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Testing geochemical models of bentonite pore water evolution against laboratory experimental data

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ABSTRACT

The determination of a bentonite pore water composition and understanding its evolution with time underpins many radioactive waste disposal issues, such as buffer erosion, canister corrosion, and radionuclide solubility, sorption, and diffusion, *inter alia*. Previous modelling approaches have tended to ignore clay dissolution–precipitation reactions, a consequence of which is that montmorillonite is theoretically preserved indefinitely in the repository system. Here, we investigate the applicability of an alternative clay pore fluid evolution model, that incorporates clay dissolution–precipitation reactions as an integral component and test it against well-characterised laboratory experimental data, where key geochemical parameters, Eh and pH, have been measured directly in compacted bentonite. Simulations have been conducted using different computer codes (Geochemist's Workbench, PHREEQC, and QPAC) to test the applicability of this model. Thermodynamic data for the Gibb's free energy of formation of MX-80 smectite used in the calculations were estimated using two different methods ('Polymer' and 'Vieillard' Models).

Simulations of 'end-point' pH measurements in batch bentonite–water slurry experiments showed different pH values according to the complexity of the system studied. The most complete system investigated revealed pH values were a strong function of partial pressure of carbon dioxide, with pH increasing with decreasing $P\mathrm{CO_2}$ (with log $P\mathrm{CO_2}$ values ranging from -3.5 to -7.5 bars produced pH values ranging from 7.9 to 9.6).

A second set of calculations investigated disequilibrium between clay and pore fluid in laboratory squeezing cell tests involving pure water (pH = 9.0) or a 1 M NaOH solution (pH = 12.1). Simulations carried out for 100 days (the same timescale as the experiments) showed that smectite remained far from equilibrium throughout, and that the lowering of pH due to smectite hydrolysis was trivial. However, extending the duration of the simulations to that required for clay–fluid equilibrium, necessitated timescales of 7 and 65 years for pure water and 1 M NaOH, respectively, but again produced relatively minor reduction in pH (in the order of 0.1–0.2 pH units). If the (equilibrium) precipitation of secondary minerals was included in the simulations, then not only was the clay–fluid equilibration period extended dramatically (from 7 to 360 years for pure water, and from 65 to 2600 years for 1 M NaOH), but concomitant changes in pH were significant, decreasing from 9.0 to 8.6 (pure water) and from 12.1 to 9.0 (1 M NaOH). Repetition of these latter calculations using an alternative method for ΔG_f^0 smectite produced an increase in equilibration time for reaction with 1 M NaOH from 2600 to 5000 years, highlighting the potential effects of the uncertainty in thermodynamic data for smectite.

A final set of calculations was carried out to investigate both the time- and space-dependent variations in pore fluid composition in laboratory in-diffusion experiments conducted for over 1200 days, initially with pure water and 'spiked' after 271 days with a Na–Ca–OH–Cl solution (pH = 11.7). Here, the sensitivity of the results to both variations in a number of parameters/conditions (porosity, reaction rate of secondary minerals, the degree of mixing of the external fluid reservoirs in the experiments, the effective diffusion coefficient) and the inclusion/exclusion of key processes (clay hydrolysis, secondary mineral precipitation, ion exchange, clay edge protonation–deprotonation reactions) was investigated. These calculations confirmed that smectite dissolution–precipitation reactions alone have an insignificant impact

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upon pH buffering over laboratory timescales and that the pH buffering observed is most likely controlled by clay protonation–deprotonation reactions, and kinetic secondary mineral (brucite + tobermorite) precipitation. Ion exchange reactions were found to have little effect on pH. Alternative data for the kinetic dissolution of smectite produced no observable differences, and the adoption of a reduced diffusion coefficient produced a poorer fit to experiment results.

In conclusion, modelling predicts that the effects of smectite dissolution on the chemistry of bentonite pore waters would be essentially undetectable over experimental time scales, but when the model is combined with plausible constraints on the precipitation of secondary minerals, significant changes in solution chemistry and mineralogy are predicted to occur over time scales that are relevant to repository near-field evolution (hundreds to thousands of years). There are remaining fundamental uncertainties related to the variable chemistry of the smectite clays, the nature of porosity in highly compacted buffer materials, the reactive surface area of smectite, and the thermodynamic properties of these clay minerals.

1. Introduction

The determination of a bentonite pore water composition and understanding the evolution of its likely chemical composition with time underpins many other repository near-field activities, such as understanding buffer erosion, canister corrosion, and radionuclide solubility, sorption, and diffusion, *inter alia* and thus plays a vital, if indirect, role in safety assessment. Key parameters in definition of this pore water composition are pH and Eh, which have major effects on canister corrosion and radionuclide solubility and migration, and concentrations (activities) of aqueous species which may accelerate metal corrosion, and/or enhance radionuclide solubilities/mobilities. Species in this category would include HS^-, HCO_3^-, SO_4^{2-} and Cl^-. An important aspect of this evaluation is not only to define a starting pore water composition, but also to gain insight into controlling processes and mechanisms, such that changes in pore water composition can be predicted when the system is subject to internal (e.g. waste thermal output) and external (e.g. water-saturation, changing host rock groundwater composition) perturbations.

Redox in bentonite pore fluids is generally assumed to be controlled by chemical equilibria involving dissolved iron species and iron-bearing minerals, such as Fe^{2+}/Fe_3O_4 (e.g. Nagra, 2002), or alternatively, by Fe^{2+}/siderite (e.g. SKB, 2006). To a certain extent, the precise controlling reactions are a site-specific issue, in that the concentrations of redox-sensitive species may be dominated by the influence of the composition of the ambient groundwater at a disposal site on the bentonite pore water.

pH is assumed to be determined through the interaction of a number of factors, such as: protonation–deprotonation reactions at clay edge sites; dissolution–precipitation reactions of trace carbonate minerals (calcite, siderite, dolomite), regulated by ion exchange reactions on clay; dissolution–precipitation reactions of the major clay mineral component (montmorillonite) of the bentonite; and the partial pressure of carbon dioxide (PCO_2) imposed by the host rock on the engineered barrier system. Different authors place different emphasis on each of the above factors, but the consensus is that the clay fraction principally acts as a cation exchanger, but with the clay being immune from dissolution–precipitation reactions, and pH being determined by the contribution from the trace carbonate mineral concentration, and the ambient PCO_2 and the buffering effects of the exchangeable cations and protolysis reactions at clay edge sites with respect to cation concentrations and pH (e.g. Nagra, 2002; Bradbury and Baeyens, 2003; Fernández et al., 2004; Ochs et al., 2004; SKB, 2006; Samper et al., 2008; Fernandez and Villar, 2010; Zheng et al., 2010). However, there are question marks concerning the thermodynamic validity of ion exchange-based models for clay (e.g. Stumm and Morgan, 1981), and a more rigorous approach employing a solid–solution model for montmorillonite has been advocated (Arthur and Wang, 2000).

A consequence of the omission of clay dissolution–precipitation reactions from pore fluid evolution models is that montmorillonite is preserved indefinitely in the near-field system, even over million-year timescales (e.g. SKB, 2006). However, this is contrary to natural systems evidence where smectite clays may undergo dissolution–precipitation reactions over assessment-relevant timescales at pH 9–10 and temperatures of 50–60 °C or lower (e.g. Savage et al., 2010). It may be concluded therefore that although an approach excluding clay mineral dissolution–precipitation may be satisfactory to interpret the results of laboratory or *in situ* experiments, it is not necessarily appropriate to be extended to the timescales of interest for repository safety assessment.

Here, we propose an alternative clay pore fluid model, one which incorporates clay dissolution–precipitation reactions as an integral component of the model and is tested against suitable well-characterised laboratory experimental data. Researchers at VTT in Finland have reported the results of laboratory experiments which have measured key geochemical parameters, Eh and pH, directly in compacted bentonite (Muurinen and Carlsson, 2007a). These measurements have been achieved by using solid-state electrodes in conjunction with standard chemical analysis of squeezed pore fluids for calibration purposes. Experiments have been conducted in diffusion cells, squeezing cells, and batch type equipment, thus providing both single ‘end-point’ type results and time- and space-dependent squeezing and in-diffusion results. Data from these experiments provide a means of testing geochemical models for bentonite pore fluid evolution and have provided the focus for the modelling activities described here.

2. Conceptual models of clay pore fluid behaviour

Intimately related to any model of the evolution pore fluid composition is the understanding of pore fluid behaviour in compacted bentonite, particularly with regard to the nature of porosity and the behaviour of fluids in close proximity to charged clay surfaces. Currently-available conceptual models for clay-pore fluid behaviour consist of either a system with different porosity types; or a system with a single porosity. Both models are discussed in more detail below.

Many researchers view compacted bentonite as possessing different types of porosity, (e.g. Kozaki et al., 1998, 2001, 2005; Bradbury and Baeyens, 2002, 2003; Fernández et al., 2004; Appelo and Wersin, 2007; Muurinen and Carlsson, 2007a; Glaus et al., 2007; Appelo et al., 2010). In this concept, ‘total porosity’ refers to the total volume of voids, without discrimination regarding location or type, whereas ‘interlamellar/interlayer porosity’ is located in the interlayer spaces of individual clay particles, between the individual tetrahedral–octahedral–tetrahedral (TOT) sheets (Bradbury and Baeyens, 2003). This is considered to be a few monolayers thick and because of its more structured nature,