Thermodynamic and fully-coupled reactive transport models of a steel–bentonite interface

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ABSTRACT

Engineered barrier system (EBS) designs for the geological disposal of high-level radioactive waste often include a bentonite buffer, the primary function of which is to protect metal waste containers or over-packs from mechanical shearing. The buffer also acts as a barrier to solute transport. One potentially dele-terious process that may occur in the buffer is the alteration of swelling clay to iron-rich minerals, some of which have a limited capacity to swell. There is a dearth of relevant natural analogues of iron–bentonite interactions, and experimental data do not provide an unequivocal indication of the conditions that will promote non-swelling clay minerals (such as berthierine) to form rather than swelling clays (such as iron-rich saponite). In addition, many of the previously-published reactive transport models of iron–bentonite or iron–claystone interfaces have not considered how 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 which suggest that the activities of major ions, especially Fe^{2+}, Fe^{3+}, Al^{3+}, H^+ and $SiO_{2(aq)}$, act as key controls on the relative stabilities of iron-rich clay minerals. In particular, they suggest that Fe-saponite is stabilised under low $fO_{2(g)}$ conditions when $SiO_{2(aq)}$ activities are buffered by quartz or more soluble silica polymorphs (e.g. chalcedony). Iron-rich 1:1 clay minerals, such as berthierine, tend to be stabilised in fluids that are quartz under-saturated. The thermodynamic models were used to inform the development of three fully-coupled reactive transport models of a steel–bentonite interface: (1) steel corrosion reaction applied on a boundary directly in contact with bentonite at a fixed rate; (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 extent and nature of the alteration predicted by the models was found to be sensitive to model con-ceptualisation. The corrosion cell assumption leads to steel corrosion products including magnetite and siderite and the alteration of primary minerals to berthierine ($\sim$2 cm thick layer forming over 100 000 years, with partial loss of montmorillonite to a depth of $\sim$9 cm). In contrast, the boundary cor-rosion assumption with a fixed steel corrosion rate leads to quicker alteration to iron-rich clay minerals. If the diffusion-limited corrosion rate assumption is made, the steel corrosion rate varies over time as the bentonite porewater composition evolves, and the spatial extent of alteration is much more limited (mil-limetre scale). Although much progress has been made, a number of uncertainties associated with mod-elling bentonite evolution remain, especially with regard to ion transport through smectite interlayers and the potential for complex couplings between chemical and physical processes.

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1. Introduction

Engineered barrier system (EBS) concepts for the geological dis-posal of high-level radioactive waste often include a bentonite buffer, the main function of which is to protect metal waste con-tainers or waste package overpacks from mechanical shear. The buffer may also act to minimise transport of corrodants to the overpack surface and to some extent may act as barrier to radionu-clide migration. The potential detrimental effect of the interaction of iron or steel canisters/overpacks on compacted bentonite in EBS designs was first identified in the late-1980s (Grauer, 1990). Of

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particular interest is the potential for alteration of the montmoril-lonite component of the bentonite to iron-rich clays, some of which may have a reduced capacity to swell (Wilson et al., 2011). Although this issue remained of interest to those waste agencies planning to employ iron or steel canisters/overpacks in their repository concepts, little more research was undertaken until new experimental and modelling studies in the late 1990s which have continued until recent times (e.g. Kamei et al., 1999; Guillaume et al., 2003; Bildstein et al., 2006; Lantenois et al., 2005; Charpentier et al., 2006; Wilson et al., 2006a, 2006b; Perronnet et al., 2007, 2008; Osacký et al., 2010; Lanson et al., 2012).

There is a dearth of relevant natural analogue data for iron–bentonite interactions under conditions relevant to radioactive waste disposal. The alteration of smectite to non-swelling minerals such as chlorite may be observed in hydrothermal and late-stage diagenetic to low grade metamorphic systems; numerous sub-aerial and sub-aqueous environments have iron-rich clays (Wilson et al., 2006a; Perronnet et al., 2008), but there are no terrestrial systems where native Fe is in contact with smectite for time periods relevant to radioactive waste disposal (many thousands of years). Interactions of clays with native iron are observed in some meteorites (Perronnet et al., 2008), but the data yield few insights as a natural analogue of iron–bentonite interactions under repository conditions.

A number of experiments investigating the stability of smectite in the presence of iron have recently been described in the literature (e.g. Guillaume et al., 2003, 2004; Lantenois et al., 2005; Charpentier et al., 2006; Wilson et al., 2006b; Perronnet et al., 2007, 2008; Osacký et al., 2010; Lanson et al., 2012). In general, these experiments include bentonite and iron present as native iron powder/coupons, magnetite (a likely steel corrosion product) and fluid (either an electrolyte solution or distilled water). However, the results of these experiments do not give an unequivocal indication of the most likely reaction pathway that may occur in an EBS, largely due to the short-term nature of the experiments (with many workers adopting the approach of applying elevated temperatures and high water/solid ratios to combat slow reaction kinetics) and issues associated with mineral meta-stabilities and differences between experimental parameters that will affect reaction kinetics (such as temperature, fluid to solid ratios, run time, fluid/solid compositions and type of iron compound).

In general, the higher temperature experiments (>250 °C) result in chlorite formation (e.g. Guillaume et al., 2003) whereas lower temperature experiments (<150 °C) tend to result in the formation of a 1:1 mineral or an altered iron-rich saponite-type smectite (e.g. Lantenois et al., 2005; Wilson et al., 2006b; Perronnet et al., 2007; Osacký et al., 2010). The experiments by Charpentier et al. (2006) were conducted under more strongly alkaline conditions than other experiments and resulted in the formation of significant amounts of iron-rich vermiculite under higher temperature conditions (300 °C). In addition to temperature, the influence of a number of other factors (iron:clay ratio, starting smectite composition) have been considered as having an influence on the identity of alteration products observed in experiments (Mosser-Ruck et al., 2010) and there has been discussion as to the mechanisms by which alteration occurs (Lantenois et al., 2005; Perronnet et al., 2007).

Experiments conducted as part of the European Union 'NF-PRO' project also provide useful insights into reactions between iron and bentonite and the influence that bentonite may have on the nature of iron corrosion (Smart et al., 2006, 2008; Carlson et al., 2006, 2007, 2008). These experiments included steel in the form of coupons, wire, and powder in the presence of either compacted or slurried bentonite (reacted with

solutions at $T = 30$–100 °C, for durations of over two years). Of particular interest is the mineralogical analysis of the experimental products. Milodowski et al. (2007, 2008, 2009a, 2009b) showed that bentonite immediately adjacent to the corroding steel wires was found to have interacted with the iron released, resulting in the formation of narrow haloes of altered bentonite and the presence of micro-fracturing. In these haloes the clay matrix was significantly enriched in iron and the apparent displacement of interlayer calcium (which re-precipitated as aragonite in a series of reaction fronts) was observed. In addition this work has shown that the thicknesses of corrosion products in compacted bentonite are vanishingly thin (less than the scanning electron microscopy imaging resolution of 0.1 μm).

A number of modelling studies have been undertaken on iron–bentonite interactions, ranging from simple thermodynamic approximations (Wilson et al., 2006a) through to more elaborate reactive transport modelling of engineered radioactive waste repository systems (Bildstein et al., 2006; Montes-H et al., 2005; Savage et al., 2010a). Many of these more recent models include complex reaction kinetics (Bildstein et al., 2006; Montes-H et al., 2005; Savage et al., 2010a). However, simple activity diagrams such as those presented by Wilson et al. (2006a) are still useful in that they allow an understanding to be developed of the influence of fixed solute activities on the relative stability of different iron-rich layer silicates. Since the models described by Wilson et al. (2006a) were published, the accuracy of the model they used to generate estimates of Gibbs free energy of formation (ΔG_f°) for 1:1 layer silicates (Chermak and Rimstidt, 1989) has been questioned (Wersin et al., 2008). In addition, other aspects of the model have been criticised (Van Hinsberg et al., 2005). Therefore, new estimates have been generated as part of the work presented here (described in Appendix A).

It is clear from the data available in the literature that iron-rich smectite (especially saponite) and 1:1 clay minerals, such as cronstedtite, odinite or berthierine, are likely bentonite alteration products. However, it is not clear as to what the precise controls are on the formation of these different clay mineral structures. In addition to this uncertainty, many of the previously-published reactive transport models of iron–bentonite or iron–claystone interfaces use a finite volume approach in which steel reacts with a volume of water that is not part of the bentonite porosity, but is present either as a gap (present prior to bentonite resaturation after repository closure) or as a fictive steel porosity (steel having no inherent porosity) to allow for growth of steel corrosion products that can then interact with the bentonite (e.g. Bildstein et al., 2006; Marty et al., 2010; Savage et al., 2010a). In such models, there is a potential for artificial dilution effects to lead to the development of water compositions in the gap that are different to those that would be likely in the bentonite pore space immediately adjacent to the steel surface once it is in contact with the bentonite. This can lead to under/over-saturation, and hence dissolution/precipitation, of minerals in the fictive volume that may not represent the likely evolution in the bentonite porespace. Moreover, in an EBS design where there is no initial gap between the steel and the bentonite, or in a concept where any such gaps are assumed to close soon after buffer resaturation, the available water to steel surface area ratio is defined by the porosity in the steel corrosion cell, and may not relate directly to the ratio of bentonite porewater to steel surface area in the real system as it evolves.

In this paper, new thermodynamic models of iron-rich clay mineral stability are presented (Section 2) and in turn, these models are used to inform the development of reactive transport models that specifically consider the process-couplings at the interface between the steel overpack and the bentonite buffer in engineered barrier systems (Section 3).