



Strål
säkerhets
myndigheten

Swedish Radiation Safety Authority

Author: David Savage

Technical Note

2012:28

Initial review of chemical and erosional
processes within the buffer and backfill
– Geochemical processes

SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Denna rapport består av en "Technical Note" inom SSM:s inledande granskning av SKB:s säkerhetsredovisning SR-Site. Syftet med denna inledande granskning av frågorna kring geokemiska processer i buffert och återfyllnad i slutförvarsanläggningen är att få en bred granskning och belysning av SR-Site med underreferenser samt att identifiera eventuella behov av kompletterande information eller förtydliganden som SKB bör tillfoga ansökansunderlaget.

Författarens sammanfattning

Slutsatsen från denna inledande granskning är att dokumenteringen i SR-Site håller en bra standard med följande undantag/brister:

- *Fullständighet*
 - Data för svälltryck av Na- och Ca-bentonit i blandade elektrolyt lösningar behövs,
 - Mer data för hydraulisk konduktivitet av Ibeco RWC bentonit behövs,
 - Experimentella och modellerings data för växelverkan mellan låg-pH cement och både MX-80 och Ibeco RWC bentonit behövs,
 - Det saknas helt redovisningen om användning av data från platsundersökningen i Forsmark (grundvattenkemi och mineraler i sprickorna) till etableringen av den troliga långsiktiga stabiliteten av lermineraler i tekniska barriärerna,
 - Det finns ett gap mellan SR-Site "data" och "modell" rapporter; ingen av dem diskuterar de konceptuella modeller som används för lerans beteende i olika säkerhetsfunktionerna.
- *Vetenskaplig trovärdighet och kvalitet*
 - Användningen av konceptuella modeller för lerans beteende och egenskaper i olika säkerhetsfunktioner bör vara konsistent (t.ex. somliga modelleringar använder en enkel porositet medan andra använder begreppet av multipel porositet),
 - Hydrolysreaktioner av leran är ignorerade i modellbeskrivningen av den långsiktiga förändringen av bentonit (illitisering, T-H-M-C-processerna, växelverkan med cement), vilket har lett till att modellerna blir orealistiska och icke konservativa.

- *Brist i relevanta modeller, data och säkerhetsfunktioner*
 - Modeller av utvecklingen i närfältet av slutförvaring (T-H-M-C-processerna, långsiktiga förändringar genom illitisering och växelverkan med cement) är bristfärdiga och icke konservativa (en kinetisk beskrivning av lerans hydrolysreaktioner behöver inkluderas i alla modeller),
 - Modellering av cement-lera-interaktionen är inadekvat och behöver revideras,
 - Illitisering och interaktion med grundvatten bör analyseras med reaktion-transport-modellering (data från naturliga system bör användas för att stöda modelleringen),
 - Modellering av utvecklingen i närfältet är inkonsekvent (vissa processer har analyserats med enkla överslagsräkningar och andra har använt reaktion-transport-modeller),
 - Analys av svälltrycks data är baserad på empiriska modeller.
- *Säkerhets betydelsefulla faktorer*
 - Säkerhetsbetydelsen av spårmineralerna (kalcit, pyrit, organiska material, etc.) i bentonit bör utvärderas kvantitativt.
- *Genomförbarhet av tillverkning, uppförande, provning, installation samt drift*
 - Begreppet utbytbarhet av bentonit (bentonite exchangeability) behöver studeras vidare (ytterligare data behövs, det finns fundamentala skillnader av egenskaperna bland olika typer av bentonit).

Efter denna granskning har ett antal nyckelfrågor identifierats som förtjäna vidare utredning av SSM. Frågorna är:

- utbytbarhet av bentonit
- svällning av leran
- mineraltransformation
 - illitisering
 - T-H-M-C-processer under den termiska perioden
 - växelverkan med cement i injekteringsbruk och pluggar
- Konsistens i konceptuella modeller av lerans beteende

Projektinformation

Kontaktperson på SSM: Jinsong Liu

Diarienummer ramavtal: SSM2010-4230

Diarienummer avrop: SSM2011-4204

Aktivitetsnummer: 3030007-4005

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

This report consists of a Technical Note in SSM's initial review phase of SKB's safety analysis SR-Site. The aim of the initial review of issues concerning geochemical processes in buffer and backfill in a final repository is to make a broad illustration and review of SR-Site together with its subordinate references, as well as to identify potential needs for complementary information or clarification which SKB should supplement to its license applications.

Summary by the author

It is concluded from this initial review that the standard of documentation in SR-Site is generally good, with the following exceptions/omissions:

- Completeness: (1) swelling pressure data for Na- and Ca-clays in mixed electrolyte solutions are needed; (2) more hydraulic conductivity data for Ibeco RWC bentonite are needed; (3) experimental and modelling data are needed for the interaction of low-pH cements with both MX-80 and Ibeco RWC bentonites; (4) there is a complete omission of the use of site characterisation data (groundwater chemistry, fracture minerals) from Forsmark to establish the likely long-term stability of clay minerals in the EBS; and (5) there is a gap between SR-Site 'data' and 'model' reports; neither discusses conceptual models used for clay behaviour in various safety functions.
- Scientific soundness and quality: (1) there needs to be a consistency of usage of conceptual models for clay properties and behaviour across different safety functions, e.g. some modelling studies employ a 'single' porosity, whilst others use a 'multiple' porosity concept; and (2) clay hydrolysis reactions are omitted from models describing long-term alteration of bentonite (illitisation, T-H-M-C processes; interaction with cements), thus rendering such models both unrealistic and non-conservative.
- Adequacy of relevant models, data and safety functions: (1) models of near-field evolution (T-H-M-C processes; long-term alteration through illitisation; and interaction with cements) are deficient and non-conservative (a kinetic treatment of clay hydrolysis reactions needs to be included throughout); (2) modelling of cement-clay interaction is inadequate and needs revision; (3) illitisation/interaction with groundwater should be analysed using

reaction-transport modelling (natural systems data should only be used in support of this); (4) modelling of near-field evolution is inconsistent (some processes are analysed using simple scoping calculations; others use reaction-transport modelling); and (5) analysis of swelling pressure data is reliant upon empirical models.

- Safety significance: the safety significance of trace minerals (calcite, pyrite, organics etc.) in bentonite should be assessed quantitatively.
- Feasibility of manufacturing, construction, testing, implementation and operation: The concept of bentonite exchangeability requires further investigation (additional data needed; there are some fundamental differences in properties between different bentonite types).

From this review, a number of key issues have been identified which would merit further investigation by SSM. These are:

- exchangeability of bentonite.
- Clay swelling.
- Mineral transformations, including
 - illitisation.
 - T-H-M-C processes during the thermal period.
 - Interaction with cement grouts and plugs.
- Consistency of conceptual models of clay behaviour.

Project information

Contact person at SSM: Jinsong Liu



Strålsäkerhetsmyndigheten

Swedish Radiation Safety Authority

Author: David Savage
Savage Earth Associates Limited, Bournemouth, U. K.

Technical Note 9

2012:28

Initial review of chemical and erosional processes within the buffer and backfill
– Geochemical processes

Date: August 2012

Report number: 2012:28 SSN: 2000-0456

Available at www.stralsakerhetsmyndigheten.se

SSN 2012:28

This report was commissioned by the Swedish Radiation Safety Authority (SSM). The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of SSM.

Summary

Clay is a fundamental component of the engineered barrier design for the KBS-3 concept and plays a key role in the performance of both the waste package buffer and disposal tunnel backfill. The main function of the clay buffer is to restrict water flow around the canister, through the selection of a material with a low hydraulic conductivity after water saturation, together with sufficient swelling pressure to ensure self-sealing. Similarly, the main function of the deposition tunnel backfill is to limit groundwater flow, again through choosing a material with a low hydraulic conductivity and suitable swelling pressure.

This document provides a review of the geochemical aspects of processes within the buffer and backfill as described in the SR-Site documentation. The review has been conducted with regard to:

- Completeness.
- Scientific soundness and quality.
- Adequacy of relevant models, data and safety functions.
- Handling of uncertainties.
- Safety significance.
- Quality in terms of transparency and traceability of information.
- Feasibility of manufacturing, construction, testing, implementation and operation.

It is concluded from this initial review that the standard of documentation in SR-Site is generally good, with the following exceptions/omissions:

- *Completeness*: (1) swelling pressure data for Na- and Ca-clays in mixed electrolyte solutions are needed; (2) more hydraulic conductivity data for Ibeco RWC bentonite are needed; (3) experimental and modelling data are needed for the interaction of low-pH cements with both MX-80 and Ibeco RWC bentonites; (4) there is a complete omission of the use of site characterisation data (groundwater chemistry, fracture minerals) from Forsmark to establish the likely long-term stability of clay minerals in the EBS; and (5) there is a gap between SR-Site 'data' and 'model' reports; neither discusses conceptual models used for clay behaviour in various safety functions.
- *Scientific soundness and quality*: (1) there needs to be a consistency of usage of conceptual models for clay properties and behaviour across different safety functions, e.g. some modelling studies employ a 'single' porosity, whilst others use a 'multiple' porosity concept; and (2) clay hydrolysis reactions are omitted from models describing long-term alteration of bentonite (illitisation, T-H-M-C processes; interaction with cements), thus rendering such models both unrealistic and non-conservative.
- *Adequacy of relevant models, data and safety functions*: (1) models of near-field evolution (T-H-M-C processes; long-term alteration through illitisation; and interaction with cements) are deficient and non-conservative (a kinetic treatment of clay hydrolysis reactions needs to be included throughout); (2) modelling of cement-clay interaction is inadequate and needs revision; (3) illitisation/interaction with groundwater should be analysed using reaction-transport modelling (natural systems data should only be used in support of this); (4) modelling of near-field evolution is inconsistent (some processes are analysed using simple scoping calculations; others use reaction-transport modelling); and (5) analysis of swelling pressure data is reliant upon empirical models.
- *Safety significance*: the safety significance of trace minerals (calcite, pyrite, organics etc.) in bentonite should be assessed quantitatively.
- *Feasibility of manufacturing, construction, testing, implementation and operation*: The concept of bentonite exchangeability requires further investigation (additional data needed; there are some fundamental differences in properties between different bentonite types).

From this review, a number of key issues have been identified which would merit further investigation by SSM. These are:

- exchangeability of bentonite.
- Clay swelling.
- Mineral transformations, including
 - illitisation.
 - T-H-M-C processes during the thermal period.
 - Interaction with cement grouts and plugs.
- Consistency of conceptual models of clay behaviour.

Contents

1. Introduction	5
2. Exchangeability of Bentonite.....	7
2.1. Composition.....	7
2.2. Hydraulic conductivity	7
2.3. Swelling Behaviour	9
2.4. Mineral Transformations.....	9
2.5. Summary.....	10
3. Clay Swelling	11
4. Mineral Transformation	13
4.1. Illitisation	13
4.2. T-H-M-C Processes.....	15
4.3. Interaction with Cement Grouts and Plugs.....	17
5. Consistency of Conceptual Models for Clay	19
5.1. Porosity Models	19
5.2. Effects of Clay Hydrolysis Reactions.....	21
5.2.1. Bentonite Pore Fluid Evolution.....	21
5.2.2. Long-Term Mineral Transformations.....	21
6. Conclusions	23
7. References.....	27
APPENDIX 1	31
Coverage of SKB Reports	31
APPENDIX 2.....	32
Suggested needs for complementary information from SKB	32
APPENDIX 3.....	33
Suggested review topics for SSM.....	33

1. Introduction

Clay is a fundamental component of the engineered barrier design for the KBS-3 concept and plays a key role in the performance of both the waste package buffer and disposal tunnel backfill. As stated in the SR-Site reports, the main function of the buffer is to restrict water flow around the canister, through the selection of a buffer material with a low hydraulic conductivity after water saturation, together with sufficient swelling pressure to ensure self-sealing (SKB, 2011, Vol I, p21). The mineralogical composition of the clay ('nominal design' is 80-85 % montmorillonite; 'accepted variation' is 75-90 % - SKB, 2010e) is a key property for the safety function of the buffer. Another aspect is that engineered barriers should be made of natural materials, stable in the long-term in the repository environment (SKB, 2011, Vol I, p60).

Similarly, the main function of the deposition tunnel backfill is to limit advective transport, again through choosing a material with a low hydraulic conductivity and suitable swelling pressure (SKB, 2011, Vol I, p21).

Geochemical properties and behaviour have a key role in defining several of the buffer safety functions (SKB, 2011, Vol I, p26), such as:

- 'Buff1' - limit advective transport by keeping
 - (a) hydraulic conductivity below 10^{-12} m s⁻¹, and
 - (b) swelling pressure above 1 MPa.
- 'Buff4' – to avoid mineral transformation through an upper limit on temperature (100 °C).
- 'Buff5' – to avoid canister sinking through maintaining a swelling pressure above 0.2 MPa.
- 'Buff6' – to limit pressure on the canister and host rock through a swelling pressure below 15 MPa and a rock temperature > -4 °C.

In addition to safety functions, one of the 'design premises' for the buffer is geochemically-based (SKB, 2011, Vol I, p178):

- swelling pressure should exceed 2 MPa.

This design premise is fulfilled when the density is in the range 1950-2050 kg m⁻³, which in turn can be achieved if the bentonite contains 75-90 wt % montmorillonite. Moreover, other geochemical constraints for the buffer are (SKB, 2010e):

- organic carbon should be < 1 wt %;
- sulphide should not exceed > 0.5 wt % (corresponding to pyrite < 1 wt %);
- total sulphur should not be > 1 wt %.

Similarly, the backfill has a single safety function, namely (SKB, 2011, Vol I, p26; SKB, 2010d):

- 'BF1' – counteract buffer expansion through maintaining a high density.

This preliminary review of geochemical processes in buffer and backfill materials has been conducted with regard to:

- Completeness.
- Scientific soundness and quality.
- Adequacy of relevant models, data and safety functions.
- Handling of uncertainties.
- Safety significance.
- Quality in terms of transparency and traceability of information.
- Feasibility of manufacturing, construction, testing, implementation and operation.

Arising from this review of SR-Site documentation, there are a number of key geochemical aspects/issues of the behaviour of the buffer and backfill that are intrinsic to the performance of the KBS-3 system which are worthy of more detailed discussion. These are:

- exchangeability of bentonite.
- Clay swelling.
- Mineral transformations, including
 - illitisation.
 - T-H-M-C processes during the thermal period.
 - Interaction with cement grouts and plugs.
- Consistency of conceptual models of clay behaviour.

These issues will be discussed in the following sections.

2. Exchangeability of Bentonite

In the SR-Site assessment, SKB has identified MX-80, a sodium montmorillonite dominated clay and Ibeco RWC, a calcium montmorillonite dominated clay as interchangeable options for the buffer material (SKB, 2011, Vol I, p180). SKB sees these materials as ‘relevant illustrations’ of possible alternatives which may be used in any repository. Fundamental to this view is that essential bentonite properties (swelling, permeability, shear strength) are achieved by a combination of sufficient density (1950-2050 kg m⁻³) and montmorillonite content (80-85 wt %) (SKB, 2011, Vol I, p178; Karnland, 2010). Karnland (2010, p16) stipulates that “*the basic mineralogical demand on the buffer material is a montmorillonite content in the range of 75 to 90 percent*”, implying that any type of montmorillonite would meet this design requirement. However, Karnland (2010, p19) goes on to state that “*a high content of potassium or some less common type of exchangeable cation will not be accepted without further investigation*”.

This section evaluates data for different bentonite types for safety-relevant properties.

2.1. Composition

Bentonite compositions can be very variable. Using available compositional data (e.g. Karnland et al., 2006; Kumpulainen and Kiviranta, 2010; Karnland, 2010; Olsson and Karnland, 2009) it can be shown that:

- Wyoming bentonites are relatively silica-rich (~ 65 % SiO₂) compared with others (< 60 % SiO₂), but it should be noted that they contain only 15 % quartz. Silica can be redistributed in the buffer in the early thermal period due to its increase in solubility with temperature.
- Indian bentonites (e.g. Kutch) are extremely rich in Fe₂O₃ (> 10 % Fe₂O₃), compared with other bentonites (< 5 % Fe₂O₃). The chemical reduction of ferric iron in the repository can lead to an increase in clay layer charge (e.g. Karnland and Birgersson, 2006, p34). The reduction of structural Fe(III) to Fe(II) tends to decrease the surface area, interlayer spacing, water swellability, and hydraulic conductivity of clay minerals (Dong, 2012).
- Greek bentonites (e.g. Ibeco RWC) are relatively rich in carbonate (> 5 % CO₃) compared with other bentonites (< 1 % CO₃). Higher carbonate contents are associated with a higher pH buffer capacity (e.g. Arcos et al., 2006).
- Sulphide is highest in Greek bentonites (> 0.5 % S). Sulphide can contribute both to buffering of redox potential and act as a supply of corrodants for the copper canister.
- Some bentonites have layer charge dominantly in octahedral layers (Wyoming, Ibeco RWC), whereas others (Indian type) have charge dominantly in the tetrahedral layer¹.

2.2. Hydraulic conductivity

Hydraulic conductivities between 10⁻¹³ and 10⁻¹⁴ m s⁻¹ have been measured in saturated bentonite in saline conditions at dry densities above about 1200 kg m⁻³ (1760 kg m⁻³ saturated density) by Karnland and co-workers (**Figure 1** – Na-bentonite and **Figure 2** - Ca-bentonite). A hydraulic conductivity 10⁻¹² m s⁻¹ is about two orders of magnitude lower than that theoretically required for mass transport being dominated by diffusion (SKB, 2010a). SKB considers that the hydraulic conductivity is primarily dependent on the geometry and composition of the buffer, the density, the ion concentration in the pore water and the temperature (SKB, 2010a).

¹ Slade et al. (Slade, P. G., Quirk, J. P., and Norrish, K., *Crystalline swelling of smectite samples in concentrated NaCl solutions in relation to layer charge*. Clays and Clay Minerals 39: 234-238, 1991.) have shown that layer charge affects swelling, with swelling decreasing as the surface density of charge increased. If the clay charge is generated in tetrahedral positions, the electrostatic attractive force between the interlayer cations and the surface will be greater than if the clay charge is generated in the more deeply buried octahedral positions. Tetrahedrally developed charge therefore plays an important role in controlling the relative swelling behaviour of smectites.

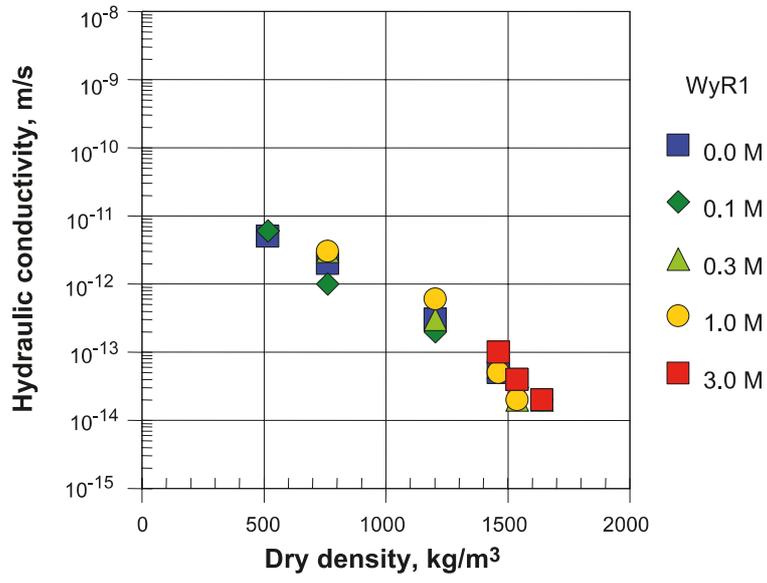


Figure 1 Hydraulic conductivity of MX-80 (WyR1) bentonite measured at different densities and molar concentration of NaCl in the saturating solution (from Karnland et al., 2006).

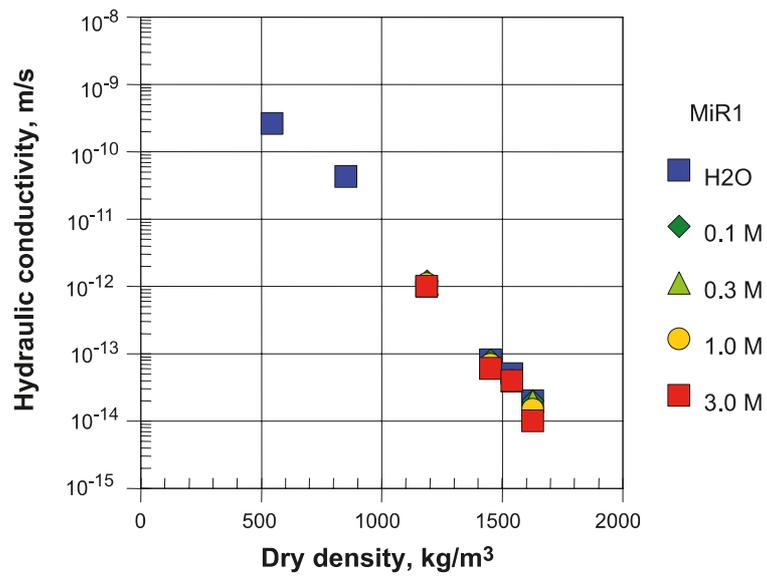


Figure 2 Hydraulic conductivity of Ibeco RWC bentonite measured at different densities and molar concentration of CaCl₂ in the saturating solution (from Karnland et al., 2006).

These Figures show that data for Na- and Ca-bentonites are similar at target compaction densities, but it can also be seen that the gradient of hydraulic conductivity with density is much greater for Ca-bentonite than the Na form, so that at 1000 kg m⁻³ dry density, the hydraulic conductivity of Ca-bentonite is about an order of magnitude greater than that for Na-bentonite. Consequently, the hydraulic conductivity of Ca-bentonite will be more susceptible to changes in density, say through erosion, than the Na-form. Pusch attributes this difference in permeability behaviour to the microstructure of the clay, with the Ca-form tending to aggregate in larger ‘stacks’ of clay lamellae than the Na-form (Pusch, 2002).

There are a number of datasets describing the hydraulic behaviour of Na-bentonites, but relatively few for Ca-bentonites and Ibeco RWC in particular. Indeed, in the SR-Site ‘Buffer, Backfill and Closure Process Report’, SKB comments that “*few tests have been performed on Ibeco RWC bentonite, but the results available indicate that the properties of this material are very similar to the properties of MX-80 at the densities considered for the buffer material*” (SKB, 2010a, p66).

Moreover, from the data available, there are fundamental differences in the pore structure of Ca- and Na-bentonites. This latter behaviour in itself need not necessarily preclude the exchangeability of bentonite types, but it is clear that there are distinctly different material properties resulting from the differences in the exchangeable cation type.

Although additional hydraulic tests on Ibeco RWC are therefore recommended, the differences in material properties between the two bentonites would still remain.

2.3. Swelling Behaviour

Details of clay swelling mechanisms are dealt with elsewhere in this report, but those relating to different bentonite types are considered here.

Experimental evidence indicates that many different types of bentonite can achieve swelling pressures that would meet performance targets for a KBS-3 buffer (e.g. Karnland, 1997a; Pusch, 1999; Karnland et al., 2006; Carlson and Keto, 2006). Whether the experimental conditions adequately represent the full range of environmental conditions that could exist in the near field of a repository at Forsmark is unclear, however.

2.4. Mineral Transformations

The subject of potential transformation of montmorillonite to other silicates is dealt with in more detail elsewhere in this report. However, regarding the behaviour of different clays:

- There is a substantial body of experimental and natural systems evidence to suggest that illitisation is inhibited by divalent interlayer cations in montmorillonite (Grauer, 1986; Grauer, 1990; Eberl, 1978; Roberson and Lahann, 1981; Yau et al., 1987; Inoue, 1983; Nadeau and Reynolds, 1981; Niu and Ishida, 2000). Ca-bentonite is thus likely to be more resistant to illitisation in the long-term than the Na-form.
- There are no mineralogical experimental data currently available for the interaction of Ca-bentonites with either OPC or low-pH cement pore fluids. There are some data available for the effects of cement pore fluids on the swelling of Ca-bentonite and some mineralogical data for the interaction of cement pore fluids with FEBEX bentonite, but this is dominated by Mg interlayer cations. Consequently, no judgement can be made regarding the relative reactivities of Na- and Ca-bentonites with cement pore fluids until further data are acquired.

2.5. Summary

The above sections show that:

- There are some fundamental differences between Ca- and Na-bentonites such as pore structure and long-term alteration that could affect the exchangeability of these materials as buffer or backfill materials and which should be further evaluated.
- Additional experimental data for different bentonite types are desirable for some issues such as long-term alteration, hydraulic properties and swelling behaviour.
- The minor mineral content of bentonites is very variable, both between different bentonites and within the same bentonite type. It is not clear whether these minerals are performance-critical or not. An assessment of this issue is desirable.

3. Clay Swelling

Smectite clays can absorb water into clay inter-layers 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 inter-layer cations (free 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. 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.

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, p23). 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 chemical activity, provided it is higher in the interlayer spaces.

For SR-Can, SKB employed a modelling approach to relate swelling pressure to saturated density (Hedin, 2004, Appendix B) which consisted of two components:

- an empirical expression relating 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.

This model fits measured data reasonably well 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).

For SR-Site however, SKB has shifted its stance regarding clay swelling behaviour and has employed an empirical correlation relating compaction density to swelling pressure (see **Figure 3**). Karnland (Karnland, 2010) noted that a plot of swelling pressures for a large number of pure montmorillonites, bentonites and other swelling clays reveals a rather wide scatter in p_{swell} when the data are plotted as a function of saturated density. Much of the scatter disappears, however, when the p_{swell} data are re-plotted in terms of an alternative parameter defined by the montmorillonite content divided by the square of the water content at full water saturation (**Figure 3**). All clay minerals with Ca^{2+} as the dominant exchangeable cation lie near the regression line shown in **Figure 3**. Clay minerals with Na^+ as the dominant cation also lie near this line at high values of X_{mont}/w_m^2 , but not at lower values (indicated in the figure by p_{swell} values enclosed by the dashed line).

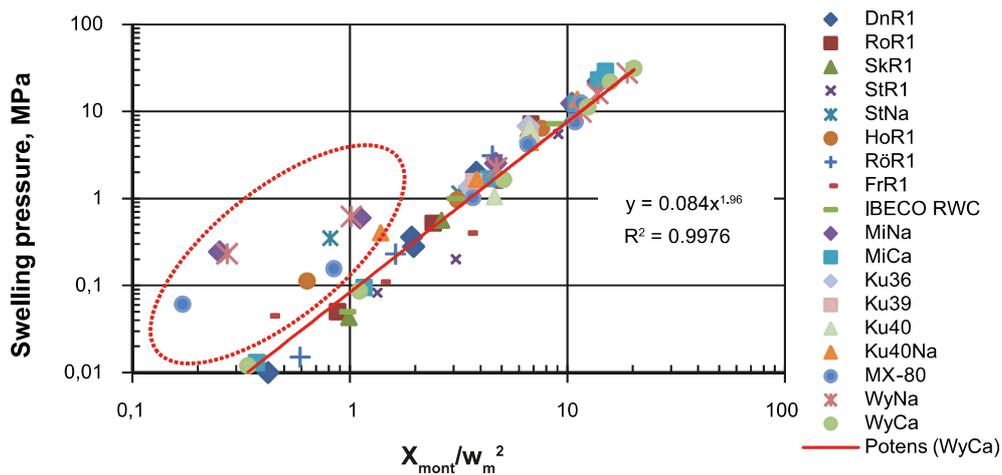


Figure 3 Plot of p_{swell} versus saturated density for a number of bentonites and swelling clays (from Karnland, 2010). The red bar indicates a range of buffer densities relevant for MX-80 and Ibeco RWC bentonites.

Karnland (Karnland, 2010) has taken the alignment around the red line in **Figure 3** to indicate that the measured relation between the variable $X_{mont}/(w_{sat})^2$ and swelling pressure is of the type $f(x) = B \cdot x^a$. The slope shows that the constant (a) has a value close to 2. Karnland thus considers that an expression for swelling pressure dominated by divalent exchangeable ions may consequently be formulated using:

$$P_s = B \cdot \left[\frac{X_{mont}}{(w_{sat})^2} \right]^a$$

The expression also appears valid for sodium bentonites in the high pressure region, which is relevant for the bentonite buffer considered in SR-Site (Karnland, 2010).

However, it should be noted that swelling behaviour has tended to be investigated in 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 empirical relationships for application in more complex fluids (realistic groundwater compositions) is necessary.

Mechanistic models to describe clay swelling are not currently available. As can be seen from the above, 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).

4. Mineral Transformation

Transformation of montmorillonite in bentonite to non-swelling minerals can impact upon processes such as swelling, hydraulic conductivity and mechanical (shear) behaviour. Although the focus on this topic has traditionally been towards the assessment for the potential conversion of montmorillonite to illite, other reactions should also be considered, such as:

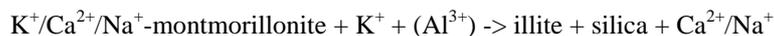
- T-H-M-C processes.
- Interaction with cement grout and plugs.

As recognised by SKB, montmorillonite stability is a complex function of temperature and groundwater composition, with key parameters in the latter including pH, and chemical activities of silica, aluminium and potassium in the aqueous phase (SKB, 2010a, p141). Indeed it is acknowledged by SKB that montmorillonite is thermodynamically unstable in groundwaters with dissolved silica concentrations matching that of quartz solubility and concentrations of silica at least as great as that of chalcedony solubility are required to stabilise montmorillonite (Figure 4). Depending upon concentrations of sodium, potassium, calcium and magnesium in groundwater therefore, montmorillonite could be transformed to illite, saponite or beidellite, or a mixture of all three minerals.

Illitisation and these other reactions are discussed in more detail below.

4.1. Illitisation

Illitisation of montmorillonite with respect to KBS-3 conditions has been discussed in detail by Karnland and Birgersson (Karnland and Birgersson, 2006), Laine and Karttunen (Laine and Karttunen, 2010), in the SR-Site main report (SKB, 2011, Volume II, p395-397) and in the Buffer, backfill and closure process report (SKB, 2010a, p 139-148). In general terms, the reaction can be written as:



So for the reaction to occur, an increase in clay layer charge and an introduction of potassium ions are required. The precise mechanism and rate of reaction are still under debate despite more than four decades of research (mainly allied to hydrocarbon exploration) (e.g. Meunier and Velde, 2004). Nevertheless, using available rates of reaction (principally those of Huang et al., 1993 and Pytte and Reynolds, 1989), the calculated conversion of smectite to illite under relevant chemical conditions and at temperatures less than 100 °C is likely to be minor according to SKB (Karnland and Birgersson, 2006).

In the SR-Site documentation, greater emphasis is placed upon mass balance and mass transfer constraints, coupled with evidence from natural analogues to suggest that illitisation of clay materials in a repository at the Forsmark Site will be limited (SKB, 2011, Volume II, p395-397). Nevertheless, the illitisation problem is complex and as described by SKB, depends upon a number of factors other than potassium availability and temperature, such as the availability of aluminium, the water/clay ratio, and silica activity (Karnland and Birgersson, 2006). Consequently, this raises an important issue, namely why this reaction is treated in SR-Site as an empirical scoping calculation, whereas other bentonite reactions (e.g. pore water evolution - Sena et al., 2011) are treated as fully-coupled reaction-transport problems using numerical computer codes. To correctly assess the potential for conversion of montmorillonite to other silicates, then reaction-transport modelling would be more appropriate.

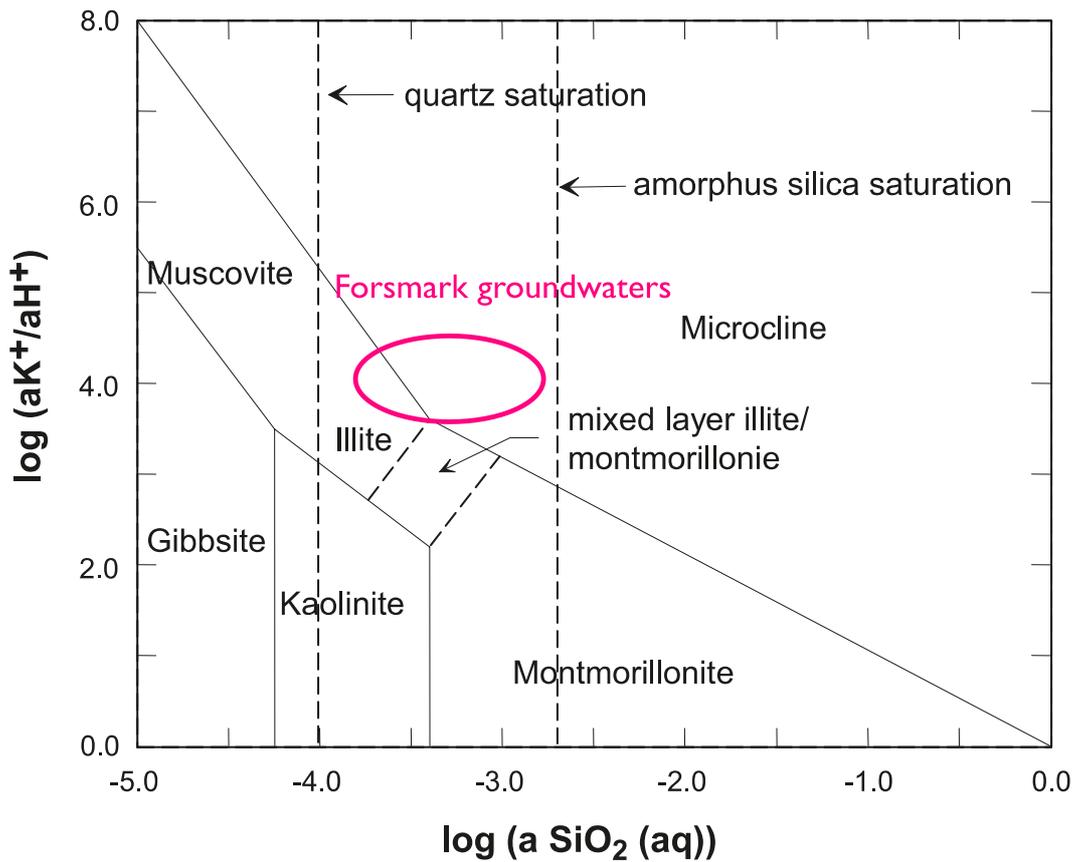


Figure 4 Mineral stability in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25 °C (modified from SKB, 2010a, p141), showing that montmorillonite is theoretically unstable in the presence of Forsmark groundwaters. Forsmark groundwater data are courtesy of Adrian Bath.

SKB has conducted detailed studies of the minerals filling fractures at the Forsmark site (SKB, 2011, Vol I, p120 and following; Figure 5), but has somehow failed to link these studies with long-term behaviour of the engineered barrier system. Consequently, any evidence (or evidence to the contrary) for the long-term stability of bentonite in the Forsmark geochemical system has not been investigated. This mineralogical evidence could be used to demonstrate long-term stability of montmorillonite or even examine evidence for previous erosion of montmorillonite by dilute groundwaters in previous glacial episodes.

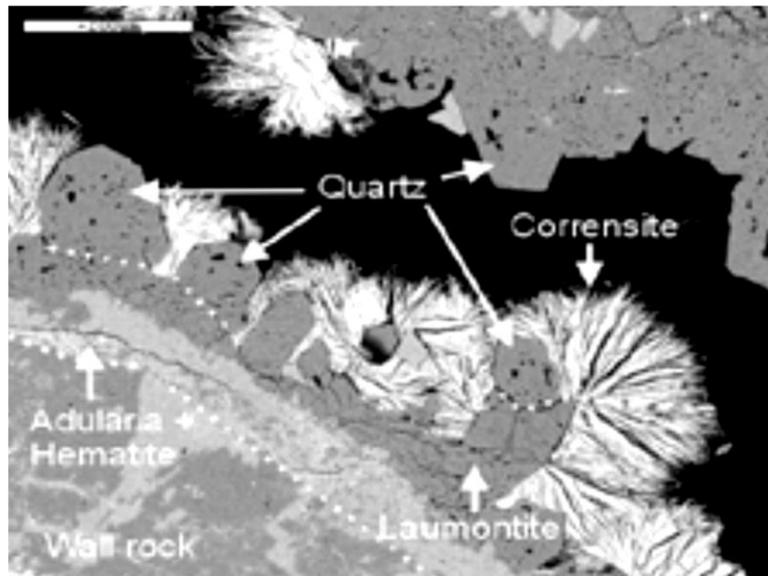


Figure 5 BSEM image of euhedral quartz and corrensite (Fe-Mg sheet silicate) from borehole KFM05A 938.00–938.18 m, growing on hematite-stained adularia (K-feldspar) and laumontite (Ca-zeolite). Scale bar is 200 μm . From Sandström et al. (Sandström et al., 2008). Corrensite dominates clay minerals in fractures at Forsmark and is a (Fe-Mg) mixed-layer chlorite-smectite mineral with some swelling properties. Although smectite is reported to occur at all depth levels at Forsmark, it is recorded as being 'minor' in abundance in comparison with corrensite, illite, saponite, and mixed-layer smectite-illite.

4.2. T-H-M-C Processes

Gradients in temperature and humidity during the period of bentonite resaturation 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.

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 buffer, water is taken up from the rock-water interface, with 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 and potential cracking. The potential issue of the buffer becoming brittle such that it could disintegrate has been raised (KASAM, 2011). Chemically within the 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.

For SR-Site, buffer resaturation has been modelled in 2-D by Åkesson et al. (Åkesson et al., 2010). However, any chemical interactions during heating and resaturation were ignored in these calculations. Instead, chemical aspects (but not mechanical effects) during resaturation are evaluated in the work reported by Sena et al. (Sena et al., 2011). However, this study does not incorporate clay mineral dissolution-precipitation reactions and focuses solely on clay ion exchange and the dissolution-precipitation of trace minerals (gypsum, anhydrite, quartz, calcite) in the buffer. Moreover, the simulations adopt equilibrium for mineral-fluid reactions and thus do not include a kinetic description of these slow reactions. Unsurprisingly, montmorillonite is preserved everywhere throughout the buffer at all times, so that in the simulations reported by Sena et al., only changes in trace mineral content and ion exchange properties are reported (Figure 6). As previously evaluated elsewhere by SSM, this modelling approach is neither realistic nor conservative (Savage et al., 2011).

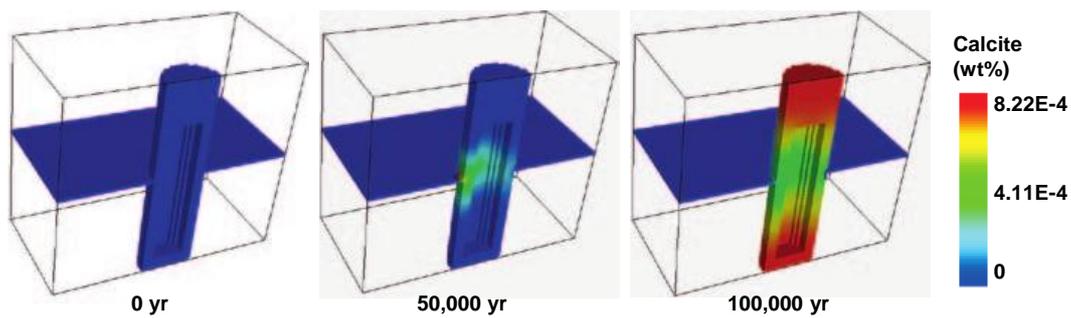


Figure 6 Evolution of calcite content in the buffer as predicted in simulations reported by Sena et al. (2010).

Hydrothermal experiments carried out by SKB with Wyoming bentonite heated to 150–200 °C have shown that cooling may lead to the precipitation of silica in various forms (SKB, 2010a, 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). For SR-Site, SKB considers that these effects will be minor, due mainly to evidence from some laboratory tests of rather short duration (SKB, 2011, Volume II, p397-398; Dueck, 2010).

Thermally-driven transformation of montmorillonite, other than consideration of illitisation (see above), is ignored in SR-Site documentation. Although experimental, analogue and modelling evidence for ‘alterations of (bentonite) impurities’ (*sic*) (e.g. sulphates, quartz, carbonates) is discussed in the ‘Buffer, backfill and closure process report’ (SKB, 2010a, p124-133), any potential transformation of montmorillonite is omitted. Previous informal interactions with SKB have indicated that this is 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). In SR-Site, SKB recognises this as an uncertainty by stating: “some of the silicate transformations are kinetically controlled and their mechanistic understanding in compacted bentonite conditions is poor. This is mainly related to clay mineral transformations (dissolution of smectite and precipitation of illite and/or kaolinite). Although these reactions occur at a very slow rate, their effect on the overall geochemical evolution is not yet clear.” (SKB, 2010a, p131).

Moreover, these omissions are perceived by SKB as an uncertainty relating to model simplification: “There are a number of accessory minerals, such as silicates, which are not included in the models, as most tend to dissolve at a very slow kinetic rate. Other silicates (usually clay minerals) precipitate at similarly slow rates. However, the dissolution-precipitation processes involving these two groups of minerals could affect the stability of montmorillonite as well as the chemical composition of the buffer porewater, thus affecting the chemical long-term evolution of the buffer” (SKB, 2010a, p131).

In an attempt to address these issues, SKB states: “In addition to the processes discussed above, the behaviour of silica and clay minerals and their effect on cementation will be addressed by performing some scoping calculations considering the present knowledge of kinetic dissolution-precipitation of smectite, silica-phases and the precipitation of alternative clay minerals (kaolinite and/or illite). These scoping calculations will give some qualitative information on the relative importance of these processes and the effect on bentonite properties, e.g. porosity changes.” (SKB, 2010a, p131). Unfortunately, this information has been unavailable for the review reported here.

4.3. Interaction with Cement Grouts and Plugs

Cement materials will be used in the construction of a spent fuel disposal facility (KBS-3V or KBS-3H) to limit the 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) (SKB, 2010c). Most of the cementitious materials will be removed before the final closure of the repository but, according to the estimates of residual materials in the KBS-3 repository (Tables 4.1-4.3 in SKB, 2010c), approximately 548 tonnes of OPC cement as rock bolt grout, 2151 tonnes of OPC cement as fracture grout, 2806 tonnes of OPC cement as shotcrete and 6.6 tonnes of other concrete materials will be left in the repository. This is of the order of 5500 tonnes of OPC cement in the entire repository. In deposition tunnels, the average amount of grout in rock fractures is envisaged to be < 20 kg per metre of tunnel, whilst shotcrete will only be used in transport tunnels where waste package deposition does not occur (SKB, 2011, Volume II, p366).

Although cement-clay interactions have been studied extensively worldwide in the last ten years, there are very few laboratory experimental studies relating to MX-80 or Ibeco RWC bentonite (Savage, 2009). Experiments conducted with these bentonites have tended to focus on swelling pressure effects (e.g. Karnland, 1997b; Karnland et al., 2007), but not on mineralogical alteration. Therefore there is a gap in data for both MX-80 and Ibeco RWC with regard to mineralogical processes at the cement-bentonite interface. In addition most, if not all, of these studies, have considered the interaction of OPC-type cement with bentonite, and not other formulations. Currently, there are only modelling studies available which address the interaction of low pH cements with bentonite (e.g. Watson et al., 2007; Lehtikoinen, 2009).

The potential reaction of cement leachates with clay-based buffer and backfill materials was looked at in detail for the KBS-3H assessment (Gribi et al., 2008) and SKB considered 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”*. SKB’s main concerns at that time were:

- 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.

For SR-Site, cement-clay interaction is discussed solely in terms of potential degradation of the backfill (Luna et al., 2006) and there is no accompanying discussion of potential effects on the buffer. Luna et al. describe a generic 2-D model 80 x 40 m in size consisting of a high transmissivity fracture intersecting a deposition tunnel filled with crushed rock and MX-80 bentonite in a 30/70 ratio. This model indicated that a pH = 9 plume could develop, but since clay mineral dissolution processes were not included in these simulations, there is limited relevance of this work. However, Luna et al. note that high-pH conditions could linger throughout the period of the first glacial cycle post-closure (120 ka). Unfortunately, there are severe limitations on the results of this study due to:

- Inappropriate choice of initial solids composition of the hydrated cement used in the simulations. Luna et al. chose a mixture of jennite, tobermorite, pyrite and calcite to represent the composition of the concrete, rather than a mix including a C-S-H gel solid-solution which other authors have found to best represent the evolving chemical composition of concrete pore fluids (e.g. Sugiyama and Fujita, 2005; Lothenbach and Winnefeld, 2006). Consequently, the solids chosen by Luna et al. will have under-estimated the high pH effects of the concrete upon the backfill and are thus non-conservative.
- Clay mineral hydrolysis reactions were not included in the simulations, thus limiting the relevance of the modelling work. Again, this is a non-conservative assumption.

Moreover, SKB states: *“a short alkaline pulse in the groundwater from low-pH cement, shotcrete and concrete is likely to form, but its effects will be negligible”* (SKB, 2011, Volume II, p318). It is considered here that this statement is unsubstantiated due to the deficiencies in the modelling reported by Luna et al. (2006).

SKB has recognised the inadequacy of the model for cement degradation described in the report by Luna et al. (Luna et al., 2006) and has produced a revised model for cement evolution (Grandia et al., 2010). This revised model contains a more realistic simulation of the dissolution of C-S-H gel, the main constituent of cement grouts. However, there is no attempt to model the interaction of cement pore water, either with rock or clay barrier materials. A conclusion of the study by Grandia et al. is: *“As a consequence, the progression of the alteration fronts in the grouted boreholes is not significant under the repository conditions for times lower than 1,000 years, and no worrying alkaline plumes are expected”* (Grandia et al., 2010). At this stage of understanding, this conclusion would appear overly optimistic.

Silica-sol based grouts may also be used to seal finer fractures. According to SKB, *“the solidified silica sol grout is similar to properties to the silica present in large quantities in the rock and fracture fillings, and may, therefore be ignored in a long-term safety context”* (SKB, 2011, Volume II, p312). It is considered here that this issue should be evaluated further.

5. Consistency of Conceptual Models for Clay

SKB uses 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 (e.g. SKB, 2010b). For example, at least three types of geochemical model are used to describe clay behaviour:

- an osmotic model has been used to describe smectite clay swelling behaviour (e.g. Karnland and Birgersson, 2006).
- 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. Sena et al., 2011).
- An empirical kinetic expression is used to describe the conversion of montmorillonite to illite (e.g. Karnland and Birgersson, 2006, Chapter 3).

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., 2009).

This lack of consistency is to a certain extent crystallised in the lack of a report in the SR-Site documentation which discusses conceptual models of clay behaviour (or behaviour of any other materials). Currently, there are ‘data’ (SKB, 2010b) and ‘model’ (SKB, 2010f) reports, neither of which adequately address conceptual models of materials behaviour.

5.1. 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 (e.g. **Figure 7**), or a system with a single porosity (e.g. **Figure 8**). This issue has been dealt with in detail for SSM elsewhere (Savage, 2011). For the multiple porosity model, the amounts of each porosity type vary with compaction density (e.g. Muurinen and Carlsson, 2007), with ‘free water’ or ‘chloride porosity’ being significantly less than the total porosity as compaction density increases.

The single porosity model has large implications for the conceptual view of pore water chemistry and hence, the trigger for buffer erosion. Since in this 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.

If calculating the evolution of porewater chemistry, it is then an important 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.

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., 2010). This would then bring greater consistency to the models of pore water evolution, clay swelling and buffer erosion.

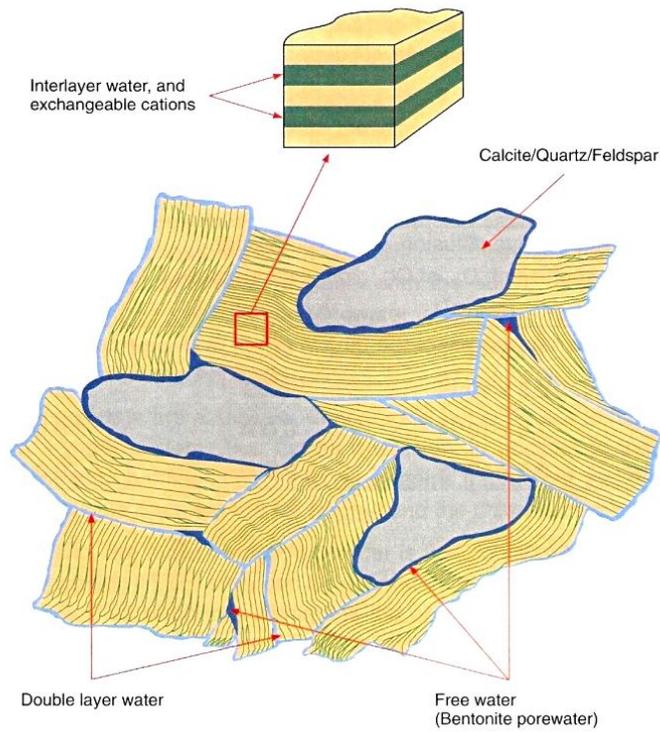


Figure 7 Schematic diagram of the nature of water in compacted bentonite according to a multiple porosity model (from Bradbury and Baeyens, 2003).

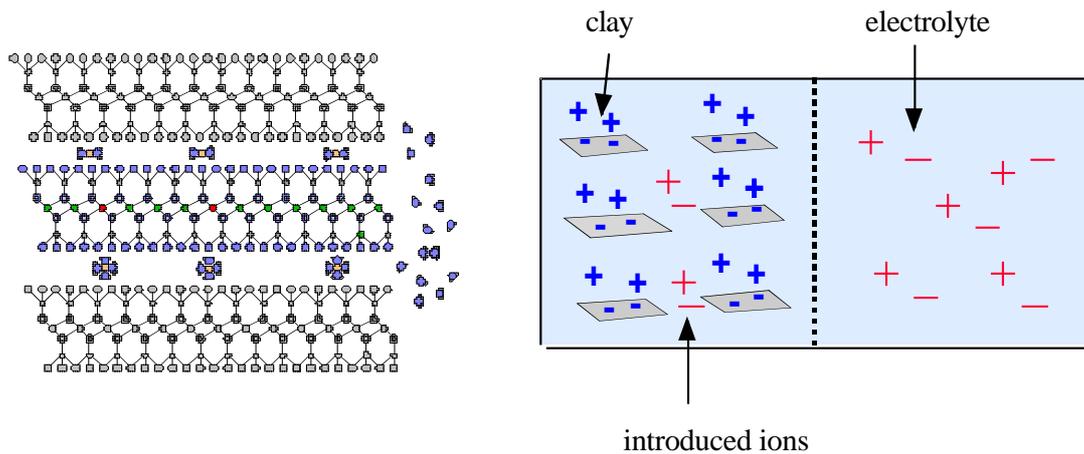


Figure 8 Schematic diagram of the nature of water in compacted bentonite according to a single porosity model (from Birgersson and Karland, 2009).

5.2. Effects of Clay Hydrolysis Reactions

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

- potential effects on pore fluid chemistry evolution, particularly pH,
- long-term transformation to other silicates, such as clays (illite, beidellite, saponite), or other silicates such as zeolites (through interaction with cement or concrete), and
- during invasion by glacial meltwaters where montmorillonite is unstable in dilute pore fluids.

This process is excluded by SKB in the modelling of barrier evolution in SR-Site.

5.2.1. 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 meltwater in glacial cycles (e.g. Neretnieks et al., 2009; SKB, 2011).

SKB's approach to modelling clay pore fluids in SR-Site is presented in the report by Sena et al. (Sena et al., 2011). 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 was excluded from these models because it was deemed to be a slow process. 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 non-conservative (Savage et al., 2010a, Savage et al., 2011).

5.2.2. Long-Term Mineral Transformations

Clay hydrolysis is also excluded from the assessment of long-term mineral transformations, with SKB relying upon empirical descriptions (e.g. Huang et al., 1993) of the long-term transformation to illite (Karnland and Birgersson, 2006, Chapter 2.4). 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 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 temperatures of 50-60 °C (e.g. Savage et al., 2010b). It may be concluded therefore that although the approach adopted by 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.

6. Conclusions

This document provides a review of the geochemical aspects of processes within the buffer and backfill as described in the SR-Site documentation. The review has been conducted with regard to:

- Completeness.
- Scientific soundness and quality.
- Adequacy of relevant models, data and safety functions.
- Handling of uncertainties.
- Safety significance.
- Quality in terms of transparency and traceability of information.
- Feasibility of manufacturing, construction, testing, implementation and operation.

Comments regarding the review of the SR-Site documentation are summarised in **Table 1**.

Table 1 Summary of comments from the review of the SR-Site documentation.

Issue	Comments
Completeness	<p>(1) Swelling pressure data for Na- and Ca-clays in mixed electrolyte solutions are needed.</p> <p>(2) More hydraulic conductivity data for Ibeco RWC are needed.</p> <p>(3) Experimental and modelling data are needed for the interaction of low-pH cements with both MX-80 and Ibeco RWC bentonites.</p> <p>(4) There is a complete omission of the use of site characterisation data (groundwater chemistry, fracture minerals) from Forsmark to establish the likely long-term stability of clay minerals in the EBS.</p> <p>(5) There is a gap between SR-Site 'data' and 'model' reports; neither discusses conceptual models used for clay behaviour in various safety functions.</p>
Scientific soundness and quality	<p>Generally good, but:</p> <p>(1) There needs to be a consistency of usage of conceptual models for clay properties and behaviour across different safety functions, e.g. some modelling studies employ a 'single' porosity, whilst others use a 'multiple' porosity concept.</p> <p>(2) Clay hydrolysis reactions are omitted from models describing long-term alteration of bentonite (illitisation, T-H-M-C processes; interaction with cements), thus rendering such models both unrealistic and non-conservative.</p>
Adequacy of relevant models, data and safety functions	<p>(1) Models for near-field evolution (T-H-M-C processes; long-term alteration through illitisation and interaction with cements) are deficient and non-conservative. A kinetic treatment of clay hydrolysis reactions needs to be included throughout.</p> <p>(2) Modelling of cement-clay interaction is inadequate and needs revision.</p> <p>(3) illitisation/interaction with groundwater should be analysed using reaction-transport modelling; natural systems data should be used in support of this.</p> <p>(4) Modelling of near-field evolution is inconsistent: some processes are analysed using simple scoping calculations; others use reaction-transport modelling.</p> <p>(5) Analysis of swelling pressure data is reliant upon empirical models.</p>
Handling of uncertainties	<p>Generally good.</p>
Safety significance	<p>Generally good, but:</p> <p>(1) The safety significance of trace minerals (calcite, pyrite, organics etc) in bentonite should be assessed quantitatively.</p>
Quality in terms of transparency and traceability of information	<p>Generally good.</p>
Feasibility of manufacturing, construction, testing, implementation and operation	<p>(1) The concept of bentonite exchangeability requires further investigation (additional data needed; there are some fundamental difference in properties of different bentonite types).</p>

7. References

- Åkesson, M., Börgesson, L., and Kristensson, O., *SR-Site Data report. THM modelling of buffer, backfill and other system components*, SKB Report TR-10-44, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Arcos, D., Grandia, F., and Domènech, C., *Geochemical evolution of the near field of a KBS-3 repository*, SKB Technical Report TR-06-16, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Arthur, R., *Handling of hydrogeochemical relations in erosion and swelling pressure models for the buffer and backfill*, STUK Technical Report STUK-TR 10, Finnish Radiation and Nuclear Safety Authority (STUK), Helsinki, Finland, 2011.
- Birgersson, M., and Karnland, O., *Ion equilibrium between montmorillonite interlayer space and an external solution*. *Geochimica et Cosmochimica Acta* 73: 1908-1923, 2009.
- Bond, A., Maul, P., Robinson, P., Savage, D., and Wilson, J.: The use of the QPAC-EBS code for modelling the evolution of engineered barrier systems with a bentonite buffer. *In Impact of Thermo-Hydro-Mechanical-Chemical (THMC) processes on the safety of underground radioactive waste repositories*. EC THERESA-TIMODAZ Conference, Luxembourg.
- Bradbury, M. H., and Baeyens, B., *Porewater chemistry in compacted re-saturated MX-80 bentonite*. *Journal of Contaminant Hydrology* 61: 329-338, 2003.
- Carlson, L., and Keto, P., *Verification of substitution of bentonites by montmorillonitic clays*, Posiva Working Report 2006-62, Posiva Oy, Olkiluoto, Finland, 2006.
- Dong, H., *Clay-microbe interactions and implications for environmental mitigation*. *Elements* 8: 113-118, 2012.
- Dueck, A., *Thermo-mechanical cementation effects in bentonite investigated by unconfined compression tests*, SKB Report TR-10-41, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Duro, L., Grivé, M., Cera, E., Gaona, X., Domènech, C., and Bruno, J., *Determination and assessment of the concentration limits to be used in SR-Can*, SKB Technical Report TR-06-2, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Eberl, D., *The reaction of montmorillonite to mixed-layer clay: the effect of interlayer alkali and alkaline earth cations*. *Geochimica et Cosmochimica Acta* 42: 1-7, 1978.
- Fernandez, A. M., and Villar, M. V., *Geochemical behaviour of a bentonite barrier in the laboratory after up to 8 years of heating and hydration*. *Applied Geochemistry* 25: 809-824, 2010.
- Grandia, F., Galindez, J. M., Arcos, D., and Molinero, J., *Quantitative modelling of the degradation processes of cement grout: Project CEMMOD*, SKB Report TR-10-25, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Grauer, R., *Bentonite as a backfill material in the high-level waste repository: chemical aspects*, Nagra Technical Report 86-12E, Nagra, Baden, Switzerland, 1986.
- Grauer, R., *The chemical behaviour of montmorillonite in a repository backfill: selected aspects*, Technical Report 88-24E, Nagra, Wettingen, Switzerland, 1990.
- Gribi, P., Johnson, L. H., Suter, D., Smith, P. A., Pastina, B., and Snellman, M., *Safety assessment for a KBS-3H spent nuclear fuel repository at Olkiluoto: Process report*, SKB Report R-08-36, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.
- Hedin, A., *Integrated near-field evolution model for a KBS-3 repository*, SKB Research Report R-04-36, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2004.
- Huang, W., Longo, J. M., and Pevear, D. R., *An experimentally derived kinetic model for smectite to illite conversion and its use as a geothermometer*. *Clays and Clay Minerals* 41, 1993.
- Inoue, A., *Potassium fixation by clay minerals during hydrothermal treatment*. *Clays and Clay Minerals* 31: 81-91, 1983.
- Karnland, O., *Bentonite swelling pressure in strong NaCl solutions. Correlation between model calculations and experimentally determined data*, SKB Technical Report TR 97-31, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1997a.
- Karnland, O., *Cement/bentonite interaction. Results from 16 month laboratory tests*, SKB Technical Report 97-32, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1997b.

- Karnland, O., *Chemical and mineralogical characterization of the bentonite buffer for the acceptance control procedure in a KBS-3 repository*, SKB Report TR-10-60, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Karnland, O., and Birgersson, M., *Montmorillonite stability with special respect to KBS-3 conditions*, SKB Technical Report TR-06-11, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Karnland, O., Olsson, S., Nilsson, U., and Sellin, P., *Mineralogy and sealing properties of various bentonites and smectite-rich clay materials*, SKB Technical Report TR-06-30, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Karnland, O., Olsson, S., Nilsson, U., and Sellin, P., *Experimentally determined swelling pressures and geochemical interactions of compacted Wyoming bentonite with highly alkaline solutions*. *Physics and Chemistry of the Earth 32*: 275-286, 2007.
- Kumpulainen, S., and Kiviranta, L., *Mineralogical and chemical characterization of various bentonite and smectite-rich clay materials. Part A: Comparison and development of mineralogical characterization methods. Part B: Mineralogical and chemical characterization of clay materials*, Posiva Working Report 2010-52, Posiva Oy, Oliluoto, Finland, 2010.
- Laine, H., and Karttunen, P., *Long-term stability of bentonite: a literature review*, Posiva Report 2010-53, Posiva Oy, Olkiluoto, Finland, 2010.
- Lehikoinen, J., *Bentonite-cement interaction – Preliminary results from model calculations*, Posiva Working Report WR 2009-37, Posiva Oy, Olkiluoto, Finland, 2009.
- Lothenbach, B., and Winnefeld, F., *Thermodynamic modelling of the hydration of Portland cement*. *Cement and Concrete Research 36*: 209-226., 2006.
- Luna, M., Arcos, D., and Duro, L., *Effects of grouting, shotcreting and concrete leachates on backfill geochemistry*, SKB Research Report R-06-107, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Meunier, A., and Velde, B., *Illite*, Springer-Verlag, Berlin, Heidelberg, 2004.
- Muurinen, A., and Carlsson, T., *Development of methods for on-line measurements of chemical conditions in compacted bentonite*. *Physics and Chemistry of the Earth 32*: 241-246, 2007.
- Nadeau, P. H., and Reynolds, R. C., *Burial and contact metamorphism in the Mancos Shale*. *Clays and Clay Minerals 29*: 249, 1981.
- Neretnieks, I., Liu, L., and Moreno, L., *Mechanisms and models for bentonite erosion*, SKB Report TR-09-35, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2009.
- Niu, B., and Ishida, H., *Different rates of smectite illitization in mudstones and sandstones from the Niigata Basin, Japan*. *Clay Minerals 35*: 163-173, 2000.
- Ochs, M., Talerico, C., Sellin, P., and Hedin, A., *Derivation of consistent sorption and diffusion parameters and their uncertainties for compacted MX-80 bentonite*. *Physics and Chemistry of the Earth 31*: 600-609, 2006.
- Olsson, S., and Karnland, O., *Characterisation of bentonite from Kutch, India and Milos, Greece - some candidate tunnel back-fill materials?*, SKB Report R-09-53, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2009.
- Pusch, R., *Is montmorillonite-rich clay of MX-80 type the ideal buffer for isolation of HLW?*, SKB Report TR-99-33, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1999.
- Pusch, R., *The buffer and backfill handbook. Part 1: Definitions, basic relationships, and laboratory methods*, SKB Technical Report SKB TR-02-20, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2002.
- Pusch, R., and Karnland, O., *Hydrothermal effects on montmorillonite. A preliminary study*, SKB Report TR-88-15, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1988.
- Pytte, A. M., and Reynolds, R. C., *The thermal transformation of smectite to illite*, In (N. D. Naeser and T. H. McCulloh eds) *Thermal History of Sedimentary Basins*, Springer-Verlag, New York, 1989.
- Roberson, H. E., and Lahann, R. W., *Smectite to illite conversion rates: effect of solution chemistry*. *Clays and Clay Minerals 29*: 129, 1981.
- Sandström, B., Tullborg, E.-L., Smellie, J. A. T., Mackenzie, A. B., and Suksi, J., *Fracture mineralogy of the Forsmark site. SDM-Site Forsmark*, SKB Report R-08-102, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.

- Savage, D., *A review of experimental evidence for the development and properties of cement-bentonite Interfaces with implications for gas transport*, Nagra Report NAB 09-30, Nagra, Wettingen, Switzerland, 2009.
- Savage, D., *An Assessment of the Impacts of Porosity Models on Bentonite Behaviour and Performance*, Unpublished Report Swedish Radiation Safety Authority, Stockholm, Sweden, 2011.
- Savage, D., Arthur, R., Watson, C., and Wilson, J., *An evaluation of models of bentonite pore water evolution*, SSM Technical Report 2010:12, Swedish Radiation Safety Authority, Stockholm, Sweden, 2010a.
- Savage, D., Arthur, R., Watson, C., Wilson, J., and Strömberg, B., *Testing geochemical models of bentonite pore water evolution against laboratory experimental data*. *Physics and Chemistry of the Earth* 36: 1817-1829, 2011.
- Savage, D., Benbow, S., Watson, C., Takase, H., Ono, K., Oda, C., and Honda, A., *Natural systems evidence for the alteration of clay under alkaline conditions: an example from Searles Lake, California*. *Applied Clay Science* 47: 72-81, 2010b.
- Savage, D., Bennett, D., Apted, M., Sällfors, G., Saario, T., and Segle, P., *International Expert Review of SR-Can: Engineered Barrier Issues. External review contribution in support of SKI's and SSI's review of SR-Can*, SKI Report 2008:10, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 2008.
- Sena, C., Salas, J., and Arcos, D., *Aspects of geochemical evolution of the SKB near field in the frame of SR-Site*, SKB Report TR-10-59, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2011.
- SKB, *Buffer, backfill and closure process report for the safety assessment SR-Site*, SKB Report TR-10-47, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010a.
- SKB, *Data report for the safety assessment SR-Site*, SKB Report TR-10-52, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010b.
- SKB, *Design, construction and initial state of the underground openings*, SKB Report TR-10-18, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010c.
- SKB, *Design, production and initial state of the backfill and plug in deposition tunnels*, SKB Report TR-10-16, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010d.
- SKB, *Design, production and initial state of the buffer*, SKB Report TR-10-15, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010e.
- SKB, *Model summary report for the safety assessment SR-Site*, SKB Report TR-10-51, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010f.
- SKB, *Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project Volumes I-III*, SKB Report TR-11-01, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2011.
- Slade, P. G., Quirk, J. P., and Norrish, K., *Crystalline swelling of smectite samples in concentrated NaCl solutions in relation to layer charge*. *Clays and Clay Minerals* 39: 234-238, 1991.
- Sugiyama, D., and Fujita, T., *A thermodynamic model of dissolution and precipitation of calcium silicate hydrates*. *Cement and Concrete Research* 36: 227-237, 2005.
- Watson, C., Benbow, S., and Savage, D., *Modelling the interaction of low pH cements and bentonite. Issues affecting the geochemical evolution of repositories for radioactive waste*, SKI Report 2007:30, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 2007.
- Yau, Y.-C., Peacor, D. R., Essene, E. J., Lee, J. H., Kuo, L.-C., and Cosca, M. A., *Hydrothermal treatment of smectite, illite, and basalt to 460 °C; comparison of natural with hydrothermally formed clay minerals*. *Clays and Clay Minerals* 35: 241-250, 1987.

Coverage of SKB Reports

Table A1-1 List of mandatory and other reports covered in the review.

Reviewed report	Reviewed sections	Comments
Mandatory Reports		
TR-11-01	SR-Site Main report: Sections 5.5; 5.6; 10.2.5; 10.3.7; 10.3.10; 10.3.12	✓
TR-10-15	Design, production and initial state of buffer	✓
TR-10-16	Design, production and initial state of the backfill and plug in deposition tunnels, chapter 6	✓
TR-10-45	FEP Report for the safety assessment SR-Site, Appendices 6 & 7	✓
TR-10-47	Buffer, backfill and closure process report for the safety assessment SR-Site, chapters 3.5 and 4.4	✓
Other Reports		
TR-06-11	Montmorillonite stability with special respect to KBS-3 conditions	✓
TR-06-30	Mineralogy and sealing properties of various bentonites and smectite-rich clay materials	✓
TR-10-18	Design, construction and initial state of the underground openings	✓
TR-10-52	Data report for the safety assessment SR-Site	✓
TR-10-59	Aspects of geochemical evolution of the SKB near-field in the frame of SR-Site	✓
TR-10-60	Chemical and mineralogical characterisation of the bentonite buffer for the control procedure in a KBS-3 repository	✓
R-06-106	Assessment of the oxygen consumption in the backfill. Geochemical modelling in a saturated backfill	✓
R-06-107	Effects of grouting, shotcreting and concrete leachates on backfill geochemistry	✓
R-09-53	Characterisation of bentonite from Kutch, India and Milos, Greece – some candidate tunnel backfill materials	✓

Suggested needs for complementary information from SKB

Table A2-1 List of questions, additional data and information required from SKB.

Item	Question
1	When will the results of scoping calculations regarding transformation of montmorillonite referred to in the 'Buffer Backfill and Closure Process Report for the safety assessment SR-Site' (TR-010-47, p131) become available?
2	Are experimental data available for the swelling of MX-80 and Ibeco RWC bentonites in samples of Forsmark groundwater?

Suggested review topics for SSM

Table A3-1 List of suggested topics requiring further additional work.

Item	Topic
1	Exchangeability of Na- and Ca-bentonites
2	Swelling behaviour of clays
3	The potential for long-term transformation of montmorillonite through illitisation, T-H-M-C processes, or interactions with cement
4	Consistency of conceptual models of clay behaviour



2012:29

The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

Strålsäkerhetsmyndigheten
Swedish Radiation Safety Authority

SE-171 16 Stockholm
Solna strandväg 96

Tel: +46 8 799 40 00
Fax: +46 8 799 40 10

E-mail: registrator@ssm.se
Web: stralsakerhetsmyndigheten.se