On the impact of temperatures up to 200°C in clay repositories with bentonite engineer barrier systems: a study with coupled thermal, hydrological, chemical, and mechanical modeling

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Abstract

One of the most important design variables for a geological nuclear waste repository is the temperature limit up to which the engineered barrier system (EBS) and the natural geologic environment can be exposed. Up to now, almost all design concepts that involve bentonite-backfilled emplacement tunnels have chosen a maximum allowable temperature of about 100 °C. Such a choice is largely based on the consideration that in clay-based materials illitization and the associated mechanical changes in the bentonite (and perhaps the clay host rock) could affect the barrier attributes of the EBS. However, existing experimental and modeling studies on the occurrence of illitization and related performance impacts are not conclusive, in part because the relevant couplings between the thermal, hydrological, chemical, and mechanical (THMC) processes have not been fully represented in the models. This paper presents a fully coupled THMC simulation of a nuclear waste repository in a clay formation with a bentonite-backfilled EBS for 1000 years. Two scenarios were simulated for comparison: a case in which the

temperature in the bentonite near the waste canister can reach about 200°C and a case in which the temperature in the bentonite near the waste canister peaks at about 100°C.

The model simulations demonstrate some degree of illitization in both the bentonite buffer and the surrounding clay formation. Other chemical alterations include the dissolution of K-feldspar and calcite, and precipitation of quartz, chlorite, and kaolinite. In general, illitization in the bentonite and the clay formation is enhanced at higher temperature. However, the quantity of illitization is affected by many chemical factors and therefore varies a great deal. The most important chemical factors are the concentration of K in the pore water as well as the abundance and dissolution rate of K-feldspar; less important ones are the concentration of sodium and the quartz precipitation rate. In our modeling scenarios, the calculated decrease in smectite volume fraction in bentonite ranges from 1-8% of the initial volume fraction of smectite in the 100 °C scenario and 1-27% in the 200 °C scenario. Chemical changes in the 200 °C scenario could also lead to a reduction in swelling stress up to 15-18% whereas those in the 100°C scenario result in about 14-15% reduction in swelling stress for the base case scenario. Model results also show that the 200 °C scenario results in a much higher total stress than the 100 °C scenario, mostly due to thermal pressurization. While cautions should be taken regarding the model results due to some limitations in the models, the modeling work is illustrative in light of the relative importance of different processes occurring in EBS bentonite and clay formation at higher than 100 °C conditions, and could be of greater use when site specific data are available.

1. Introduction

Geological repositories for disposal of high-level nuclear waste generally rely on a multi-barrier system to isolate radioactive waste from the biosphere. The multi-barrier system typically consists of the natural system (NS), which includes the repository host rock and its surrounding subsurface environment, and the engineered barrier system (EBS), which comprises the waste canister and in many design concepts a smectite clay-based buffer or backfill. Clay/shale formations have been considered as a host rock throughout the world and are being studied at several underground research laboratories, e.g., Toarcian argillites at the Tournemire site, France (Patriarche et al., 2004), Opalinus Clay at the Mont Terri, Switzerland (Bossart et al., 2002), and Boom Clay at the Mol site, Belgium (Barnichon and Volckaert, 2003). An EBS composed of clay-based material such as bentonite is routinely considered in the design of nuclear waste repositories. Both host clay rock and EBS bentonite have low permeability, low diffusion rates, high retention capacity for radionuclides, and the capability of swelling that could seal fractures induced by damage due to tunnel excavation, ventilation, and/or heating.

Radioactive waste (spent fuel) emanates a significant amount of thermal energy due to decay processes, which causes temperature increases in the surrounding environment particularly in the early stages of waste emplacement. The temperature to which the EBS and natural rock can be exposed is one of the most important design variables for a geological repository, because it determines waste package spacing, distance between disposal galleries, and therefore the overall size (and cost) of repository for a given amount of heat-emanating waste (Horseman and McEwen, 1996). This is especially important for a clay repository, because argillaceous rocks have relatively small heat conductivity. A thermal limit of about 100 °C or lower is imposed unanimously in all disposal concepts throughout the world despite their differences in design concepts (Hicks et al., 2009). Chemical alteration and the subsequent changes in mechanical

properties are among the determining factors. A high temperature could result in chemical alteration of buffer and backfill materials (bentonite) within the EBS through illitization and cementation, which compromise the function of these EBS components by reducing their plasticity and capability to swell when wetting and to maintain swelling pressure (Pusch and Karnland, 1996; Pusch et al., 2010; Wersin et al., 2007). The swelling capability of clay minerals within the bentonite is important for sealing gaps between bentonite blocks, between bentonite and other EBS components, and between the EBS and the surrounding host rock, inhibiting the water infiltration into EBS and subsequently the corrosion of canister, and suppressing the microbial activity. The swelling capacity loss due to illitization therefore will comprise these beneficial features of EBS. Chemical alteration may also occur in the near-field host rock, which could reduce the clay capability for self-sealing within the excavation damaged zone (EDZ). As a result of the low permeability of a clay rock, a high temperature may induce significant pore pressure build-up (through pore water expansion and vaporization) in the near field, which could generate adverse mechanical deformation (such as fracturing), damaging the integrity of the host rock (Horseman and McEwen, 1996).

Regarding the concern of chemical alteration and the associated mechanical changes, Wersin et al. (2007), after reviewing a number of data sets, concluded that the criterion of 100°C for the maximum temperature within the bentonite buffer is overly conservative. Their conclusion was based on their findings that no significant changes in bentonite hydraulic properties occur at temperatures of at least 120°C under wet conditions and that bentonite is chemically stable to much higher temperature under dry conditions. The impact of a high temperature on bentonite and clay host rock behavior, and the consequences on repository performance, are largely open questions for a clay repository system. While various studies shed light on certain aspects of this

question, there is a lack of studies that integrate the relevant THMC processes and consider the interaction between the EBS and host rock. In this paper, we use coupled THMC modeling to evaluate the chemical alteration and mechanical changes in EBS bentonite and the NS clay formation under various scenarios, attempting to provide useful information for decisions on temperature limits and motivate more studies on this issue.

2. A review of the chemical and mechanical alteration in EBS and clay formation

A number of studies have been conducted to evaluate the chemical, mechanical and geological alteration in bentonite and clay-rock formations as a result of hydration and/or heating at temperatures ranging from 30 to 300°C. Illitization, the transformation of smectite to illite, has caught great attention of researchers because it results in a loss of smectite which in turn causes a loss in the swelling capacity. Illitization is evident in geological systems (Wersin et al., 2007), as exemplified by several natural analogue studies (Pusch and Madsen, 1995; Kamei et al., 2004; Cuadros 2006; Casciello et al., 2011). Illite/smectite mixed-layer clay is commonly observed in clayey sediments, and deep formations typically contain more illite than shallow formations (Cuadros, 2006), which leads to a conclusion that smectite is gradually transformed to illite during diagenesis.

Various laboratory experiments have been conducted to evaluate the degree of illitization in bentonite. These experiments typically involve hydrating bentonite samples with various types of solutions and exposing each sample to a range of temperature conditions for a given time period. Pusch et al. (2010) summarized two laboratory studies. In one study, samples of MX-80 bentonite saturated with weakly brackish water were heated from one end and contacted at the other end with a solution that contained about 300 ppm Na^+ and 10 ppm K^+ for one year. The temperature was about 130°C at the heated end and 90°C at the other end. Comparison of

untreated and hydrothermally treated clay showed that there were almost no differences geochemically, but the treated sample became stiffer. In another study (Pusch et al., 1991, cited in Pusch et al., 2010), a clay sample was placed into large vessels with initially distilled water. Then the samples were heated to 200 °C. The most noticeable chemical change was the dissolution of calcite. K- and Na-feldspar dissolved slightly at 130 °C but completely dissolved at 200°C. Increase in shear strength was also observed. In another study, Mosser-Ruck and Cathelineau (2004) heated Na- and Ca-smectite at 150°C for two months in batch experiments. Three types of experimental solutions were used: 0.01 M NaOH , 1 M K₂CO₃ and mixtures of 1 or 3 M KCl with 10⁻⁴ or 10⁻² M KOH. No chemical alteration was observed in the experiment with NaOH solution, whereas transformation of low-charge smectite to high-charge smectite was observed for K solutions, with byproducts of quartz, feldspars, zeolites and calcium silicate hydrates (CSH). Caporuscio et al. (2012) conducted batch experiments with bentonite from Colony, Wyoming, consisting of smectite with minor mineral impurities (feldspar, silicas, zeolites, pyrite). The samples were saturated with Na-Ca-K-Cl-based brine representing in situ concentrations and were heated at ~160 bar and 125° to 300°C for one month. No significant mineralogical alteration of smectite was observed, and illite was not formed during these reactions.

Pacovsky et al. (2005) performed a *Mock-Up* test on the Czech candidate buffer material “RMN” under repository-like conditions for two years. This buffer consisted of highly compacted blocks of clay with 75% Ca-Fe-montmorillonite, 10% finely ground quartz, and 5% graphite powder. The sample was emplaced in a cylinder, heated from inside with a constant temperature of 95°C and saturated from the outside with solution that primarily contained Na and Cl. Chemical and mechanical changes exhibited spatial heterogeneity, with the most significant

change occurring near the heater. Significant dissolution of the Fe-montmorillonite was observed, leading to the precipitation of iron minerals and causing cementation within the entire buffer. However, the dissolution of montmorillonite did not lead to the formation of illite. On the contrary, intergrowth of illite and kaolinite that was obvious in untreated clay dissolved near the heater after being exposed to heating and hydration. Also observed was a drop in swelling pressure and increase in hydraulic conductivity in the hot part of the buffer. The material from the Pacovsky et al. (2005) *Mock-Up* test was also analyzed in Stríček et al. (2009). Their results showed that no recrystallization occurred and the cation exchange capacity did not show any systematic changes.

While laboratory and *Mock-Up* tests have greatly improved the understanding of geochemical and mechanical alterations in EBS bentonite at high temperature, findings from these studies must be taken cautiously, because the experimental conditions deviate considerably from actual repository conditions, for example, with regards to the timing of re-saturation versus timing of maximum temperature, the mechanical constraints, and the availability of water. Eventually, one has to rely on field scale experiments to study the alterations at conditions representing a geological repository. Results from a large-scale 5-year field experiment at SKB's underground laboratory at Äspö (Pusch et al., 2010) allow for a careful evaluation of the alteration of clay minerals in bentonite by comparing hydrothermally treated and untreated samples. This test was conducted with a very dense MX-80 clay buffer surrounding a full-size copper-lined KBS-3 canister in an 8-meter-deep, 1.75 m diameter deposition hole in granite. The surface temperature of the canister was maintained at 85°C for a couple of years and at successively lower temperatures later in the experiment. The properties of a sample taken from the vicinity of the heater were analyzed. Chemical alteration of the montmorillonite was quite

complicated; depending on the type of montmorillonite, different changes occurred.

Montmorillonite in MX-80 bentonite can generally be grouped into two types: (1)

montmorillonite with a normal charge as the end member of an illite/smectite mixed layers

series, and (2) low-charge montmorillonite as the end member of dioctahedral vermiculite–

smectite mixed layer phases. The frequency of Type 1 montmorillonite within the illite/smectite

mixed layers in the hydrothermally treated clay was actually higher than that of untreated clay,

whereas the fraction of Type 2 montmorillonite dropped in heated clay in comparison with

untreated clay. But the overall interlayer charge of both montmorillonite types decreased, due to

the replacement of original Mg in the octahedral layer by Al. In comparison with the untreated

bentonite, the hydrothermally treated sample had hydraulic conductivity two to three orders of

magnitude higher but almost the same swelling pressure. Pusch et al. (2010) mentioned that the

increase in hydraulic conductivity was probably caused by an alteration in micro-structural

particle morphology. In a Temperature Buffer Test (Åkesson, 2012), the 0.63 m thick cylindrical

blocks that is composed of MX-80 bentonite was heated internally and hydrated externally for

about 6 years. The temperature near the heater fluctuated around 140 to 160 °C and the inner

parts of the bentonite blocks reached full saturation in about 4.7 years. Mineralogical analyses of

the samples taken after dismantling of the test showed no changes in smectite composition,

although an increase in the Ca concentration in the interlayer space was observed for the inner

sample.

Numerical modeling has also been used to study the chemical alteration in the EBS bentonite and NS clay formation for longer time frames ranging from 1000 to 100,000 years. The

geochemical changes in 1 m thick, fully saturated MX-80 bentonite, sandwiched by a canister

and a geological fluid, were simulated by Montes-H et al. (2005a) under a constant temperature

of 100°C. In the model, the MX-80 bentonite was pre-treated with a Ca and Na chloride solution. The bentonite was composed of 85% Na/Ca-montmorillonite and 15% accessory minerals. Their simulations showed that Na/Ca-montmorillonite converted to Ca-montmorillonite by cation exchange reactions, and there was a minimal neo-formation of saponites, vermiculites and chlorites. The swelling capacity of EBS bentonite was just slightly affected over the 1000-year simulation period, based on an evaluation using a simplified method in which swelling capacity is a function of the volume of swelling clay. In fact, Montes-H et al. (2005b), using the same method, predicted that the loss of swelling capability is only about 11% to 14% compared to unheated samples, even if Na/Ca-montmorillonite is completely converted to Ca-montmorillonite. Marty et al. (2010) used a model setup similar to that in Montes-H et al. (2005a), except that the host rock was the Callovo-Oxfordian argillite, and the corrosion of a steel canister was specifically considered. Their model showed that significant illitization (about 40% loss in smectite) occurred near the EBS-NS interface during a 10,000-year simulation period, and that several Fe^{+2} minerals, such as chlorite and Fe-saponite, formed near the canister.

There are also some laboratory tests that focus exclusively on mechanical and hydrological property changes due to temperature increase. Villar and Lloret (2004) and Lloret and Villar (2007) reported that the swelling capacity of clay (FEBEX bentonite) decreased at temperatures around 30-80°C, although the influence of temperature was less evident when the confining stress was high. On the other hand, the measured increase in hydraulic conductivity with temperature was less than expected on the basis of thermal changes in water kinematic viscosity. The transfer induced by temperature between intra-aggregate adsorbed water and inter-aggregate free water may explain most of the features observed, taking into account that the physical characteristics (e.g., density and viscosity) of water in these two states are different. Martín and

Barcala (2005) reported an overheating event in a *Mock-Up* experiment for FEBEX bentonite (ENRESA, 2000). The event was also analyzed in detail by Sanchez et al. (2005) using coupled THM modeling and a double-structure constitutive model of the bentonite. During the temperature transient in which the temperature increased up to 200°C and exceeded 100°C for a few days, the total stress increased significantly due to the effects of thermally induced stresses and drying of the bentonite. However, after the transient, the total stress reduced to levels lower than prior to the transient, possibly indicating irreversible structural changes and reduced swelling capacity. However, Pusch (2000) and Pusch et al. (2003) found that the swelling pressure of compacted bentonite was not significantly affected by heating up to 125°C.

Several observations can be generalized from these studies: (1) although illitization is widely observed in geological systems (e.g., Pusch and Madsen, 1995), this process has not been conclusively confirmed for EBS bentonite in either small-scale laboratory experiments or large-scale *Mock-Up* and *in situ* or field tests; (2) not forming illite does not mean smectite stays unaltered — rather, smectite undergoes various changes, including transformation of low-charge smectite to high-charge smectite (Mosser-Ruck and Cathelineau 2004), conversion of Na/Ca-montmorillonite to Ca-montmorillonite (Montes-H et al., 2005a), dissolution of the Fe-montmorillonite (Pacovsky et al., 2005), and an increase in interlayer charge of montmorillonite as observed in one field scale test (Pusch et al., 2010); (3) the role of dissolved K^+ in illitization and/or smectite alteration is well recognized in natural analogue studies (Cuadros, 2006) and supported by some laboratory studies (Mosser-Ruck and Cathelineau, 2004), but could be debatable in terms of the source of K^+ (e.g. from the surrounding formations by transport or the dissolution of some minerals) and the interference of other cations; (4) as a result of heating, increase in permeability is observed in most studies, but the change in swelling capacity is

inconclusive; (5) there is a lack of long-term, high temperature experimentation under a range of conditions.

Our literature review shows that the chemical alteration in the EBS bentonite and the NS clay formation is a complicated process depending on the geochemical conditions, and that the degree of mechanical and hydrological changes, either caused directly by temperature increases or by associated geochemical reactions, is still a matter of debate. In this paper, we examine how illitization depends on geochemical conditions and in turn how swelling stress is affected by illitization while EBS bentonite and NS clay formation undergo simultaneously hydrological and thermal changes. We specifically target the illitization and subsequent stress changes because illitization is one of the determining factors that lead to a thermal limit of 100 °C or below in most disposal concepts.

3. Model development

3.1 Simulator

The numerical simulations are conducted with TOUGHREACT-FLAC, which sequentially couples the multiphase fluid flow and reactive transport simulator, TOUGHREACT (Xu et al., 2011), with the finite-difference geomechanical code FLAC3D (Itasca, 2009). TOUGHREACT can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity, and can accommodate any number of chemical species present in liquid, gas, and solid phases. A variety of subsurface thermal, physical, chemical, and biological processes are considered in TOUGHREACT under a wide range of conditions of pressure, temperature, water saturation, ionic strength, pH and Eh. The major chemical reactions include aqueous complexation, acid-base, redox, gas dissolution/exsolution, cation exchange mineral

dissolution/precipitation, and surface complexation. FLAC3D is a numerical modeling code for mechanical analysis of soil and/or rock in three dimensions

(<http://www.itascacg.com/software/flac3d>).

The coupling of TOUGHREACT and FLAC was developed in Zheng et al. (2011) to provide the necessary numerical framework for modeling fully coupled THMC processes. It was equipped with a linear elastic swelling model (Zheng et al., 2012; Rutqvist et al., 2014) to account for swelling as a result of changes in saturation and pore water composition. In this study, the linear elastic swelling model is further extended by incorporating the effect of changes in the abundance of swelling clay on stress.

3.2 Modeling scenario

We apply TOUGHREACT-FLAC to coupled THMC processes associated with a hypothetical bentonite-buffered nuclear waste repository in clay rock, a repository example that involves a horizontal nuclear waste emplacement tunnel at 500 m depth (Figure 1) (Rutqvist et al., 2014). The Z-axis is set as vertical, while the horizontal Y- and X-axes are aligned parallel and perpendicular to the emplacement tunnel, respectively (Figure 1) in this 2-D model. Note that while the canister is modeled as a heat source with mechanical properties of steel, the THC changes in the canister and their interactions with EBS bentonite are not considered here for the sake of simplicity.

An initial stress field is imposed by the self-weight of the rock mass. Zero normal displacements are prescribed on the lateral boundaries of the model. Vertical displacements are prevented at the bottom. An open boundary is applied to the liquid pressure at top and bottom and initially the model domain is in hydrostatic state. The initial temperature at the top is about

11 °C, with a thermal gradient of 27 °C/km, the initial temperature at the bottom is 38 °C. The model simulation was conducted in a non-isothermal mode with a time-dependent heat power input (Rutqvist et al., 2014), adopted from representative heating data from the U.S. DOE's Used Fuel Disposition campaign, for pressurized water reactor (PWR) used fuel.. This heat load is then scaled in the 2D model to represent a certain line load, which depends on the assumed spacing between individual waste packages along an emplacement tunnel. The heat load for the “low-T” case corresponds to an initial thermal power of 3144W for a 4-PWR-element waste package, with surface waste deposition of 60 years, a 50-m spacing between emplacement tunnels, and 3-m spacing between the 5-m long packages. The heat load for the “high T” case represents similar waste package and spacing, except with only 20 years surface waste deposition. Initially the EBS bentonite has a water saturation of 65% and the clay formation is fully saturated. From time zero, the EBS bentonite undergoes simultaneously re-saturation, heating, chemical alteration, and stress changes.

3.3 Mechanical Model

While development of a more comprehensive and rigorous chemical-mechanical model is underway (Davis et al., 2013), in this paper we use a linear elastic swelling model that is extended by incorporating changes in the abundance of swelling clay to evaluate the consequence of illitization on swelling stress in EBS bentonite. The mechanical model for the clay formation is the same as in Rutqvist et al. (2014).

Rutqvist et al. (2011) included a linear elastic swelling model that under mechanically constrained conditions results in a swelling stress, σ_s , that is linearly proportional to the saturation:

$$d\sigma_s = 3K\beta_{sw}ds_l \quad (1)$$

where K is the bulk modulus, S_l is the water saturation and β_{sw} is a moisture swelling coefficient (dimensionless). In this report, β_{sw} is 0.048, calibrated based on the swelling pressure of 1 MPa for Kunigel-V1 bentonite (Börgesson et al. 2001) under the condition that bentonite is saturated with dilute solution (e.g. deionised water), and K is 20 MPa (Rutqvist et al., 2011).

To consider the swelling due to both moisture and chemical concentration changes, we include the stress due to a change of ion concentration in the pore water and abundance of swelling clay:

$$d\sigma_s = 3K\beta_{sw}ds_l - A_n dC + A_{sc} dm_s \quad (2)$$

where A_n is a constant that linearly relates ion concentration (C) variation and the corresponding stress change. A_{sc} is a constant that relates the change in mass fraction of swelling clay, m_s , to change in stress.

A_n is typically calculated from swelling pressures measured using different solution (e.g. deionised water versus 1 M NaCl solution) to saturate the bentonite. Laredj et al. (2010) proposed the following expression for A_n :

$$A_n = \frac{(5.312 \ln C - 23.596)}{\sqrt{C}} - \frac{7.252 \times 10^{-4}}{C^2} \quad (3)$$

An empirical value for A_{sc} is derived through a linear regression of swelling pressure versus smectite mass fractions as shown in Figure 2, and A_{sc} is the slope of the linear correlation. However, probably because these bentonite materials differ not only in the mass fraction of smectite, but also in other properties, these data points are fairly scattered, which makes it impossible to establish an unique linear regression between swelling pressure change and mass fraction change of smectite. We therefore chose a linear correlation line cross the measured swelling pressure for Kunigel VI bentonite and use the slope of this line as the value of A_{sc} which is $2.5 \times 10^6 \text{ Pa}^{-1}$. The non-uniqueness of linear regression between swelling pressure and mass fraction of smectite leads to uncertainty of A_{sc} , a sensitivity run with A_{sc} of $9.3 \times 10^6 \text{ Pa}^{-1}$ was therefore conducted to illustrate how the choice of A_{sc} affects the calculated swelling pressure, although A_{sc} of $9.3 \times 10^6 \text{ Pa}^{-1}$ is less likely for Kunigel-VI bentonite because the measured swelling pressure for Kunigel-VI bentonite is much lower than that calculated from the fitting line with a slope of $9.3 \times 10^6 \text{ Pa}^{-1}$.

More sophisticated and realistic mechanical models are available in the literature and have been successfully used for bentonite and clay formation, such as state surface approach (e.g. Nguyen et al., 2005) and dual structure Barcelona Expansive Clay model (Alonso et al., 1999; Sánchez et al., 2005). In this paper, we use a rather simple elastic model because it allows us to incorporate the contribution from chemical component and parameters for the model can be relatively easily calibrated as discussed above.

3.4 Chemical Model

In this generic case (non-site specific), it is assumed that the EBS buffer is composed of Kunigel-V1 bentonite (Ochs et al., 2004) and that the host rock properties are representative of the Opalinus Clay formation (Bossart 2011; Lauber et al., 2000). The mineral compositions of the bentonite and clay formation are listed in Table 1. The mineralogical composition of Opalinus Clay varies remarkably because of the spatial heterogeneity in mineralogical composition and the analytical method used. For example, Bossart (2011) summarized measured mineralogical composition from various sources, and reported that the illite/smectite mixed layer ranges from 5% to 11%. However, Lauber et al. (2000) reported that the illite/smectite mixed layer ranges from 14% to 22%. In this paper, the mineralogical compositions (Table 1) are the average values given in Bossart (2011) and Lauber et al. (2000).

The pore-water compositions of the bentonite (Sonnenthal et al., 2008) and the clay formation (Fernandez et al., 2007) are listed in Table 2.

Mineral dissolution/precipitation is kinetically controlled. The kinetic law for mineral dissolution/precipitation is given in Xu et al. (2011):

$$r = kA \left| \left(1 - \left(\frac{K}{Q} \right)^\theta \right) \right|^\eta \quad (4)$$

where r is the kinetic rate, k is the rate constant (mol/m²/s) which is temperature dependent, A is the reactive surface area per kg water, K is the equilibrium constant for the mineral–water reaction written for the destruction of one mole of mineral, and Q is the reaction quotient.

Exponents θ and η are fitting parameters, for simplicity, they are assumed equal to 1 in this paper.

The kinetic rate constants can usually be summed for three mechanisms (Lasaga et al., 1994):

$$k = k_{25}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{198.15} \right) \right] + k_{25}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{198.15} \right) \right] \alpha_H^{n_H} \\ + k_{25}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{198.15} \right) \right] \alpha_H^{n_{OH}} \quad (5)$$

where subscripts *nu*, *H* and *OH* indicate neutral, acid, and alkaline mechanisms, respectively, *E* is the activation energy, *k*₂₅ is the rate constant at 25 °C, *R* is gas constant, *T* is the absolute temperature, *a* is the activity of the species, and *n* is a power term (constant). It should be noted that reaction rates depend on the reactive surface area *A* in Equation (4), which is a function of the product of the specific surface area and the volume fraction of each mineral. Therefore, the calibrated values of specific surface area and volume fraction should be viewed as arbitrary and non-unique (co-linearly varying) values, the product of which is relevant but not each value separately.

The kinetic rates and surface areas for the minerals considered in the model were taken mostly from Xu et al. (2006) (Table 3). However, the illitization rate (the rate of illite precipitation and smectite dissolution) was calibrated (Liu et al., 2013) based on the measured illite percentage in an illite/smectite (I/S) mixed layer from Kinnekulle bentonite, Sweden (Pusch and Madsen, 1995). The thermodynamic data were taken from the Data0.dat.YMPv4.0, an EQ3/6 (Wolery, 1993) database qualified by the U.S. Department of Energy for the Yucca Mountain project.

3.5 Thermal and Hydrological Model

The model considers non-isothermal two phase (air and water) flow, with each individual phase fluxes given by a multiphase version of Darcy's Law. For the vapor flow in the air phase, in addition to Darcy flow, mass transport can also occur by diffusion and dispersion according to Fick's law. The effective vapor diffusion coefficient is the product of porosity, tortuosity and molecular diffusion coefficient. Porosity and tortuosity are given in Table 4 and the molecular diffusion coefficient is $1.034 \times 10^{-5} \text{ m}^2/\text{s}$. Both conductive (Fourier's law) and convective heat flux are considered in the model. The basic mass and energy balance equations as well as the equations for fluxes are given in Pruess et al. (2012). The capillary pressure is calculated by van Genuchten function as:

$$P_{cap} = -\frac{1}{\alpha} \left([S^*]^{1/m} - 1 \right)^{1-m} \quad (6)$$

where P_{cap} is the capillary pressure (Pa), $S^* = (S_l - S_{lr}) / (1 - S_{lr})$ and S_l is the water saturation, S_{lr} is the residual water saturation. S_{lr} is 0.1 for bentonite and 0.01 for clay formation. The values of α and m are given in Table 4. Table 4 also lists other thermal and hydrodynamic parameters used in the model. The majority of these parameters are taken from Sonnenthal et al. (2008) for the EBS bentonite and Thury (2002) for the NS clay formation. Permeability for the clay formation is from Soler (2001) and that for the bentonite is from JNC (2000).

3.6 Model limitations

The modeling work presented in the paper aims to improve the understanding of the coupled processes contributing to chemical and mechanical alteration in EBS bentonite and NS clay formation for a generic case. The model results presented in the next section are constrained by

some limitations/assumptions in the model, which readers should be aware of when understanding the model results. First, illitization is simulated as a dissolution-precipitation process, i.e., the dissolution of smectite and neo-formation of illite, with the illitization rate calibrated against field data (Pusch and Madsen, 1995). It is known that illitization could also occur through solid state transformation by substitution of intracrystal cations (e.g., Cuadros and Linares, 1996), which is not considered in our model. Second, the current mechanical model for the NS clay formation is not tied with chemical variables, i.e., mechanical-chemical coupling is only considered in the EBS bentonite. Third, the mechanical-chemical coupling is calculated using an extended linearly elastic swelling submodel, but a more rigorous approach linking chemistry and mechanics is needed for more realistic simulation. Development of linkages between chemistry and mechanics, taking advantage of the framework provided by a dual-structure model implemented in TOUGHREACT-FLAC (Davis et al. 2013) is ongoing. Fourth, in the current model, the canister serves only as a heat source; chemical changes on the surface of the canister are neglected for simplification. Further model analysis is needed to consider chemical changes at the canister, specifically the release of Fe^{+2} , which might enhance the dissolution of smectite by forming chlorite or other types of iron-rich clay minerals. Finally, it is noteworthy that simulations were only conducted for a period of 1,000 years because the simulator was not fast enough for longer simulation time periods and coupled process effects are most pronounced in the first 1,000 years. The computational efficiency of the simulator needs to be improved and simulations for longer time, e.g. 100,000 years, are warranted.

4. Model results

4.1 TH evolution

The evolution of heat release from decaying waste is shown in Figure 1. The heat release rates have been adjusted to make two cases for comparison: a “high T” case, in which the temperature near the canister can reach 200 °C; and a “low T” case, in which the temperature near the canister peaks at about 100 °C. In this paper, the temporal evolution at four monitoring points (see Figure 1 for their positions) is used to present thermal, hydrological, chemical and mechanical results: point A is inside the bentonite near the canister, point B is inside the bentonite and near the EBS-NS interface, point C is inside the clay formation and near the EBS-NS interface, and point D is inside the clay formation at a distance from canister of 10 m. The temperature evolution at the four monitoring points A, B, C, and D is shown in Figure 3. In the “high T” case, the EBS bentonite is above >120 °C during most of the 1000 years of simulation period, except for the very early time, and reaches a peak temperature of about 200 °C near the canister. In the “low T” case, temperature remains below 85 °C in most of simulation times. It takes about 20 years for the low T case to fully saturate EBS bentonite, and about 25 years for the “high T” case (Figure 4). Pore pressure increases as a result of re-saturation and heating. The “high T” case exhibits much higher pore pressure than the “low T”, with a difference of about 5 MPa after 1000 years (Figure 5). The clay formation near the EBS-NS interface (point C) goes through desaturation (Figure 4), which interestingly lasts much longer for the “low T” case than the “high T” case. This is because the higher temperature leads to a higher pore pressure (Figure 5) in the EBS bentonite which reduces desaturation in the clay formation and higher pore

pressure in the EBS bentonite lower the hydraulic pressure gradient and therefore the flow of water towards the EBS bentonite.

4.2 Chemical alteration of the EBS and the NS clay formation

In this section, we focus on hydrothermally induced changes to clay minerals, especially smectite and illite, in bentonite and clay formation. Clay minerals are compositionally complex hydrous aluminum silicates and have a continuous sheet structure. While consensus has not yet been reached with regard to the details of the reaction process (Wersin et al., 2007), there is agreement that in general two mechanisms could be in play when smectite transitions to illite (Wersin et al., 2007): (1) a solid state transformation by substitution of intracrystal cations (e.g., Cuadros and Linares, 1996); or (2) a dissolution–precipitation process (e.g., Mosser-Ruck et al., 1999). Either transformation process could occur, depending on the physico-chemical conditions (Cuadros and Linares, 1996). In our current model, we consider only the second illitization mechanism, i.e., the dissolution of smectite and the precipitation of illite. The first mechanism, albeit being proposed, is still of debate, and more importantly the reaction rate is hard to determine and seldom reported, which is why the first mechanism is not considered in the current model. Although illitization is the focus when discussing chemical alterations of the EBS bentonite and NS clay formation, changes of other minerals are briefly illustrated as well because they are either the byproducts or interfere with the illitization process.

4.2.1 The base case

As mentioned in the previous section, illitization is modeled as the dissolution of smectite and precipitation of illite. The overall reaction can be written as:

Note that in the current model, Na-smectite, a smectite with Na dominating the interlayer cations, is used. If Ca-smectite is used, Ca is involved in the reaction as well. Many factors can affect the chemical reactions, such as the initial water-mineral disequilibrium in bentonite (since the water used for making bentonite blocks is not necessarily in equilibrium with the mineral phase in bentonite, and it takes time to reach that equilibrium), as well as the thermal and hydrological disturbances in response to emplacement.

In the base model which uses the parameter values listed in Tables 1 to 4, calculated results confirm that the clay formation undergoes a small degree of illitization similar to the process widely observed in geological systems (e.g. Wersin et al., 2007; Pusch and Madsen, 1995). This is illustrated by the smectite dissolution at point C and D in Figure 6 and illite precipitation at point C and D in Figure 7. The volume fraction of smectite decreases by only about 0.002 (or 6% of the initial amount) in 1000 years. When the temperature is higher (“high T” case), illitization at point D in the clay rock is clearly accelerated, resulting in a decrease of 0.015 (or 43% of the initial amount) in the smectite volume fraction after 1000 years. At point C, located near the EBS-NS interface, more hydrological and chemical interactions take place between the bentonite and the clay formation. Subsequently, more smectite dissolves and more illite precipitates. For the “high T” case, the smectite volume fraction decreases by 0.035, a 100% loss of smectite.

Illitization also occurs in the EBS bentonite, as shown by the smectite and illite volume fraction changes at points A and B in Figures 6 and 7. Although smectite precipitate and illite

dissolves for a short time period between 15 to 30 years near the canister (point A) because evaporation lead to the increase in concentration of Mg and Na and the water from clay formation that carries K has not arrived yet, in the long run illitization (smectite dissolve and illite precipitates) proceeds after the arrival of incoming water. In addition to temperature effects, illitization is affected by the initial disequilibrium between the pore-water solution and the mineral phase. Initially, the pore water in the bentonite buffer is oversaturated with respect to illite and undersaturated with respect to smectite. In addition, the pore water in the clay formation contains a much higher concentration of K and Al, and thus provides a source of Al and K for the EBS bentonite alteration through diffusion and advection, which is manifested by the increase in Al and K concentrations at point A (Figure 8). Note that the increase in Al and K concentrations in bentonite is caused not only by diffusion and advection, but also by the dissolution of other minerals, such as K-feldspar and quartz. The pore water in the clay formation also has a higher concentration of Mg and Na, which inhibits illitization. But it seems that the factors in favor of illitization outpace those against illitization. At the end of 1000 years, the smectite volume fraction in the bentonite decreases by 0.035 (or 11%) for the ‘high T’ case and 0.006 (or 2%) for the “low T” case, which corresponds to an illite volume fraction increase of similar magnitude. Clearly the “high T” case demonstrates stronger illitization than the “low T” case.

Dissolution of K-feldspar and precipitation of quartz are also observed in the model results. Their effect on illitization will be discussed in the following section. Calcite dissolution, as observed in a laboratory test reported in Pusch et al. (1991), is also shown in our current simulations, but occurs in the EBS bentonite only during the hydration period. Calcite dissolution plays a less significant role in illitization, but is important in controlling the acid-base

conditions in the EBS and NS. Models also show small amount of precipitation of chlorite and kaolinite in EBS bentonite (near the canister) and clay formation, as shown in Figure S1 and S2 in the supplementary material.

4.2.2 The effect of pore water composition

If illitization takes place via the dissolution of smectite and neo-formation of illite, as assumed in the current simulations, it must be initiated by changes in concentrations of relevant chemical species in the aqueous phase. Among these ionic species, K plays a key role; its importance for illitization has been well recognized (e.g., Pusch and Karnland, 1996; Wersin et al., 2007). In a sensitivity study presented in this section, the initial concentration of K in the pore water of the clay formation is increased to 0.01 mol/L, which is about four times that of the base case. The 0.01 mol/L value is close to the K concentration in sea water. Such a high K concentration in the pore water of clay formation would be possible if there is sea water intrusion, or if the clay formation has marine origin and the diagenesis process has not consumed too much K.

An increase in the initial K concentration in the pore water of clay formation moderately increases the illitization in the clay formation, as illustrated by the illite precipitation at point C and D in Figure 9, and by the smectite dissolution at point C and D in Figure 10. It demonstrates the importance of dissolved K over the course of illitization. At Point D in the clay formation, illitization incorporates most of the K into the mineral phases and eventually reduces the K concentration to a low level (see Figure S3 in the supplementary material). In Point C, closer to the bentonite interface, this reduction is faster and occurs earlier, partially because of illitization

that occurs locally and partially because of the transport of K to bentonite buffer, indicating that the clay formation would not be sustained source of K for illitization in bentonite in the long run. Increasing the initial K concentration in the pore water of clay formation seems to have a rather moderate effect on illitization in the bentonite (see results at point A and B in Figures 9 and 10). We observe that the magnitude of illitization clearly decreases with distance from the NS-EBS interface, a result of decreasing amount of K being transported. Although such observation demonstrates that an external source of K is relevant for illitization in bentonite, the pore water of clay formation may not be the only source of K, or the major one.

As mentioned above, an increase in the K concentration in the pore water of clay formation has a fairly limited effect on the illitization in bentonite; largely because the migration of K from the clay formation to the bentonite is retarded by illitization occurring along the pathway. This raises the question, how is illitization in bentonite affected if the initial pore water in bentonite contains more K? To answer this question, we conducted a sensitivity run in which the concentration of K in the pore water of the bentonite is one order of magnitude higher (see Figures S4 and S5 in the supplementary data), and we observed significant enhancement of illitization in the bentonite. This result suggests that illitization might be a concern if the bentonite material initially contains more K, or if the water that is used to fabricate bentonite blocks or pellets has a high initial K concentration. Note also that one of the byproducts of illitization is the precipitation of quartz. As the illitization is enhanced when the concentration of K in the pore water of bentonite increases, the production of quartz increases as well. The cementation by quartz (or amorphous SiO_2 minerals) might lower the swelling capacity of bentonite and increase the brittleness of the bentonite.

According to the illitization reaction, this process may be suppressed if the concentration of Na in pore water of bentonite is higher. In a sensitivity run, we increased the concentration of Na in the pore water of bentonite. Model results (See Figures S6 and S7 in Supplementary Material) show that for the “high T” scenario, the volume fraction of smectite decreases by about 0.025 (or 8%) in the sensitivity run, compared to a decrease of 0.035 (or 11%) in the base run near the canister, whereas for the “low T” case, smectite dissolution is very limited in the sensitivity run. Near the EBS- NS interface, we observe similar behavior. All these findings suggest that illitization is inhibited by the higher concentration of Na in the pore water of bentonite. This might be the reason why no chemical alteration was observed in the experiment with a Na solution reported in Mosser-Ruck and Cathelineau (2004) and Caporuscio et al., (2013). The use of a bentonite mixture with a smaller K or a higher Na concentration in the pore water could be a mitigating measure if illitization is a concern for higher temperature repository designs.

4.2.3 The effect of accessory minerals

Although the role of K in illitization and/or smectite alteration is well recognized in natural analogue studies (e.g., Cuadros, 2006) and supported by some laboratory studies (Mosser-Ruck and Cathelineau, 2004), the source of K is not well understood. Pusch and Madsen (1995) realized that the concentration of K in the external source for illitization in the bentonite layer used in their concept was probably unrealistically high. As shown in the previous section, adjusting the initial K concentration in the clay formation has relatively limited effect on the illitization in bentonite. This suggests that if illitization of bentonite backfill occurs, the clay formation may not be the major source of K. The sensitivity analyses presented in this section show that K-feldspar could be a more important source.

Figures 11 and 12 shows the smectite dissolution and illite precipitation in a sensitivity run in which *K*-feldspar is not part of the mineral assemblage in both the bentonite and the clay formation, i.e., there is no *K*-feldspar dissolution. Near the canister (see smectite dissolution and illite precipitation at point A in Figures 11 and 12), the illitization in the bentonite for the “no *K*-feldspar” scenario is dramatically inhibited in comparison with that in the base case. In the “no feldspar” case, the smectite volume fraction only decreases by about ~0.001–0.003 which is approximately one order of magnitude lower than that in the base case. The following reaction clearly shows the importance of feldspar dissolution for illitization: it provides not only *K* but also *Al*.

Near the NS-EBS interface, the illitization in the bentonite is also significantly suppressed (see smectite dissolution and illite precipitation at point B in Figures 11 and 12), but to a lesser degree than near the canister. In the simulation bentonite near the NS-EBS interface still receives *K* from the clay formation, whereas illitization near the canister depends almost entirely on the dissolution of feldspar for the supply of *K*. Points C and D in Figures 11 and 12 illustrate that illitization in the clay formation is less dependent on the presence of feldspar, as there is an initially high concentration of *K* that can sustain some degree of illitization.

As the dissolution rate of silicate minerals (e.g., Zhu, 2005) can vary by orders of magnitude, we conduct another sensitivity run in which the *K*-feldspar dissolution rate is increased by two orders of magnitude. As expected, illitization in the bentonite is enhanced, and the smectite

volume fraction decreases by 0.085 near the EBS-NS interface and 0.055 near the canister (see results at points A and B in Figures 13 and 14). This means that 18–27% of the initial smectite volume fraction (0.314) in bentonite dissolves. In the clay formation, illitization is also accelerated, and eventually all smectite is transferred to illite, as shown by the plateau of the volume fraction change of smectite and illite at points C and D in Figures 13 and 14.

Because quartz precipitation is a product of illitization, it is conceivable that the illitization process might be faster if the quartz precipitation rate were to increase. To test this notion we increased the quartz precipitation rate by two orders of magnitude in a sensitivity run. Apparently, more quartz precipitates in the bentonite and the clay formation as the reaction rate increases. But the clay formation is more affected by the faster quartz precipitation rate than the bentonite. In addition to the reaction rate, the saturation index is another limit to mineral precipitation (or dissolution). As shown by these simulations, illitization is part of the complex reaction network, which is dependent on the pore water chemistry, mineralogical composition, reaction rates, the interaction between EBS bentonite and NS clay formation, and the change of all these conditions associated with heating and hydration. This is probably why illitization is not consistently observed in laboratory studies.

4.3 Mechanical changes

In this section we estimate how the chemical changes observed above may affect the mechanical behavior of the EBS bentonite related to the evolution of swelling and total stress. We limit our analysis to the effects of ion concentration and illitization on swelling and do not include other potential effects of chemical changes on mechanics, such as changes in mechanical properties due to cementation. Besides, the current mechanical model is not tied with chemical

variables for the NS clay formation. Mechanical-chemical coupling (calculated via an extended linear elastic swelling model) is only considered in the EBS bentonite.

4.3.1 The base case

Figures 15 and 16 show the stress changes at point A and B for both “low T” and “high T” cases. Several processes combine to drive the stress in bentonite up to around 5.1 MPa for the “low T” and 11.5 MPa for the “high T” case after 1000 years, including the increase in pore pressure due to hydration and thermal pressurization (a processes caused by the difference in thermal expansion of the fluid and solid host rock), bentonite swelling, and thermal expansion. In comparison with the “low T” case, clearly the stronger thermal pressurization in the “high T” case leads to much higher stress in the bentonite. For both the “high T” and “low T” cases, the total stress within the buffer is produced mostly by pore pressure and less by swelling and thermal stress.. More details on thermal pressurization mechanisms and effects can be found in Rutqvist et al. (2014).

The constitutive relationship described by Equation (2) provides an opportunity to evaluate the effect of chemical changes on swelling stress. The mechanical results presented in this section are based on the chemical results in Section 4.2. In order to isolate the contributions from ion concentration changes versus smectite mass fraction changes, to swelling stress changes, we present three sets of swelling stress calculations. In the first set, denoted in Figures 17 and 18 as “ $\sigma=f(Sl,C,Sc)$ ”, the swelling stress is calculated according to Equation (2) as a function of liquid saturation changes (Sl), ion concentration (C) changes, and smectite mass fraction (Sc) changes. In the second set, denoted as “ $\sigma=f(Sl,C)$ ”, the contribution from smectite mass changes in Equation (2) is disregarded, and the swelling stress is only a function of liquid saturation and ion

concentration. In the third set, denoted as “ $\sigma=f(SI)$ ”, all chemical effects are neglected, and the swelling stress is only a function of liquid saturation changes.

At early time (< 20 years), results for “ $\sigma=f(SI,C,Sc)$ ” and “ $\sigma=f(SI,C)$ ” cases are indistinguishable (Figures 17 and 18), which indicates that smectite mass fraction changes have not yet contributed to the stress change, because the volume fraction of smectite shows significant changes only after about 20 years (see Figure 6). Ion concentration changes start to affect stress at early times (< 20 years) and maintain such effect afterwards. Initially bentonite near the canister undergoes desaturation and therefore negative swelling stress (see Figure 17 for changes at point A). Table 5 shows the swelling stress calculated for those three cases and the contribution of ion concentration and smectite mass fraction change to the swelling stress reduction at point A by the end of the 1000-year simulation. In general, the changes in the ionic concentration of the pore water in bentonite have a fairly moderate effect on swelling stress, about 14% swelling stress reduction due to chemical change for the “low T” case and 15% swelling stress reduction for the “high T” case at point A (Figure 17). The stress changes near the EBS-NS (point B) interface behave similarly to those near the canister, except the stress starts to increase earlier; the stress after 1000 years is similar as well. The pore water ion concentration changes in bentonite lead to about 15% swelling stress reduction for the “low T” case and 18% swelling stress reduction for the “high T” case (see Figure 18). In terms of the total stress, the decrease of swelling stress accounts for about 1.4-1.7% reduction of the total stress.

As shown by Equation (2), the reduction of swelling stress by the dissolution of smectite depends of the values of A_{sc} , the constant that linearly relate the swelling stress with the abundance of smectite. In the “high T” base case, A_{sc} is $2.5 \times 10^6 \text{ Pa}^{-1}$, which leads to about 15-

18% reduction of swelling stress (see Figures 17 and 18). In sensitivity runs with A_{sc} of 9.3×10^6 Pa^{-1} , the swelling stress reduction due to the dissolution of smectite is around 32-40% (see Figure S8 in the supplementary data).

Our mechanical model for the clay formation is equivalent to that in Rutqvist et al. (2014), and therefore the stress response in the clay formation is the same. Except for swelling, the mechanical model for the clay formation is not tied to chemical variables, which prevents further analysis of the effects of chemical changes on the mechanical behavior in the clay formation. In the future, a constitutive relation that incorporates the chemical component within the mechanical model for the clay formation will be implemented. Based on this development, we will be able to analyze the effects of chemical changes on mechanical behavior in a clay formation.

4.3.2 Stress changes for a simulation with the maximum dissolution of smectite

The model results for the base case suggest that the loss of smectite (via illitization) results in a maximum 18% reduction in swelling pressure, but only minimal decrease in total stress, partially because the loss of smectite is only 11% for the “high T” case and much less for the “low T” case. In Section 4.2.3, we evaluated several chemical scenarios and found that if the dissolution rate of K-feldspar is higher, more dissolution of smectite occurs, with a maximum as high as 27% for the “high T” case. The calculated swelling stress for this “ $r(\text{K-feldspar}) \times 100$ ” case was calculated using two A_{sc} (a constant that relates the changes in mass fraction of swelling clay) values: 2.5×10^6 Pa^{-1} and 9.3×10^6 Pa^{-1} . In the “high T” base case, the chemical changes lead to about 16% and 18% reduction in swelling stresses at points A and B, respectively; whereas the pore water ion composition changes in the sensitivity case lead to further reduction of

swelling stress — a decrease of 20% and 26% at points A and B, respectively if an A_{sc} of 2.5×10^6 Pa^{-1} is used, and a decrease of 46% and 70% at points A and B, respectively if an A_{sc} of 9.3×10^6 Pa^{-1} is used (Figures S9 and S10 in the supplementary material). This sensitivity analyses illustrate the potential magnitude of reduction in swelling stress due to dissolution of smectite and the dependence of model results on the choice of A_{sc} . 46% and 70% reduction in swelling stress is somewhat unrealistic because an A_{sc} of 9.3×10^6 Pa^{-1} is quite unlikely for Kunigel-VI bentonite (see Figure 2), but it illustrates the importance of having a reliable A_{sc} . When the model is applied to a site-specific scenario, ideally A_{sc} should be measured experimentally by varying the smectite content for the same type of bentonite. In terms of the total stress, the decrease of swelling stress in the sensitivity cases still accounts for fairly small reduction of the total stress, even for the 70% reduction in swelling stress at point B for “r(K-feldspar)*100” case with A_{sc} of 9.3×10^6 Pa^{-1} , decrease in swelling stress only lead to 6% decrease in total stress. However, one of the functions of the swelling stress is to provide mechanical support to the tunnel walls to seal any fractures in the disturbed rock zone and to prevent further failure during thermal-stress peak. The stability in the excavation disturbed zone depends on local effective stress evolution where the confining stress from the bentonite swelling plays a critical role (Rutqvist et al., 2014).

It is noteworthy that this generic model uses Kunigel-VI bentonite as the EBS backfill material. Kunigel-VI bentonite has a fairly low swelling pressure comparing with other bentonites such as FEBEX bentonite (ENRESA, 2000): 1 MPa for Kunigel-VI bentonite versus 5

MPa for FEBEX bentonite. Therefore, the percentage of reduction in swelling stress could be lower if FEBEX bentonite is assumed in the model.

5. Concluding remarks

This study investigates the impact of elevated temperature (100 and 200°C) on the bentonite backfill and near-field clay host rock in a geologic repository for radioactive waste. We use coupled THMC modeling to evaluate the chemical alteration and associated mechanical changes in a generic repository and consider the interaction between EBS Kunigel-V1 bentonite and the NS clay formation. Two main scenarios were developed for comparison: a “high T” case in which the temperature near the waste package can reach about 200 °C and a “low T” scenario in which the temperature peaks at about 100 °C.

Our model results indicate the occurrence of some degree of illitization in the NS clay formation, as previously revealed by several natural analogue studies, and also show that some of illitization occurs in the EBS bentonite. Other potential chemical alterations include the dissolution of K-feldspar and calcite, and the precipitation of quartz, chlorite, and kaolinite. In general, illitization in the bentonite and clay formation is enhanced at the higher temperature. However, the quantity of illitization, expressed as the smectite volume fraction change, is affected by many chemical factors and subsequently varies a great deal, which could be the reason that illitization is not consistently observed in laboratory studies. The most important chemical factors are the concentration of K and dissolution rate of K-feldspar; less important are the concentration of Na and the quartz precipitation rate. The decrease in smectite volume fraction in bentonite ranges from 0.004 to a maximum of 0.085, or up to about 27% of the initial volume fraction of smectite for the 200 °C scenario. The smectite volume fraction in the clay

formation decreases moderately in some cases, but in other cases it decreases as much as 0.035, fully depleting the initial smectite.

Higher temperature leads to much higher stress in the near-field, caused by thermal pressurization in the low permeability rock surrounding and connected to the emplacement tunnel. During this period of strong thermal stresses, smectite dissolution causes only minimal changes in the simulated total stress. Chemical changes including the changes in pore water ion concentration and smectite volume fraction lead to a reduction in swelling stress up to 16-18% for the base case. However, more dissolution of smectite under some chemical conditions and the variation of the key parameters could result in further reduction of swelling and total stress up to 26%, which could have significant mechanical effects such as reduction of stress at the tunnel walls, and relaxation of fractures in the disturbed rock zone. While this modeling exercise improves understanding of the coupled processes that contribute to chemical and mechanical alteration in the EBS bentonite and NS clay formation, the results should be interpreted cautiously because of the limitations and assumptions in the model as discussed in Section 3.6. .

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List of Tables

Table 1. Mineral volume fraction (dimensionless, ratio of the volume for a mineral to the total volume of medium) of the EBS bentonite (Ochs et al., 2004) and the clay formation (Bossart, 2011; Lauber et al., 2000) used in the model.

Table 2. Pore water composition of EBS bentonite (Sonnenthal et al., 2008) and clay host rock (Fernandez et al., 2007).

Table 3. Kinetic properties for minerals considered in the model (Xu et al., 2006).

Table 4. Thermal and hydrodynamic parameters. Data for bentonite taken from Sonnenthal et al. (2008) and JNC (2000). Data for clay formation taken from Thury (2002) and Soler (2001).

Table 5. Swelling stress (MPa) calculated for three cases at the end of 1000-year simulation at point A. The difference in the swelling stress between cases $\sigma=f(SI)$ and $\sigma=f(SI,C)$ is the contribution of ion concentration change on the swelling stress reduction, and the difference in swelling stress between cases $\sigma=f(SI)$ and $\sigma=f(SI,C,Sc)$ is the contribution of both ion concentration and smectite mass fraction change on the swelling stress reduction (see the last column in term of percentage).

List of Figures

Figure 1. Domain for the test example of a bentonite back-filled horizontal emplacement drift at 500 m (Rutqvist et al., 2014). Modeling monitoring points: A: inside the bentonite near the canister, B: inside the bentonite and near the EBS-NS interface, C: inside the clay rock formation and near the EBS-NS interface, D: inside the clay rock formation at a distance of 10 m from the canister. “High T”: 200 °C; “Low T”: 100°C.

Figure 2. Swelling pressure versus mass fraction of smectite for various bentonites. ▲, FEBEX bentonite (ENRESA, 2000); ●, Montigel bentonite (Bucher and Muller-Vonmoos, 1989); □, Kunigel VI bentonite (JNC, 1999); ○, Kunigel bentonite (Konime and Ogata, 1996), ◆ are data for reference material from Czech, Danish, Friedland, Milos Deponit CA-N, Kutch (Indian) and Wyoming MX-80 (Karnland et al., 2006). The lines are linear regression curves.

Figure 3. Temperature evolution at points A, B, C, and D.

Figure 4. The temporal evolution of water saturation at points A, B, C, and D.

Figure 5. The temporal evolution of pore pressure at points A, B, C, and D (note that before the bentonite becomes fully saturated, it is gas pressure rather than pore pressure).

Figure 6. The temporal evolution of smectite volume fraction at points A, B, C, and D. The initial volume fraction of the smectite in bentonite is 0.314 (see Table 1), so in comparison with initial amount, smectite volume fraction decrease by about 11% () at point A, similarly we can obtain the decrease percentage at the rest of points)

Figure 7. The temporal evolution of illite volume fraction at points A, B, C, and D.

Figure 8. The temporal evolution of Al and K concentration at point A (near the canister).

Figure 9. Temporal evolution of illite volume fraction at point A, B, C and D for base and sensitivity case: K concentration in the clay formation equal to 0.01 mol/L.

Figure 10. Temporal evolution of smectite volume fraction at points A, B, C, and D for base and sensitivity case with K concentration in the NS clay formation equal to 0.01 mol/L.

Figure 11. Temporal evolution of smectite volume fraction at point A, B, C and D for base and sensitivity case: no K-feldspar dissolution.

Figure 12. Temporal evolution of illite volume fraction at point A, B, C and D for base and sensitivity case: no K-feldspar dissolution.

Figure 13. Temporal evolution of smectite volume fraction at point A, B, C and D for base and sensitivity case: K-feldspar dissolution rate is two orders of magnitude higher.

Figure 14. Temporal evolution of illite volume fraction at point A, B, C and D for base and sensitivity case: K-feldspar dissolution rate is two orders of magnitude higher.

Figure 15. Simulation results of mean total stress, pore pressure, and thermal stress at point A for the “low T” and “high T” scenario, respectively.

Figure 16. Simulation results of mean total stress, pore pressure, and thermal stress at point B for the “low T” and “high T” scenario, respectively.

Figure 17. Simulation results of swelling stress at point A for the “low T” (100°C) and “high T” (200°C) scenarios, respectively. Stress (σ) as a function of: liquid saturation (Sl), pore water ion concentration (C) and mass fraction smectite (Sc) changes.

Figure 18. Simulation results of swelling stress at point B for the “low T” (100°C) and “high T” (200°C) scenarios, respectively. Stress (σ) as a function of: liquid saturation (Sl), pore water ion concentration (C) and mass fraction smectite (Sc) changes.