Reactive transport modelling of shale-bentonite interactions in a hypersaline environment☆

James C. Wilson [a], [*], Steven Benbow [b], Richard Metcalfe [b], Helen Leung [c]

[a] Quintessa Ltd., 633/635 Birchwood Boulevard, Warrington WA3 7QU, United Kingdom
[b] Quintessa Ltd., The Hub, 14 Station Road, Henley-on-Thames, Oxfordshire RG9 1AY, United Kingdom
[c] Nuclear Waste Management Organization, 22 St. Clair Avenue East, 6th Floor, Toronto, Ontario M4T 2S3, Canada

ARTICLE INFO

ABSTRACT

Bentonite is a widely considered sealing material for radioactive waste repositories and its behaviour has been studied in a variety of settings. In Ontario Power Generation's Deep Geological Repository (DGR) design for low and intermediate level radioactive waste, a reference 70:30 bentonite/sand mixture is the most voluminous component of the proposed shaft sealing system, in addition to cement- and asphalt-based components. In this study, the long-term durability of the bentonite in contact with sedimentary wall rocks of the shaft and highly-saline porewater was assessed. The possible significance of reactions between bentonite and high-salinity, magnesium-rich porewater for the sealing properties of bentonite has hitherto received less attention than reactions such as smectite illitization, iron-bentonite interactions and cement-bentonite interactions.

Fully-coupled reactive transport models were developed to simulate the evolution of the interface between the bentonite/sand mixture and the Georgian Bay Shale, which forms the wall rocks of the shaft overlying the Cobourg Formation (limestone), within which it is proposed to locate the repository. The highly saline nature of the shale porewater led to a Pitzer approach being used to model mineral solubilities. The 'base case' simulation suggests that there will be rapid partial replacement of Na–montmorillonite with Ca-montmorillonite in the bentonite/sand, with K-montmorillonite then replacing Ca-montmorillonite over longer timescales (tens of thousands of years). Over 100,000 years, minor alteration of the primary minerals at the shaft seal-rock interface occurred in this model, resulting in a reduced porosity alteration zone with a thickness of a few centimetres. The main alteration product in the bentonite/sand was saponite, whereas in the shale, it was analcime (which was included as a representative sodium-rich framework silicate). A number of variant cases were also developed that explored the effects of model discretisation and geochemical assumptions (controls on dissolved silica concentrations) on calculated system evolution. The variation in discretisation led to minor differences in the evolution of the system, especially with regard to porosity. The assumption that quartz buffers the initial dissolved silica concentrations instead of amorphous silica (the 'base case' assumption) resulted in kaolinite forming along with saponite in the bentonite/sand, and kaolinite forming in preference to analcime in the host rock. However, none of the simulations resulted in a significant increase in bentonite-sand porosity over 100,000 years and most of the thickness of the bentonite/sand shaft seal remained unaltered. Hence the models suggest that the performance of the DGR bentonite/sand shaft seals in contact with hypersaline porewater should not be detrimentally affected.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Designs for radioactive waste disposal facilities, especially Deep Geological Repositories (DGRs), often include bentonite as a buffer around higher-level waste/spent fuel containers and as a backfill/sealing material (e.g., Madsen, 1998; Wilson et al., 2011). Although much work has been undertaken to understand the potential long-

term durability of bentonite in radioactive waste repositories, especially in relation to smectite illitization, iron-bentonite interactions and cement-bentonite interactions (Metcalfe and Walker, 2004; Karnland and Birgesson, 2006; Savage et al., 2007; Wersin and Snellman, 2008; Wilson et al., 2011, 2015; *inter alia*), relatively little attention has been given to modelling the potential for bentonite to react with highly-saline water compositions, especially those with a high concentration of magnesium. Highly-saline groundwater occurs in many sedimentary rock settings. This is the case for Ontario Power Generation's (OPG) proposed Deep Geologic Repository (DGR) for Low and Intermediate Level Radioactive Waste (L&ILW) near the existing Western Waste Management Facility at the Bruce nuclear site in Canada (OPG, 2011).

The proposed DGR would be constructed about 680 m below ground surface. The host rock of the DGR is the Cobourg Formation (limestone). This formation is overlain by about 200-m of shales (Georgian Bay Shale), and a further 400-m sequence of predominantly argillaceous formations. The DGR shafts will be sealed primarily with a bentonite/sand mixture, although there will be a concrete monolith at the level of the DGR and shallower concrete bulkheads to provide mechanical support as well as an initial low-permeability barrier. A reference composition of 70/30 wt% bentonite/sand mixture has been adopted for the DGR shaft seal design.

Experimental studies on the interaction of bentonite with saline solutions and brines show that ion exchange occurs within the bentonite and that smectite persists as the dominant type of clay mineral over laboratory timescales (Kaufhold and Dohrmann, 2009; Herbert et al., 2008; Suzuki et al., 2008). The experiments reported in the literature consider a range of solution compositions and ionic strengths, those presented by Suzuki et al. (2008) included simulated seawater, whereas the Herbert et al. (2008) bentonite-water interaction experiments considered eight different solutions covering a wide range of pH (5.3–13.2) and salinities (ionic strengths from 0 to 15.5 M). Based on TEM-EDX analyses of the samples, Herbert et al. (2008) report changes in layer composition and suggest that ultimately, smectite could be altered to non-swelling minerals such as kaolinite or pyrophyllite. However, these were not identified by XRD analysis.

In addition to experimental data on smectite stability under saline conditions, natural analogue studies of bentonite-seawater interaction have showed little, if any structural modification of smectite layers due to saline water intrusion (e.g. Fernandez et al., 2005; Pérez del Villar et al., 2005). However, it appears that relevant natural analogue studies for bentonite-hypersaline fluid interactions have yet to be identified.

Preliminary thermodynamic modelling by Wilson et al. (2011) suggests that Mg-rich fluids (high activity ratios of $Mg^{2+}/[H^+]^2$) could favour saponite (trioctahedral Mg-rich smectite) stability (chalcedony buffering silica activity). Additional calculations (Fig. 1) using the same approach suggest this may also be the case where dissolved silica concentrations are buffered by quartz (the lowest solubility silica polymorph) or amorphous silica (which is more soluble than chalcedony). These models are termed 'preliminary' given that not all possible clay compositions are included in the databases available in Geochemist's Workbench® format, including the database 'thermo.com.v8. r6+' that was used to construct the diagrams given by Wilson et al. (2011), and those in Fig. 1. Of particular note is the absence of vermiculite in the database. Vermiculite is often observed as a weathering product of mica in soils or as a product of hydrothermal alteration of basic and ultra-basic rocks and may form during metamorphism (Wilson, 2013). In addition to saponite as a candidate bentonite alteration product, recent work undertaken for the Cyprus Natural Analogue Project

(CNAP) has found palygorskite associated with bentonite under alkaline conditions at pH ~ 10 (Alexander et al., 2012, 2013). Thermodynamic modelling of palygorskite stability by Birsoy (2002) suggests that it tends to be stabilised by very high dissolved silica activities. It has been suggested that palygorskite could precipitate from silica and Mg-rich solutions derived from amorphous silica and decomposing Mg-rich smectite (Wilson, 2013).

In this paper, reactive transport models are presented in order to explore the possible evolution of the bentonite/sand mixture as it reacts with the argillaceous rock in the presence of hypersaline porewater with a significant concentration of magnesium. The models have been designed carefully to gain insights into the key reactions, taking into account as far as possible, uncertainties in thermodynamic and kinetic data. Specifically, the paper describes interactions between the bentonite/sand mixture and shale of the Georgian Bay Formation, which is taken as representative of the argillaceous lithologies present in the rock sequence above the DGR's host rock through which shafts will be constructed. Of particular interest, is how the hydraulic properties of the bentonite/sand shaft seal could evolve over time, and whether alteration to the primary mineralogy is likely to be detrimental to the desired properties of the shaft-sealing materials. Potentially detrimental evolution could include a dramatic increase in porosity, which in turn would increase the capacity of diffusive transport of solutes (including any contaminants released from wastes and transported to the shaft). Alternatively, the alteration of swelling clay to non-swelling clay could result in 'stiffening' and the potential for the development of fractures that may become advective flow paths.

2. Methods

2.1. Numerical simulation of coupled processes

The reactive transport models presented in this paper were developed using the computer software 'QPAC' (Quintessa, 2010). QPAC is a multi-physics, finite-volume code that has a dedicated reactive transport module. The code uses a finite-volume discretisation approach and is capable of solving fully-coupled nonlinear problems. The code has been widely applied to the modelling of engineered barrier systems (Watson et al., 2009; Savage et al., 2010a, 2010b, 2010c; Watson et al., 2013; Wilson et al., 2015). The following processes were included in the reactive transport models: (1) mineral dissolution/precipitation reactions (kinetic treatment); (2) aqueous speciation (equilibrium); (3) solute diffusion; and (4), coupled porosity evolution. Advective flow in the deep formations at the Bruce site is negligible (Intera, 2011) and was therefore not included. The simulations were specified to proceed until 100 000 years and assumed fully water-saturated conditions. Ion exchange was not included as a specific process, as the addition of instantaneous ion exchange processes to the fully-coupled approach taken for mineral dissolution-precipitation, solute transport and aqueous speciation using the Pitzer model (and the large number of parameters it includes) led to numerical difficulties. The implementation of the Pitzer approach in fully-coupled reactive transport model codes introduces greater nonlinearity in the relationships between the solved variables. Instead, smectite end-member compositions were included as discrete minerals (Sections 2.2). Prototypes of the reactive transport simulations were built using the Davies equation, and in these models ion exchange was optionally included as a fully-coupled process without modelling issues. However, little difference was observed between the prototypes using either approach, supporting the choice to omit ion exchange processes in the Pitzer simulations.

The effective diffusion D_{eff} (m^2/s) was modelled in the 'base