

Prospects for coupled modelling

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ISBN 978-952-478-734-5 (print, Edita Prima Oy, Finland 2012)
ISBN 978-952-478-735-2 (pdf)
ISSN 1796-7171

SAVAGE David (Savage Earth Associates Ltd). *Prospects for coupled modelling. STUK-TR 13. Helsinki 2012. 44 pp.*

Keywords: KBS-3 concept, bentonite, T-H-M-C-B processes, interaction, coupled modelling, future capabilities

Executive summary

Clay-based buffer and tunnel backfill materials are important barriers in the KBS-3 repository concept for final disposal of spent nuclear fuel in Finland. Significant changes can be expected to occur to the properties and behaviour of buffer and backfill, especially during re-saturation and through the thermal period. Reactions will occur in response to thermal and chemical gradients, induced by the thermal output of the spent fuel and at interfaces between different barrier materials, such as cement/clay, steel/clay etc. Processes of ion exchange, mineral dissolution and precipitation, and swelling can lead to significant re-distribution of mass and evolution of physical properties so that reliable predictive modelling of future behaviour and properties must be made.

This report evaluates the current status of modelling of buffer and backfill evolution and tries to assess the potential future capabilities in the short- to medium-term (5–10 years) in a number of technical areas:

- Non-isothermal (T-H-M-C-B) modelling and the potential for cementation.
- The consistency of models.
- Swelling pressure.
- Cement-bentonite interactions.
- Iron-bentonite interactions.
- Mechanical (shear) behaviour.
- Bentonite erosion.

A key issue for all topics is the issue of up-scaling of models and data from laboratory and *in situ* experiments to the physical and temporal scales of interest to safety assessment. Information from analogue systems may help in some instances, but care needs to be taken that models employed are fit for purpose.

Relatively little progress has been made in the area of T-H-M-C-B modelling in that models developed thus far have addressed T-H-M or T-H-C problems, but modelling the interaction of M (mechanical) and C (chemical) processes has been very limited, in part due to a lack of understanding of process couplings. Chemical processes have been mainly restricted to cation exchange, surface complexation and the (equilibrium) dissolution-precipitation of trace minerals in the bentonite. New computer codes are now emerging (with some currently tested and in use) that can combine mechanical and chemical processes in a more satisfactory manner and it is to be expected that greater progress will be made in this area in the next 5–10 years.

There is much debate currently surrounding the nature of porosity in compacted bentonite. Some researchers favour a single porosity model, whereas others prefer a multiple porosity description. This debate impacts upon a whole range of important processes such as clay swelling, ionic transport, pore fluid evolution and bentonite erosion *inter alia*. There is much research focused

on this topic and it is anticipated that progress will be made through the Äspö EBS Task Force and BRIE Projects in the near to medium future.

Clay dissolution-precipitation reactions have been omitted from most pore fluid evolution and T-H-M-C-B modelling studies in the past, mainly due to the limitation of computer codes, but also due to a perception of the potential minor impact of such processes. In future, it is likely that these reactions will be included in near-field evolution models, bringing greater consistency between the modelling of pore fluid evolution and clay alteration (e.g. illitisation).

Clay swelling is currently evaluated using empirical correlations of swelling pressure with compaction density, coupled with Donnan exclusion in saline groundwaters. Swelling is excluded from other models of near-field interactions, but could relatively easily be incorporated into future models. It is considered unlikely that a mechanistic understanding of clay swelling will be developed in the next 5–10 years, but it is believed that clay swelling will be brought into more modelling studies of near-field evolution.

Cement-bentonite interactions are currently treated as a T-H-C process in coupled models, but clay swelling could feasibly be incorporated into future models. There is strong non-linear coupling between chemical and physical processes and it is considered unlikely that changes in permeability/diffusivity will be able to be predicted in the short to medium term. The ability to predict porosity changes is currently limited by the capabilities to model mineral growth. Although a theoretical framework to model growth exists, progress is hampered by a lack of critical data such as mineral-fluid interfacial free energies. It is unlikely that this situation will improve significantly in the next 5–10 years.

Models of iron-bentonite interactions are similar to those of cement-bentonite in that processes are strongly coupled in a non-linear fashion. This problem is also treated as a T-H-C issue, but modelling progress is held back by uncertainties surrounding the nature of the products of iron-bentonite interaction and key reaction mechanisms. However, these uncertainties could be reduced significantly in the next 5–10 years. Processes concerning gas (chemical and physical) are excluded from current models of iron-bentonite interactions, but it is likely that these will be included in future models of this type.

Most modelling of the mechanical behaviour of bentonite during shear relies on a constitutive law for elasto-plastic behaviour. There are new models being developed which move away from the conventional T-H-M soils approach which treats bentonite as an elasto-plastic porous medium with water or air occupying a notional porosity with the inclusion of additional process models to take into account the very high observed water suctions, intrinsic permeability variation and macroscopic swelling

of partially saturated compacted bentonite. It is likely that this type of model will be considered for bentonite material properties in future calculations of this type.

The currently-available model of bentonite erosion accounts for forces that control the expansion of bentonite from a deposition hole into a fracture (dynamic force-balance model), and for the effects of particle and ionic concentrations on the viscosity of the expanded bentonite (viscosity model). The force-balance and viscosity models have been combined into an overall model of buffer erosion, which accounts for both the Brownian motion of individual clay colloids into the flowing groundwater and for the advection of sols that form within the fracture as the bentonite expands and becomes less dense and less viscous. In this model, there is no explicit link between the chemical composition of groundwaters, ion exchange in the bentonite, the formation of sols, and the mechanical effects of the erosion process. In reality however, bentonite erosion is a coupled H-M-C problem and it is likely that coupled computer codes incorporating mechanical and chemical processes will be used in future to address this issue.

SAVAGE David (Savage Earth Associates Ltd). Kytkeytyjen mallien tulevaisuudennäkymät loppusijoituksen turvallisuusperustelussa. STUK-TR 13. Helsinki 2012. 44 s.

Avainsanat: KBS-3-konsepti, bentoniitti, T-H-M-C-B-prosessit, vuorovaikutus, kytketty mallinnus, tulevaisuuspotentiaali

Tiivistelmä

Rakennetuissa päästöesteissä voi odottaa tapahtuvan merkittäviä muutoksia loppusijoitustilojen uudelleensaturoitumisen, tilojen termisen vaiheen ja myöhempien vaiheiden aikana. Muutosten ajavina voimina toimivat tiloihin syntyvät termiset ja kemialliset gradientit ja niistä seuraavat monet vuorovaikutukset. Tässä työssä pyritään arvioimaan erityisesti kapselipuskurin ja tunnelitäytteen evoluution kuvaamiseen käytettyjen mallinnusmenetelmien nykytilaa ja tulevaisuudennäkymiä 5–10 vuoden aikavälillä. Kaikissa mallinuksissa keskeisen ongelman muodostaa laboratoriotulosten ja *in situ* -kokeiden skaalaaminen turvallisuusarvioinnin kannalta mielekkäisiin fyysisiin ja ajallisiin mittakaavoihin. Luonnonanalogoista saatava informaatio saattaa varauksin olla avuksi näissä skaalauksissa.

Kytkeytyissä T-H-M-C-B-malleissa on tapahtunut jonkin verran edistystä, jos mallinnus on jaettu T-H-C- ja T-H-M-osamallinuksisiin. Mekaanisten (M) ja kemiallisten (C) vuorovaikutusten mallinuksissa on vain rajallista edistymistä johtuen osin puutteellisesta prosessiymmärryksestä. Uusien mallinnusohjelmien avulla mekaanisten ja kemiallisten prosessien kytkeminen onnistunee paremmin lähitulevaisuudessa.

Tiivistetyn bentoniitin huokoisuuden luonnetta T-H-C-malleissa kuvataan nykyisellään kahdella ristiriitaisella tavalla. Ristiriitaisuutta pystytään oletettavasti ratkomaan muutamien vuosien kuluessa. Savimineraalien liukenemis–saostumisreaktiota ei ole huomioitu kytkeytyissä mallinuksissa. Jatkossa nämä reaktiot todennäköisesti sisällytetään lähialueen mallinuksisiin. Bentoniitin paisumista mallinnetaan nykyisin vain empiirisin mallein. On luultavaa, että mallinnustehtävät ulotetaan lähitulevaisuudessa yhä enemmän käsittämään myös paisumista, mutta samalla on epätodennäköistä, että paisuminen kyettäisiin mekanistisesti hallitsemaan. Sementti–bentoniitti -vuorovaikutukseen liittyy useita kiinnostavia prosesseja, mutta tietojen puuttumisen vuoksi niitä ei kyetä kunnolla mallintamaan. Tilanne ei ilmeisesti lähitulevaisuudessa oleellisesti parane. Myös rauta–bentoniitti -vuorovaikutuksiin liittyy epälineaarisia kytkentöjä, mutta näihin liittyviä epävarmuuksia luultavasti pystytään pienentämään lähitulevaisuudessa. Rauta–bentoniitti -vuorovaikutukseen liittyvä kaasun tuotanto todennäköisesti sisällytetään mallein tulevaisuudessa.

Leikkaussiiroksen kohteeksi joutuvaa bentoniittia kuvataan uusissa mallinuksissa elasto-plastisena huokoisena materiaalina, johon voidaan lisäksi sisällyttää useita T-H-M käyttäytymiseen vaikuttavia muuttujia. Tämä mallinnustapa todennäköisesti jatkuu lähitulevaisuudessa. Nykyisin käytössä oleva bentoniitin eroosiomalli hyödyntää varaustasapainoja ja viskositeettimuutoksia. Eksplisiittiset linkit systeemin kemiallisiin muutoksiin kuitenkin puuttuvat. Tulevaisuudessa luultavasti kytketään sekä kemialliset että mekaaniset prosessit bentoniittieroosion kuvaukseen.

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1 Introduction

Clay-based buffer and tunnel backfill materials are important barriers in the KBS-3 repository concept for final disposal of spent nuclear fuel in Finland (TKS-2009 – Posiva, 2010). Properties of these materials that can affect repository performance include:

- low hydraulic conductivity that reduces transport of corrodants to the canister and transport of radionuclides to the geosphere;
- a low chemical activity of water that prevents the survival of microorganisms that could be detrimental to the long-term integrity of the canister;
- a swelling pressure to establish tightness and self-sealing ability as well as sustaining contacts with the host rock and the canister; and
- a sufficiently high deformability to absorb a certain amount of rock movements, preventing the canister from being ruptured.

These properties should be achieved both in the design (present) and target (future) states. However, as Posiva point out (TKS-2009, Posiva, 2010, p295): *“the performance targets, and requirements and the target properties of the host rock consider those properties of the EBS and host rock that are essential for the safety functions, but their fulfilment can usually be examined only indirectly, by modelling”*. This places modelling (conceptual and numerical) in a key role in repository design and safety assessment.

Changes can be expected to occur to the properties and behaviour of buffer and backfill, especially during re-saturation and through the thermal period. Reactions will occur in response to thermal and chemical gradients, induced by the thermal output of the spent fuel and at interfaces between

different barrier materials, such as cement/clay, steel/clay etc. Processes of ion exchange, mineral dissolution and precipitation, and swelling can lead to re-distribution of mass and evolution of physical properties so that reliable predictive modelling of future behaviour and properties must be made.

This report evaluates the current status of modelling of buffer and backfill evolution and tries to assess the potential future capabilities in the short- to medium-term (5–10 years) in a number of technical areas:

- Non-isothermal T-H-M-C(B) evolution and potential for cementation.
- Consistency of models.
- Swelling pressure.
- Cement-bentonite interactions.
- Iron-bentonite interactions.
- Mechanical (shear) behaviour.
- Bentonite erosion.

1.1 Process Up-scaling

An issue common to all the above technical areas is the problem of up-scaling data from laboratory and in situ experiments to the physical and temporal scales relevant to models used to inform safety assessment. This may mean ensuring that all processes relevant to long-term barrier evolution are included (e.g. the need to include mineral dissolution-precipitation reactions in models of bentonite pore fluid evolution – Savage et al., in press), that key parameters are scaled accordingly (e.g. reactive surface area of minerals – Maher et al., 2009), that natural systems evidence is sought to confirm the relevance/magnitude of selected reactions (e.g. Savage, 2011b), and/or that system simplifications to model at larger scales are appropriate.

A schematic illustration of this point is shown in Figure 1:

- laboratory experiments can provide quantitative mineral dissolution rates, ion exchange data, pore fluid compositional data, and data on (fast) mineral growth.
- *In situ* experiments can provide data concerning the spatial scale of pore fluid alteration (at short timescales).
- Industrial analogues provide a bridge between well-constrained short-term laboratory data and the somewhat less well-constrained data from natural systems.
- Where available, natural analogues can help up-scaling by placing short-term experimental evidence in context (suitability of reaction mechanisms; mineral dissolution and growth rates; selection of secondary minerals; evidence for physical properties changes).

Up-scaling is thus a common thread to the discussions of each of the technical issues presented in this report.

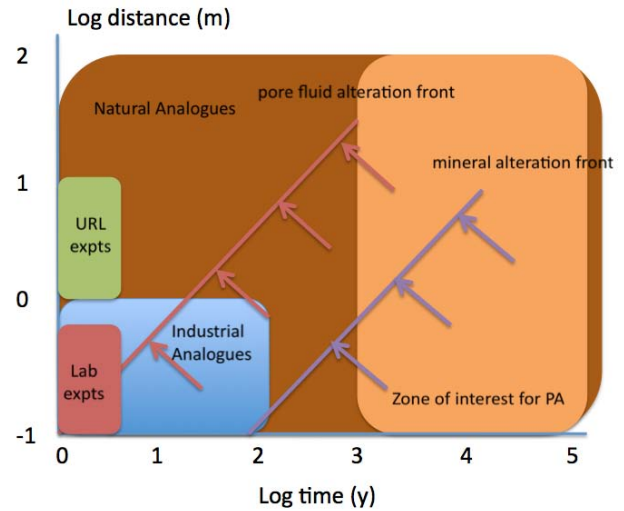


Figure 1. Schematic illustration of the differing space and temporal scales associated with different data sources and those required for performance assessment (PA). The positions of hypothetical pore fluid and mineral reaction fronts are schematic and their locations will be a function of site-specific groundwater flow/diffusion and the nature of the interfacial reaction concerned (from Savage, 2011b).

2 Non-isothermal (T-H-C-M-B) modelling and potential for cementation

2.1 Background

Gradients in temperature and humidity during the period of bentonite re-saturation and beyond may lead to the redistribution of mass, alteration of the montmorillonite clay content, and potentially to the cementation of mineral grains within the buffer. Water uptake is a slow process because of the very low permeability of the buffer or backfill and the surrounding fractured hard rock. Flow through the rock is mainly through fractures, which control the rate and location of incoming water for saturating the bentonite, such that wetting and swelling could be uneven over its interface with the rock, resulting in uneven swelling pressure. In general, the uptake of water from the bentonite will create a negative pressure, which will dehydrate the rock in the immediate vicinity.

As heat is released from waste packages, processes involved in the evolution of the bentonite buffer include thermally induced distribution of initial pore water in the clay during the early thermal phases. On the outer part of the bentonite buffer, water is taken up from the rock-water interface, with potential swelling of the bentonite in this region. On the inner part of the bentonite buffer, next to the waste canister, moisture content decreases (desiccation), with potential shrinkage. Chemically within the bentonite buffer, there may be the dissolution of buffer minerals and precipitation of chemical compounds so that mass is redistributed around the buffer according to dependence of mineral solubility with temperature.

Hydrothermal experiments carried out by SKB with Wyoming bentonite heated to 150–200°C have shown that heating and cooling may lead to the precipitation of silica in various forms (SKB, 2010, p126). The precipitation could cause cementation effects, including a strength and stiffness increase,

which has been demonstrated in several laboratory investigations (Pusch and Karnland, 1988). In the Buffer Mass Test at Stripa (90°C maximum temperature), the buffer was analysed with respect to the distribution of silica, but no definite conclusion could be drawn regarding possible enrichment in the coldest part. However, the study of cooling-related precipitation of silica was confirmed by a coupled modelling study of the Kinnekulle analogue (Pusch et al., 1988).

Posiva has recognised the potential importance of such processes and considers mineral transformation and cementation as a key R&D task requiring further studies (TKS-2009, Posiva, 2010, p372).

2.2 Analysis

Modelling in this topic area generally falls into one of two categories:

- T-H-M modelling, focusing on the mechanical response to gradients in temperature and humidity. Chemical effects are for the most part ignored (e.g. Rutqvist et al., 1999; Birkholzer et al., 2005; Rutqvist and Tsang, 2008; Bond and Watson, 2008; Bond et al., 2010a).
- T-H-C(B) modelling focusing on the chemical response to gradients in temperature and humidity. Mechanical effects are ignored (e.g. Pusch et al., 1988; Arcos et al., 2000, 2008; Arthur and Zhou, 2005; Samper et al., 2008b; Itälä, 2009; Fernández et al., 2011).

There are very few, if any modelling studies that consider both mechanical and chemical properties of bentonite. In the past, this has arisen principally because of insufficient computing power, but more recently due to a perceived lack of understanding of mechanical-chemical couplings (e.g. SSM comments on the SR-Can safety assessment – Savage et al.,

2008, p12). Some examples that have considered T-H-M-C(B) interactions are discussed below.

Samper and co-workers have produced a coupled model of the FEBEX mock-up test at the Grimsel URL in Switzerland using the INVERSE-FADES-CORE computer code (Zheng and Samper, 2008). Their coupled T-H-M-C model accounts for thermal and chemical osmosis and bentonite swelling with a state-surface approach. The model reproduces measured temperature and cumulative water inflow data and fits relative humidity data at the outer part of the buffer, but underestimates relative humidities near the heater. Zheng and Samper believe that dilution due to hydration and evaporation near the heater are the main processes controlling the concentration of conservative species while surface complexation, mineral dissolution/precipitation and cation exchange also affect reactive chemical species. Results of sensitivity analyses to chemical processes show that pH is mostly controlled by surface complexation on clay while dissolved cation concentrations are controlled by clay cation exchange reactions. However, it should be noted their model did not include kinetic mineral dissolution-precipitation processes and completely ignored the potential dissolution of montmorillonite. The model also assumed that all water is accessible to solutes for transport and geochemical reactions, thus ignoring any potential discretisation of water into different structural types (e.g. Bradbury and Baeyens, 2003). The model also excluded CO₂ degassing and dissolution processes, which would impact significantly upon predicted carbonate precipitation and pH.

Thomas and co-workers have developed the COMPASS computer code which implements a fully coupled thermo/hydro/mechanical formulation for unsaturated clays, including certain aspects of reactive chemical transport (Seetharam et al., 2007). The model includes conduction, convection and latent heat transfer; moisture transfer in both the liquid and vapour phases due to liquid and vapour gradients; and chemical transfer due to both advection and hydrodynamic dispersion are also considered. The heat transfer formulation includes flow due to conduction, convection, and latent heat of vaporisation. Moisture movement in both liquid and vapour form, caused by pressure gradients is governed by Darcy's law, and vapour transfer due to diffusion is represented by a modified Philip

and de Vries approach, (Ewen and Thomas, 1989). Chemical transport is governed by advection and hydrodynamic dispersion. Geochemical interaction is incorporated using an equilibrium-based approach. MINTEQA2, a geochemical model is utilised to solve the chemical equilibrium equations (Allison et al., 1991). Chemical reactions included are ion exchange reactions involving major cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺) and precipitation–dissolution of trace minerals (calcite, dolomite, anhydrite and halite). The dissolution of major silicates (smectite, quartz) or kinetics was not considered, thus omitting any assessment of the redistribution of silica. Finally, the stress/strain behaviour of the clay is represented with an elasto-plastic constitutive relationship and is governed by a stress equilibrium equation (Thomas and He, 1995). An elastic constitutive deformation model was implemented in their model.

Xie et al. have assessed the chemical composition of porewaters extracted from compacted bentonite subjected to simultaneous heating and hydration with a non-isothermal reactive transport model by coupling the geochemical software PHREEQC with the object-oriented FEM simulator GeoSys/RockFlow (Xie et al., 2006). Reactive transport modelling included heat transport, two-phase flow, multicomponent transport and geochemical reactions in the liquid phase, i.e. ion exchange, mineral dissolution/precipitation and equilibrium reactions (but not kinetic reactions). The coupling processes are shown schematically in Figure 2. Time is discretised using Euler timesteps, whilst spatial discretisation is by the Finite Element Method. For each timestep, two-phase flow and heat transport are calculated. Because these two processes are strongly coupled via material properties, the program iterates between them. Reactive mass transport is separated using an operator splitting technique and a two-step non-iterative sequential approach. In the first step, conservative transport is calculated for all chemical components based on the phase velocities calculated for two-phase flow, while in the second step the geochemical reactions are simulated. In this work, transport and reactions are calculated only in the liquid phase. For the reaction step, the geochemical program PHREEQC, version II (Parkhurst and Appelo, 1999) is employed. Unlike other modelling teams, Xie et al. simulated the dissolution and precipitation of aluminosilicates as well as trace

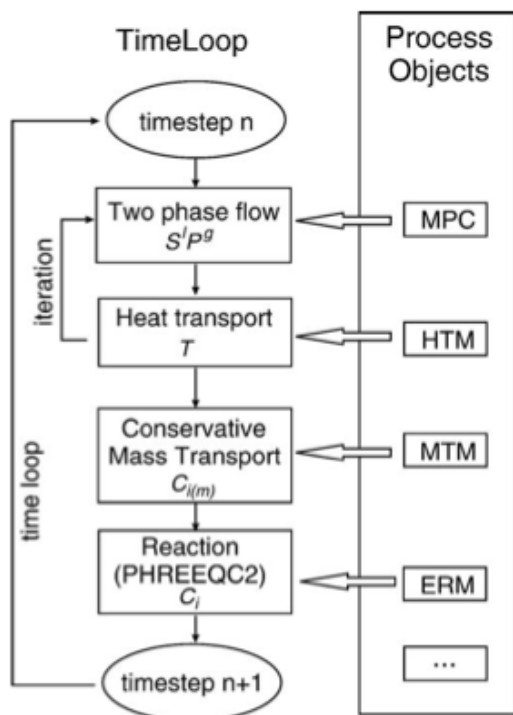


Figure 2. Schematic representation of the coupling concept used in GeoSys/RockFlow. (from Xie et al., 2006).

minerals such as calcite and gypsum, although only as equilibrium reactions (Figure 3). According to Xie et al., simulations show that the easily soluble minerals in bentonite determine the porewater chemistry. Temperature affects both two-phase flow and geochemical reactions. Porosity change due to dissolution/precipitation was low during the

experiment. However, changes of the effective porosity caused by bentonite swelling can be very large.

Historically, there have been fundamental differences in the representation of porosity and water disposition between T-H-C and T-H-M modelling studies. Quintessa has tried to tackle this problem by developing a model for the porosity and water disposition in bentonite in its QPAC computer code that is more detailed than models used to date in most T-H-M modelling studies under variably saturated conditions (Bond et al., 2010a, Bond et al., 2010b; Quintessa, 2010). The new model moves away from the conventional T-H-M soils approach which treats bentonite as an elasto-plastic porous medium, with water or air occupying a notional porosity with the inclusion of additional process models to take into account the very high observed water suctions, intrinsic permeability variation and macroscopic swelling of partially saturated compacted bentonite. It replaces the empirical parameterisation usually employed in T-H-M models with a direct representation of the water disposition, pore structure and relevant processes, albeit at an abstracted level. This new model differentiates between water which can be considered to be 'bound' or otherwise immobile (specifically water held in bentonite interlayer sites and double layers) and water which is 'free' or mobile, comprising liquid water and water vapour. The disposition of the water is then constrained using thermodynamic data derived directly from laboratory studies to

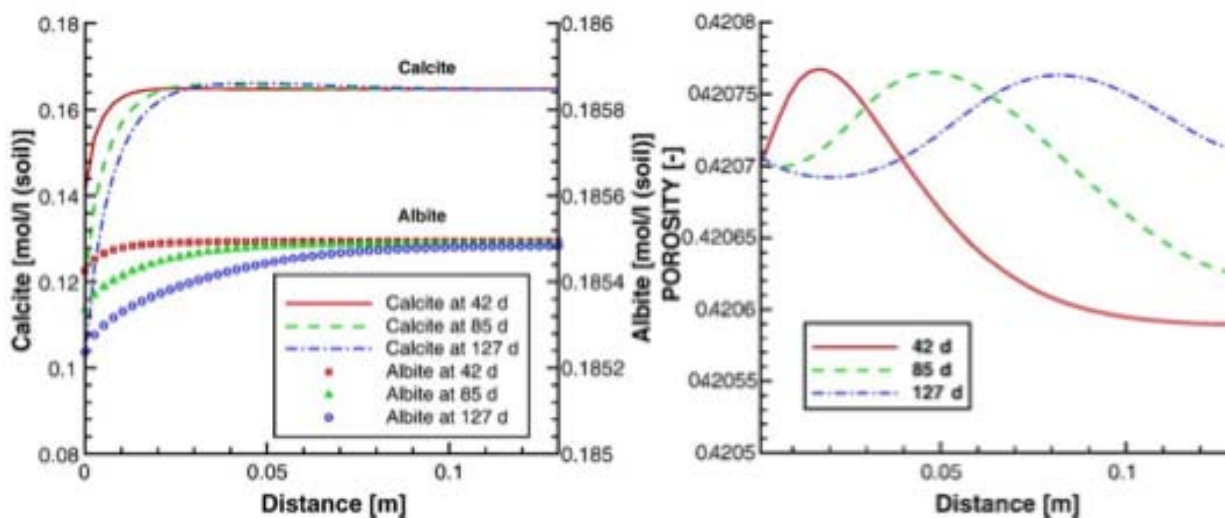


Figure 3. Mineral dissolution/precipitation (left), and porosity change (right) for the compacted bentonite (from Xie et al., 2006).

give a localised energy balance (including bentonite free energy and rock stress) which allows a bound water retention curve to be dynamically evaluated. In addition, a simple mass and volume balancing approach allows the micro-scale changes in porosity and bentonite grain volume to be converted into a macro-scale bulk volume change and water retention capacity. Indeed, the model largely abandons the concept of ‘porosity’ as a useful term when describing the state of fluids in bentonite, naturally considering ‘capacities’ to hold different types of water dependent on the physical and chemical condition of the bentonite. Migration of liquid water, air and water vapour is handled using conventional multi-phase-flow theory with some simple adjustments to selected parameterisation (mainly relative permeability and suction curves) to take into account the different water and air distribution models. The new model has been successfully applied to a series of benchmarking studies in the EU THERESA project (for SSM). To date, Quintessa has not applied this model to T-H-M-C problems, but the QPAC code is capable of addressing important issues in this topic area (Quintessa, 2010).

2.3 Up-scaling issues

The issue of up-scaling has been addressed through the ‘calibration’ of models through the results of *in situ* tests (e.g. Arcos et al., 2002, 2008; Arthur and Zhou, 2005; Samper et al., 2008b; Zheng et al., 2010), and also by investigation of natural analogues (e.g. Pusch et al., 1988). However, the key process of thermally-driven clay dissolution has been omitted from most models (e.g. Arcos et al., 2002, 2008; Samper et al., 2008b; Zheng et al., 2010).

2.4 Summary

Most current models either tackle T-H-C or T-H-M problems, with very few being capable of addressing the combination of mechanical and chemical processes. Some computer codes (QPAC, COMPASS, INVERSE-FADES-CORE) are now capable of handling simple C-M couplings. Although the re-distribution of silica under a thermal gradient could be modelled by these codes, the process of cementation cannot.

2.5 Future prospects

It may be realised from the above discussions that currently, relatively few computer codes and

modelling teams are capable of modelling T-H-M-C interactions. Microbiological aspects (B) are completely absent from these codes despite considerable interest in the published literature in the role of microbes in a whole range of geochemical processes. However, the last five years has seen the first steps in coupling chemistry to the more established T-H-M modelling that has occurred over the last twenty years through projects such as DECOVALEX.

Posiva and SKB are developing their capabilities in this area through the EBS Task Force and BRIE (Bentonite Rock Interaction Experiment) projects. In the former, two benchmark data sets are to be prepared to which modelling can be applied using alternate porosity concepts (multi-porous, including Diffuse Double Layer, and ion-equilibrium) (Steeffel et al., 2010). In addition, it has been decided that it would be advantageous to couple the Donnan equilibrium (or ionic equilibrium) calculations with calculations of swelling pressure in the CrunchFlow computer code (Steeffel et al., 2010). Steeffel et al. also recommend that processes such as thermosmosis, microstructure evolution, existence of different states of water in the bentonite, and existence of a threshold hydraulic gradient for water flow be incorporated in future computer codes for T-H-M-C (Steeffel et al., 2010).

Notwithstanding the efforts of Posiva and SKB in this area, it seems likely that in the next 5-10 years we will see the following incorporated into T-H-M-C-B modelling:

- Kinetics of mineral dissolution and growth. This process is already included in T-H-C models and is thus a matter of time before incorporation into T-H-M-C modelling.
- Discretisation of different water types in bentonite. This is effectively already included in codes such as QPAC (Quintessa, 2010) and CrunchFlow (Steeffel et al., 2010).
- Donnan exclusion.
- Clay swelling. This is already included in some codes.
- Two-phase flow with participation of gas in geochemical reactions.
- Inclusion of some microbiological processes, such as catalysis of inorganic reactions.

However, it is considered unlikely that the effects of cementation could be quantitatively included in such models over this timescale.

3 Consistency of models

3.1 Background

Posiva and SKB use several seemingly independent and unconnected geochemical modelling approaches to address various aspects of the chemical evolution of the clay and clay pore fluids in the repository system. For example, at least three geochemical models are used to describe clay behaviour:

- An osmotic model is used to describe smectite clay swelling behaviour (e.g. Karnland and Birgersson, 2006; Hedin, 2004).
- Ion-exchange and clay surface site protonation / deprotonation models (usually developed in PHAST or PHREEQC) are used to describe long-term pore fluid evolution and interaction with groundwater (e.g. Hedin, 2004; Arcos et al., 2006).
- An empirical kinetic expression is used to describe the conversion of montmorillonite to illite (e.g. Karnland and Birgersson, 2006).

In addition, Posiva and SKB are considering use of a fourth model to describe the conversion of montmorillonite to non-swelling berthierine, as a result of interactions between the clay and the corroding cast iron insert (Karnland and Birgersson, 2006).

Moreover, a single porosity model is used to describe clay swelling (Birgersson and Karnland, 2009), whereas a multiple porosity model is used to describe pore fluid evolution (Arcos et al., 2006), ionic transport (Ochs et al., 2006) and bentonite erosion (Neretnieks et al., 2010).

3.2 Analysis

3.2.1 Porosity models

The conceptual understanding of the nature of porosity in compacted bentonite has an impact upon several safety-relevant processes, such as:

- The evolution of pore fluid chemistry with time.
- Bentonite erosion.

- Ionic transport.
- Clay swelling.

Currently, there is much debate surrounding this issue, but in general, researchers envisage either a system with different porosity types, or a system with a single porosity.

Multiple porosity model

Many researchers view compacted bentonite as possessing different types of porosity, (e.g. Kozaki et al., 1998, 2001, 2005; Bradbury and Baeyens, 2002, 2003; Muurinen and Carlsson, 2007; Glaus et al., 2007) (Figure 4):

- ‘total’ porosity which refers to the total volume of voidage, without discrimination regarding location or type.
- ‘interlamellar/interlayer’ water, located in the interlayer spaces of individual clay particles, between the individual tetrahedral-octahedral-tetrahedral (TOT) sheets (Bradbury and Baeyens, 2003). This is considered to be a few monolayers thick and because of its more structured nature, is likely to have different properties from so-called ‘free’ water.
- ‘external’ water can be viewed as being of two types:
 - that which consists of water in electrical double layers on the surfaces of the clay particles (‘double layer water’);
 - ‘free water’ (Bradbury and Baeyens, 2003) or ‘chloride’ porosity (Muurinen and Carlsson, 2007), which consists of water as interconnected thin films on the outside of clay stacks and also as films surrounding other minerals (e.g. quartz) in the bentonite.

The amounts of each porosity type vary with compaction density in bentonite according to Muurinen and Carlsson (2007), with ‘free water’ or ‘chloride

porosity' being significantly less than the total porosity as compaction density increases. If calculating the evolution of porewater chemistry, it is then a moot point which 'porosity' should be considered to evaluate solute concentrations. Seemingly, some authors opt to use the 'free' or 'geochemical' porosity (e.g. Fernandez and Villar, 2010), whilst others use 'total' porosity (e.g. Arcos et al., 2006). Clearly, this can lead to confusion and different results from the same basic assumptions.

In terms of ionic transport, diffusion of cations is envisaged to take place both through the interlamellar porosity and the free porosity, whereas diffusion of chloride and other anions takes place solely through the free porosity (e.g. Glaus et al., 2007). At high ionic strengths, diffusion of cations is thought to take place preferentially through the free porosity. This interpretation leads to an effective diffusion coefficient which varies according to ionic strength.

Single porosity model

An alternative conceptual model to that described above is offered by Karnland and co-workers (Karnland et al., 2002; Birgersson and Karnland, 2009) which consists of a bentonite-pore fluid system consisting of one porosity type and where pore fluid composition is controlled by ion equilibria within the interlamellar pore space involving two basic processes:

- Donnan equilibrium which reduces concentrations of external ions compared with external pore fluids;
- Cation exchange, which affects systems only with more than one type of cation.

Consequently, the clay-pore fluid system is envisaged to consist of clay particles acting as macro-ions, and the entire clay-water system may be viewed as a 'polyelectrolyte'.

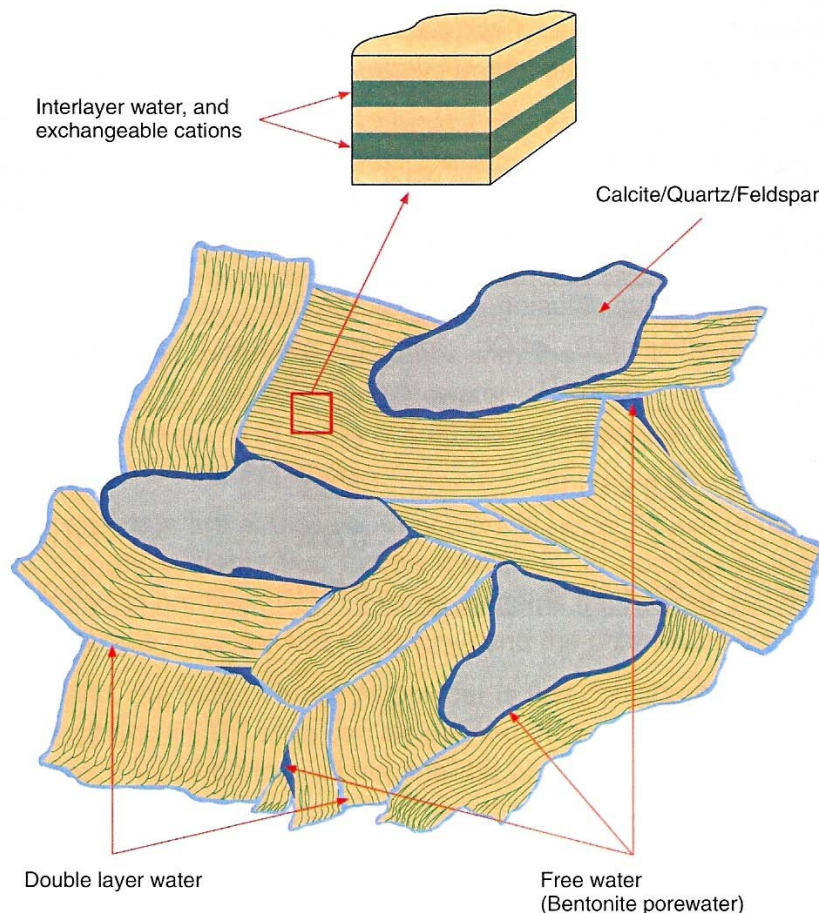


Figure 4. Schematic diagram of the nature of water in compacted bentonite (from Bradbury and Baeyens, 2003).

Birgersson and Karnland (2009) argue that the acceptance of the existence of only one type of porosity in compacted bentonite obviates the need to describe two separate methods of describing anion and cation diffusion and thus their model brings a greater symmetry to the understanding of ionic transport in compacted bentonite. Thus removing all but one type of pore structure greatly reduces the amount of model parameters to one, the interlayer pore diffusivity (D_c). Furthermore, the single pore type model is not only consistent with, but also allows for calculation of, the swelling pressure under various physicochemical conditions (Karnland et al., 2005; Birgersson et al., 2008).

The findings of the Birgersson and Karnland (2009) also have large implications for the conceptual view of pore water chemistry and hence, the trigger for buffer erosion. Since in their model, the major part of cations and anions reside in the interlayer pores, this volume is of crucial importance and cannot be ignored in characterising the bentonite pore water chemistry. This approach is thus in sharp contrast to the ‘multiple porosity’ model where pore fluid is considered to reside in the ‘free water’ porosity only.

3.2.2 Effects of clay hydrolysis reactions

Clay hydrolysis (dissolution) reactions can be important in two areas of safety-relevant processes in buffer and backfill, namely through:

- potential effects on pore fluid chemistry evolution, particularly pH and,
- long-term transformation to other silicates, such as clays (illite, beidellite, saponite), or other silicates such as berthierine (through interaction with steel canister components) and zeolites (through interaction with cement or concrete).

Routinely, however, this process is ignored in the modelling of barrier evolution.

Bentonite pore fluid evolution

Geochemical models of clay pore fluid evolution have two key roles in a safety assessment. Firstly, geochemical modelling is used to define a pore fluid for radionuclide solubility and transport calculations within the bentonite buffer once canister perforation has occurred (e.g. Duro et al., 2006),

and secondly, the modelled clay pore fluid cation composition is used as a ‘switch’ to turn on or off buffer erosion processes during intrusion of melt-water in glacial cycles (e.g. Neretnieks et al., 2010; SKB, 2011).

Posiva and SKB’s approach to modelling clay pore fluids is presented in reports by Arcos et al. (2006) and Hedin (2004). This model is based primarily around assumed chemical equilibrium between Na^+ , K^+ , Ca^{2+} , and Mg^{2+} aqueous species and cation exchange sites on montmorillonite, but also includes protonation-deprotonation of clay edge surface sites, and dissolution-precipitation of the trace mineral constituents, calcite and gypsum. This model is based on short-term laboratory experiments aimed at characterising clay pore fluids to establish chemical boundary conditions for laboratory sorption experiments (e.g. Bradbury and Baeyens, 2003).

Clay hydrolysis has been excluded from these models because: “*the process of smectite dissolution is, nevertheless, very slow... Thus, it seems reasonable to consider smectite dissolution as a process of minor importance in the geochemical evolution of the system*” (Arcos et al., 2006, introduction to Section 4.2.1). This exclusion of clay hydrolysis from models attempting to simulate the long-term evolution of the near-field system has recently been challenged as being unrealistic and unconservative (Savage et al., 2010a, in press).

Long-term mineral transformations

Clay hydrolysis is also excluded from the assessment of long-term mineral transformations, with Posiva and SKB relying upon empirical descriptions (e.g. Huang et al., 1993) of the long-term transformation to illite (Karnland and Birgersson, 2006). The role of clay hydrolysis in the potential transformation of montmorillonite to other silicates is also ignored (Karnland and Birgersson, 2006).

A consequence of the omission of clay hydrolysis reactions from Posiva and SKB’s models is that montmorillonite is preserved indefinitely in the near-field system, even over million-year timescales. However, this is contrary to natural systems evidence where smectite clays may undergo dissolution-precipitation reactions over assessment-relevant timescales at pH as low as 9 and tempera-

tures of 50–60°C (e.g. Savage et al., 2010b). It may be concluded therefore that although the approach adopted by Posiva/SKB may be satisfactory to interpret the results of laboratory or *in situ* experiments, it is not necessarily sufficient to be extended to the timescales of interest for safety assessment.

3.3 Up-scaling Issues

There is a need for models to be ‘fit for purpose’, in other words, that they consider all processes of relevance to bentonite evolution in the long-term. A good case in point is the general omission of clay dissolution-precipitation processes from models of bentonite pore fluid evolution (see comments under ‘Bentonite Pore Fluid Evolution’, above).

3.4 Summary

Models of a number of safety-relevant processes such as clay swelling, pore fluid evolution, ionic transport and colloidal properties/erosion in compacted bentonite use inconsistent assumptions concerning the nature of porosity, and the number and type of chemical reactions involved. This inconsistency in approach limits confidence in the understanding of these processes.

3.5 Future prospects

3.5.1 Porosity models

The investigation of porosity models for compacted bentonite is an explicit goal of the Äspö EBS Task Force Project (TKS-2009 – Posiva, 2010, p376). It seems almost certain therefore that some rationalisation of these models will take place in the next 5-10 years. Conceivably, it could be envisaged that a transition exists between a multiple porosity type at low to medium compaction densities and a single porosity type at high compaction densities (e.g. Bond et al., 2010b). This would then bring consistency to the models of pore water evolution, clay swelling and buffer erosion.

3.5.2 Clay hydrolysis reactions

To a certain extent, the exclusion of clay hydrolysis reactions from porewater evolution models is a result of inadequacies of computer codes such as PHAST (Parkhurst et al., 2004) and PHREEQC (Parkhurst and Appelo, 1999). Newer codes with more efficient use of computer resources mean that kinetic mineral dissolution-precipitation reactions could be included currently without overt penalty to simulation times. It is likely that these reactions will be included in future simulations of this type in the next 5–10 years.

4 Swelling pressure

4.1 Background

Smectite clays can absorb water into clay interlayers with the most important parameters being:

- the surface density of charge of the clay (swelling decreases with increasing charge density);
- the charge and solvation behaviour of the interlayer cations (swelling is greatest for ions such as sodium); and
- the electrolyte concentration or activity of water (swelling decreases with increasing salinity of the contacting solution).

Two categories of swelling are generally observed: *innercrystalline swelling* caused by the hydration of the exchangeable cations in the dry clay; and *osmotic swelling*, resulting from concentration gradients in ion concentrations between clay surfaces and pore water.

Models that have been proposed to describe the swelling pressure of clays have been reviewed by Karnland (1997), Savage (2005), Agus and Schanz (2008) and Arthur (2011) *inter alia*. These models can be classified as follows:

- *Empirical models* relate swelling pressure to the interlamellar distance between individual clay particles (Low, 1979, 1980). The models are relatively simple to use, but model parameters must be calibrated experimentally and results are not always easy to obtain or are physically meaningful (Grauer, 1986).
- *Diffuse double-layer (DDL) models*, which relate swelling pressure to repulsive interactions arising from the overlap of electrical double layers associated with the charged surfaces of clay particles, but are difficult to apply to highly compacted clays due in part to structural modi-

fications of water that occur in the interlamellar regions of clay particles (e.g. Low, 1987).

- *DLVO (Derjaguin-Landau-Verwey-Overbeek) models* are a permutation on the DDL models and have their basis in colloid chemistry but cannot in general be applied to clay swelling (Grauer, 1986). DLVO theory predicts a decreasing surface repulsion of clay platelets with increasing electrolyte concentration which becomes an attraction at high ionic strengths. For very small interparticular distances, the theory predicts an attraction for all ionic strengths, which is contrary to experimental evidence. The DLVO model thus suffers the same weaknesses as double-layer theory.
- *Thermodynamic models* describe the macroscopic properties of the clay-water system and do not lend themselves to consideration of microscopic properties (Sposito, 1972). This model is based on the connection between swelling pressure and the relative partial free energy, based on equilibrium thermodynamics.

4.2 Analysis

Posiva and SKB employ an empirical modelling approach that can be used to relate swelling pressure to saturated density as described by Hedin (Hedin, 2004) and consists of two components:

- An empirical expression which relates swelling pressure to the density of solids and an aqueous phase assuming the latter is initially pure water.
- An assumption of Donnan equilibrium to calculate changes in swelling pressure that would result if the clay were saturated with a salt solution of some specified composition.

The expression relating swelling pressure to density is:

$$P_s^{fresh} = AT \left(\exp \left(B \frac{\rho_{solid}(\rho_{day} - \rho_{water})}{\rho_{water}(\rho_{solid} - \rho_{day})} \right) - 1 \right) \quad (1)$$

where A and B are fitting parameters, T is temperature ($^{\circ}\text{K}$), and ρ_{day} , ρ_{water} , and ρ_{solid} are the densities of saturated clay, water, and solid clay particles, respectively. The correction applied for salinity is:

$$P_s^{saline} = \sqrt{(P_s^{fresh})^2 + (2RTC\alpha_d)^2} - 2RTC\alpha_d \quad (2)$$

where P_s is the swelling pressure in kPa, R is the gas constant [8.314 J/($^{\circ}\text{K}\cdot\text{mole}$)] and α_d (dimensionless) is the tabulated degree of dissociation for the external NaCl solution of concentration C .

This model fits measured data reasonably well (Figure 5) and shows that the effects of salt concentration on swelling pressure tend to diminish with increasing saturated density. As pointed out by Arthur, this good agreement is somewhat conditional, however, because the relation between swelling pressure and saturated density for pure-water conditions is based entirely on empirical observations (Arthur, 2011). Moreover, Arthur points out that the assumption of ideal Donnan behaviour upon which this modelling approach is based may

not be valid for highly compacted buffer materials (Arthur, 2011).

As originally pointed out by Grauer, osmotic swelling (and models thereof) is insignificant where bentonite water contents are less than 30% (about three interstitial water layers in the montmorillonite structure), in other words, in most repository conditions (Grauer, 1986). Osmotic swelling operates over larger distances than innercrystalline swelling and in sodium montmorillonite can result in total separation of clay layers. Because the interlayer ions are fixed for electrostatic reasons, water is taken up into the interlayer spaces to balance concentration, provided there is a higher concentration in the interlayer spaces.

Osmotic swelling depends to a large extent on the electrolyte concentration and the valency of the dissolved ions. Innercrystalline swelling, on the other hand, depends only slightly on these factors.

4.3 Up-scaling issues

Models developed thus far have been relevant to simple chemical systems only, i.e. Ca-bentonite in CaCl_2 solutions or Na-bentonite in NaCl solutions. To be more realistic, further development of these models for application in more complex fluids is necessary.

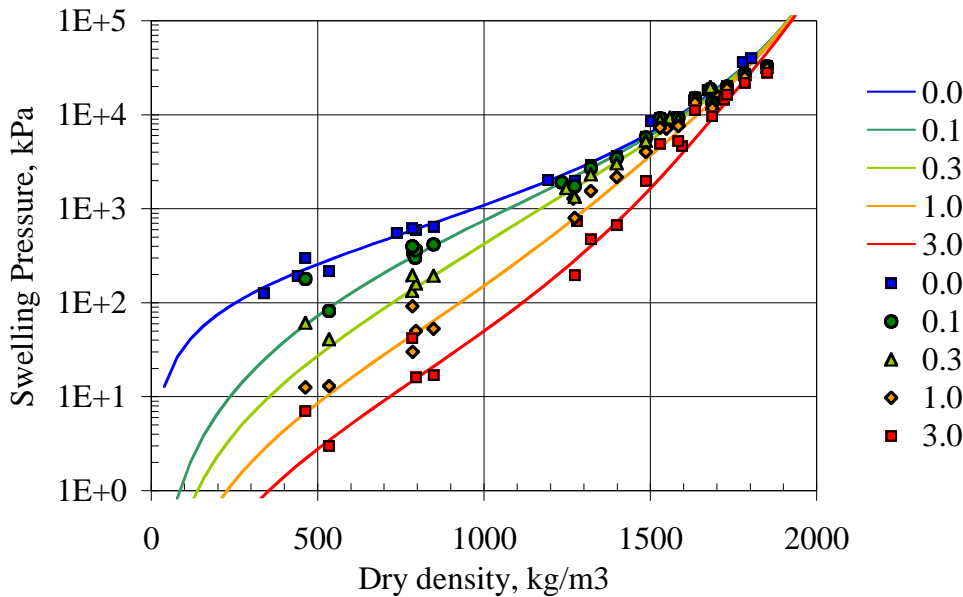


Figure 5. Measured and calculated swelling pressures for MX-80 bentonite in NaCl solutions of different concentrations (M). Modelled data are shown as lines, physical measurements as points (from Karnland et al., 2005).

4.4 Summary

Posiva and SKB rely upon an empirical model of clay swelling correlated with compaction density, together with incorporation of Donnan exclusion to account for swelling in saline fluids. Models are valid only for simple chemical compositions and not complex groundwaters.

4.5 Future prospects

Mechanistic models to describe clay swelling are not currently available. Alternative models that attempt to account for the thermodynamic and microstructural properties of compacted clays have been developed, but they rely on empirical evidence to establish a relation between swelling pressure and clay density for a limiting case in which the saturating solution is pure water (Arthur, 2011). Fully empirical approaches can accurately relate

swelling pressures to various measures of the swelling-clay content of clay-based materials, but these approaches have so far been applied only to simplified systems in which the aqueous phase consists of pure water or simple NaCl or CaCl₂ solutions. It is unlikely that a wholly mechanistic model of clay swelling will be developed in the next 5–10 years.

Thus far, clay swelling has generally been considered in isolation to other near-field processes and has not been included in T-H-M-C calculations. However, the relatively simple nature of equations (1) and (2) lend themselves to incorporation into some T-H-M-C models. It is to be expected that such estimates of swelling pressure will be routinely incorporated into T-H-M-C models developed over the next few years.

5 Cement-bentonite interactions

5.1 Background

Cement and other construction materials will be used in the construction of a spent fuel disposal facility (KBS-3V or KBS-3H) to limit groundwater inflow (grouting), to stabilise the rock (shotcrete, castings of rock bolts), to construct plugs and seals (e.g. drift end plugs, compartment plugs), to fill, for example, anchoring holes, and for operational safety purposes (floors, supporting walls etc) (Gribi et al., 2008, Appendix F). Chemical and mineralogical reaction zones develop between cement and bentonite due to contrasting chemical properties of the two materials, with reactions proceeding through a number of processes, such as:

- Diffusive transport of cement pore fluids into compacted bentonite which will lead to mixing with bentonite pore fluids and initiation of reaction of clay minerals with hyperalkaline fluids from the cement. Counter-diffusion of bentonite pore fluids into the cement will lead to growth of carbonates (aragonite, calcite) at the interface and a decrease in porosity.
- Mixing and reaction of cement pore fluids with the entrained pore fluid in compacted bentonite. Sharp gradients in pH (and partial pressure of carbon dioxide) across the interface encourage the rapid precipitation of solid carbonates, such as aragonite and calcite, and hydroxides such as brucite ($\text{Mg}(\text{OH})_2$), leading to a decrease in porosity.
- Fast exchange of cations in cement pore fluids (principally K, Na, and Ca) for cations (principally Na^+ in MX-80 bentonite) in interlayer sites in montmorillonite, leading to a decrease of swelling pressure.
- Fast protonation-deprotonation reactions at clay edge sites. Typically, such sites can neutralise 55 moles of hydroxyl ions per cubic metre of MX-80 bentonite (at 2000 kg m^{-3} water-saturated compaction density).
- Slow hydrolysis of montmorillonite and other minerals present, either as additives (e.g. quartz sand), or as accessory minerals. At elevated pH, such reactions consume hydroxyl ions, thus chemically neutralising the advancing cement pore fluids. These reactions lead to an increase in porosity and a decrease in swelling pressure.
- Precipitation of secondary minerals such as clays, hydroxides, carbonates, calcium silicate hydrates, and aluminosilicates such as zeolites and feldspars. These reactions may be relatively fast (e.g. hydroxides, carbonates, calcium silicate hydrates), or relatively slow (e.g. clays, zeolites, feldspars).

All of the above processes require the presence of an aqueous fluid phase: firstly, cement leaching will not occur to any significant degree under less than fully-saturated conditions; and secondly, transport and reaction of cement leachates with bentonite will not occur in unsaturated conditions.

Previous studies have highlighted that cement-bentonite interactions are strongly non-linear, with a complex interplay between fluid transport, clay ion exchange and dissolution, secondary mineral growth, and consequent changes in physical properties (porosity, permeability, swelling pressure) of the bentonite (Figure 6).

Posiva considers that the highly reactive high-pH fluids from cementitious materials could in principle constitute a threat to the long-term stability of the buffer and other bentonite components (Gribi et al., 2008, p140): *“the reaction of the cement-conditioned alkaline water with the buffer will result in mineral dissolution and formation of new phases. Consequently, it is likely that the hydraulic and chemical properties of both the cementitious materials themselves and any bentonite that comes into contact with high-pH fluids will change”*.

Posiva's main concerns are:

- montmorillonite dissolution leading to change in swelling pressure, porosity, and hydraulic conductivity;
- bentonite cementation by secondary phases leading to fracturing, with the possibility of advective transport, and;
- formation of alteration products, and their consequences for the properties of altered clay.

A detailed review of likely processes and issues regarding the presence of cementitious materials is contained in Appendix F of the Process report of the recent KBS-3H study (Gribi et al., 2008).

5.2 Analysis

Modelling of cement-bentonite interactions has been studied extensively in the last twenty years (e.g. Fritz and Madé, 1991; Savage et al., 2002, 2010a, 2010b, in press; Oda et al., 2004; Takase, 2004; Fernández et al., 2007; Watson et al., 2007, 2009a, 2009b; Ueda et al., 2007; Yamaguchi et al., 2007; Marty et al., 2009, 2010; Lehikoinen, 2009). Most of these studies relate to the interaction of OPC-type cements with bentonite, but a few are relevant to so-called 'low pH' cements (Watson et al., 2007; Lehikoinen, 2009; Savage et al., 2010b).

Early attempts at cement-clay modelling used an assumption of local equilibrium (e.g. Fritz and Madé, 1991; Gaucher et al., 2004), but although computationally efficient, this approach does not

capture the fine structure of potential alteration zones (e.g. Marty et al., 2009). Marty et al. have also emphasised the need to consider the fineness of computational meshes to accurately reproduce potential alteration (Marty et al., 2009).

For the most part, the capability of currently-available reaction-transport codes exceeds the level of understanding of the various reaction couplings (e.g. Figure 6) in the system. For example, aqueous speciation, mineral solubility, (pH-dependent) mineral dissolution kinetics, solid-solutions, cation exchange and surface complexation are all adequately accommodated in modern reaction-transport codes. Codes now also have the capability to tackle the effects of changing porosity upon diffusion coefficients, but the exact specification (using Archie's Law) remains problematic *a priori* (e.g. Kosakowski et al., 2009). Calculations are mostly in 1-D, but some codes have the capability to tackle 2-D, albeit with longer simulation times. The modelling of mineral growth is key in determining the rate of change of physical properties such as porosity (and potentially permeability), but currently remains problematic. Most modellers either assume a fast rate (local equilibrium), or the same rate equation (but reversed) as that for dissolution, neither of which may be correct. Some researchers have attempted to use data from natural systems to constrain the growth rates of secondary minerals (e.g. Savage et al., 2010b).

The role of secondary minerals in governing the

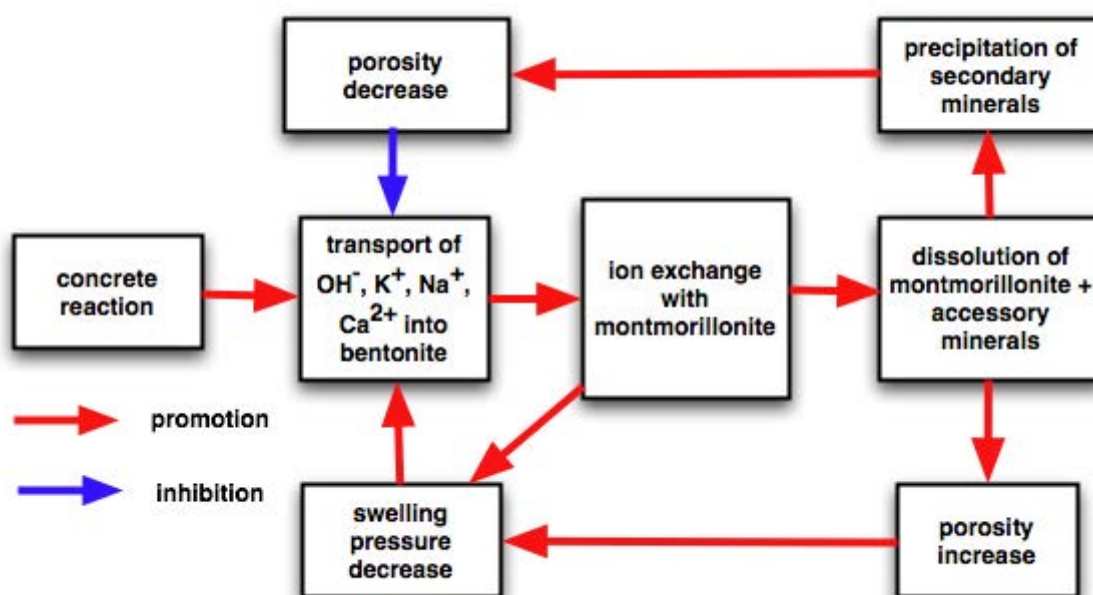


Figure 6. Cement-bentonite interaction as a coupled non-linear system (after Takase, 2004).

potential alteration of bentonite by hyperalkaline fluids has been reviewed (e.g. Gaucher and Blanc, 2006; Savage et al., 2007) and is principally through the influence on solution chemistry (notably pH) and the associated effects on the rate and mechanism, of mineral dissolution (e.g. Oda et al., 2004; Vieillard et al., 2004), together with changes to porosity which affect mass transport. The rate of growth of secondary minerals can have a profound effect upon the dissolution rates of primary minerals, and hence, the overall rate of bentonite degradation (e.g. Maher et al., 2009; Savage et al., 2010b). The choice of secondary minerals in predictive modelling can have a large impact upon the estimated amount of alteration (e.g. Oda et al., 2004). In general, the selection of secondary minerals has tended to follow one of two paths:

1. Computer code chooses (e.g. Gaucher and Blanc, 2006); or
2. Expert judgment (e.g. Savage et al., 2007).

Option (1) above is only really possible where: (a) accurate and reliable thermodynamic data for all possible secondary minerals are available; and (b) secondary mineral growth is unaffected by kinetics and the growth of metastable products. Unfortunately, neither of these conditions pertain to the cement-bentonite system, and thus option (2) currently remains the only logical choice. Consequently, data from analogue systems become extremely important in informing expert judgement (e.g. Savage, 2011b).

5.3 Up-scaling issues

Data from natural and industrial analogues have already been used to help define the following in up-scaled models of cement-clay interaction:

- reaction mechanisms (e.g. Savage et al., 2007; De Windt et al., 2008);
- the physical scale of alteration (e.g. De Windt et al., 2008); and
- kinetic data for mineral dissolution and growth (Savage et al., 2010b).

However, up-scaling changes in reactive mineral surface area and physical properties (e.g. permeability) remains a problem.

5.4 Summary

Cement-bentonite interaction is modelled as a T-H-C process. In general, the capability of currently-available reaction-transport codes exceeds the level of understanding of the various reaction couplings in the system. However, modelling of porosity-permeability evolution still remains uncertain.

5.5 Future prospects

Computer models used to describe cement-bentonite interaction have thus far focused on T-H-C type interactions with little or no discussion of mechanical processes. It is likely that this topic will see progress in the next 5–10 years, with the addition at least of the effects of changes to swelling pressure incorporated into model processes.

The modelling of mineral growth remains the most uncertain area of modelling of cement-bentonite interactions. To model mineral growth, the critical issue is the reactive surface area (A), and especially how it may change with time. Typically in reaction-transport modelling, A is kept constant with time. However, for a secondary mineral, surface area is initially created by nucleation and is subsequently modified by crystal growth and dissolution and by crystal ripening. Nucleation is an extremely important process to consider, since at supersaturation levels above a critical value, its rate may be very large, and therefore it may control the rate at which surface area is generated. In addition, the process of Ostwald ripening, whereby smaller crystals with higher solubility dissolve and re-precipitate as larger crystals is important to include in the analysis as ripening counteracts rapid surface area generation by nucleation. Although theoretical approaches to model such processes exist (e.g. Steefel and Van Cappellen, 1990; Fritz et al., 2009), they have not been applied extensively due to a lack of relevant data for mineral-fluid interfacial free energies *inter alia*. However, it has been recognised that the interaction of cement pore fluids with rocks and other engineered barrier components may well develop through an Ostwald Step type sequence of alteration (e.g. Savage et al., 2007) which will demand greater consideration of such processes in future modelling studies.

6 Iron-bentonite interactions

6.1 Background

In the KBS-3H design, Posiva report that in addition to the processes relevant to KBS-3V, significant geochemical interactions between the supercontainer shell and buffer will take place (iron/smectite interaction, iron silicate formation, cation exchange, etc.) (TKS-2009 – Posiva, 2010). These processes may affect buffer density, swelling pressure, hydraulic conductivity and other properties. According to Posiva, the effects are locally limited at early stages, but may develop with time and affect larger parts of the buffer (TKS 2009 – Posiva, 2010).

Although mineral transformation of the buffer is expected to proceed slowly, due to the slow diffusive migration rate of Fe(II), which is retarded by sorption, and the slow kinetics of the transformation processes, there is evidence from some laboratory experiments that transformation processes can proceed rapidly, even at relatively low temperatures (Lantenois et al., 2005). Moreover, experiments investigating the corrosion of steel in compacted bentonite (Carlson et al., 2007) have shown that the hydraulic conductivity of bentonite may be substantially increased by steel-bentonite interactions on a relatively short timescale.

Although some modelling studies (Wersin et al., 2008) have shown that the zone undergoing mineral transformation may remain spatially limited (a few centimetres) for very long times, this work did not address changing physical properties of the bentonite with time (either increased hydraulic conductivity or cementation by corrosion products), nor the kinetics of clay transformation (e.g. Savage et al., 2010c).

An essential feature of iron-bentonite interactions is that they are strongly coupled in a non-linear fashion:

- Anaerobic corrosion of steel supplies ferrous ions and hydrogen gas at the interface with benton-

ite. Sorption of ferrous ions on the clay may act as a ‘pump’, driving steel corrosion. Migration of pulses of gas through bentonite will provide a pathway for aqueous species such as dissolved iron.

- Ion exchange/sorption of Fe²⁺ on clay will retard its migration through the bentonite, but may be linked to long-term mineralogical transformation processes.
- Corrosion of steel may be linked to smectite transformation through chemical reduction of structural Fe³⁺ in the clay.
- Anaerobic corrosion of iron, coupled with clay transformation processes serve to increase pore fluid pH, thus accelerating clay dissolution.
- Transformation of montmorillonite to non-swelling minerals will change the physical properties of the bentonite, potentially further enhancing transport through the clay.

It is thus important to incorporate this strong coupling between different processes in any modelling of the iron-bentonite system, and moreover, not to focus on individual sub-systems without due account of process coupling.

6.2 Analysis

The potential detrimental effects of the interaction of iron or steel canisters/overpacks with compacted bentonite in waste package buffers was first identified by Nagra in the mid-1980’s (Grauer, 1986, 1990; Savage, 1986). Although this issue remained of concern to some waste agencies, little more research was done until Andra and JAEA initiated new experimental and modelling studies in the late 1990’s (e.g. Kamei et al., 1999; Guillaume et al., 2003; Neaman et al., 2003; Lantenois et al., 2005; Charpentier et al., 2006; Wilson et al., 2006a, 2006b; Perronnet et al., 2007a, 2007b; Ishidera et al., 2008; Mosser-

Ruck et al., 2010; Fukushi et al., 2010). Posiva and SKB followed suit in the middle of the last decade, carrying out reviews and experiments as part of their KBS-3H research programme (e.g. Marcos, 2003; Smart et al., 2006a, 2006b, 2008; Carlson et al., 2006, 2007, 2008; Wersin and Snellman, 2008; Milodowski et al., 2009a, 2009b). These experiments have been followed up by several modelling studies, carried out mainly in the last five years (Montes-H et al., 2005; Bildstein et al., 2006; Hunter et al., 2007; Wersin et al., 2008; Samper et al., 2008a; Savage et al., 2010c; Marty et al., 2010; Lu et al., 2011).

Modelling studies have treated this issue as a T-H-C problem, with most models predicting that magnetite is the principal steel corrosion product, along with significant alteration of the clay minerals of the bentonite to a mixture of non-swelling silicates, such as chlorite, berthierine or cronstedtite and zeolites. Like models of cement-bentonite interaction, mineral dissolution-precipitation reactions were originally treated as equilibrium reactions (e.g. Montes-H et al., 2005; Bildstein et al., 2006), but are now treated kinetically (Savage et al., 2010c; Lu et al., 2011), and processes of aqueous

speciation, cation exchange and clay edge protolysis are all included (e.g. Hunter et al., 2007; Wersin et al., 2008; Savage et al., 2010c). Some authors have focused on the principal reaction products being the formation of iron oxides such as magnetite with accompanying sorption of Fe on clay surfaces (e.g. Hunter et al., 2007; Samper et al., 2008a; Lu et al., 2011), whereas others have tried to model the growth of iron-bearing aluminosilicates (e.g. Wersin et al., 2008; Savage et al., 2010c; Marty et al., 2010).

Some key issues for modelling of iron-bentonite interactions arising from these studies are:

- The choice of Fe solubility-limiting solids at the corroding steel surface is important, since this defines the concentration of iron at the canister boundary and hence, the concentration gradient of Fe across the bentonite. Some authors have chosen to use solids with very low solubilities, such as magnetite or pyrite (e.g. Bildstein et al., 2006; Wersin et al., 2008), but there is mineralogical evidence that more soluble, poorly crystalline iron oxyhydroxide may be more relevant (e.g. Figure 7 – Milodowski et al., 2009a).

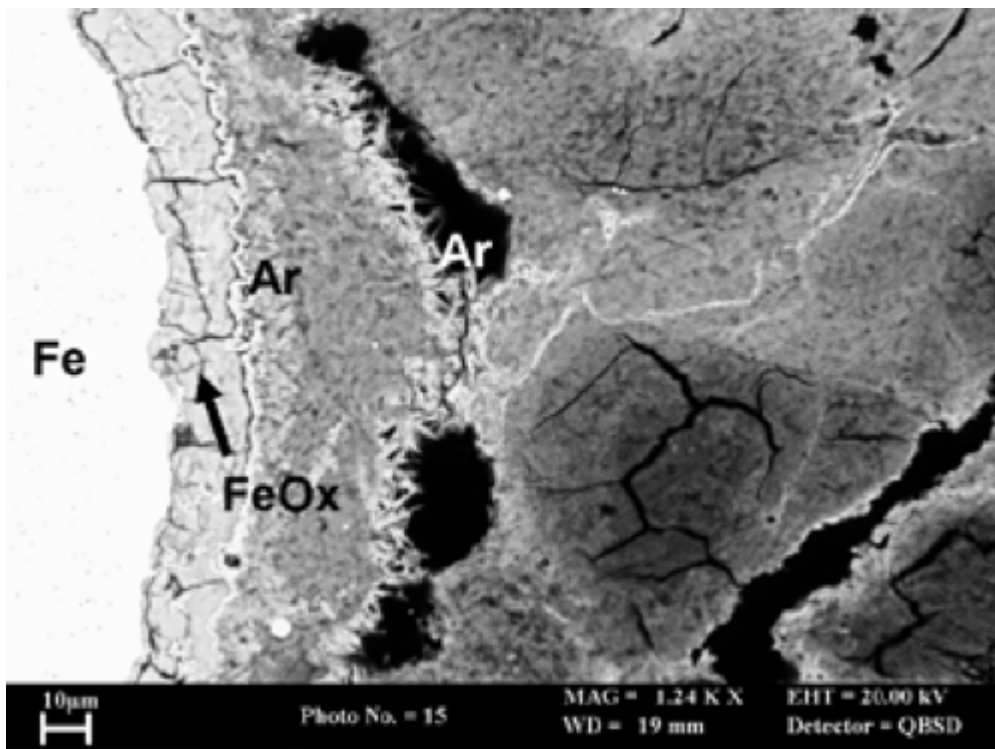


Figure 7. BSEM photomicrograph showing aragonite needles (Ar) lining open shrinkage fractures within the alteration halo in bentonite around a corroded steel wire. The surface of the steel (Fe) is corroded and coated in gel-like iron oxide (FeOx). Clay matrix enriched in Fe appears brighter than unaltered clay (from Milodowski et al., 2009a).

- There is strong evidence that the physical properties of compacted bentonite in contact with steel degrade over very short timescales. For example, samples of bentonite from corrosion experiments (e.g. Carlson et al., 2008) show increased hydraulic conductivity after only 3 years of reaction.
- Detailed mineralogical investigation of compacted bentonite from steel corrosion experiments show greatest penetration of Fe into the bentonite matrix along hairline microfractures that radiate outwards from the corroding metal. Milodowski et al. (2009b, p52) consider that: “*The early formed fractures may have represented potentially important pathways for gas and solute transport during the course of the experiments. The irreversible shrinkage of the bentonite, as a result of interaction with Fe released from corroding iron or steel may therefore be significant in evaluating the long-term behaviour of the bentonite seal and the transport of gas and solutes around corroding waste canisters emplaced in bentonite backfill*”.
- Iron-bentonite interaction is a strongly coupled process, such that it is relatively uninformative to separate ‘sub-systems’ for modelling analysis.

6.3 Up-scaling issues

From a laboratory experimental perspective, up-scaling has involved either high temperatures (e.g. Mosser-Ruck et al., 2010) and/or high water/clay ratios (e.g. Lantenois et al., 2005) in an attempt to accelerate reactions over short timescales. However, this has led to confusion over the nature of potential reaction mechanisms and products of iron-bentonite interaction that should be incorporated into models of long-term interactions.

There is a shortage of relevant natural analogue data (iron is unstable in the geological environment), but it is conceivable that industrial (anthropogenic) analogues could be used in future to better constrain models of long-term evolution.

6.4 Summary

The nature of iron-bentonite interaction is similar to the cement-bentonite problem, i.e. physicochemical processes are strongly coupled, but the former includes the additional complexity of modelling the evolution of redox in the system. Unlike cement-bentonite interaction however, the understanding of

reaction mechanisms and products of iron-bentonite interaction is much more limited, principally due to a lack of supporting data from analogues.

6.5 Future prospects

One of the principal hindrances to the advancement of modelling of iron-bentonite interactions is the ambiguity and uncertainty relating to the results of laboratory experiments in that the type and amounts of solid products of studies published thus far appear to be strong functions of time, temperature, water/clay ratio, and clay and pore fluid compositions (Savage et al., 2010c). For example, the products of high temperature experiments (> 250°C) are dominated by chlorite, whereas lower temperatures produce berthierine, odinite, cronstedtite, or Fe-rich smectite, depending upon initial clay composition and water/clay ratio. A plausible explanation of these data is that the sequence of alteration of bentonite by Fe-rich fluids proceeds via an Ostwald step sequence. Although natural systems evidence is not completely analogous to waste package corrosion scenarios (there are no natural occurrences of carbon steel, for example), the low-temperature diagenesis of iron-rich sedimentary rocks shows that magnetite is rare (Tucker, 1991), and that chlorite is the common Fe-silicate in ancient sandstones, but does not occur in sediments younger than 1 Ma (Odin, 1990). The mixed ferrous-ferric silicates, odinite and cronstedtite occur in recent, shallow (< 60 m depth), warm (> 20°C) tropical sediments but do not occur in ancient sediments older than 1 Ma (Odin, 1990). It may be concluded that chlorite is the likely most stable Fe-silicate phase, but its formation is kinetically inhibited and occurs through an Ostwald step process via odinite, cronstedtite, and/or berthierine precursors. Older specimens of odinite (> 1000 a) tend to have greater proportions of interstratified 14 Å layers than younger specimens, and this is taken to indicate that unstable odinite transforms to a more chlorite-like mineral upon shallow burial (Bailey, 1988). Rationalisation/synthesis of this information from laboratory experiments is likely to occur over the next 5–10 years, thus providing sounder boundary conditions for future predictive modelling.

Comments regarding modelling the kinetics of growth of secondary minerals under the Cement-Bentonite Section are also relevant here.

Hydrogen, generated as part of the anaerobic

corrosion of steel, has been ignored in simulations carried out thus far, except as a monitor of the overall corrosion rate of the steel. Some experimental studies suggest that hydrogen may act as a catalyst

for the chemical reduction of aqueous sulphate (e.g. Truche et al., 2009). It is likely that more explicit inclusion of hydrogen and its effects will be incorporated into future models of this system.

7 Mechanical (shear) behaviour

7.1 Background

Fractures in the host rock crossing a deposition hole may be activated and sheared by an earthquake. The buffer in a deposition hole acts as a cushion between the canister and the rock, which reduces the effect of rock shear substantially. A lower density for the buffer yields softer material and a reduced effect on the canister. However, at the high density that is suggested for a repository the stiffness of the buffer is relatively high. The stiffness is also a function of the rate of shear, which means that there may be a substantial damage on the canister at very high shear rates. According to TKS-2009 (TKS-2009 – Posiva, 2010, p292), the buffer should be plastic enough to mitigate the effects of minor rock shear movements on the canisters. Posiva place an upper bound of 2050 kg m^{-3} for buffer density so that the canister is protected during rock shear movements.

An elastic-plastic material model is used to

simulate the behaviour of the bentonite where the stress-strain relations have been derived from laboratory tests (e.g. Figure 8), using computer codes such as ABAQUS (Börgesson and Hernelind, 2010). The material model is made a function of both the density and the strain rate at shear. ABAQUS is a general-purpose finite element program designed for both linear and non-linear stress analyses. Since the shear is fast and takes place under undrained conditions, the density is unchanged during the tests. However, strain rate varies largely with both the location of the elements and time.

7.2 Analysis

The currently-used material model for bentonite has been described by Hernelind (Hernelind, 2010). The bentonite buffer is modelled using only total stresses that do not include the pore water pressure, since shear and compression are fast during the

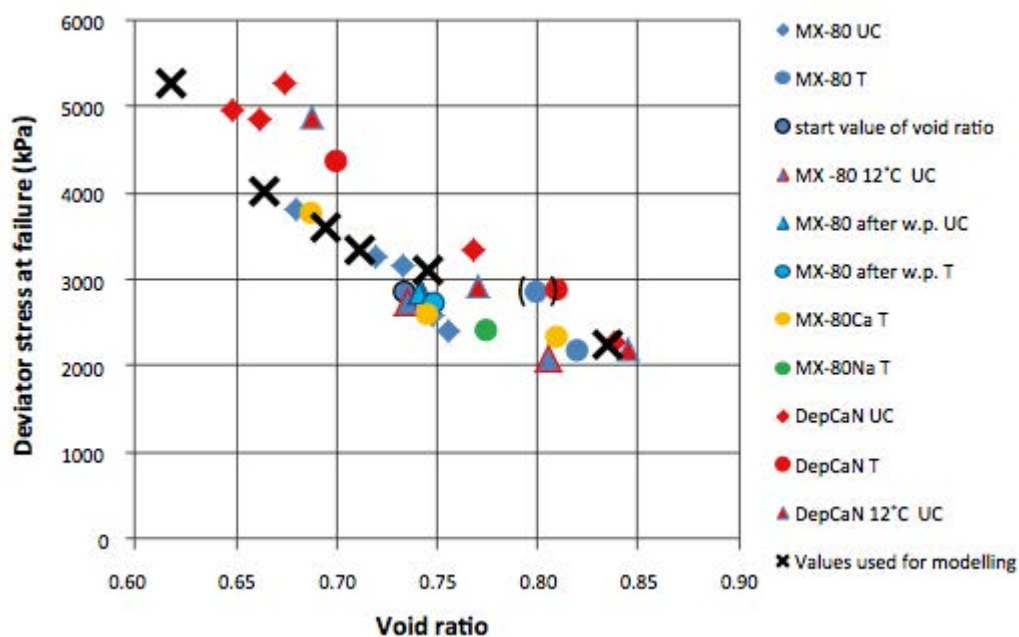


Figure 8. Measured deviator stress at failure as a function of void ratio for different bentonites at different test techniques (from Börgesson and Hernelind, 2010). The relation used for MX-80 in the calculations is marked with x and relates to a strain rate of 10^{-4} s^{-1} .

earthquake. The most important properties of the bentonite for rock shear are the stiffness and the shear strength. These properties vary with bentonite type, density and rate of strain. Ca-bentonite has higher shear strength than Na-bentonite and the shear strength increases with increasing density and strain rate.

Since it cannot be excluded that the Na-bentonite MX-80 will be ion-exchanged to Ca-bentonite the properties of Ca-bentonite is used in the modelling by Posiva and SKB. The acceptable density at saturation of the buffer material is 1950–2050 kg m⁻³ which is covered by the models below.

The material model in ABAQUS is expressed with von Mises' stress σ_j that describes the 'shear stress' in three dimensions according to:

$$\sigma_j = \left(\frac{(\sigma_1 - \sigma_3)^2 + (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2}{2} \right)^{1/2} \quad (3)$$

where σ_1 , σ_2 and σ_3 are the principal stress components. The material model defines the relation between the stress and the strain and is partitioned into elastic and plastic parts. A von-Mises model is normally used to model the undrained behaviour of soft cohesive soils, whereas a Mohr-Coulomb model is normally used to represent a drained stress-strain behaviour of sands.

Bentonite is modelled as a linear elastic material combined with von Mises plastic hardening. The plastic hardening curve is made a function of the strain rate of the material. The reason for the latter relation is that the shear strength of bentonite is sensitive to the strain rate. It increases about 10% for every factor of ten increase in strain rate. Since the rock shear at an earthquake is very fast (1 m s⁻¹) the influence is strong and the resulting shear strength will be different at different parts of the buffer. Experiments (Börgesson and Hernelind, 2010) show that Young's modulus (E) is also dependent on strain rate but in the calculations presented by Hernelind (2010), this has been neglected and a representative stiffness has been chosen.

The material model is parameterised using data from laboratory studies (e.g. Börgesson et al., 1995, 2004; Börgesson and Hernelind, 2006). The results of the studies and the resulting material model used for SR-Site are described in two separate reports (Börgesson and Hernelind, 2010; Dueck et al., 2010). The material used for the modelling in SR-Site differs from the material used for the scale

tests, since MX-80Ca (MX-80 ion-exchanged from Na-bentonite to Ca-bentonite) is used as reference buffer material in SR-Site while unaffected MX-80 was used in the scale tests.

Geochemical transformation of the buffer can lead to a material with different properties than the original buffer. The effect of a rock shear through such a buffer may of course have different consequences than those through the original buffer. According to Hernelind (2010), a 8.75 cm thick annulus of cemented bentonite around the canister produces an effect of rock shear that is more severe than an unaltered bentonite due to the increased stiffness of the buffer. However, the properties of cemented bentonite are not known in detail so the calculation must be regarded as an example rather than as a prediction (Hernelind, 2010).

7.3 Up-scaling issues

Models of mechanical shear behaviour are dependent upon laboratory experiments for input data and mechanisms. It is difficult to see what analogue data may exist to help scaling for the long-term, but conceivably, field examples of faulting of bentonite beds could help confirm shear mechanisms.

7.4 Summary

An elastic-plastic material model is used to simulate the behaviour of the bentonite where the stress-strain relations have been derived from laboratory tests, using computer codes such as ABAQUS. The material model is made a function of both the density and the strain rate at shear. These models are dependent upon laboratory experiments for input data and mechanisms and are thus questionable in terms of temporal and physical scales.

7.5 Future prospects

Most modelling of the mechanical behaviour of bentonite relies on a constitutive law for elastoplastic behaviour such as the 'BBM' (Barcelona Basic Model) (Alonso et al., 1990). This, in turn, is an extension of the modified 'Cam-Clay' model (Roscoe and Burland, 1968). The BBM has some limitations for expansive clays such as bentonite and has been extended to the Barcelona Expansive Model, 'BExM' (Alonso et al., 1999). An alternative approach called the Bentonite Elastoplastic Swelling Pressure and Contact Stress-based model, 'BESC' has recently been suggested (Åkesson and

Kristensson, 2008). This latter model is formulated as two differential equations for elastic and plastic strains, respectively.

There are new models being developed which move away from the conventional T-H-M soils approach which treats bentonite as an elasto-plastic porous medium with water or air occupying a notional porosity with the inclusion of additional process models to take into account the very high observed water suctions, intrinsic permeability

variation and macroscopic swelling of partially saturated compacted bentonite (e.g. Bond et al., 2010a). These models replace the empirical parameterisation usually employed in T-H-M models with a direct representation of the water disposition, pore structure and relevant processes, albeit at an abstracted level. It is likely that this type of model will be considered for bentonite material properties in future calculations of this type.

8 Bentonite erosion

8.1 Background

The bentonite buffer in a KBS-3 repository for spent nuclear fuel may be susceptible to mass losses by erosion should the constituent clay minerals be suspended as colloids that are then transported away from deposition holes in flowing groundwater. Bentonite erosion could occur in various scenarios, including those involving the migration of glacial meltwaters to repository depths, because stable suspensions of clay colloids tend to form in aqueous solutions that are relatively dilute (e.g. Miller and Marcos, 2007).

Figure 9 illustrates the key features of a conceptual model of buffer erosion (Birgersson et al., 2009). The figure represents a vertical cross section through a portion of a KBS-3V deposition hole that is intersected by a horizontal fracture. Free swelling of bentonite from the deposition hole outward into the fracture is resisted by frictional forces acting within the bentonite and at the rock interface. The maximum penetration distance is reached when these counteracting forces equilibrate. Bentonite density and swelling pressure then decrease rapidly with increasing distance in the fracture. The rheological properties of the bentonite change

accordingly from those of a solid \rightarrow gel \rightarrow fluid. Clay colloids form near this front, and are lost by diffusion into the flowing groundwater. Bentonite fluids (i.e. dispersions of bentonite colloids in water, not solids or gels) may also be lost by advection. More bentonite then extrudes into the fracture from the deposition hole to restore equilibrium. The resultant loss of bentonite results in a decrease in buffer density.

Neretnieks et al. (2010) have developed a model of buffer erosion that accounts for forces that control the expansion of bentonite from a deposition hole into a fracture (dynamic force-balance model), and for the effects of particle and ionic concentrations on the viscosity of the expanded bentonite (viscosity model). The force-balance and viscosity models have been combined into an overall model of buffer erosion, which accounts for both the Brownian motion of individual clay colloids into the flowing groundwater and for the advection of sols that form within the fracture as the bentonite expands and becomes less dense and less viscous. The force-balance model is based on the assumption that expansion of the buffer outward from a deposition hole into an intersecting fracture is controlled by a number of forces



Figure 9. Conceptual model of buffer erosion (from Birgersson et al., 2009). The swelling pressure and density of bentonite in the fracture decreases exponentially with increasing distance, z , and, at a given distance, with decreasing fracture aperture, a .

acting on the individual clay particles (Neretnieks et al., 2010). These forces include the gravity and buoyant force, forces resulting from changes in the chemical potential in a concentration gradient (diffusional force), van der Waals attractive forces between clay particles, repulsive forces between the particles resulting from charges within and on the surfaces of the particles (diffuse double layer forces), and frictional forces acting on the particles as they move through the aqueous phase as a result of imbalances among the other forces.

8.2 Analysis

This ‘force-balance model’ has been used to predict changes in the density and volume fraction of clay particles in the expanded bentonite. The viscosity model was developed to relate changes in volume fraction of clay particles to corresponding changes in the viscosity of bentonite gels/sols (Moreno et al., 2011; Neretnieks et al., 2010). The model is based on the concept of a co-volume of a colloidal particle, with the co-volume being defined as the volume over which a given particle can rotate freely without touching other particles in a colloidal suspension. It is determined both by the physical size of the particle as well as by interactions involving the particle’s electrical double layer and those of its nearest neighbours. The co-volume thus depends on the physical volume fraction and on properties of the colloidal suspension, such as the ionic composition of the aqueous phase, that control the effective thickness of the electrical double layer.

The buffer erosion model was evaluated by for an idealised case of two-dimensional groundwater flow in a horizontal fracture intersecting a deposition hole (Moreno et al., 2011). The fracture aperture was assumed to be 1 mm. Bentonite was assumed to consist of pure Na-montmorillonite and the groundwater was represented by a dilute NaCl solution. The Darcy flow equation, solute diffusion equations, and governing equations underpinning the force-balance and viscosity models were evaluated simultaneously using a numerical solver.

The force-balance model of Neretnieks et al. (2009) uses a DLVO-based representation of attractive and double-layer forces applied to an idealized system of pure Na-montmorillonite in a simple NaCl electrolyte solution.

8.3 Up-scaling issues

Confirmation that the process of bentonite (clay) erosion operates at all could be assessed through the investigation of the abundance of montmorillonite in fracture mineral assemblages in drillcore at sites in Scandinavia. A preliminary evaluation of this approach has been made through the SSM investigation of the bentonite erosion process, where it was concluded that there was no evidence from drillcore at Forsmark, Sweden that any preferential removal of montmorillonite in fractures at shallow depths had occurred due to the downward migration of glacial meltwaters (Savage, 2011a). This could be extended to evaluate drillcore data from sites elsewhere (e.g. in Finland).

8.4 Summary

The understanding of mechanical erosion (piping) is at a very low level and available models are semi-empirical at best.

Posiva and SKB have developed a model of chemical erosion that accounts for forces that control the expansion of bentonite from a deposition hole into a fracture (dynamic force-balance model), and for the effects of particle and ionic concentrations on the viscosity of the expanded bentonite (viscosity model). The process of buffer erosion is not relevant to concepts developed in other international programmes, so the availability of alternative models is limited.

8.5 Future prospects

The model of bentonite erosion employed by Posiva/SKB is purely physical in the sense that chemistry (the composition of glacial meltwaters) is only employed as a ‘switch’ to turn on/off the empirical erosion equation at various stages of repository evolution as necessary. In the current model, there is no explicit link between the chemical composition of groundwaters, ion exchange in the bentonite, the formation of sols, and the mechanical effects of the erosion process. In reality however, bentonite erosion is a coupled H-M-C problem and it is likely that coupled computer codes will be used in future to address this issue. It is envisaged that in future, this H-M-C approach will be used to model the erosion process.

9 Conclusions

The status and future prospects for modelling for the following technical areas have been reviewed:

- Non-isothermal (T-H-C-M-B) modelling and the potential for cementation.
- The consistency of models.
- Swelling pressure.
- Cement-bentonite interactions.
- Iron-bentonite interactions.
- Mechanical (shear) behaviour.
- Bentonite erosion.

A key issue for all topics is the issue of up-scaling of models and data from laboratory and *in situ* experiments to the physical and temporal scales of interest to safety assessment. Information from analogue systems may help in some instances, but care needs to be taken that models employed are fit for purpose.

Relatively little progress has been made in the area of T-H-M-C-B modelling and thus far, models have been developed to address T-H-M or T-H-C problems, but modelling the interaction of M (mechanical) and C (chemical) processes has been very limited, in part due to a lack of understanding of process couplings. Chemical processes have been mainly restricted to cation exchange, surface complexation and the (equilibrium) dissolution-precipitation of trace minerals in the bentonite. New codes are now emerging that can combine mechanical and chemical processes in a more satisfactory manner and it is to be expected that greater progress will be made in this area in the next 5-10 years.

There is much debate currently surrounding the nature of porosity in compacted bentonite. Some researchers favour a single porosity model, whereas others prefer a multiple porosity description. This debate impacts upon a whole range of important processes such as clay swelling, ionic transport, pore fluid evolution and bentonite erosion *inter alia*.

There is much research focused on this topic and it is anticipated that progress will be made through the Äspö EBS Task Force and BRIE Projects in the near to medium future.

Clay dissolution-precipitation reactions have been omitted from most pore fluid evolution and T-H-M-C-B modelling studies in the past, mainly due to the limitation of computer codes, but also due to a perception of the potential minor impact of such processes. In future, it is likely that these reactions will be included in near-field evolution models, bringing greater consistency between the modelling of pore fluid evolution and clay alteration (e.g. illitisation).

Clay swelling is currently evaluated using empirical correlations of swelling pressure with compaction density, coupled with Donnan exclusion in saline groundwaters. Swelling is excluded from other models of near-field interactions, but could relatively easily be incorporated into future models. It is considered unlikely that a mechanistic understanding of clay swelling will be developed in the next 5–10 years, but it is believed that clay swelling will be brought into more modelling studies of near-field evolution.

Cement-bentonite interactions are currently treated as a T-H-C process in coupled models, but clay swelling could feasibly be incorporated into future models. There is strong non-linear coupling between chemical and physical processes and it is considered unlikely that changes in permeability/diffusivity will be able to be predicted in the short to medium term. The ability to predict porosity changes is currently limited by the capabilities to model mineral growth. Although a theoretical framework to model growth exists, progress is hampered by a lack of critical data such as mineral-fluid interfacial free energies. It is unlikely that this situation will improve significantly in the next 5–10 years.

Models of iron-bentonite interactions are similar to those of cement-bentonite in that processes are strongly coupled in a non-linear fashion. This problem is also treated as a T-H-C issue, but modelling progress is held back by uncertainties surrounding the nature of the products of iron-bentonite interaction and key reaction mechanisms. However, these uncertainties could be reduced significantly in the next 5–10 years. Processes concerning gas (chemical and physical) are excluded from current models of iron-bentonite interactions, but it is likely that these will be included in future models of this type.

Most modelling of the mechanical behaviour of bentonite during shear relies on a constitutive law for elastoplastic behaviour. There are new models being developed which move away from the conventional T-H-M soils approach which treats bentonite as an elasto-plastic porous medium with water or air occupying a notional porosity with the inclusion of additional process models to take into account the very high observed water suctions, intrinsic permeability variation and macroscopic swelling of partially saturated compacted bentonite. It is likely that this type of model will be considered for

bentonite material properties in future calculations of this type.

The currently-available model of bentonite erosion accounts for forces that control the expansion of bentonite from a deposition hole into a fracture (dynamic force-balance model), and for the effects of particle and ionic concentrations on the viscosity of the expanded bentonite (viscosity model). The force-balance and viscosity models have been combined into an overall model of buffer erosion, which accounts for both the Brownian motion of individual clay colloids into the flowing groundwater and for the advection of sols that form within the fracture as the bentonite expands and becomes less dense and less viscous. In this model, there is no explicit link between the chemical composition of groundwaters, ion exchange in the bentonite, the formation of sols, and the mechanical effects of the erosion process. In reality however, bentonite erosion is a coupled H-M-C problem and it is likely that coupled computer codes, incorporating mechanical and chemical processes will be used in future to address this issue.

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