

# Reactive Transport Modelling of Bentonite Shaft Seals under Hypersaline Conditions

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## 1. Introduction / Background

Bentonite is a widely considered sealing material for radioactive waste repositories (e.g., Madsen, 1998; Wilson et al., 2011) and its behaviour has been studied in a variety of settings. Ontario Power Generation's Deep Geological Repository (DGR) design for low and intermediate level radioactive waste would be constructed about 680 m below ground surface. The host rock of the DGR is the Cobourg Formation (limestone) of Ordovician age. 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 70:30 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.

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. Interactions around the secondary concrete sealing materials in the shaft were assessed separately (Quintessa, 2011).

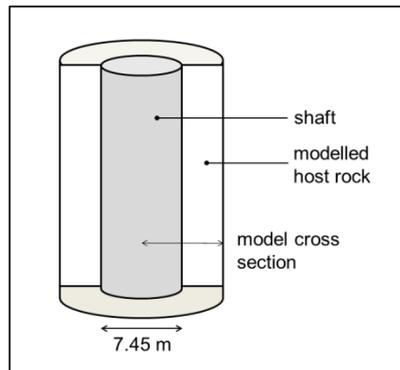
Groundwaters in the Georgian Bay Shales are expected to be highly saline and Mg-rich. The possible significance of reactions between bentonite and such waters for the sealing properties of bentonite have hitherto received less attention than reactions such as smectite illitization, iron-bentonite interactions and cement-bentonite interactions (e.g. Metcalfe and Walker, 2004; Karnland and Birgesson, 2006; Savage et al., 2007; Wilson et al., 2011; *inter alia*).

Experimental studies on the interaction of bentonite with saline solutions and brines with a wide range of salinities and pH 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). 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. Natural analogue studies can yield more detail on the possible long-term effect of these interactions. Studies of bentonite-seawater interaction (Fernández et al. 2005; Pérez del Villar et al. 2005) have shown little, if any structural modification of smectite layers due to saline water intrusion. However, natural analogue studies for bentonite-hypersaline fluid interactions have yet to be identified.

The potential for alteration of the bentonite/sand mix due to interactions with the Georgian Bay Shale groundwaters over performance-relevant timescales of up to 100 000 y was investigated using reactive transport models. Reactive transport modelling activities were informed by the development of activity diagrams to help understand the stability of the clay minerals.

## 2. Concept and Model Details

A schematic representation of the region around shaft-rock system is shown in Figure 2-1. The dimensions shown correspond to the ventilation shaft, rather than the wider main shaft in the DGR, as the smaller diameter shaft has less sealing material and therefore a greater potential that alteration will affect performance. An Excavation Damaged Zone (EDZ) is expected to a depth of 1.1 m around the shaft.



**Figure 2-1 Schematic of the shaft-rock system. The rock comprises intact Georgian Bay Shale and an EDZ of depth 1.1 m. The seal is a 70:30 bentonite/sand mix.**

Reactive transport models were developed to simulate the evolution of the interface between the bentonite / sand mixture and the Georgian Bay Shale. Radially symmetric 1-D models were constructed, with an outer radius of 10 m, at which distance it was assumed that the *in situ* groundwater was unaffected by interactions with the bentonite. The 1.1 m thick EDZ region was represented as a region of Georgian Bay Shale with increased porosity (14.2%) and enhanced effective diffusion ( $1.7 \times 10^{-12} \text{ m}^2/\text{s}$  compared to the intact rock (7.1% and  $8.6 \times 10^{-13} \text{ m}^2/\text{s}$  respectively). Simplified initial mineral assemblages that were specified in the modelling are shown in Table 2-1. The simulations were specified to run until 100 000 years.

**Table 2-1 Simplified compositions of bentonite/sand mix and Georgian Bay Shale.**

Bentonite / Sand		Georgian Bay Shale	
Mineral	Vol.%	Mineral	Vol.%
Montmorillonite(Na)	44.82	Calcite	8.93
Quartz	1.53	Dolomite	9.76
Cristobalite	1.74	Quartz	26.08
Calcite	0.50	Chlorite	14.66
Gypsum	0.59	Illite	33.47
Sand (quartz)	21.82		
Porosity	29.00	Porosity <sup>1</sup>	7.1
<b>TOTAL</b>	<b>100.00</b>	<b>TOTAL</b>	<b>100.00</b>

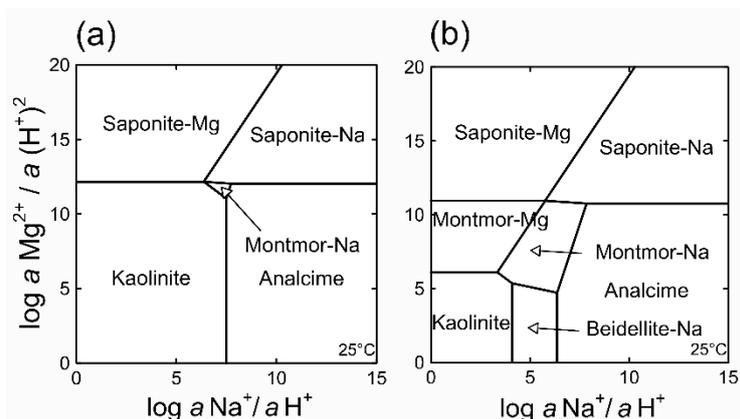
1. Note that in the reactive transport models an enhanced porosity is assumed in the host rock at the Excavation Damaged Zone, and initial mineral volumes are scaled accordingly.

Mineral dissolution/precipitation kinetics were fully coupled with porosity evolution. Diffusion of solutes was coupled to the evolving porosity using a linear Archie's Law ( $D_{eff} = \theta D_{pore}$ , where  $D_{eff}$  is the effective diffusion coefficient,  $\theta$  is the porosity and  $D_{pore}$  is the porewater diffusion coefficient). The formulation allows the effective diffusion to tend to zero if porosity becomes completely clogged. For this reason, minimum grid cell sizes must be chosen to be representative

of the thickness of clogging that would be expected to be needed in the real system in order to completely prevent diffusion of solutes. A thickness of 1 cm was chosen for the simulations.

Both rock and engineered materials were allowed to undergo alteration via dissolution/precipitation reactions. The salinity of the Georgian Bay Shale porewater is sufficiently high (ionic strength = 7.65 M) that it was necessary to use the Pitzer approach (Pitzer, 1991) to obtain more accurate activities of aqueous species than would be provided by standard Debye-Hückel models. Pitzer data from the Yucca Mountain Project ‘YPP’ database was used to model ion activities in the highly-saline groundwaters (USDOE, 2007). Thermodynamic data for the minerals species were taken from the database ‘thermo.com.V8.R6+’ (based on the EQ3/6 database generated by Lawrence Livermore National Laboratory, sometimes referred to as the ‘LLNL’ dataset).

Potential secondary minerals that could form in the system were identified after considering the available supporting experimental data and natural analogue data. Additionally, a supporting investigation of mineral stability was undertaken to determine the most stable clay minerals in the system  $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  using the ‘thermo.com.V8.R6+’ database. The activity diagrams produced suggest that if bentonite comes into contact with water compositions which have a relatively high  $\text{Mg}^{2+}/(\text{H}^+)^2$  activity ratios, montmorillonite could undergo alteration to magnesium-rich clay minerals such as saponite (tri-octahedral smectite) (Figure 2-2), if kinetically feasible. Saponite is observed in weathered rocks and soil, especially those rich in ferromagnesian minerals and it can be found in lake and ocean sediments and hydrothermal systems (Wilson, 2013).



**Figure 2-2 Activity diagrams for the system  $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  at  $T = 25\text{ }^\circ\text{C}$ ,  $P = 1\text{ bar}$ . Diagram (a) has dissolved silica activity set at quartz equilibrium; diagram (b) has it set at amorphous  $\text{SiO}_2$  equilibrium. The diagram includes clay minerals and analcime as a representative sodium-rich framework silicate (albite, paragonite and pyrophyllite were suppressed).**

The complete set of potential secondary minerals that were identified in the preliminary thermodynamic modelling are listed in Table 2-2. Illite was not included as a bentonite alteration product, as empirical models of smectite illitization show that it is likely to be negligible over the considered timescales under conditions of low temperature ( $< 100\text{ }^\circ\text{C}$ ) and near-neutral pH, even when relatively high concentrations of  $\text{K}^+$  are present (e.g., Karnland and Birgersson, 2006; Quintessa, 2011). Given that the ambient temperature is expected to be low in the main part of DGR ( $\sim 22\text{ }^\circ\text{C}$ ) due to a lack of radiogenic heating (Quintessa, 2011), and shaft seals are at even shallower depths, and hence lower temperature, K-smectite minerals were included instead.

**Table 2-2 Potential alteration products included in reactive transport simulations**

<b>Mineral</b>	<b>Composition</b>
<b><i>Bentonite Alteration Products</i></b>	
Brucite	Mg(OH) <sub>2</sub>
Saponite (Na, Mg, K, Ca)	(Na <sub>0.33</sub> / K <sub>0.33</sub> / Ca <sub>0.165</sub> / Mg <sub>0.165</sub> ) Mg <sub>3</sub> Si <sub>3.67</sub> Al <sub>0.33</sub> O <sub>10</sub> (OH) <sub>2</sub>
Beidellite (Na, Mg, K, Ca)	(Na <sub>0.33</sub> / K <sub>0.33</sub> / Ca <sub>0.165</sub> / Mg <sub>0.165</sub> ) Al <sub>2</sub> Si <sub>3.67</sub> Al <sub>0.33</sub> O <sub>10</sub> (OH) <sub>2</sub>
Montmorillonite (Mg, K, Ca, Na)	(Na <sub>0.33</sub> / K <sub>0.33</sub> / Ca <sub>0.165</sub> / Mg <sub>0.165</sub> ) Al <sub>1.67</sub> Mg <sub>0.33</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Kaolinite	Al <sub>2</sub> SiO <sub>5</sub> (OH) <sub>4</sub>
Analcime	Na <sub>0.96</sub> Al <sub>0.96</sub> Si <sub>2.04</sub> O <sub>6</sub> · H <sub>2</sub> O
Sepiolite	Mg <sub>4</sub> Si <sub>6</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O
Palygorskite	Mg <sub>2.84</sub> Al <sub>1.8</sub> Si <sub>7.73</sub> O <sub>20</sub> (OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> · 4H <sub>2</sub> O
<b><i>Host Rock Alteration Products</i></b>	
Analcime	Na <sub>0.96</sub> Al <sub>0.96</sub> Si <sub>2.04</sub> O <sub>6</sub> · H <sub>2</sub> O
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>

Dissolution / precipitation reaction kinetics were represented using a Transition State Theory (TST) approach with the reaction rate depending on the acid, neutral, base and carbonate concentrations in the porewater:

$$\frac{dm}{dt} = A(m) \left( k_1 a_{H^+}^{n_1} + k_2 + k_3 a_{H^+}^{n_3} + k_4 f_{CO_2}^{n_4} \right) \left( \frac{Q}{K} - 1 \right).$$

Here,  $m$  (mol) is the abundance of the mineral in question,  $A(m)$  (m<sup>2</sup>) is its reactive surface area (which depends upon its abundance),  $k_{1,2,3,4}$  (mol/m<sup>2</sup>/s) are the rate constants for acid, neutral, base and carbonate mechanisms respectively, and  $n_{1,3,4}$  are dimensionless catalysis constants for acid, base and carbonate rates respectively.  $a_{H^+}$  is the activity of  $H^+$ ,  $f_{CO_2}$  is the fugacity of  $CO_2$  and  $Q$  and  $K$  are the ion activity product and equilibrium constant for the mineral.

The compilation of kinetic data by Palandri and Kharaka (2004) was used as the primary data compilation ( $k$  and  $n$  values) for silicate and carbonate minerals. Kinetic data for montmorillonite dissolution from Rozalén et al. (2008) was refitted to the form above and was used as a proxy for saponite, beidellite and palygorskite.

Measured values of dissolved silica concentrations are not available for the Georgian Bay Shale, so different assumptions regarding silica buffering were tested in the models (amorphous silica or quartz buffering was assumed). The models were implemented in Quintessa's QPAC software and the simulations explored the evolution of the bentonite/sand mixture over 100 000 years.

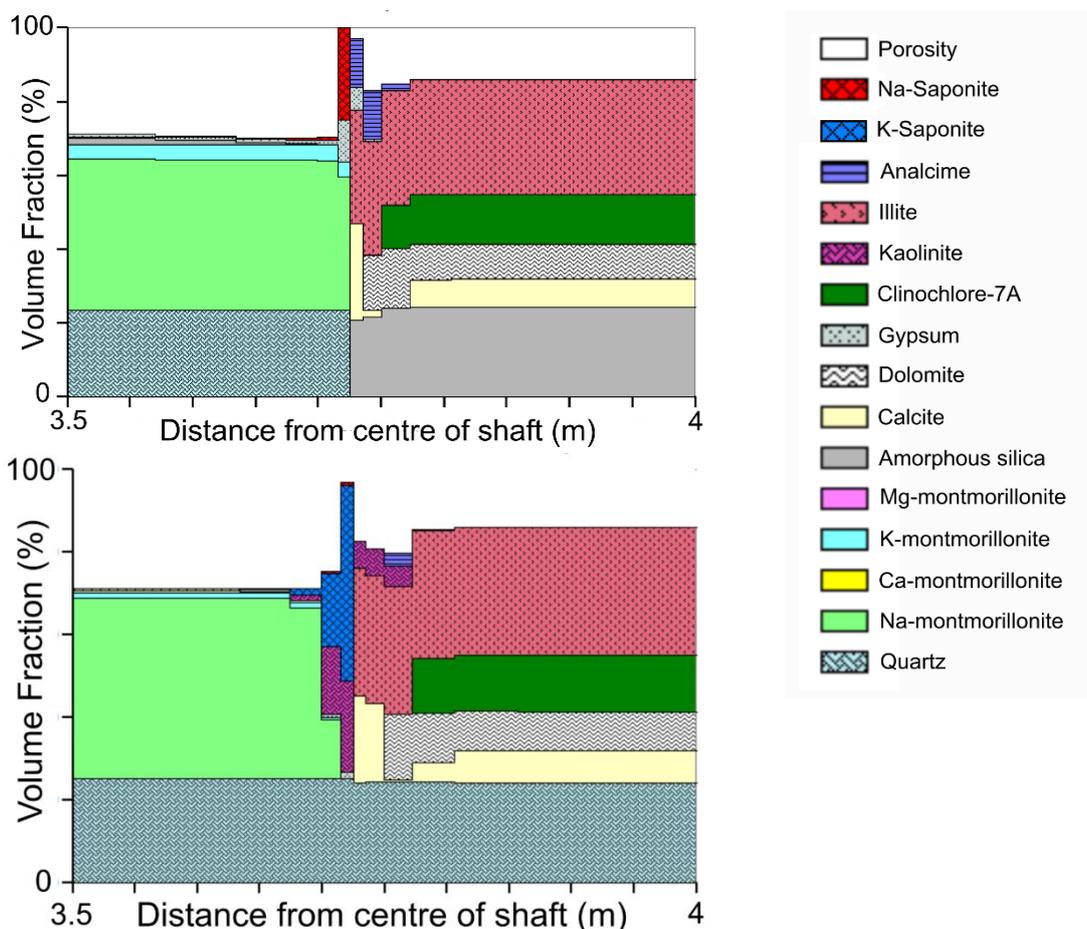
### 3. Results

Mineral volume fractions in the system at 100 000 y are shown in Figure 3-1 for the amorphous silica and quartz buffering assumptions for silica in the Georgian Bay Shale groundwater.

Over 100 000 years, minor alteration of the primary minerals at the shaft seal-rock interface occurred in the simulation assuming amorphous silica buffing in the Georgian Bay Shale (Figure 3-1, top). This results in an alteration zone in which porosity becomes clogged over 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). Partial ion exchange of the Na-montmorillonite to K-montmorillonite was seen across the bentonite.

Specifying quartz buffering in the Georgian Bay Shale leads to greater amounts of alteration. By 100,000 years, primary montmorillonite had been replaced completely by K-saponite and kaolinite in the bentonite/sand near the shale to a depth of around 2 cm. Porosity was reduced in this region to 3%, but was not completely clogged (unlike the amorphous silica buffering case). The overall difference in the pattern of silicate mineral evolution in the shale is due to the lower dissolved silica activity in the shale porewater which leads to the stabilisation of kaolinite rather than analcime.

The findings in all variant cases that were considered in the study was that alteration of the primary phases is restricted to a narrow (<5 cm) band around the shaft seal-rock interface.



**Figure 3-1** Volume fraction plots for bentonite/sand – shale interface at 100 000 years assuming amorphous silica-buffering (top) and quartz buffering (bottom) in the Georgian Bay Shale. The coordinates on the x axes refer to the distance from the centre of the shaft.

#### 4. Conclusions

None of the simulations predicted 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 bentonite/sand shaft seals in contact with hypersaline porewater should not be detrimentally affected. With regard to implications for shaft seal performance in the DGR, there was no significant increase in bentonite/sand porosity and the predicted alteration of primary montmorillonite (although more extensive than in the base case) is

confined to the volume near to the interface with the shale, most of the bentonite/sand remaining unaltered (apart from partial replacement of Na-montmorillonite by K-montmorillonite).

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