

# Exchangeability of bentonite buffer and backfill materials

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ISBN 978-952-478-732-1 (print, Edita Prima Oy, Finland 2012)  
ISBN 978-952-478-733-8 (pdf)  
ISSN 1796-7171

*SAVAGE David (Savage Earth Associates Ltd), ARTHUR Randy (Intera Inc). Exchangeability of bentonite buffer and backfill materials. STUK-TR 12. Helsinki 2012. 56 pp.*

**Keywords:** engineered barrier, canister buffer, tunnel backfill, bentonite, montmorillonite, performance assessment, performance target

## 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. One issue that is relevant to material properties is the degree to which different bentonite compositions can be regarded as interchangeable. In Posiva's current repository design, the reference bentonite composition is MX-80, a sodium montmorillonite dominated clay. Posiva would like to be able to use bentonite with Ca-montmorillonite as the dominant clay mineral. However, at this stage, it is not clear what supporting data need to be acquired/defined to be able to place the state of knowledge of Ca-bentonite at the same level as that of Na-bentonite.

In this report, the concept of bentonite exchangeability has been evaluated through consideration of how bentonite behaviour may be affected in six key performance-relevant properties, namely

- mineralogical composition and availability of materials
- hydraulic conductivity
- mechanical and rheological properties
- long-term alteration
- colloidal properties
- swelling pressure.

The report evaluates implications for both buffer and backfill.

Summary conclusions are drawn from these sections to suggest how bentonite exchangeability may be addressed in regulatory assessments of engineered barrier design for a future geological repository for spent fuel in Finland. Some important conclusions are:

- There are some fundamental differences between Ca- and Na-bentonites such as colloidal behaviour, 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 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.

Posiva's view that assessments of the exchangeability of different bentonite types as buffer materials should be based on performance requirements for this engineered barrier seems reasonable, but the level of understanding needed to adequately support such assessments is not clear and would seem to depend on the types of requirements being considered. Assessments addressing long-term safety requirements may be the

most challenging because these requirements relate to a target state of the buffer that will not be attained until hundreds or thousands of years have elapsed since the initial state, and to subsequent interactions involving the buffer with continuously evolving near-field conditions. Should such assessments be based in whole or in part on experimental testing, then it is important to consider whether the experimental conditions are appropriate and defensibly bounding with respect to conditions expected in the near field over long periods of time. Assessments based on modelling should consider whether the models adequately represent thermal, mass-transport, chemical/mineralogical and mechanical processes controlling bentonite-water interactions, whether the reliability of the models has been verified to the extent possible in relation to relevant experimental and natural systems studied, and whether model results can be sensibly related to safety-relevant physical, thermal and rheological properties of the buffer.

*SAVAGE David (Savage Earth Associates Ltd), ARTHUR Randy (Intera Inc). Bentoniittimateriaalien vaihdettavuus loppusijoituskonseptin kapselipuskurissa ja tunnelitäytössä. STUK-TR 12. Helsinki 2012. 56 s.*

**Avainsanat:** tekniset päästöesteet, kapseli puskuri, tunnelitäyte, bentoniitti, montmorilloniitti, turvallisuusperustelu, toimintakykytavoite

## Tiivistelmä

Saviin perustuvat puskuri- ja tunnelitäyttömateriaalit ovat suunnitellulle KBS-3 loppusijoituskonseptille tärkeitä päästöesteitä. Materiaaliominaisuuksia tutkittaessa tärkeä kysymys on, missä määrin saatavilla olevat eri bentoniittimateriaalit ovat keskenään vaihtokelpoisia. Posiva on suunnittelulähtökohtiensa vertailutasoksi määritellyt Na-montmorilloniittivaltaisen saven, ns. MX-80 bentoniitin. Posiva haluaa varata mahdollisuuden käyttää myös Ca-montmorilloniittivaltaista savea sulkurakenteissaan. Bentoniitti-materiaalien vaihdettavuus edellyttää kuitenkin lisätietojen hankkimista Ca-bentoniitista, jotta tietämys siitä saataisiin samalle tasolle kuin Na-bentoniitin.

Tässä raportoinnissa todetaan seuraavien näkökohtien olevan tärkeitä bentoniitteja tarkasteltaessa:

- Ca- ja Na-bentoniitin kesken on joitakin olennaisia eroja kuten kolloidinen käyttäytyminen, huokosrakenne ja muuttumisilmiöt aikojen kuluessa. Nämä erot voivat vaikuttaa kapselipuskuri- ja tunnelitäyttömateriaalien vaihdettavuuteen ja näiden erojen merkitystä tulisi edelleen arvioida.
- Kokeellisista tutkimuksista saatavat tulokset ovat toivottavia erityisesti pitkällä aikavälillä bentoniiteissa tapahtuvien mineralogiaan (muuttumiseen), hydraulisiin ominaisuuksiin ja paisuntaominaisuuksiin liittyvien muutosten selvittämisessä.
- Bentoniittien aksessorinen mineraalisisältö on hyvin vaihteleva sekä eri bentoniittien välillä että myös saman bentoniittityypin sisällä. Aksessoristen mineraalien turvallisuusmerkityksestä ei ole selvää käsitystä. Arviot ovat toivottavia.

Posivan mukaan vaihtokelpoisuuden arviointi tulee perustua rakennettujen päästöesteiden toimintakykyvaatimusten täyttymiseen. Näkemys on perusteltu, mutta samalla arviointiin tarvittavan riittävän ymmärryksen osittaminen ei ole selvää ja näyttää riippuvan siitä mitä tai millaisia vaatimuksia tarkastellaan. Pitkäaikaisturvallisuuden osittamiseen liittyvät vaatimukset ovat haasteellisimpia, sillä ne liittyvät päästöesteiden tavoitetiloihin, jotka saavutetaan esimerkiksi puskurin tapauksessa vasta satojen tai tuhansien vuosien kuluttua. Jos arvioinnit perustuvat kokonaan tai osittain kokeelliselle tutkimukselle, on tärkeää osoittaa, että koejärjestelyt ovat perusteluja tulevaisuuden odotettavissa oleviin olosuhteisiin nähden. Mikäli arvioinnit perustuvat mallinnuksiin, tärkeiksi nousevat kysymykset siitä, huomioivatko mallit relevantit fysikaaliskemialliset kytkökset ja ovatko ne riittävän verifioituja käytettävissä oleviin kokeellisiin ja luonnonanalogioiden tutkimuksiin.

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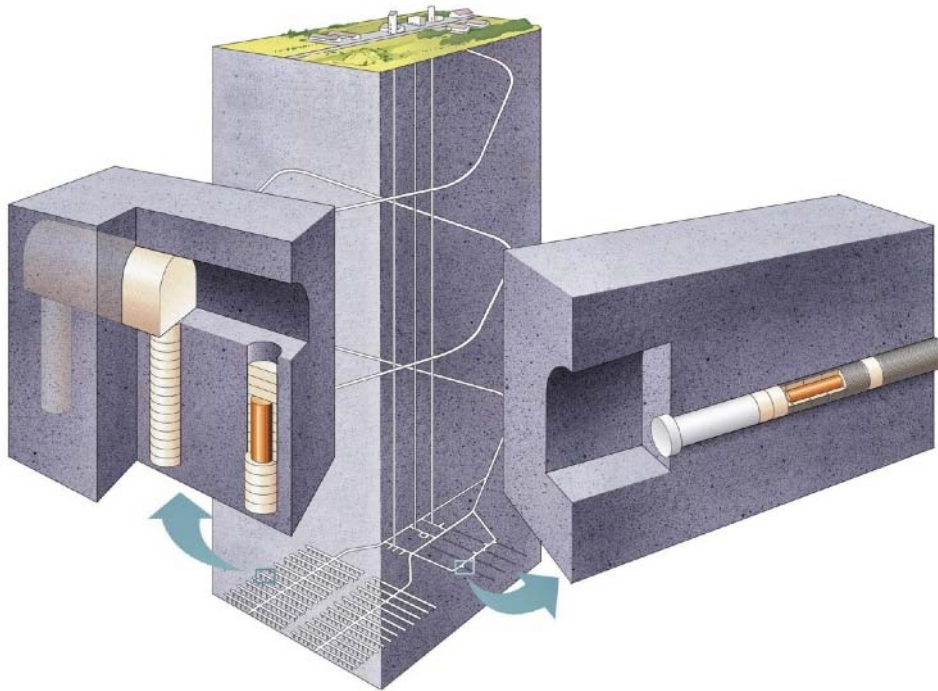
# 1 Introduction

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 (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 and sustain 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.

One issue that is relevant to the above material properties is the degree to which different bentonite compositions can be regarded as interchangeable. In Posiva's current repository design, the reference bentonite composition is MX-80, a sodium montmorillonite-dominated clay. Posiva would like to be able to use bentonite with Ca-montmorillonite as the dominant clay mineral. However, at this stage, it is not clear what supporting data need to be acquired/defined to be able to place the state of knowledge of Ca-bentonite at the same level as that of Na-bentonite.

The report evaluates implications for both buffer and backfill. The design of the buffer is described in TKS-2009 (Posiva, 2010) and Juvankoski and Marcos (2009) (Figure 1) where buffer functions are described as:



**Figure 1.** The KBS-3V (left) and KBS-3H (right) are alternative realisations of the KBS-3 spent fuel disposal method. KBS-3V is the reference variant in the construction licence application and its accompanying safety case. (from Posiva, 2010, p285).

- to isolate the canister from the near-field bedrock and processes therein;
- to support the canister in its installation position;
- to absorb minor near-field rock movements, and
- to prevent flow of groundwater in the gap between the canister and the bedrock in such a way that mass transport between the bedrock and the canister occurs mainly by diffusion.

The buffer material is high-grade compacted bentonite. The reference bentonite type is MX-80, a Wyoming sodium bentonite with a montmorillonite content above 75%. Posiva believes that as long as a bentonite type contains greater than 75% montmorillonite, it can be considered as a suitable candidate for substitution for MX-80 in the future (Juvankoski and Marcos, 2009).

According to TKS-2009 (Posiva, 2010, p188) the requirements for the buffer are:

- sufficiently low hydraulic conductivity in order to prevent advection;
- sufficient swelling pressure in order to ensure tightness and self-sealing ability as well as to prevent microbiological activity and the sinking of the canister;
- sufficiently small pore structure in order to prevent the migration of radionuclides with colloids.

The buffer must also guarantee sufficient protection of the canister against small rock dislocations, bearing in mind the canister properties, the selected buffer material and the rock conditions prevailing at Olkiluoto. The buffer properties themselves must not, as a consequence of the heat released from the canister, change to an extent that would be detrimental (Posiva, 2010, p188).

A complication of discussing the applicability of exchangeability of clay to the tunnel backfill is that a final design has yet to be chosen by Posiva (or SKB). The backfill concept currently consists of a foundation bed, and pre-compacted blocks and pellets (Hansen et al., 2009) (Figure 2). According to Hansen et al. (2009), three different materials are being considered for the compacted clay blocks which constitute the bulk of the backfill:

- Friedland clay, with an estimated maximum swelling clay content of 30%.
- Milos B bentonite clay (Ibeco RWC), with an estimated amount of swelling clay of 50–60%.

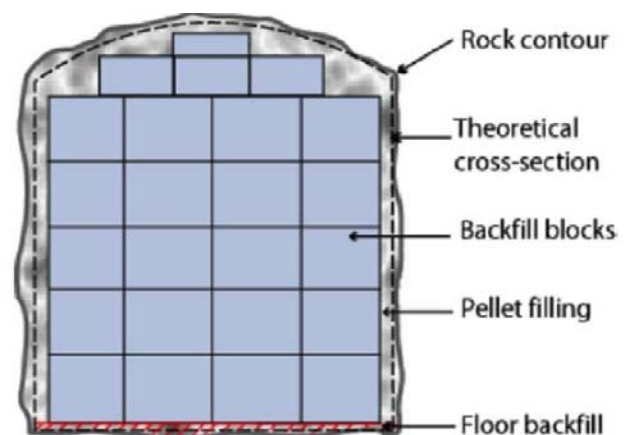
- A mixture of bentonite and ballast, with a minimum bentonite content of 40% (of which over 70% is composed of swelling minerals).

Hansen et al. consider that the target state will be achieved once the backfill has been completely saturated with water and the functional requirements as a result of the saturation have been met. The saturation may last from 50 to 1000 years. Erosion, piping, or defects in the self-sealing process may inhibit achievement of the target state (Hansen et al., 2009).

The target functions for the backfill are (Hansen et al., 2009):

- to prevent the creation of preferential flow paths,
- to keep the buffer in place in the deposition hole,
- to support the surrounding rock, and
- not to jeopardise the function of canister, buffer or bedrock.

According to Posiva, the prevention of flow paths has been identified as the key factor in system evolution and performance (Hansen et al., 2009). If there are no preferential flow paths, the groundwater cannot rapidly transport potentially harmful components through the backfill to the buffer or canister. One of the most probable places where preferential flow path(s) could develop is at the interface between the backfill and the rock. The backfill needs a tight contact with the surrounding host rock in order to function as desired (Hansen et al., 2009). In order to achieve such a tight contact,



**Figure 2.** Schematic cross section of a backfilled tunnel. The three main components of the block backfill are 1) pre-compacted backfill blocks, 2) pellet filling and 3) material placed underneath the blocks to provide stable foundation for the block assemblage. From Keto et al. (2009).

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the backfill must develop a swelling pressure of 100 kPa (Hansen et al., 2009).

## 1.1 Structure of the report

In this report, the concept of bentonite exchangeability has been evaluated through consideration of how bentonite behaviour may be affected in six key performance-relevant properties, namely:

- mineralogical composition and availability of materials
- hydraulic conductivity

- mechanical and rheological properties
- long-term alteration
- colloidal properties
- swelling pressure.

Summary conclusions are drawn from these sections to suggest how bentonite exchangeability may be addressed in regulatory assessments of engineered barrier design for a future geological repository for spent fuel in Finland.

## 2 Mineralogical composition and availability of materials

### 2.1 Buffer

The mineralogical composition of clays used for the buffer is an essential issue in understanding the long-term evolution of bentonite materials and also affects, among others, the composition of pore water, the susceptibility for erosion, and transport of radionuclides (Kumpulainen and Kiviranta, 2010). Consequently, mineralogical composition affects the designs of buffer and backfill components. Currently, the sole mineralogical aspect of the buffer design is that it should contain more than 75% of montmorillonite (Posiva, 2010, p364). This implies that any type of montmorillonite (Na, Ca, K, Mg) would meet this design requirement.

Posiva report that MX-80 sodium bentonite has been used in buffer block manufacturing tests and in material tests (Posiva, 2010, p364). Calcium bentonite (Deponit CaN) from the Greek island of Milos has also been tested as an alternative type of bentonite. These materials are also options for the raw material for the pellets possibly used in the buffer structure. China and India have also been considered as potential bentonite suppliers (Posiva, 2010, p193). Posiva state that the final selection of bentonite will be governed by quality, the security of supply and availability that spans a sufficiently long period of time. A study has been conducted on this issue (Ahonen et al., 2008).

The reference bentonite selected is MX80, which is the commercial name of a Wyoming sodium bentonite with montmorillonite content above 75%. Chemical analyses of some candidate bulk materials (from Kumpulainen and Kiviranta, 2010) are shown in Table 1. This shows, *inter alia*, that:

- Wyoming bentonites are relatively silica-rich (~ 65% SiO<sub>2</sub>) compared with others (< 60% SiO<sub>2</sub>), 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 are extremely rich in Fe<sub>2</sub>O<sub>3</sub> (> 10%), compared with other bentonites (< 5%). The chemical reduction of ferric iron in the repository can lead to an increase in clay layer charge and a decrease in swelling (e.g. Karnland and Birgersson, 2006).
- Greek (> 5% CO<sub>3</sub>) and Friedland (> 2% CO<sub>3</sub>) bentonites are relatively rich in carbonate compared with the other bentonites (< 1% CO<sub>3</sub>). Higher carbonate contents are associated with a higher pH buffer capacity (e.g. Arcos et al., 2006).
- Organic carbon is highest in the Friedland bentonites (> 0.25%). This can contribute not only to controlling redox potential but can also act as a potential complexant of radionuclides.
- Sulphide is highest in the 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.

The mineralogical analyses of the bulk materials are shown in Table 2. This shows that:

- smectite content is highest in the Wyoming bentonites (> 75%) and lowest in the Friedland bentonites (< 25%).
- Quartz content is very high in the Friedland bentonites (> 20%).
- Pyrite content is highest in the Greek bentonites (> 1%).

The information in Table 2 therefore suggests that MX-80, Deponit CaN ('AC200'), and possibly Kutch ('Basic Star') are the only bentonites that would fulfil the design requirements set out by Posiva.

**Table 1.** Chemical compositions of bulk bentonite materials (from Kumpulainen and Kiviranta, 2010).

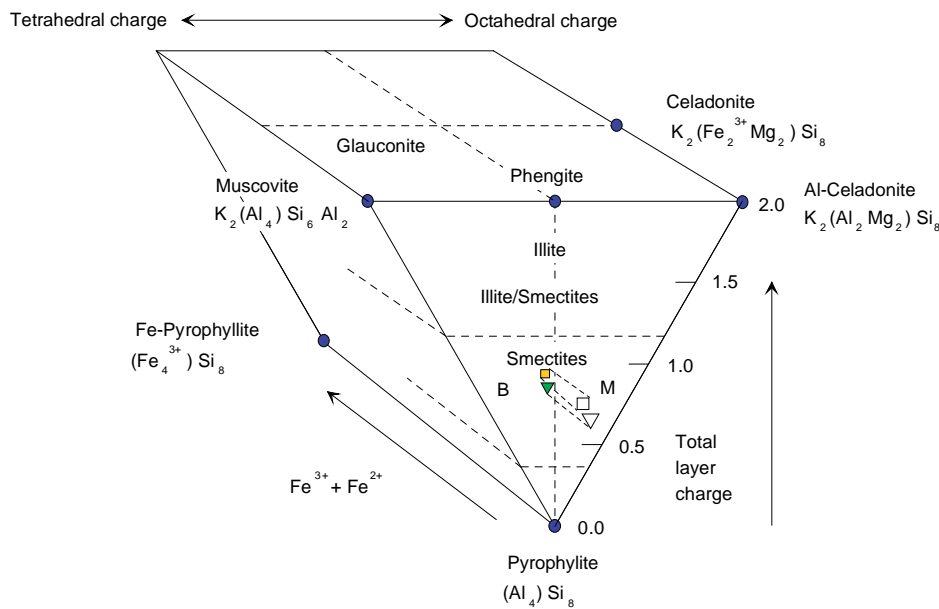
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	CO <sub>2</sub>	Org C	SO <sub>3</sub>	S	LOI	H <sub>2</sub> O
<b>Wyoming, USA</b>															
ABM MX-80	65.37	18.70	3.59	0.36	0.15	2.34	1.29	2.19	0.53	0.79	0.14	0.14	0.20	5.36	9.49
Volclay	64.32	19.00	3.30	0.48	0.15	2.56	1.66	2.03	0.62	0.99	0.15	0.08	0.18	5.70	8.40
WyMX-80	64.88	18.92	3.28	0.37	0.15	2.41	1.23	2.05	0.59	0.62	0.13	0.07	0.22	5.90	9.76
<b>Milos, Greece</b>															
ABM DepCaN	57.66	16.96	4.71	0.20	0.75	3.26	5.04	0.90	0.98	5.12	0.02	0.35	0.62	8.94	12.79
ABM DepCaN <sub>2</sub>	57.71	17.02	4.66	0.28	0.75	3.28	5.09	0.89	0.91	4.90	0.01	0.28	0.62	8.78	12.79
AC200	56.38	17.07	5.01	0.42	0.78	3.49	4.73	2.97	0.59	5.60	0.00	0.20	0.39	8.16	9.88
<b>Kutch, India</b>															
ABM Asha	51.15	21.23	13.40	0.07	1.20	2.02	0.73	2.02	0.06	0.36	0.02	0.01	0.02	8.11	11.71
Basic Starbentonite	54.21	17.44	12.63	0.54	1.35	2.78	1.63	1.40	0.14	0.68	0.01	0.24	0.16	7.71	8.81
Ca-Starbentonite	58.24	15.27	11.52	0.01	1.52	3.14	1.67	1.62	0.21	0.32	0.00	0.25	0.17	6.65	12.44
HLM-Starbentonite	55.31	15.48	13.52	0.99	1.66	2.46	1.21	2.45	0.22	0.97	0.00	0.04	0.03	6.67	14.72
<b>Friedland, Germany</b>															
ABM Friedland	60.61	17.28	4.46	2.62	0.95	1.93	0.48	1.09	2.94	2.40	0.31	0.53	0.39	7.25	4.01
SM Friedland	60.17	17.41	5.28	2.24	0.93	2.06	0.63	1.19	2.67	2.03	0.27	0.70	0.47	0.95	7.72

**Table 2.** Mineralogical composition of bentonites investigated by Kumpulainen and Kiviranta using the Rietveld method (from Kumpulainen and Kiviranta, 2010).

Minerals	Wyoming, USA			Milos, Greece		Kutch, India				Friedland, Germany	
	ABM MX80	WyMX80	Volclay	ABM DepCaN	AC200	ABM Asha	Basic Star	HLM Star	Ca-Star	ABM Friedland	SH Friedland
Smectite	83.7	76.3	76.3	68.0	76.8	55.1	73.0	65.6	81.3	19.2	23.9
Illite	0.1	1.8	1.8	8.7	5.7	13.4	7.0	11.6	2.6	32.2	34.8
Kaolinite						22.7	4.0	5.8	2.2	9.7	8.5
Calcite	0.5	0.7	0.7	7.2	5.8	0.7	1.9	1.1	0.9		
Muscovite	5.3	8.3	8.3	4.7	4.7		4.9	3.0	4.8	5.2	4.3
Dolomite				1.1	0.4						
Quartz	3.8	4.8	4.8	0.7	0.2		0.8	2.2	2.3	28.5	23.1
Plagioclase	1.5	2.3	2.3	1.5	0.0	1.4	0.5	2.9	0.5	0.5	0.9
Siderite										2.7	1.6
Cristobalite	1.9	0.4	0.6				0.4	0.0	0.3		
Tridymite	2.6	1.6	1.6	2.8	1.7	0.0	0.4	0.3	0.2		
Gypsum	0.7	1.2	1.2	1.6	1.2	0.9	1.5	1.2	1.6	1.2	2.0
Goethite				1.0	0.4	3.1	1.8	4.5	1.4		
Hematite		0.4	0.4	0.5	0.7	0.3	1.5	0.5	0.6		
Maghemite						1.6	1.5	0.4	0.5		
Magnetite	1.2	1.4	1.4	1.0	0.8					0.1	
Anatase	0.1	0.0	0.1	0.5	0.3	0.7	0.7	0.9	0.9		
Pyrite	0.7	0.8	0.8	0.9	1.4					0.7	0.8
Zircon		0.1	0.1								

**Table 3.** Structural formulae and layer charge data for smectites in bentonites investigated by Kumpulainen and Kiviranta (2010).

Bentonite	Formula	Tet charge	Oct charge	Total charge
<b>Wyoming</b>				
MX-80	$\text{Na}_{0.49}\text{Ca}_{0.13}\text{Mg}_{0.05}\text{Al}_{2.99}\text{Fe}^{3+}_{0.33}\text{Fe}^{2+}_{0.02}\text{Mg}_{0.43}\text{Si}_{8.00}\text{Al}_{0.00}\text{O}_{20}(\text{OH})_4$	0.449	-1.123	-0.674
WyMX-80	$\text{Na}_{0.51}\text{Ca}_{0.17}\text{Mg}_{0.05}\text{Al}_{3.11}\text{Fe}^{3+}_{0.39}\text{Fe}^{2+}_{0.03}\text{Mg}_{0.52}\text{Si}_{7.70}\text{Al}_{0.30}\text{O}_{20}(\text{OH})_4$	-0.300	-0.425	-0.725
Volclay	$\text{Na}_{0.54}\text{Ca}_{0.16}\text{Mg}_{0.06}\text{Al}_{3.09}\text{Fe}^{3+}_{0.38}\text{Fe}^{2+}_{0.03}\text{Mg}_{0.56}\text{Si}_{7.65}\text{Al}_{0.35}\text{O}_{20}(\text{OH})_4$	-0.351	-0.406	-0.757
<b>Milos, Greece</b>				
Deponit CaN	$\text{Na}_{0.22}\text{Ca}_{0.28}\text{Mg}_{0.23}\text{Al}_{2.91}\text{Fe}^{3+}_{1.44}\text{Fe}^{2+}_{0.01}\text{Mg}_{0.57}\text{Si}_{8.00}\text{Al}_{0.00}\text{O}_{20}(\text{OH})_4$	0.055	-0.788	-0.733
AC200	$\text{Na}_{0.75}\text{Ca}_{0.05}\text{Mg}_{0.07}\text{Al}_{2.79}\text{Fe}^{3+}_{0.59}\text{Fe}^{2+}_{0.01}\text{Mg}_{0.74}\text{Si}_{7.47}\text{Al}_{0.53}\text{O}_{20}(\text{OH})_4$	-0.534	-0.334	-0.867
<b>Kutch, India</b>				
Asha	$\text{Na}_{0.75}\text{Ca}_{0.13}\text{Mg}_{0.10}\text{Al}_{2.28}\text{Fe}^{3+}_{1.17}\text{Fe}^{2+}_{0.01}\text{Mg}_{0.48}\text{Si}_{7.67}\text{Al}_{0.33}\text{O}_{20}(\text{OH})_4$	-0.327	-0.658	-0.986
Basic Star bentonite	$\text{Na}_{0.41}\text{Ca}_{0.24}\text{Mg}_{0.15}\text{Al}_{2.38}\text{Fe}^{3+}_{1.22}\text{Fe}^{2+}_{0.00}\text{Mg}_{0.60}\text{Si}_{7.20}\text{Al}_{0.80}\text{O}_{20}(\text{OH})_4$	-0.805	0.004	-0.801
HLM Star bentonite	$\text{Na}_{0.66}\text{Ca}_{0.11}\text{Mg}_{0.09}\text{Al}_{2.03}\text{Fe}^{3+}_{1.56}\text{Fe}^{2+}_{0.00}\text{Mg}_{0.56}\text{Si}_{7.28}\text{Al}_{0.72}\text{O}_{20}(\text{OH})_4$	-0.724	-0.143	-0.867
Ca-Star bentonite	$\text{Na}_{0.46}\text{Ca}_{0.24}\text{Mg}_{0.14}\text{Al}_{2.20}\text{Fe}^{3+}_{1.27}\text{Fe}^{2+}_{0.00}\text{Mg}_{0.69}\text{Si}_{7.37}\text{Al}_{0.63}\text{O}_{20}(\text{OH})_4$	-0.634	-0.198	-0.832
<b>Friedland, Germany</b>				
Friedland	$\text{Na}_{0.58}\text{Ca}_{0.03}\text{Mg}_{0.10}\text{Al}_{2.22}\text{Fe}^{3+}_{1.09}\text{Fe}^{2+}_{0.18}\text{Mg}_{0.59}\text{Si}_{7.80}\text{Al}_{0.20}\text{O}_{20}(\text{OH})_4$	-0.196	-0.515	-0.711
SH Friedland	$\text{Na}_{0.63}\text{Ca}_{0.02}\text{Mg}_{0.07}\text{Al}_{2.10}\text{Fe}^{3+}_{1.34}\text{Fe}^{2+}_{0.70}\text{Mg}_{0.48}\text{Si}_{7.14}\text{Al}_{0.86}\text{O}_{20}(\text{OH})_4$	-0.860	0.141	-0.719



**Figure 3.** Ideal end-member minerals in the pyrophyllite – mica series with potassium as charge-compensating cation, and approximate compositional ranges for illite and smectite. B denotes beidellite, M denotes montmorillonite. The compositional positions of MX-80 and Deponit CaN are represented by triangles and squares, respectively. All formulae are related to the basic  $\text{O}_{20}(\text{OH})_4$  cell. From Karnland and Birgersson (2006).

**Table 4.** Results of XRD analyses of five consignments of Wyoming MX-80 material (from Karnland et al., 2006). The consignments were delivered around 1980 (WySt), 1995 (WyL1), 1999 (WyL2), 2001 (WyR1) and WyR2). Wym denotes the mean value of the six analysed samples. Plus and minus denote the maximum deviations from mean values. Data are in wt % of the total material.

	WySt	WyL1	WyL2	WyR1	WyR1m	WyR2	Wym	plus	minus
Montmorillonite	82.5	79.5	79.8	82.7	83.9	80.0	81.4	2.5	1.9
Illite	0.7	0.8	0.7	0.8	0.8	0.7	0.8	0.1	0.1
Anatase	0.4	0.1	0.2	0.3	0.0	0.2	0.2	0.2	0.2
Calcite	1.3	0.0	0.0	0.1	0.0	0.0	0.2	1.1	0.2
Cristobalite	0.2	1.4	2.5	0.6	0.7	0.0	0.9	1.6	0.9
Goethite	0.0	0.0	0.1	0.0	0.0	0.6	0.1	0.5	0.1
Gypsum	1.4	0.7	0.9	0.7	0.8	1.1	0.9	0.5	0.1
Hematite	0.5	0.9	0.1	0.2	0.4	0.0	0.4	0.5	0.3
Lepidocrocite	0.3	0.5	0.9	0.4	0.4	0.5	0.5	0.4	0.2
Magnetite	0.4	0.1	0.1	0.1	0.1	0.1	0.2	0.3	0.1
Microcline	0.0	0.3	0.0	0.0	0.0	0.0	0.1	0.2	0.0
Muscovite	2.4	5.1	2.6	3.5	4.4	2.5	3.4	1.7	1.0
Orthoclase	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.2	0.0
Plagioclase	4.6	2.4	4.0	3.2	2.3	4.7	3.5	1.2	1.2
Pyrite	0.8	0.6	0.6	0.6	0.3	0.9	0.6	0.3	0.3
Quartz	2.6	2.5	3.8	3.0	2.8	3.2	3.0	0.8	0.5
Tridymite	1.7	5.0	3.8	3.9	3.1	5.1	3.8	1.3	2.1

Clay mineral formulae and layer charge data in the bentonites studied by Kumpulainen and Kiviranta are shown in Table 3. This shows that:

- Indian bentonites have a large amount of ferric iron in the octahedral layer of the smectite. As pointed out by Karnland and Birgersson (2006), possible chemical reduction of this ferric iron will lead to a layer charge increase, which could accelerate long-term transformation of the clay into a non-swelling silicate.
- As pointed out by Kumpulainen and Kiviranta, the Wyoming smectites are beidellitic montmorillonites (octahedral charge > tetrahedral charge) and the Kutch smectites are montmorillonitic beidellites (octahedral charge < tetrahedral charge) (e.g. Figure 3).

Table 4 shows results of analyses of different batches of Wyoming MX-80 bentonite, delivered in 1980 ('WySt'), 1995 ('WyL1'), 1999 ('WyL2') and 2001 ('WyR1' and 'WyR2') to SKB (data from Karnland et al., 2006) which highlights the variability/consistency of bentonite product delivered in that period. It may be seen from Table 4 that:

- the montmorillonite content is consistently at or above 80 wt%;

- As might be expected, there is a large variability in minor components such as calcite, gypsum, muscovite, plagioclase and tridymite.

Slade et al. (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. This interpretation is consistent with the behaviour of vermiculites which have very high tetrahedral charges and high swelling (Skipper et al., 2006).

Cation exchange data for candidate bentonites are shown in Table 5 (from Kumpulainen and Kiviranta, 2010). This shows that total cation exchange capacities for bentonites from Wyoming, Greece, and India are similar at about 0.9–1.0 eq kg<sup>-1</sup>, whereas that for Friedland Clay is about a factor of four less. Exchange sites are dominated by sodium in the Wyoming, Indian, and German bentonites, whereas Deponit CaN from Greece is dominated by Ca and Mg.



**Table 5.** Cation exchange data for bentonites investigated by Kumpulainen and Kiviranta (2010).

	% of Exchange Sites				CEC (eq/kg)
	Na	K	Ca	Mg	
<b>Wyoming</b>					
MX-80	71	2	20	7	0.84
WyMX-80	69	2	23	7	0.85
Volclay	69	2	21	8	0.89
<b>Milos, Greece</b>					
Deponit CaN	29	2	38	31	0.82
AC200	84	2	6	8	0.95
<b>Kutch, India</b>					
Asha	76	1	13	10	0.90
Basic Star bentonite	51	1	30	19	0.92
HLM Star bentonite	76	1	13	11	1.00
Ca-Star bentonite	55	1	29	16	1.00
<b>Friedland, Germany</b>					
Friedland	76	6	4	13	0.26
SH Friedland	83	5	2	9	0.31

## 2.2 Backfill

According to TKS-2009 (Posiva, 2010, p255), limitations have been set for the composition of the backfill material by stating that it must not contain organic, oxidising, or other potentially harmful agents in amounts that would significantly impair the functioning of the buffer, copper canister or the surrounding rock. Posiva say that no exact limits on the chemical composition of the backfill material have been specified so far, but the chemical composition of the materials will be taken into account in safety analyses (Posiva, 2010, p256). The backfill of the deposition tunnels comprises pre-compacted blocks and pellets that fill the space between the blocks and the rock, and a floor backfill which will be emplaced separately (Figure 2).

### 2.2.1 Foundation bed materials

Two different materials have been selected for the candidates of foundation bed materials: a mixture of bentonite and ballast (40/60) and bentonite pellets.

The most important properties of the foundation bed are the self-sealing capacity and the hydraulic conductivity, which should be below  $10^{-10} \text{ m s}^{-1}$ . According to Hansen et al. (2009), the swelling ability of the floor backfill is less important, as it will be located under the blocks whose main function will be to produce the swelling pressure. The bentonite and

ballast mixture will be chosen for its good mechanical properties (Hansen et al., 2009). This means that the mixture should have a good resistance against erosion, thus minimising the risk of channel formation from the backfill into the deposition hole. Based on preliminary results, the mixture also shows sufficient self-sealing phenomena (Hansen et al., 2009). Pellets were chosen as another candidate material, because it has low permeability, but the mechanical instability and compressibility may be problematic (Hansen et al., 2009).

The current reference design is a mixture of bentonite and crushed rock (40/60). The bentonite is high quality sodium activated Ca-bentonite (Milos), which has a montmorillonite content of over 75%. The crushed rock is from ONKALO and the grain size of that is less than 8 mm. The water content of the mixture during emplacement is around 17% and the dry density of the mixture is  $1750 \text{ kg m}^{-3}$  after emplacement.

### 2.2.2 Block materials

Three candidate materials for the blocks have been selected (Hansen et al., 2009):

- Friedland Clay from Germany;
- bentonite and ballast mixture (40/60%); and
- Milos B bentonite with a montmorillonite content of 50–60%.

**Table 6.** Chemical analyses of Cebogel pellets, Minelco granules and Milos bentonite (from Keto et al., 2009).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	S	C
Cebogel pellets	53.1	16.8	5.2	3.8	5.4	3.5	0.6		0.45	
Minelco granules	52.0	16.8	5.1	4.0	6.7	2.7	0.8		0.34	
Milos bentonite	48.7	17.3	4.8	3.0	9.3	0.7	0.3	0.8	0.47	0.59

**Table 7.** Exchangeable cation content and cation exchange capacity (CEC) of Cebogel pellets, Minelco granules and Milos bentonite (from Keto et al., 2009). Units are cmol kg<sup>-1</sup>.

	Exchangeable Cations				CEC
	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	
<b>BaCl<sub>2</sub> method</b>					
Cebogel pellets	13.3	0.9	7	78.3	99.5
Minelco granules	10.9	1.0	8.8	62.2	82.9
Milos bentonite	32.6	1.7	19.9	21.3	75.5
<b>NH<sub>4</sub> acetate method</b>					
Cebogel pellets	12.2	1.4	8.0	81.3	103.0
Minelco granules	18.7	1.4	13.2	65.7	99.0
Milos bentonite	71.8	1.2	19.9	18.4	111.3

The current reference design is Friedland Clay, with an initial water content of 7–8%. The dry density of individual blocks is greater than 2000 kg m<sup>-3</sup>, and the dry density of the block assembly is designed to be greater than 1950 kg m<sup>-3</sup> after emplacement.

### 2.2.3 Pellets

The pellet material considered for the deposition tunnel consists of 100% bentonite (Hansen et al., 2009). The bentonite pellets are made of high-grade bentonite that has a montmorillonite content over 75%.

The reference design is ‘Cebogel’ pellets of compressed high quality sodium activated Ca-bentonite (Milos) and an initial water content of 13%. Water is added to the mixture in the nozzle during emplacement and the dry density after emplacement is 1000 kg m<sup>-3</sup> with a total water content greater than 26%. Chemical analyses (Table 6) for these materials show that sulphur contents are broadly comparable, whereas no data are currently available for the organic carbon content of the Cebogel and Minelco products.

Cation exchange data (Table 7) show that exchange sites in Cebogel and Minelco are dominated by sodium, whereas Milos is dominated by calcium and magnesium. The total CEC (Table 7 – as deter-

mined by NH<sub>4</sub> acetate) is approximately 1.0 eq kg<sup>-1</sup> for all materials.

## 2.3 Analysis

Posiva has yet to decide on a final version of its backfill design, so it is difficult to comment in detail on the effects of the choice of materials. However, in broad terms, the following can be stated:

- The swelling pressure of the backfill has to be sufficient to support the tunnel walls (> 0.2 MPa – Hansen et al., 2009). The Milos B bentonite can generate a greater swelling pressure (at a given dry density) than either the Friedland Clay or compacted blocks of clay/ballast mix. Consequently, it is more critical that the installation densities of the latter are achieved so that sufficient swelling pressure can be generated.
- In terms of potential harmful impurities, Friedland Clay has the highest content of organic carbon, whereas Deponit CaN has the highest content of reduced sulphur (bisulphide) of the various candidate materials. However, without some sort of system analysis of safety consequences for different concentrations of these impurities, it is difficult to make a judgement concerning the relative suitability of the various materials.

## 2.4 Summary

- A wide range of sources and compositions of bentonite is being considered by Posiva. Currently, only MX-80, Deponit CaN and possibly Kutch 'Basic Star' meet buffer design requirements of containing > 75% smectite.
- Different bentonites contain different amounts of potentially safety-relevant contaminants such as organic carbon and sulphide minerals. Since Posiva has not defined specific concentration limits for these impurities, it is difficult to compare different bentonite materials with regard to this issue.
- Kutch bentonites have high contents of ferric iron in octahedral layers. Chemical reduction of this iron over the long-term would increase layer charge and reduce swelling. This feature makes this bentonite type less suitable than others under consideration.
- Different batches of MX-80 analysed over a period of twenty years show a consistent content of montmorillonite (~ 80 wt%), but a large variability in the content of some minor minerals.
- Bentonites from Wyoming and Greece have a cation exchange capacity in the order of 1 eq kg<sup>-1</sup>, but have different charge compensating cations. Wyoming and Indian bentonites have exchange sites dominated by Na, whereas Greek bentonites have sites dominated by Ca and Mg.
- Some bentonites have layer charge dominantly in octahedral layers (Wyoming, Deponit CaN), whereas others (Indian type) have charge dominantly in the tetrahedral layer.
- The design for the tunnel backfill is not yet certain, so it is difficult to comment other than:
  - Backfill materials consisting of Friedland Clay or clay/ballast mixes require greater precision in achieving densities to achieve design swelling pressures than bentonites such as Milos clay.
  - It is difficult to make a judgement concerning the relative suitability of the various materials with regard to impurities in the absence of some sort of system analysis of safety consequences for different concentrations of these components.

## 3 Hydraulic conductivity

### 3.1 Buffer

#### 3.1.1 Safety functions and performance targets

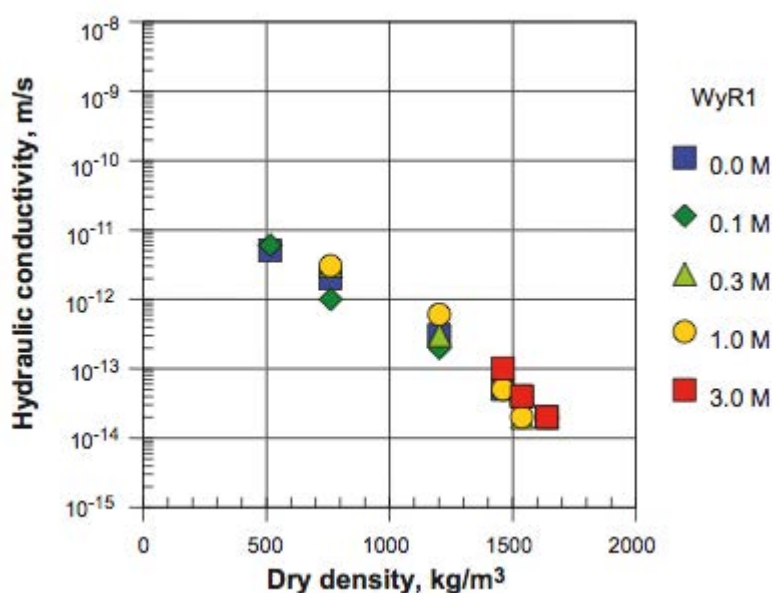
According to TKS-2009 (Posiva, 2010, p292), “the buffer should be impermeable enough that the movement of water is insignificant and that diffusion is the dominant transport mechanism for both the corrosive agents present in the groundwater that may degrade the canisters and for the radionuclides that may be released from canisters”.

Posiva’s performance target for fluid transport is fulfilled when the hydraulic conductivity is less than  $10^{-12}$  m s<sup>-1</sup>. If the buffer saturated density falls within the target range (1950–2050 kg m<sup>-3</sup>), then the performance target for hydraulic conductivity is also expected to be upheld given the expected evolution of groundwater salinity at repository depth and assuming no physical changes of the buffer, due, for example, to alteration or freezing (Posiva, 2010, p300).

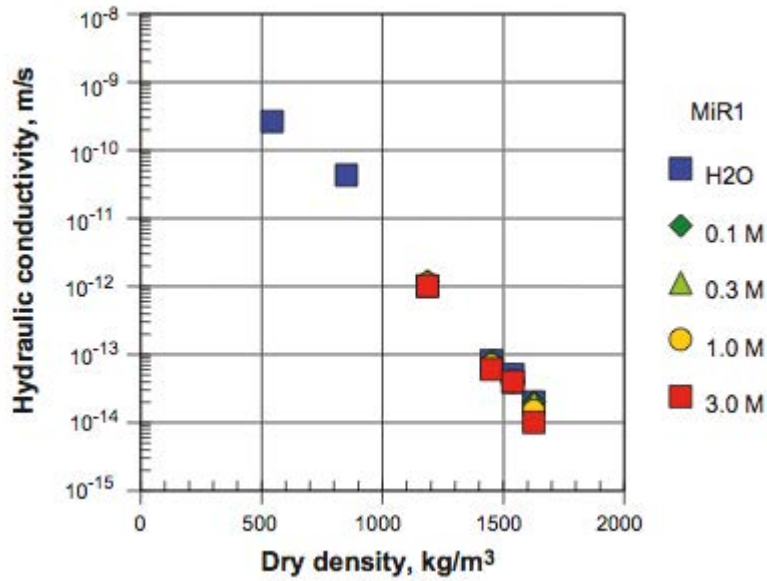
#### 3.1.2 Analysis

Experimental data are available for water flow in saturated buffers at the laboratory scale (e.g. Pusch et al., 1987). There are no relevant data from in situ experiments or natural systems.

Hydraulic conductivities between  $10^{-13}$  and  $10^{-14}$  m s<sup>-1</sup> have been measured in saturated bentonite in saline conditions at dry densities above about 1200 kg m<sup>-3</sup> (1760 kg m<sup>-3</sup> saturated density) by Karnland and co-workers (Figure 4 – Na-bentonite and Figure 5 – Ca-bentonite). A hydraulic conductivity of  $10^{-12}$  m s<sup>-1</sup> is about two orders of magnitude lower than that theoretically required for mass transport being dominated by diffusion (SKB, 2010). SKB consider 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, 2010). Regarding the latter, higher temperatures decrease the viscosity of



**Figure 4.** 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 5.** Hydraulic conductivity of Deponit CaN (MiR1) bentonite measured at different densities and molar concentration of CaCl<sub>2</sub> in the saturating solution (from Karnland et al., 2006).

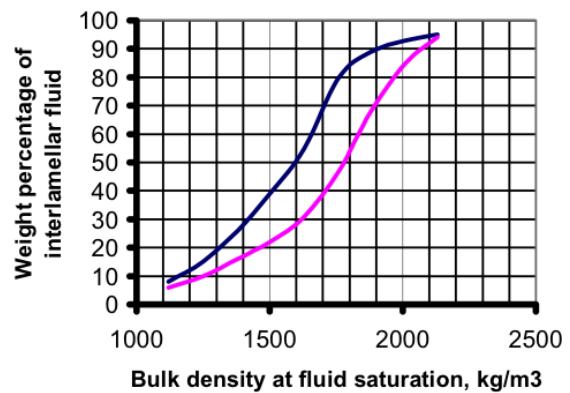
water thus increasing permeability, but can also affect the microstructure (e.g. Villar and Lloret, 2004).

It may be seen from Figure 4 and Figure 5 that although the dependence of hydraulic conductivity upon compaction density is strong, the dependence of pore water salinity is weak (weaker than that for swelling pressure, for example). It should be noted however that these data concern Na-bentonite percolated with NaCl solutions and Ca-bentonite percolated with CaCl<sub>2</sub> solutions and not *vice versa*. No data are currently available for these alternative systems.

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<sup>-3</sup> 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). These larger stacks have larger voids associated with them. The number of lamellae in stacks in Na-bentonite is typically 3–5, but up to 10 for the Ca

form (Pusch, 2002). Pusch emphasises this point by comparing the theoretical fraction of interlamellar pore water in each type of clay at different saturated bulk densities (Figure 6). From this Figure, Pusch concludes that at a given density, there is more ‘free’ pore water in Ca-bentonite at a given density than in the Na form. However, the diagram demonstrates that in both clay types the fraction of interlamellar water is large at higher densities and since this fraction is ‘immobile’ at normal hydraulic gradients, it is clear that the hydraulic conductivity of a dense buffer is very low, irrespective of the type of adsorbed cation. Pusch goes on to state that for low densities the difference between the two forms



**Figure 6.** Theoretical fraction of total porewater in montmorillonite that is in interlamellar positions. Upper curve represents Na clay and the lower curve Ca clay (from Pusch, 2002).

becomes obvious, however, and for densities lower than 1600–1800 kg m<sup>-3</sup> Ca-smectite becomes very conductive because of the lack of microstructural continuity and coherence.

Likos and Wayllace confirm Pusch's observations by noting that water uptake, volume change, and swelling pressure are all more significant for Ca-Mg-type bentonites than a Wyoming-Na-type bentonite in water vapour sorption experiments using compacted bentonites in controlled humidity environments (Likos and Wayllace, 2010). 'Plastic yielding', evident as a peak in the relationship between swelling pressure and relative humidity was more evident and occurred at a lower relative humidity for Ca-Mg bentonite. Likos and Wayllace attribute this behaviour to the limited capacity for interlayer swelling in Ca-Mg bentonites and corresponding structural collapse induced by the onset of water uptake in larger intra-aggregate and inter-aggregate pores. They also note that the number of mineral layers making up quasi-crystals within the clay aggregates is larger for divalent cation systems, with as many as 400 face-to-face oriented layers for Ca-smectite and perhaps 20 layers for Na-smectite at 1000 bar.

Regarding water content Muurinen has noted that in Deponit CaN, the interlamellar space contributes more to the chloride porosity than in sodium bentonite (Muurinen, 2009). Owing to the thinner double layers in the divalent bentonite there is probably very little exclusion in the so-called 'soft fraction' of the bentonite. In the Deponit CaN samples the water amount in the soft fraction of the clay decreases more quickly with the increasing density than in the MX-80 samples, which supports the greater increase of hydraulic conductivity with decreasing compaction density.

## 3.2 Backfill

### 3.2.1 Safety Targets and Functions

According to Posiva (Posiva, 2010, p301), "*the backfill shall limit the advective mass transport along the deposition tunnel (advective migration)*" thereby:

- restricting the flow of groundwater in the tunnel; and
- limiting the transport of harmful substances in the tunnel.

Posiva concludes that the tunnel backfill should "*be impermeable enough so that water flow is negligible and the deposition tunnels do not significantly alter the bedrock hydrology (over the longterm)*" (Posiva, 2010, p293). The accompanying performance target for the hydraulic conductivity of the backfill is  $< 10^{-10}$  m s<sup>-1</sup>. Since hydraulic conductivity (along with swelling pressure and compressibility) are all strong functions of dry density, requirements of 1740, 1510, and 1240 kg m<sup>-3</sup> have been defined for a 40/60 clay/ballast mix, Friedland Clay, and Milos B bentonite, respectively (Hansen et al., 2009). Hansen et al. go on to note that the greatest safety margin regarding dry density has been achieved with Milos B bentonite, and the lowest with the 40/60 mixture.

### 3.2.2 Analysis

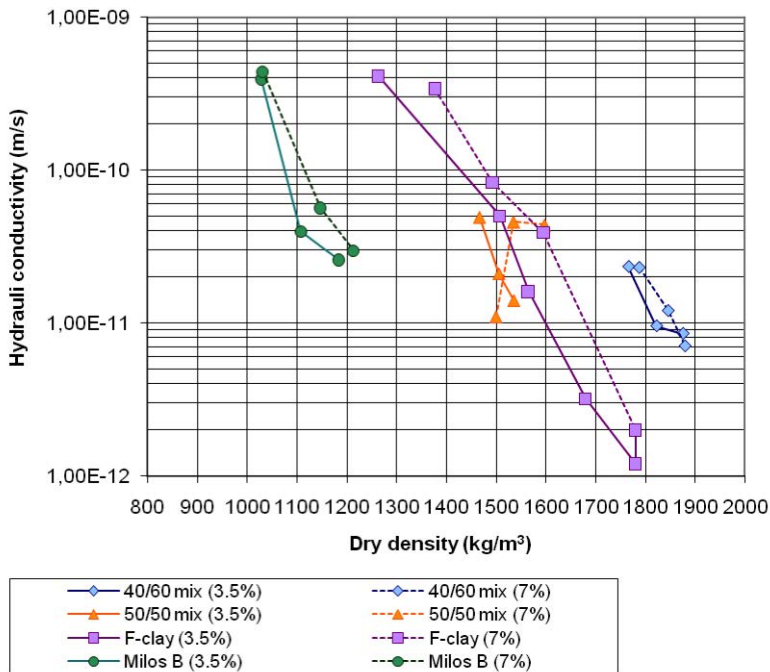
The safety target of  $< 10^{-10}$  m s<sup>-1</sup> for the hydraulic conductivity of the backfill is less challenging than that for the buffer. Indeed, for compacted blocks of clay, Pusch et al. (1987) have shown that this value could be achieved with as little as 10% swelling clay in the compacted blocks at a saturated density of 2000 kg m<sup>-3</sup>.

The hydraulic conductivities of the various backfill components are shown in Figure 7. It may be seen from this Figure that to achieve the target hydraulic conductivity of  $10^{-10}$  m s<sup>-1</sup>, compaction densities of at least 1800 (60/40 ballast/clay mix), 1450 (50/50 ballast/clay mix), 1500 (Friedland Clay), and 1100 (Milos B clay) kg m<sup>-3</sup>, respectively, are required. These are similar, but not identical, to values suggested by SKB (Johannesson and Nilsson, 2006). Consequently, greatest demands are placed upon the ballast/clay mixes in terms of required compaction densities to achieve the target hydraulic conductivities.

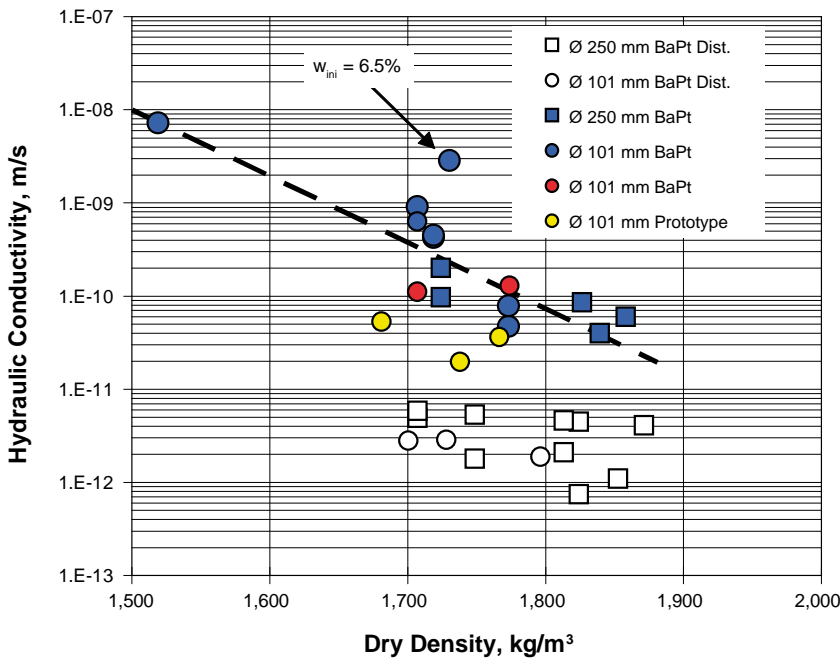
In terms of field tests, only a mix of 30% MX-80 and 70% crushed rock has been evaluated, in the Prototype Repository and Backfill and Plug tests at Äspö (Johannesson and Nilsson, 2006) (Figure 8). This shows that a dry density of at least 1750 kg m<sup>-3</sup> is required to reach the target hydraulic conductivity of  $10^{-10}$  m s<sup>-1</sup>. This backfill type has since been discarded by SKB and Posiva.

Hydraulic conductivity data determined by SKB for a variety of pure clays are shown in Figure 9 and those for clay-ballast mixtures in Figure 10. Again, both these Figures show a wide range of required

dry density, according to clay type and proportion of clay in clay/ballast mixtures. For example, Figure 9 shows a dry density, from as little as 1100 kg m<sup>-3</sup> for Milos bentonite, to as much as 1500 kg m<sup>-3</sup> for Friedland Clay.



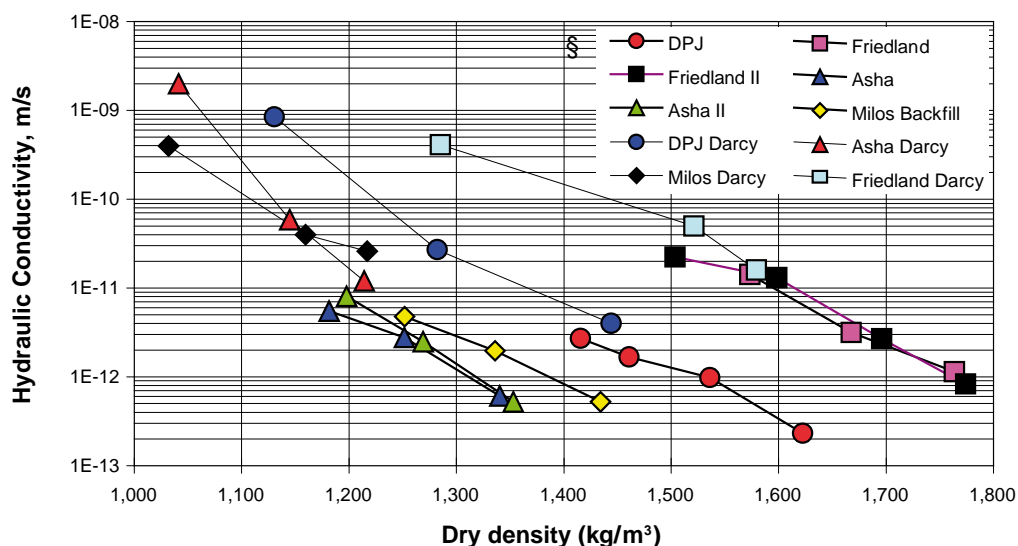
**Figure 7.** Hydraulic conductivity of the candidate backfill materials (bentonite- ballast mixtures 40/60 and 50/50, Friedland clay (F-clay) and Milos bentonite (Milos B)). From Hansen et al. (2009).



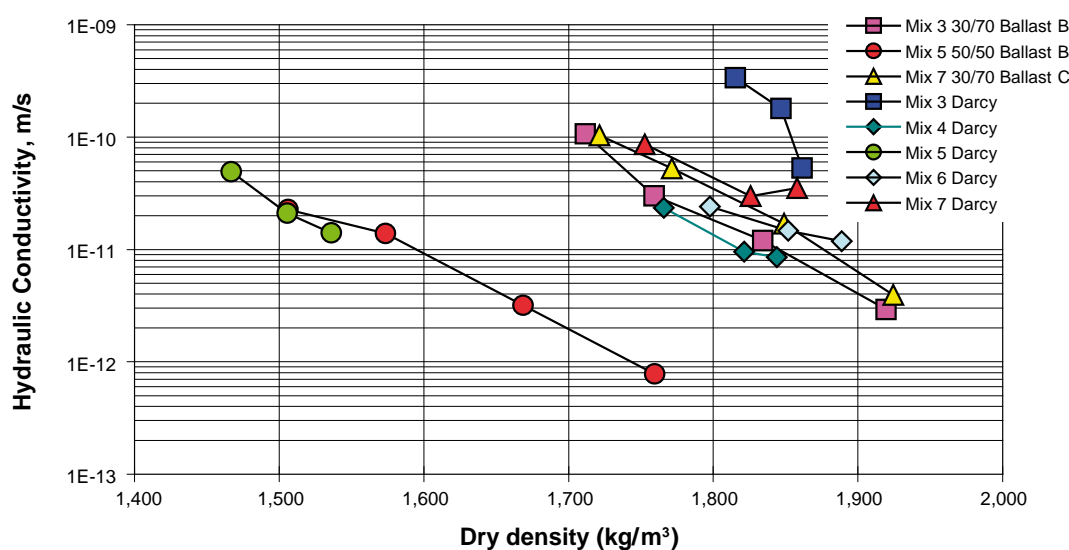
**Figure 8.** Hydraulic conductivity for a 30/70 mixture (30% MX-80 and 70% crushed rock) backfill type plotted as function of the dry density from the Backfill and Plug (BaPt) and Prototype Repository ('Prototype') tests at Äspö (from Johannesson and Nilsson, 2006).

However, because of the sensitivity of hydraulic conductivity to achieved compaction density (Figure 9 and Figure 10), and because of the difficulties of backfill emplacement (e.g. potential for: non-homogeneous installation; application of bentonite

pellets to void spaces; piping problems, etc – Bennett, 2010), a bentonite with a lower dependence of hydraulic conductivity upon density, such as a Na-bentonite, could be preferred for this function.



**Figure 9.** The hydraulic conductivity of natural clays plotted as function of the dry density (from Johannesson and Nilsson, 2006).



**Figure 10.** Hydraulic conductivity of clay-ballast mixtures evaluated from the oedometer tests together with tests results from other determinations of hydraulic conductivity plotted as a function of the dry density of the samples (from Johannesson and Nilsson, 2006).



### 3.2.3 Summary

There are a number of datasets describing the hydraulic behaviour of Na-bentonites, but relatively few for Ca-bentonites and Deponit CaN in particular. Indeed, in the SR-Site 'Buffer, Backfill and Closure Process Report', SKB comments that "*few tests have been performed on Deponit CaN 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, 2010, 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 interchangeability 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 tests on Deponit CaN are therefore recommended, the differences in material properties between the two bentonites would still remain.

## 4 Mechanical and rheological properties

### 4.1 Buffer

#### 4.1.1 Safety functions

Mechanical interactions between the buffer and the canister arise from the buffer through the clay matrix. Both compressive stresses and shear stresses are generated in the clay (SKB, 2010). According to TKS-2009 (Posiva, 2010, p292), the buffer should be:

- *plastic* enough to mitigate the effects of small rock movements on the canisters, and
- *stiff* enough to support the weight of the canisters and keep the canister in position in the deposition hole.

For SKB, the safety functions relating to the mechanical and rheological properties of the buffer are those concerning the ‘damping of rock shear’ (‘Buff3’) and ‘prevent canister sinking’ (‘Buff5’) (SKB, 2011, Volume I, Figure 8-2). The safety criterion for the former is that the buffer saturated density should be less than  $2050 \text{ kg m}^{-3}$ , whereas for the latter, it is defined by swelling pressure being greater than 0.2 MPa. The main determinant of the creep rate and resulting canister sinking is the magnitude of the mobilised shear strength (shear stress divided by shear strength), which results in increased sinking. The shear strength decreases with decreasing swelling pressure. These effects are relevant to the ‘shear load scenario’ during glacial loading and post-glacial earthquakes (e.g. SKB, 2011, Vol III, p617). The design premises require that the canister should remain intact after a 5 cm rock shear movement at a rate of  $1 \text{ m s}^{-1}$  for buffer material properties of a  $2050 \text{ kg m}^{-3}$  Ca-bentonite (SKB, 2011, Vol II, p481). Canister sinking is treated as a special case of the buffer advection scenario so that for a deposition hole that has experienced loss of buffer mass due to erosion/colloid release such that advective conditions prevail, this safety function cannot be guaranteed. However, if advective

conditions do exist, the fact that the canister sinks is of secondary importance (SKB, 2011, Vol II, p542).

#### 4.1.2 Analysis

Ca-bentonite has been selected for stress-strain calculations by SKB as a conservative choice because of its greater density, swelling pressure and deviatoric strength under design conditions (SKB, 2011, with the material model reported in Börgesson et al., 2010, and shear calculations reported by Börgesson and Hernelind, 2010). New experimental data have been reported by Dueck et al. (2010), which update those utilised in the SR-Can assessment (Börgesson and Hernelind, 2006).

These data show that Deponit CaN has greater deviatoric stress values (generally 1MPa greater) at a given void ratio than those for the Na-form of MX-80. Unusually, the Ca-exchanged form of MX-80 (orange dots) behaves more closely to MX-80 (blue and green dots) than Deponit CaN (red dots) (Figure 11).

Regarding the possibility of using natural systems data, SKB reports (SKB, 2010, p190):

*“No natural analogues concerning mechanical behaviour have been studied. Manmade bentonite seals are made in completely different ways (mixtures with low density) and natural bentonites have unknown histories. The existence of relevant natural analogues is probably very limited and difficult to evaluate”.*

Pusch gives a generalised expression of the shear strength  $q$  as a function of the mean effective stress  $p$  (Pusch, 2002):

$$q = ap_b$$

where  $a = q$  for  $p = 1 \text{ kPa}$ , and  $b$  is the slope of  $\log p/\log q$  diagrams. Pusch notes that the strength parameter,  $a$  of Ca-bentonite is twice that of the sodium form and is increased by the presence of

saline groundwater (Table 8). Note that Börgesson et al. consider that Moosburg bentonite shows (unexplained) larger deviator stress values at failure than Deponit-CaN under similar conditions (Börgesson et al., 2010 – data not shown here) and they consider that Moosburg bentonite differs substantially from what may be expected from ion-exchanged MX-80 and/or Deponit CaN.

### 4.2 Backfill

According to TKS-2009 (Posiva, 2010, p301), the mechanical properties of the backfill should:

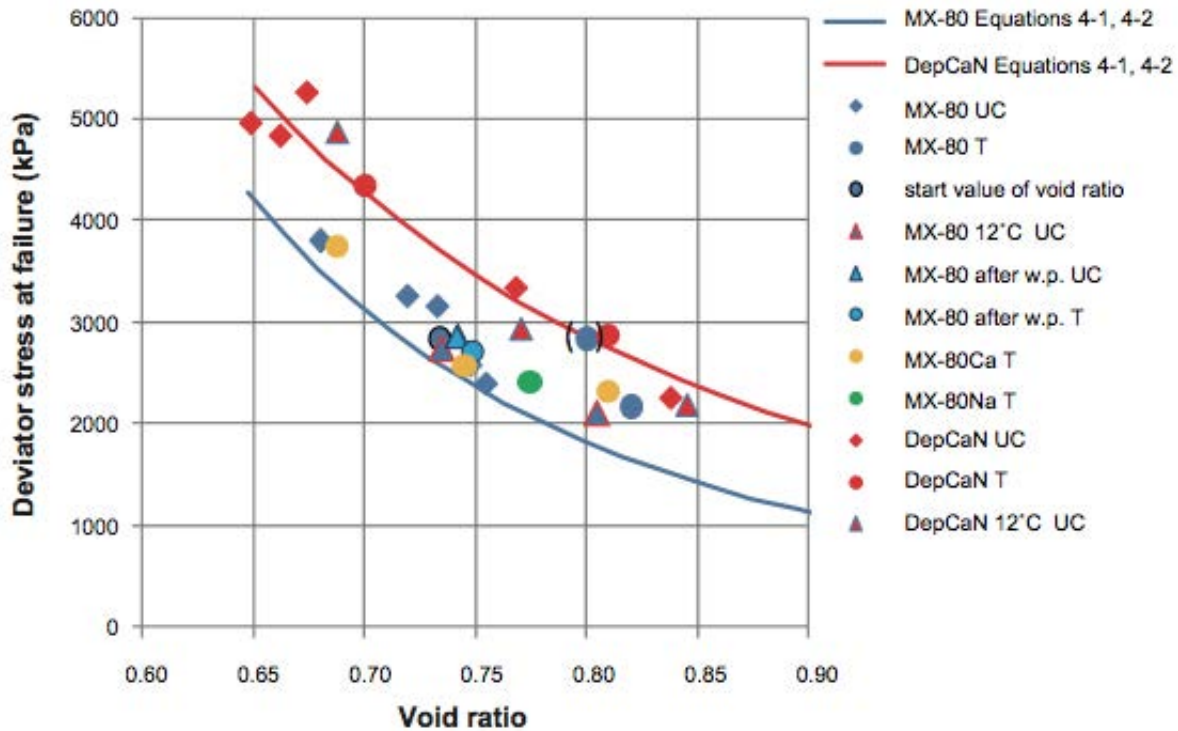
- Keep the buffer in place by restricting expansion into the deposition tunnel. The compressibility of the backfill material depends on the composition, saturation rate and density of the backfill material components and the amount of void in the structure.
- Protect the rock from surrounding mechanical disturbance by maintaining a certain swelling pressure to support the strength of the tunnel walls. The swelling pressure generated by the backfill material depends on the amount, density and saturation rate of the expanding materials. These mechanical properties need to be maintained even as a result of, for example, mineralogical change.

**Table 8.** Strength parameter *a* of bentonites interpreted from triaxial tests (from Pusch, 2002).

Bentonite	<i>a</i> (dimensionless)	Pore water
MX-80 (Na)	2.8	Pure water
IBECO (Na)	2.9	Pure water
MX-80 (Na)	3.5	3.5 % NaCl
Moosburg (Ca)	5.5	Pure water

According to TKS 2009, surveys of the interaction between the filling structure and the buffer and the optimisation of the backfill in terms of composition, production and placement will continue during the next TKS period (Posiva, 2010, p271).

Hansen et al. (2009) also state that the compression of the backfill caused by the swelling of the buffer should not be large enough to allow the saturated density of the buffer to decrease below 1950 kg m<sup>-3</sup>. Also, they state that the compressibility of the backfill depends not only on the compression properties of the backfill materials but also on the backfill geometry and free void space in the tunnel, i.e. the compressibility needs to be studied as a function of the backfill structure. In addition, the compressibility is different at different saturation states of the backfill.



**Figure 11.** Results from unconfined compression tests (UC) and triaxial tests (T) on MX-80 (blue), MX-80Na (green), MX-80Ca (orange) and Deponit CaN (red). From Dueck et al. (2010).

**Table 9.** Dry densities ( $\text{kg m}^{-3}$ ) for different backfill materials required to fulfil target properties of the buffer (from Johannesson and Nilsson, 2006).

Material	Hydraulic Conductivity ( $< 10^{-10} \text{ m s}^{-1}$ )	Swelling Pressure ( $> 200 \text{ kPa}$ )	Deformation properties (buffer saturated density $\geq 1950 \text{ kg m}^{-3}$ )
Asha 230 (Indian bentonite)	1120	1050	1160
Milos bf	1090	1060	1240
DPJ (Czech bentonite)	1220	1240	1400
Friedland Clay	1400	1350	1510
30/70 mixture	1700–1800	1730–1800	1690
50/50 mixture	1280	1450	1560

The compressibility and deformation behaviour of the backfill materials are described in detail in Johannesson and Nilsson (2006, p. 28), Johannesson (2008, p. 19–20) and in Kuula-Väisänen et al. (2008, Chapter 4). Modelling has been carried out with analytical calculations (Johannesson and Nilsson, 2006; Johannesson, 2008) and numerical modelling (Korkiala-Tanttu, 2008).

The densities required for various backfilling materials to maintain the target saturated density of the buffer ( $1950 \text{ kg m}^{-3}$ ) are shown in Table 9 (from Johannesson and Nilsson, 2006), along with other key properties, hydraulic conductivity and swelling pressure. From this Table, it may be seen that the requirements for the mechanical properties are the most demanding and in terms of material, the clay/ballast mixtures require the highest density. The reference material, Friedland Clay lies between the bentonite clays (Asha, Milos bf and DPJ) and the clay/ballast mixtures in terms of necessary density.

The backfill materials must also have a sufficient self-sealing ability (sealing of the piping channels

within the backfill due to swelling of the backfill materials) after saturation (Hansen et al., 2009). Keto et al. (2009) have shown that the self-sealing ability of Friedland is sufficient when the degree of block filling is  $>70\%$ .

### 4.3 Summary

Posiva and SKB have conservatively chosen Ca-bentonite (Deponit CaN) for calculations of mechanical behaviour, because of its higher strength, swelling pressure and density, in the belief that if this bentonite type meets safety requirements, then other (e.g. Na-dominated) bentonite types will also be adequate.

Consideration of the mechanical properties of tunnel backfill is complicated by the lack of a final specification for this material. From tests carried out this far, it is clear that clay-ballast mixtures have the greatest demands in terms of required density. Of the pure clays, Friedland Clay performs the least satisfactorily, but is the current reference clay for the compacted blocks in the backfill design.

## 5 Long-term alteration

Alteration of clay in the buffer and backfill are similar processes and are here considered together rather than as separate sections. Differences in treatment are highlighted as necessary.

### 5.1 Safety targets and functions

TKS-2009 states that: “*the buffer temperature shall remain sufficiently low, in order to prevent thermally induced mineral transformation*” (Posiva, 2010, p298). This is particularly relevant during the early evolution of the repository when there is significant heat generation by the spent fuel. This requirement is necessary for the buffer to fulfil its other safety functions. For both Posiva and SKB, this performance target is  $< 100^{\circ}\text{C}$ . For SKB, this issue is evaluated through the ‘Buff4’ safety function, ‘resist transformation’ (SKB, 2011, Vol I, Figure 8-2). This criterion is principally based upon the temperature-dependent rate of transformation of montmorillonite to non-swelling illite. The evidence for this transformation has been evaluated in detail (e.g. SKB, 2010; Karnland and Birgersson, 2006).

Although illitisation has been the focus of most clay mineral alteration studies and concerns, other mineral transformations may be equally or more important resulting from:

- interaction with groundwaters which could include beidellitisation or saponitisation in addition to illitisation;
- interaction with cement grouts and concretes;
- interaction with iron/steel canister/insert materials.

### 5.2 Thermodynamic stability

The thermodynamic stability of smectites, and clays in general, have been debated for a number of decades, so that a comprehensive discussion of this issue is outside the scope of this document. Nevertheless, this debate has centred principally

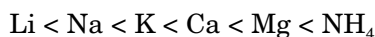
on the status of clays as a thermodynamic phase. Some authors consider that because of the heterogeneity of composition of clay minerals, and smectites in particular, they cannot be considered as single phases in a thermodynamic sense (e.g. Lippmann, 1981; May et al., 1986). However, some of the problems arising from this heterogeneity can be avoided if clay minerals are considered as solid-solutions (e.g. Aagaard and Helgeson, 1983; Fritz, 1985; Ransom and Helgeson, 1994; Ransom and Helgeson, 1995; Arthur and Wang, 2000; Vidal and Dubacq, 2009). The preservation of clays over multi-million year timescales is an indication of their long-term stability, but some authors would view clays as ‘metastable micas’, so in other words, any transformation of clays to more thermodynamically stable solids such as micas may be very slow.

An analysis of the stability of montmorillonite in deep groundwaters at Forsmark, Sweden has suggested control of major cations through montmorillonite-saponite coexistence (e.g. Figure 12). Stability fields for Na- and Ca-montmorillonite in Figure 12 are small in comparison with saponitic clays, suggesting that the latter may be more stable under Forsmark conditions.

### 5.3 Cation exchange

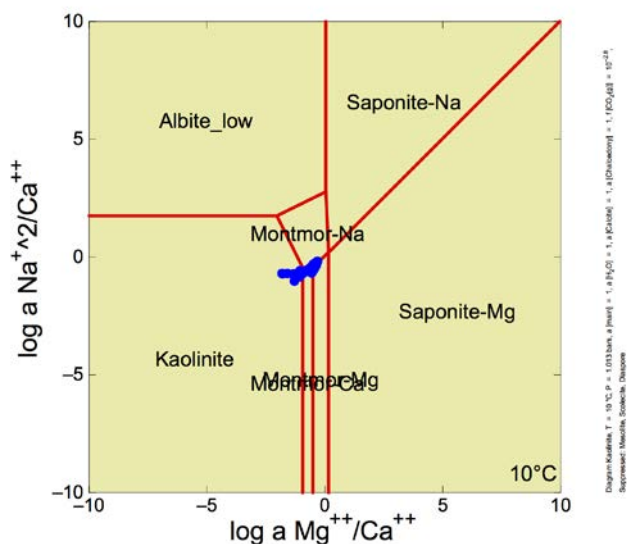
In smectite clays such as montmorillonite, clay layers bear a permanent negative charge compensated by counterions located between them (inter-layer space). These counterions are the origin of two features of clay behaviour: swelling; and cation exchange. The former refers to the entrance of water into the clay, while the latter involves the replacement of natural counterions like  $\text{Na}^+$  by other ions initially in the aqueous solution in contact with the mineral, and the concomitant release of  $\text{Na}^+$  to the solution. Studies have shown that, under a given set of conditions, various cations are not equally

replaceable and do not have the same replacing power. In principle, the following law of replacement applies (e.g. Pusch, 2002):



This implies preferential replacement of e.g.  $\text{Na}^+$  by  $\text{Ca}^{2+}$  rather than vice versa. According to the current paradigm for ionic exchange in clays, specific interactions between the ions and the clay surface, or the hydration properties of ions in the clay interlayer, are the driving force for ion exchange (Rotenberg et al., 2009). The origin of clay selectivity has been explained by a number of arguments (Rotenberg et al., 2009):

- the size of hydrated cations, compared to the interlayer spacing;
- the ability to lose a water molecule at the clay surface, thus forming a stronger inner-sphere complex;
- the hydration state in the interlayer; or
- the polarisability that influences the formation of surface complexes.



**Figure 12.** Mineral stabilities in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$  at  $10^\circ\text{C}$ .  $\text{Al}^{3+}$ ,  $\text{SiO}_{2(\text{aq})}$  and  $\text{Ca}^{2+}$  activities were fixed by kaolinite, chalcedony and calcite respectively at a  $\log f\text{CO}_{2(\text{g})} = -2.8$  bars. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A.H. Bath, pers. comm.). This suggests control of Na/Ca ratios in groundwater by montmorillonite-saponite coexistence. Note the narrow stability fields for montmorillonite in comparison with saponite. From Savage (2011).

These microscopic features are then thought to weigh in favour of the interactions of clay interlayers with larger cations. However, considering only the properties of the clay phase to infer properties of cation exchange can lead to erroneous conclusions since it is the hydration free energy difference, i.e. the contribution of the water phase, that leads to an overall exchange of small ions for larger ones (e.g.  $\text{Na}^+$  for  $\text{Cs}^+$ ) (Rotenberg et al., 2009).

Moreover, the replacement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by  $\text{Na}^+$  in montmorillonite increases as the concentration of  $\text{Na}^+$  in the solution increases (cation exchange is a stoichiometric reaction and the law of mass action holds, implying that an increased concentration of the replacing cation causes greater exchange). Selectivity varies with electrolyte concentration, so that the more dilute the solution, the greater the selectivity.

The effects of concentration depend on the kind of cation that is being replaced and also on the valence of the cation. The complexity of cation exchange processes is indicated by the fact that with cations of about similar replacing power and the same valence, dilution has a relatively small effect on the exchange, while with cations of different replacing power and different valence (e.g.  $\text{Na}^+$  versus  $\text{Ca}^{2+}$ ), dilution produces significant differences in exchange.

Compaction may also affect cation exchange by reducing the activity of water and thereby reducing the hydration of aqueous species (e.g. Wang et al., 2003). Cations with a low hydration tendency, such as Cs, therefore accumulate in the interlayer space, whereas highly hydrated cations such as sodium tend to accumulate in the bulk water where water is easily available for hydration (Van Loon and Glaus, 2008).

Laine and Karttunen (2010) report that Olkiluoto groundwater at repository depth may be either saline Na-Ca-Cl type or highly saline Ca-Na-Cl type and that the interface between these two groundwater types is very close to repository level. Groundwater salinity and Ca/Na increase with depth. According to Laine and Karttunen, these compositions favour exchange towards a Ca-dominant composition. This is confirmed by experiments which showed cation exchange towards a Ca-dominant composition when bentonite interacts with Olkiluoto saline groundwater (Muurinen and Lehikoinen, 1999). Consequently, reaction of Na-

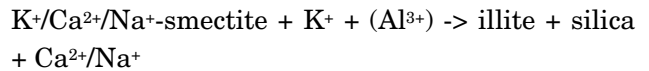
bentonite with Olkiluoto-type groundwater would lead to a progressive replacement of Na by Ca<sup>2+</sup> (e.g. note the similarity of exchange composition in Figure 13 and Figure 14).

#### 5.4 Interaction with Groundwater

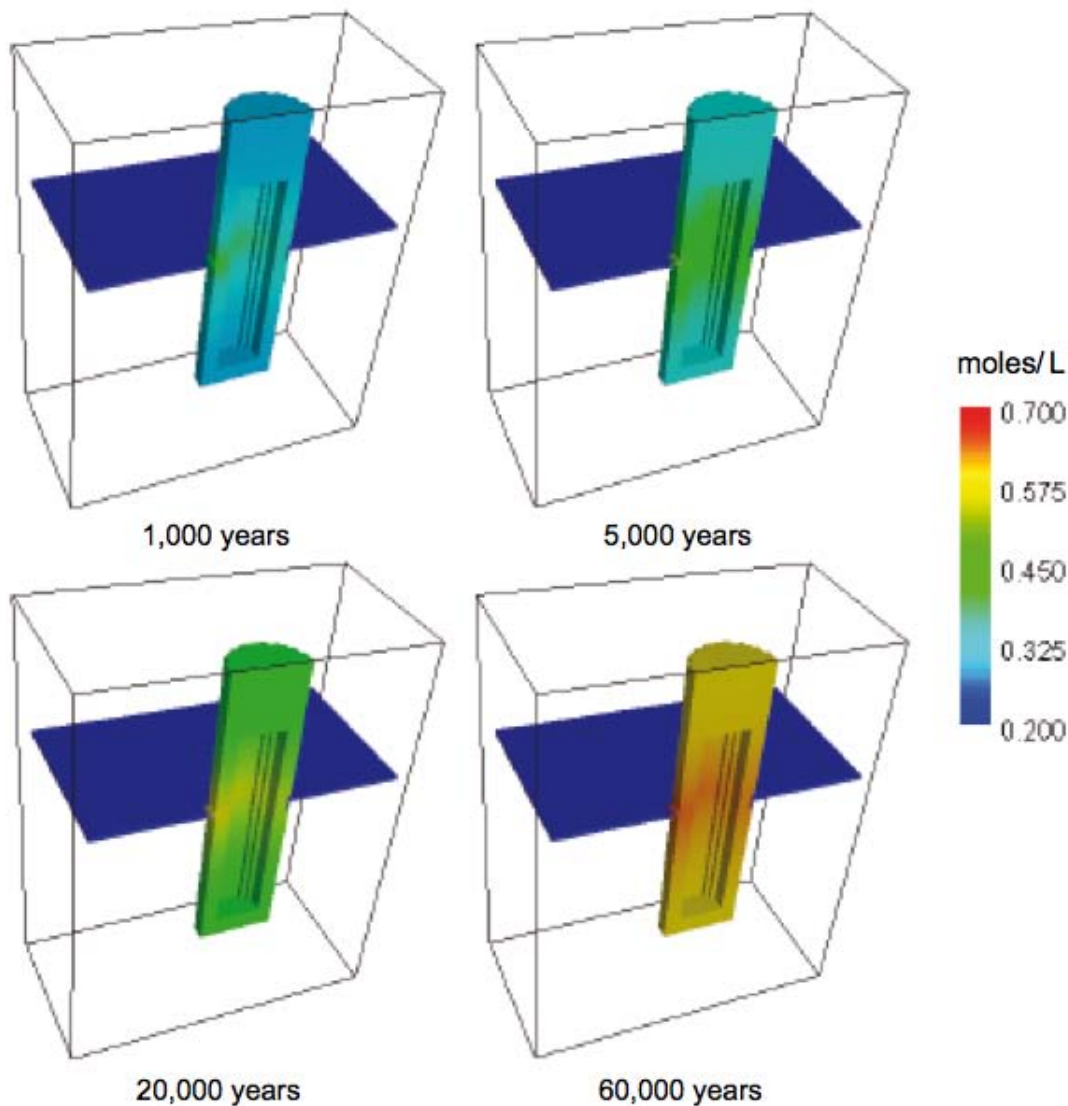
Interaction of clay with groundwater could lead to beidellitisation or saponitisation reactions inter alia, as well illitisation. For example, the potential saponitisation of montmorillonite in bentonite by groundwaters at Forsmark, Sweden has been discussed recently (Savage, 2011), but the greatest attention has been placed upon illitisation reactions.

Illitisation of montmorillonite with respect to KBS-3 conditions has been discussed in detail by Karnland and Birgersson (2006) and Laine and

Karttunen (2010). 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 activity and the precipitation rate of silica in and from the aqueous phase can also affect illitisation. 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



**Figure 13.** Predicted evolution of Ca occupancy in the exchanger of MX-80 bentonite during interaction with groundwater at the Forsmark site, Sweden (from Arcos et al., 2006).

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 (Karnland and Birgersson, 2006). Karnland and Birgersson note however that neither of these models addresses factors such as the availability of aluminium, the water/clay ratio, or silica activity.

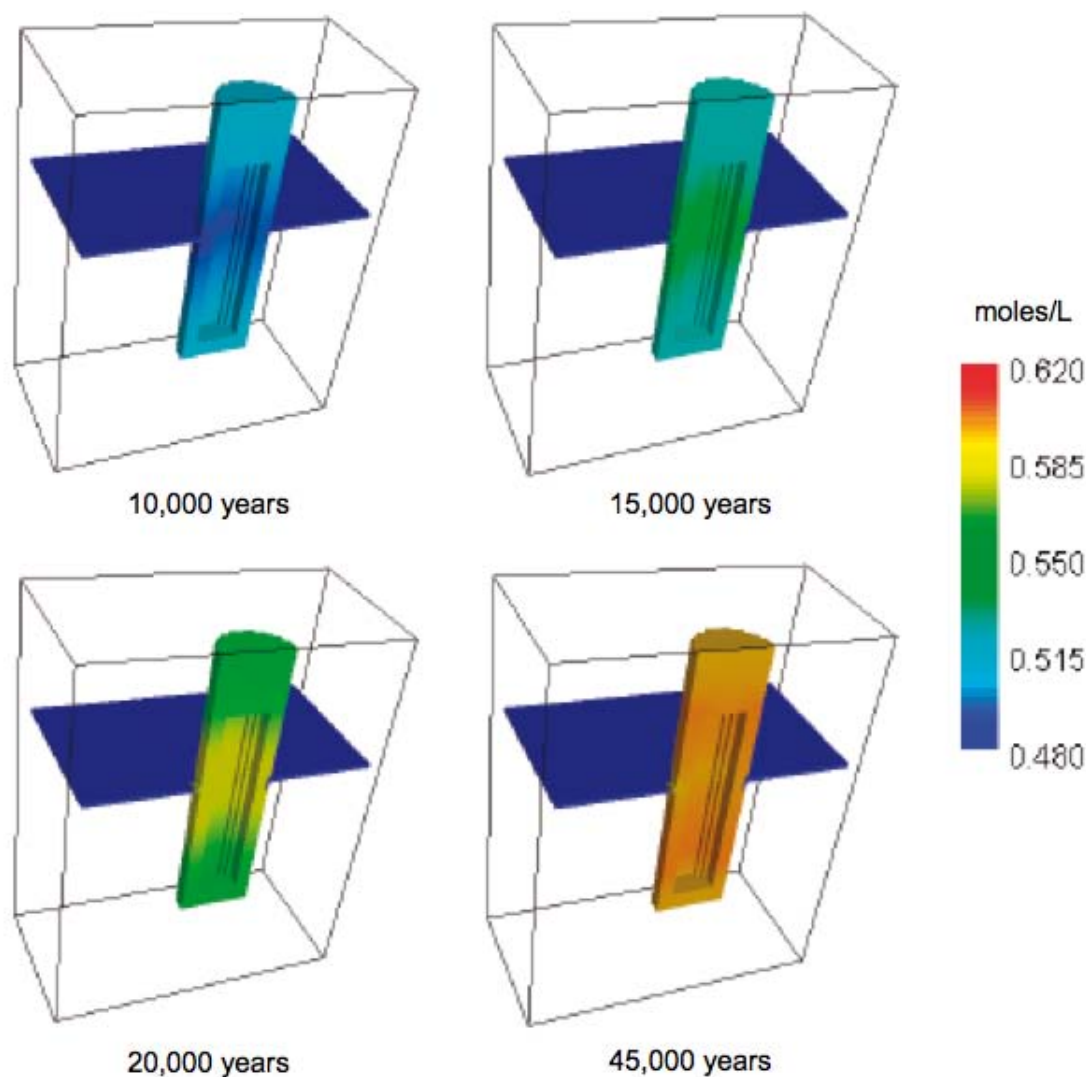
The reactivity of different types of montmorillonite clays is not really addressed by Karnland and Birgersson (2006) or Laine and Karttunen (2010). However, Grauer (1986, 1990) observed that Ca-montmorillonite is less prone to illitisation than the sodium form, citing evidence from both experimental (e.g. Eberl, 1978; Roberson and Lahann, 1981; Yau et al., 1987; Inoue, 1983) and natural system studies (e.g. Nadeau and Reynolds, 1981). Other

authors also report smectite compositional effects on the rate of illitisation (e.g. Niu and Ishida, 2000).

Despite this evidence, the precise effects of smectite composition upon the mechanism of illitisation are not clear.

## 5.5 Interaction with cement/concrete

Cement and other construction materials will be used in the construction of a spent fuel disposal facility (KBS-3V or KBS-3H). Posiva state that the purposes of such materials are 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)



**Figure 14.** Predicted evolution of Ca occupancy in the exchanger of Deponit CaN during interaction with groundwater at the Forsmark site, Sweden (from Arcos et al., 2006).



(Gribi et al., 2008, Appendix F). Concrete will also be used for temporary construction elements (walls, intermediate floors, doors). 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-3H repository, between 1.2 and 1.8 million kg of cement will be left in the entire repository. Of these, an average of 2 600 to 3 900 kg of cement will be located in each drift (Hagros, 2007).

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). Despite no cement-bearing component being in direct contact with the bentonite in the supercontainer and distance block unit in the KBS-3H design, potential effects on the buffer arising through indirect contact of alkaline cementitious pore water transported from a grouted fracture by groundwater to the supercontainer area through the fractured rock network have been evaluated by Posiva (from a mass balance perspective). From these calculations,

Posiva show that an outer zone of buffer of 4 cm thickness could be altered over a period of 100 000 years (Gribi et al., 2008).

Cement-clay interactions have been studied extensively worldwide in the last ten years, through laboratory experiments (e.g. Madsen, 1998; Ichige et al., 1998; Kubo et al., 1998; Vigil de la Villa et al., 2001; Fujiwara et al., 2002; Ramírez et al., 2002; Nakayama et al., 2004; Yamaguchi et al., 2007), computer simulations (e.g. De Windt et al., 2001; Savage et al., 2002; Gaucher et al., 2004; Watson et al., 2007; Marty et al., 2009; Watson et al., 2009), and a few analogue investigations (e.g. Tinseau et al., 2006; Arcilla et al., 2009; Honrado et al., 2009; Savage et al., 2010a).

Surprisingly, there are very few laboratory experimental studies relating to MX-80 or Deponit CaN bentonite (Savage, 2009). Experiments conducted with these latter 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 Deponit CaN with regard to mineralogical processes at the cement-bentonite interface. Reaction of cement/cement pore fluids with FEBEX bentonite is characterised by pore blocking with Mg-bearing solids such as brucite, sepiolite and Mg-clays (e.g. Cuevas et al., 2006).

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).

There is evidence for reactivity of montmorillonite in the pH range 9–10 at the Searles Lake analogue in California, USA (Savage et al., 2010a). Appreciable dissolution of montmorillonite is inferred to have occurred, with the precipitation of illite, K-feldspar and analcime. These observations are in contrast with the results of the modelling studies described above, probably due to advection being the primary mode of fluid transport in the Searles Lake diagenetic system.

## 5.6 Interaction with iron/steel

Interaction of bentonite with iron/steel is especially relevant to the KBS-3H concept where currently, the supercontainer is envisaged to be made of steel. Any interaction of steel with bentonite, could potentially include:

- saturation of clay cation exchange/sorption sites with  $\text{Fe}^{2+}$ ;
- mineral transformation of smectite to non-swelling sheet silicates such as berthierine;
- perturbation of buffer physical properties such as decreased swelling and/or increased hydraulic conductivity.

Laboratory experimental studies of the corrosion of iron in clay show that corrosion product layers are generally thin ( $< 1 \mu\text{m}$ ) with magnetite, siderite, or 'green rust' occurring depending upon temperature and ambient  $\text{PCO}_2$  (Johnston et al., 1985; Allen and Wood, 1988; Hermansson, 2004; Carlson et al., 2007). However, the results of experiments to characterise the mineralogical products of iron-bentonite interaction are not unequivocal because the inevitable short-term nature of laboratory experimental studies introduces issues of metastability and kinetics. Factors influencing bentonite alteration include: reaction time, temperature, water/clay ratio, and clay and pore fluid compositions. For example, high temperature experiments ( $> 250^\circ\text{C}$ ) are dominated by iron chlorite (Cathelineau et al., 2005), whereas lower temperatures produce berthierine, odinite, cronstedtite, or Fe-rich smectite (e.g. Lantenois et al., 2005; Wilson et al., 2006), depending upon initial clay composition and water/clay ratio.

This ambiguity of experimental data has been interpreted as evidence for the relevance of Ostwald step processes in bentonite alteration (Savage et al., 2010b). The models by Savage et al. demonstrate in particular, the potential influence of mineral growth kinetics and the treatment of surface areas for mineral nucleation and growth. This contrasts with modelling studies of iron-bentonite interactions which have emphasised equilibrium (infinite rate) mineral growth (e.g. Montes-H et al., 2005). Some studies have attempted to consider mineral growth kinetics (e.g. Bildstein et al., 2006; Marty et al., 2010), but little work has been undertaken on the effects of using different kinetic data/rate laws.

Overviews of iron-bentonite interactions are described in the recent KBS-3H assessment Process

(Gribi et al., 2008) and Summary (Smith et al., 2008) reports, and in more detail in a number of underlying reports:

- a literature review (Marcos, 2003);
- a summary of the status of international research (Wersin and Snellman, 2008);
- as applied to the Olkiluoto Site (Wersin et al., 2008),
- as linked to gas behaviour (Johnson et al., 2008), and
- in evidence from steel corrosion experiments in compacted bentonite (Carlson et al., 2008; Milodowski et al., 2007, 2009).

In conclusion, Posiva believe that considerable uncertainties exist regarding iron-bentonite interactions (Gribi et al., 2008, p140) so that:

- further experimental work should include measurements of swelling pressure and hydraulic properties, including gas transport properties of altered bentonite.
- The potential effect of  $\text{H}_2$  on Fe-clay interactions and on reduction of structural iron in smectite should be experimentally investigated.
- From a modelling perspective, it would be useful to include reaction kinetics for smectite transformation in the KBS-3H conceptual model to obtain a more realistic description of the evolution of the iron front.

Currently, all the experimental data in the literature refer to either Na-bentonites such as MX-80 or Kunipia-F, or natural clays, such as the Callovo-Oxfordian mudstone from Bure, France. Some experimental studies have been conducted with the French 'FoCa' clay (Perronnet et al., 2007), but this clay is not directly analogous to the Ca-bentonites under consideration by Posiva and SKB. According to the SR-Site Buffer Process Report (SKB, 2010, p151), iron-bentonite interactions are being studied in the Alternative Buffer Materials (ABM) project at the Äspö HRL. Eleven different compacted clays have been placed in contact with an iron heater at  $130^\circ\text{C}$  in three different packages (Eng et al., 2007). Experimental durations are from two to more than five years. It is not clear whether other experimental studies between Ca-bentonite and steel canister materials are being carried out, but Posiva may turn to the use of a titanium supercontainer to avoid this issue altogether (Posiva, 2010, p479).

## 5.7 Summary

Long-term interaction of bentonite with groundwater is likely to lead to dominance of calcium on the cation exchange site in montmorillonite, regardless of the initial composition of the bentonite.

There is a substantial body of experimental and natural systems evidence to suggest that illitisation is inhibited by divalent interlayer cations in montmorillonite. 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.

A similar story exists for the interaction of bentonite with iron or steel canister materials. There are no experimental data currently available for Ca-bentonite. This issue is being addressed in the ABM test at Äspö where initial data will become available in 2012. Consequently, no judgement can be made regarding the relative reactivities of Na- and Ca-bentonites with iron or steel canister materials.

## 6 Colloidal properties

### 6.1 Safety functions

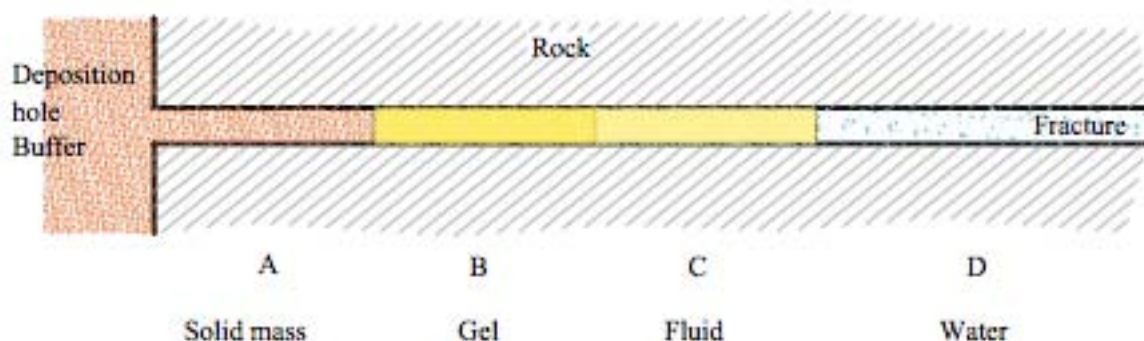
The colloidal properties of bentonites are important mainly because the buffer may become susceptible to significant mass losses by erosion should the constituent clay minerals be suspended as colloids that are then transported away from deposition holes in flowing groundwater. This type of erosion could occur in repository scenarios involving the transient migration of very dilute solutions, such as glacial meltwaters, to repository depths because stable suspensions of clay colloids tend to form in aqueous solutions that are relatively dilute. Erosion could adversely impact safety functions of the buffer because the corresponding performance targets generally depend, either directly or indirectly, on the buffer's density. Buffer erosion was determined to be a key contributor to risk in the SR-Can safety assessment (SKB, 2006).

### 6.2 Analysis

SKB recently carried out a detailed evaluation of buffer erosion (Neretnieks et al., 2009; Birgersson et al., 2009; Moreno et al., 2011). Apted et al. (2010) considered related concepts and potential safety consequences from a regulatory perspective.

The basic conceptual model considered in these studies is illustrated in Figure 15, which shows 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 friction forces acting within the bentonite and at the rock interface. Bentonite density and swelling pressure decrease rapidly with increasing distance in the fracture, and rheological properties change accordingly from those of a solid  $\rightarrow$  gel  $\rightarrow$  fluid (which may also include a semi-fluid phase). Fluid properties are identical to those of groundwater at the penetration front. Clay colloids form near this front, and are lost by diffusion into the flowing groundwater. Bentonite fluids, which are considered to be dispersions of bentonite colloids in water (i.e., 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 mass loss of bentonite from the deposition hole results in a decrease in buffer density.

Neretnieks et al. (2009) developed a model of buffer erosion that accounts for forces that would control the expansion of bentonite from a deposition



**Figure 15.** Conceptual model of buffer erosion (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,  $a$ .

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 were 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 would be controlled by a number of forces acting on the individual clay particles (Neretnieks et al., 2009). 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 friction forces acting on the particles as they move through the aqueous phase as a result of imbalances among the other forces. Because changes in particle velocity are expected to be slow as the buffer expands, acceleration can be neglected and the sum of all these forces must then be equal to zero.

The force-balance model was used to predict changes in the density and volume fraction ( $\varphi$ ) of clay particles in the expanded bentonite. The viscosity model was developed to relate changes in  $\varphi$  to corresponding changes in the viscosity of bentonite gels/sols (Moreno et al., 2011; Neretnieks et al., 2009). The model is based on the concept of a co-volume of a colloidal particle. The co-volume is 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

**Table 10.** Predicted erosion rates and corresponding penetration distances of bentonite in fractures (Neretnieks et al., 2009).

Water velocity (m yr <sup>-1</sup> )	Erosion rate (g yr <sup>-1</sup> )	Penetration distance (m)
0.10	11	34.6
0.32	16	18.5
0.95	26	11.5
3.15	43	7.0
31.50	117	2.1
315.00	292	0.5

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.

Model results are summarized in Table 10 (Neretnieks et al., 2009). As can be seen, the erosion rate was predicted to increase, and the length of the fracture penetrated by bentonite to decrease, with increasing groundwater velocity. The erosion rate was found to be proportional to the water velocity (raised to the power 0.41), and also proportional to the fracture aperture. The erosion rate and fracture penetration distance for the two lowest water velocities were extrapolated from model results for the four higher water velocities because the numerical method became unstable when the velocity was less than about 0.95 m yr<sup>-1</sup>. Neretnieks et al. (2009) noted that the erosion rate for a given water velocity could be higher or lower than the values given in the Table because the effects of ion transport on the viscosity have not been adequately accounted for in systems containing both Na<sup>+</sup> and Ca<sup>2+</sup> ions. These authors concluded that it was not possible to affirm based on the present state of knowledge that the erosion of smectite gels cannot occur to a considerable extent.

The results of the buffer-erosion studies carried out by SKB have been used to support the SR-Site safety assessment (SKB, 2011). Studies are also planned in Posiva's programme to experimentally evaluate the potential for buffer erosion as a function of groundwater and bentonite composition, and to evaluate filtration mechanisms that could potentially minimize or prevent erosional mass losses

of bentonite from a deposition hole (Posiva, 2010, p369). It should also be noted that Birgersson et al. (2009) developed an alternative modelling approach to that described above based on variations in the rheological properties of bentonite as a function of water content.

### 6.3 Summary

Considering the above analysis in relation to the exchangeability of bentonites based on their colloidal properties, it can be noted that the interaction energy between like-charged colloidal clay particles becomes strongly attractive at relatively small inter-particle separation distances if the counterions in the electrical double layer separating the particles are divalent and if the surface-charge density is large (Kjellander et al., 1988; Pegado et al., 2008). This attractive force, due to so-called ion-ion correlations, is important for montmorillonite clays

if exchangeable Ca/Na molar ratios are greater than about 90/10 (e.g., Birgersson et al., 2009). In such cases the attractive force is sufficiently strong that the minerals cannot expand to form gels or sols. On the other hand, montmorillonites having Ca/Na < 90/10 can form gels or sols if counterion concentrations are below a critical coagulation concentration.

These observations are relevant because they suggest that buffer materials composed of essentially pure Ca-montmorillonites would be much more resistant, if not completely impervious, to the effects of colloid formation and chemical erosion than buffer materials composed of mixed Na/Ca-montmorillonites having Ca/Na < 90/10. As noted in the preceding section, however, buffer materials with montmorillonite predominantly in the Ca form initially could become more sodic with time due to ion-exchange reactions resulting from contact of the buffer with repository groundwaters.

## 7 Swelling pressure

Swelling clays such as montmorillonites and other smectites will expand freely when contacted by water. Should the clays be confined within an enclosed volume, such as a deposition hole or tunnel in a KBS-3 repository, the expansion will be limited and a pressure will develop within the clay. This pressure is referred to as the swelling pressure ( $p_{swell}$ ). The swelling-pressure of KBS-3 buffer materials is considered in this section. The backfill is not considered in detail because important aspects of its design are still under investigation by Posiva.

### 7.1 Safety functions

The swelling pressure is important in relation to repository performance because many performance targets for the buffer (and backfill) are defined in terms of this parameter (e.g., Posiva, 2010, p298). These targets include the prevention of significant microbial activity ( $p_{swell} > 2$  MPa); the provision of sufficient tightness and self-sealing ability ( $p_{swell} > 1$  MPa); and the prevention of canister sinking ( $p_{swell} > 0.1$  MPa). Also, because swelling pressure and hydraulic conductivity are closely related, a performance target to prevent significant advective transport can be stated in terms of hydraulic conductivity ( $K < 10^{-12}$  m s<sup>-1</sup>) (Posiva, 2010, p298) or swelling pressure ( $p_{swell} > 0.1$  MPa) (SKB, 2006). Similarly for the backfill, the performance target of  $K < 10^{-10}$  m s<sup>-1</sup> corresponds to  $p_{swell} > 0.2$  MPa for an assumed groundwater salinity of 35 g l<sup>-1</sup> (Pastina and Hellä, 2006).

### 7.2 Analysis

Various types of models that have been proposed to account for physical, mineralogical and surface-chemical processes controlling the swelling pressure of clay-based materials have been reviewed by Karnland (1997a), Dixon (2000), Savage (2005) and Agus and Schanz (2008). Empirical models relate  $p_{swell}$  to the interlamellar distance between individ-

ual 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  $p_{swell}$  to repulsive interactions arising from the overlap of electrical double layers associated with the charged surfaces of clay particles (e.g., Yong et al., 1992; Komine and Ogata, 1994, Komine and Ogata, 1996 – see also Sridaharan, 1997), are based on well-established theoretical concepts for colloidal systems (e.g., Kruyt, 1952; Adamson, 1967), but are difficult to apply to highly compacted clays due in part to structural modifications of water that occur in the interlamellar regions of clay particles (e.g., Low, 1987).

With these modelling limitations in mind, Dixon (2000) proposed that a database of experimental measurements could instead be constructed and used to establish empirical correlations between  $p_{swell}$  and clay dry density. An example is shown in Figure 16, where swelling pressures determined in tests involving various bentonites and aqueous solutions are plotted as a function of the ‘effective clay dry density’ (ECDD = dry mass of clay divided by the volume occupied by the clay plus the void volume). Dixon (2000) noted that the regression lines shown in the figure are similar, indicating little influence of salt on the swelling behaviour as long as the ECDD is above about 0.9 Mg m<sup>-3</sup>. The limited number of available measurements at high salt concentrations generates significant uncertainty in the regression results, however.

A similar approach has been proposed recently by Karnland (2010), who 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 (Figure 17). Much of the scatter disappears, however, when the

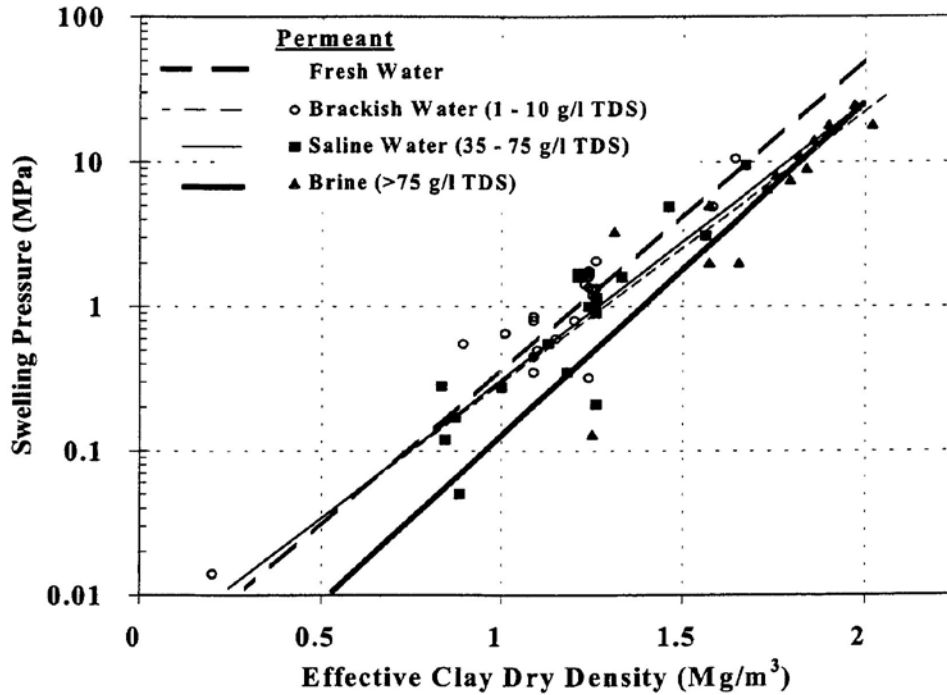


Figure 16. Empirical correlations between experimental measurements of pswell and effective clay dry density (Dixon 2000). The lines in the figure represent the results of regression analyses for tests involving fresh water, brackish water, saline water and brine.

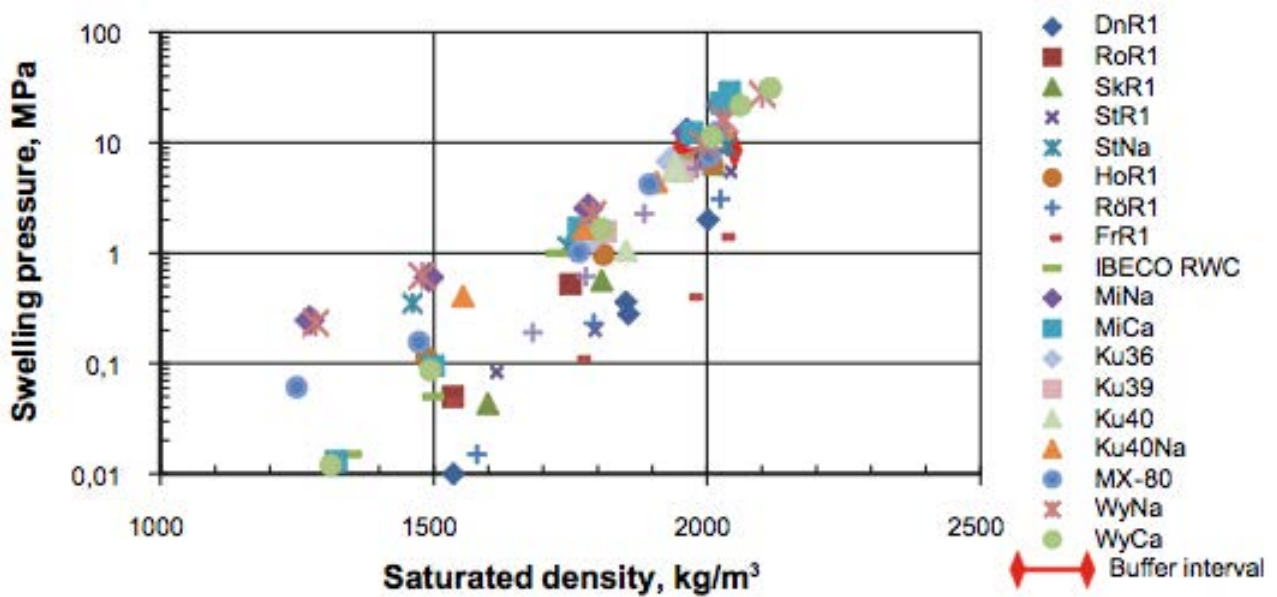


Figure 17. Plot of pswell versus saturated density for a number of bentonites and swelling clays (from Karnland, 2010). The red bar indicates a range of buffer densities relevant for MX-80 and IBECO RWC bentonites.



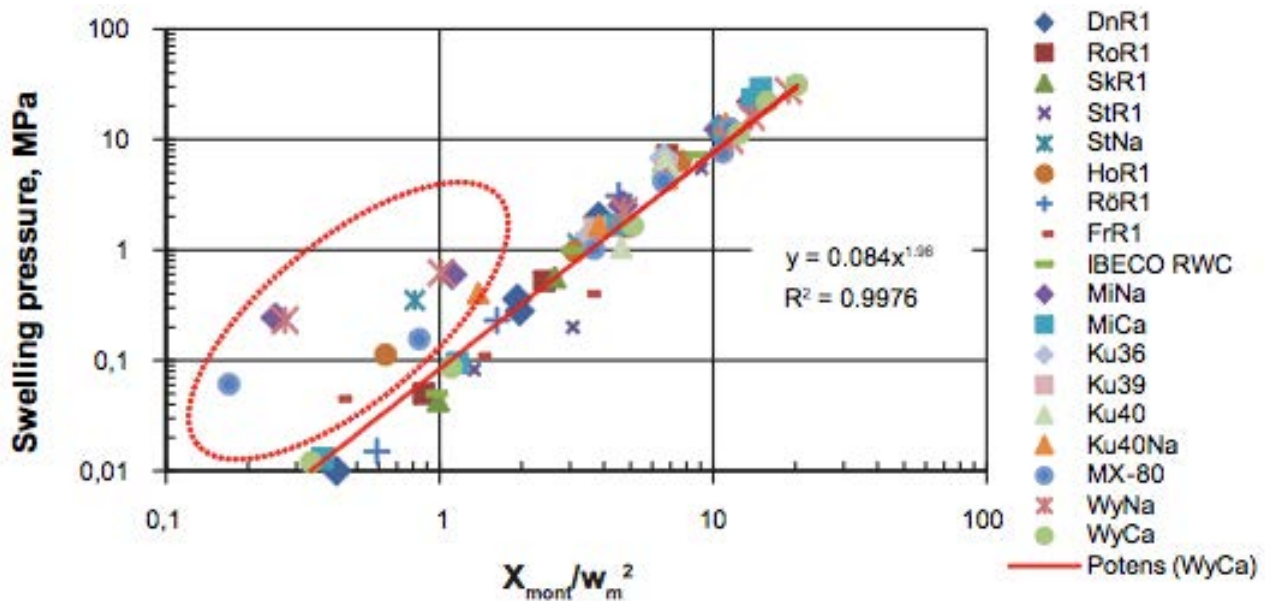
$p_{swell}$  data are re-plotted in terms of an alternative parameter defined by the montmorillonite content divided by the square of the water content at full water saturation (Figure 18). All clay minerals with  $\text{Ca}^{2+}$  as the dominant exchangeable cation lie near the regression line shown in Figure 18. Clay minerals with  $\text{Na}^+$  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).

It is worth noting that both of the above approaches were based on the results of experiments in which relatively simple aqueous solutions were used. Dixon (Dixon, 2000) considered variations in environmental conditions only in terms of a range of groundwater salinities. Karnland (2010) based his approach on the results of experiments in which pure water, or simple NaCl or  $\text{CaCl}_2$  solutions, were used (Karnland et al., 2006). In studies of the effects of salt solutions on swelling pressure, however, Herbert and Moog (1999, 2000) and Herbert et al. (2004) have shown that other aspects of solution chemistry can strongly affect swelling pressure. For example, Herbert and Moog (2000) found that in tests involving MX-80 bentonite and saturated NaCl solutions  $p_{swell}$  increased with increasing Mg content if the K concentration was held constant, and that K played

the dominant role in affecting  $p_{swell}$  in a series of tests in which both Mg and K varied.

An empirical modelling approach that can be used to relate  $p_{swell}$  to saturated density was described by Hedin (2004) based on the study of Karnland et al. (2002). The approach consists of two steps. The first involves the use of an empirical expression to relate  $p_{swell}$  to the densities of solids and an aqueous phase assuming the latter is initially pure water. The second step uses the concept of the Donnan equilibrium to calculate changes in  $p_{swell}$  that would result if the clay were then to come into contact with a salt solution of some specified composition. Results, such as shown in Figure 19, are at least qualitatively consistent with experimental observations, which indicate that the effects of salt concentration on swelling pressure tend to diminish with increasing saturated density. This good agreement is somewhat conditional, however, because the relation between  $p_{swell}$  and saturated density for pure-water conditions is based entirely on empirical observations. An analysis by Arthur (2011) suggests that the assumption of ideal Donnan behaviour upon which this modelling approach is based may not be valid for highly compacted buffer materials.

There is some evidence to show that increasing temperature decreases bentonite swelling pressure



**Figure 18.** Plot of swelling pressures shown in Figure 18 as a function of the montmorillonite content ( $X_{mont}$ ) and water content at full water saturation ( $w_m$ ) (Karnland, 2010). The latter variable is defined as the mass of water divided by the total mass of solids.

(e.g. Pusch, 1980; Villar and Lloret, 2004). For example, Pusch (1980) noted increasing temperature to 70°C decreases the swelling pressure by approximately 30–50% of that measured at 25°C.

### 7.3 Effects of freezing on swelling pressure

Birgersson et al. (2008, 2010) and Schatz and Martikainen (2010) have carried out a number of experimental and modelling studies of the effects of freezing on bentonite buffer and backfill materials. The impetus for these studies comes from the possibility that future permafrost conditions could possibly extend to the depths of a KBS-3 repository in Finland or Sweden. The effects of freezing on the swelling pressure were the primary focus of these studies.

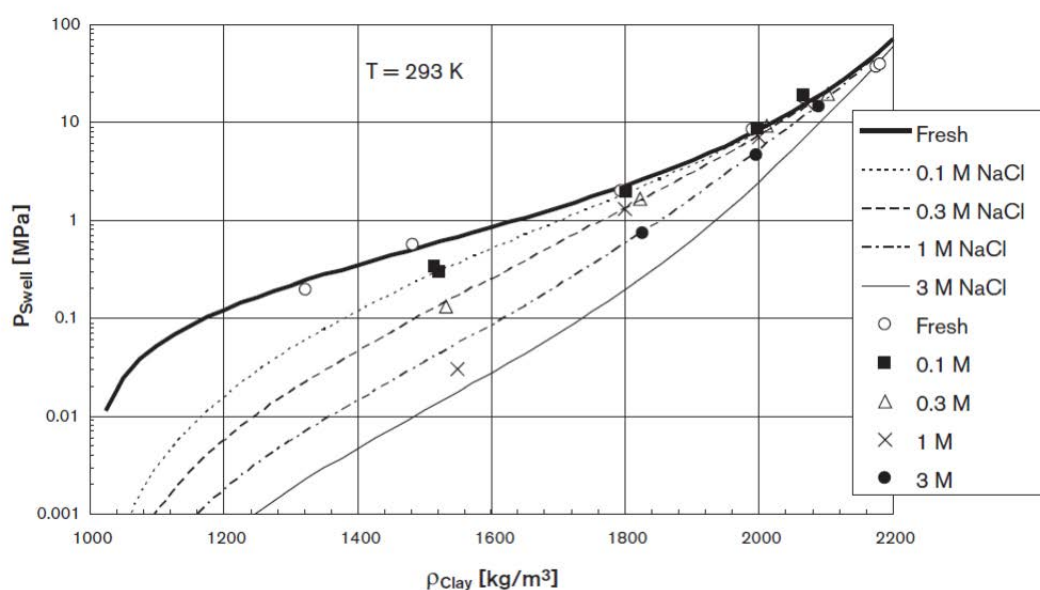
Birgersson et al. (2008, 2010) used a thermodynamic approach to develop a relation between  $p_{swell}$  and temperature given by:

$$p_{swell}(w, \Delta T) = p_{swell}(w, 0^\circ\text{C}) + \frac{\Delta S(w)}{v_{clay}(w)} \Delta T$$

where  $\Delta T$  represents a difference in temperature, measured from 0°C,  $\Delta S(w)$  stands for the difference between the molar entropy of water in bentonite and the molar entropy of bulk water,  $v_{clay}(w)$  refers to the molar volume of water in bentonite, and  $w$

denotes the bentonite's mass ratio of water to solids. Because there is a phase change at 0°C,  $\Delta S(w)$  must have different values depending on whether  $\Delta T$  is positive or negative. Above 0°C,  $\Delta S(w)$  is uniformly small over a range of relevant bentonite densities, and changes in  $p_{swell}$  are therefore also small under such conditions. Below 0°C,  $\Delta S(w)$  is a large positive number and  $p_{swell}$  must therefore decrease rapidly with decreasing temperature until a critical temperature,  $T_c$ , is reached at which point  $p_{swell} = 0$  MPa. This is considered to be the freezing point of bentonite because ice cannot form until swelling pressure is lost (Birgersson et al., 2010). It should be noted however, that other authors have different definitions of the freezing point (e.g. Kozłowski, 2009), such as the freezing point in the soil–water system being comprehended as the temperature,  $T_f$ , at which the equilibrium freezing of liquid soil water (i.e. its solidification) begins. This temperature corresponds to the 0°C for pure free water and in the case of the soil–water system is lower than 0°C.

Experimental results are in reasonably good agreement with model predictions (e.g. Figure 20) (Birgersson et al., 2010; Schatz and Martikainen, 2010). An important assumption in the model is that there exists only one type of pore in compacted bentonites.



**Figure 19.** Comparison of calculated and experimental  $p_{swell}$  values as a function of bentonite density for various NaCl concentrations (Hedin, 2004).

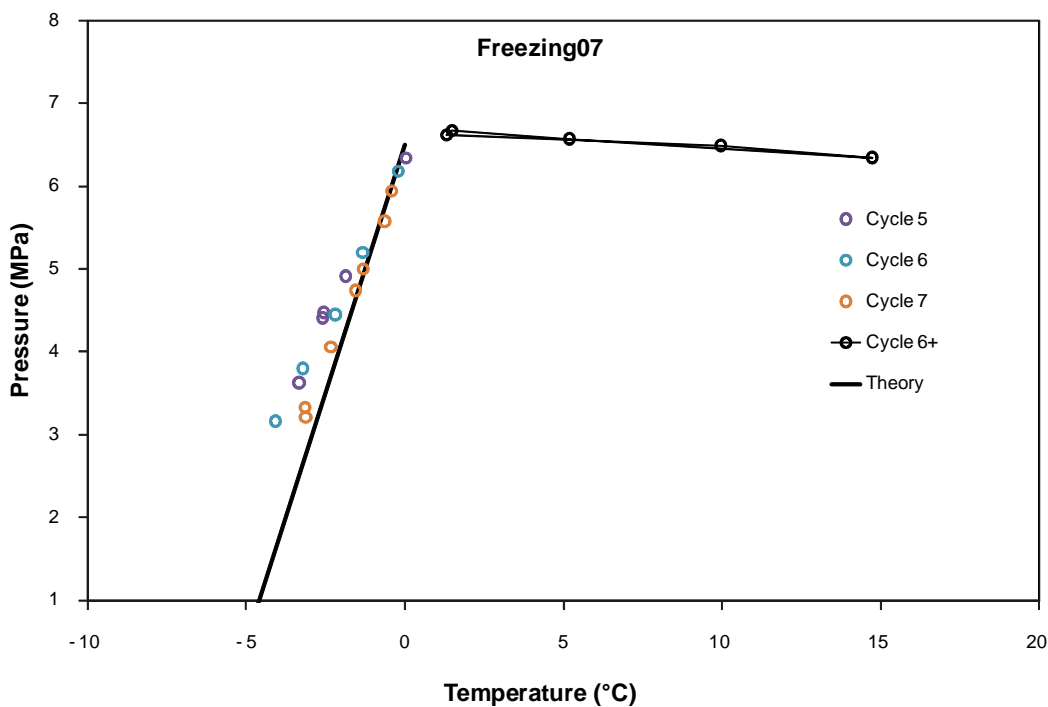
From the viewpoint of bentonite exchangeability it is interesting to note that for all densities investigated in the studies mentioned above, the rapid drop in  $p_{swell}$  when  $T < 0^\circ\text{C}$  depends only on the difference in molar entropy between bulk water and ice, and is therefore independent of bentonite type (Birgersson et al., 2010). The critical temperature at which bentonite freezes, however, depends on the swelling pressure at  $0^\circ\text{C}$  and is therefore a function of density, montmorillonite content, layer charge, etc. Schatz and Martikainen (2010) found no significant differences in the freeze-thaw behaviour of MX-80 and Deponit CaN bentonites.

## 7.4 Summary

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 Olkiluoto is unclear, however.

Mechanistic models that could be used to help address this question are not presently available. Alternative models that attempt to account for the thermodynamic and microstructural properties of compacted clays have been developed, but they presently 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. 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  $\text{CaCl}_2$  solutions.



**Figure 20.** Comparison of measured swelling pressures in Deponit CaN bentonite (symbols) with predictions made using the thermodynamic model (lines) (Birgersson et al., 2010). Each cycle refers to a single freeze-thaw cycle.

## 8 Conclusions

As the Finnish regulator, STUK has the authority to independently evaluate the technical merits of any justifications from Posiva concerning the use, or ‘exchangeability’, of different bentonite types as buffer materials in a KBS-3 repository at Olkiluoto. In this section we use the preceding discussions as a basis for commenting on the adequacy of understanding that STUK should expect to see in support of such justifications. The backfill is not included in this analysis because important aspects of its basic design, manufacture and installation are still under investigation.

### 8.1 Exchangeability in relation to buffer performance

Posiva’s views on bentonite exchangeability are based on performance requirements for the buffer. The TKS-2009 report notes, for example, that “... *buffer components will be manufactured from the reference bentonite (sodium bentonite, type MX-80) and/or some other alternative bentonite type that meets the performance requirements set for buffer material(s)*” (emphasis added) (Posiva, 2010, p. 193). In this context, performance requirements presumably relate to the design basis (Juvankoski and Marcos, 2009) and therefore include long-term safety requirements, initial-state requirements and technical requirements (Posiva, 2010, p. 187).

As noted in the Introduction, the long-term safety requirements are based on two primary safety functions (Posiva, 2010, p. 288):

- to contribute to mechanical, geochemical and hydrogeological conditions that are predictable and favorable to the canister, and to protect canisters from external processes that could compromise the safety function of complete containment of the spent fuel and associated radionuclides, and
- to limit and retard radionuclide releases in the event of canister failure.

To achieve these functions the buffer must have (e.g., Posiva, 2010, p. 188):

- sufficiently low hydraulic conductivity to minimise advective solute transport,
- sufficient swelling pressure to ensure tightness and self-sealing ability, as well as to prevent major microbiological activity and canister sinking,
- sufficiently small pore structure to prevent the migration of radionuclides with colloids, and
- sufficient plasticity to protect the canister from the effects of minor rock-shear movements.

Also, heat released from the canister must not change any buffer properties to an extent that would adversely affect buffer performance, the swelling pressure within the buffer must develop quickly enough to prevent thermal spalling of the adjacent host rock, and the buffer must not endanger the performance of other engineered barriers.

The initial state is the starting point for assessments of long-term safety and is defined for the buffer by conditions prevailing in the near field when the buffer has been successfully installed around a canister. Initial-state requirements address the gap between the buffer and canister and between the buffer and rock (Posiva, 2010, p. 190). The water content of buffer blocks, the dry density of the blocks and the average dry density of the buffer, from which the average saturated density can be calculated, are also initial-state requirements. Target values for these requirements have not been fully designed, but tentative values have been specified for the case of blocks composed of MX-80 bentonite produced by isostatic compression.

Technical requirements include manufacturing requirements and installation requirements. Manufacturing requirements concern the acquisition and quality assurance of raw materials, storage and handling of these materials, and the

production of buffer components, including blocks, rings and pellets (Ahonen et al., 2008; Juvankoski, 2010; Laaksonen, 2010). Installation requirements concern the handling of buffer components, filling of the gap between the buffer and rock, removal of deposition-hole protections and filling the top of the deposition hole (Juvankoski and Marcos, 2009). Manufacturing and installation requirements are still under investigation (Posiva, 2010, p193).

The design basis for the buffer takes into account these long-term safety requirements, initial-state requirements and technical requirements. The current design basis calls for (Posiva, 2010, p. 190; Juvankoski and Marcos, 2009):

- a montmorillonite content greater than 75 wt%,
- a saturated density between 1950 and 2050 kg m<sup>-3</sup>,
- sufficient ductility to protect the canister from shear-type dislocations in the rock of up to 100 mm, and
- temperatures < 100°C.

Posiva believes this design basis will ensure that the buffer's safety functions are met once a target state has been achieved. The target state is expected to evolve from the initial state through an early transient period during which the buffer becomes fully saturated with groundwater, and radiogenic heat from the spent fuel is largely dissipated by conduction into the surrounding rock (e.g., Posiva, 2010, Section 6.1.3).

Posiva's view that the exchangeability of different bentonite types should be assessed in relation to the performance requirements discussed above seems reasonable. The level of understanding necessary to adequately support such assessments is not clear, however, and would seem to depend on the type of requirements being considered. Assessments of exchangeability in relation to initial-state or technical requirements may be relatively straightforward, for example, because they can be evaluated by direct observations and measurements, and because it is reasonable to expect that any alternative bentonite types would be subjected to the same quality-assurance standards and laboratory-scale and block-scale testing as the reference MX-80 material.

Assessments based on long-term safety requirements may be more problematic, however. These requirements relate to a target state of the buffer that

will be attained only after hundreds or thousands of years have elapsed since the initial state, and to subsequent interactions involving the buffer with a continuously evolving near-field environment. In such cases decisions as to what qualifies as an adequate level of understanding in justifications from Posiva regarding bentonite exchangeability may have to be based largely on expert judgement, and may therefore be subject to differences of opinion. Factors that we believe STUK should consider when evaluating any such justifications in relation to long-term safety requirements are discussed below.

## 8.2 Exchangeability in relation to performance targets

Because the long-term safety requirements discussed above are quite general, Posiva has defined a number of more specific "performance targets" for the buffer (e.g., Posiva, 2010, Section 6.1.4). These targets relate to properties that are either measurable or otherwise observable by modelling or other means. Posiva believes that if these targets are achieved then it can be assumed that the buffer's safety functions will be met. Because the targets relate to the buffer, it follows that they must be achievable regardless of the type of bentonite used as the buffer material.

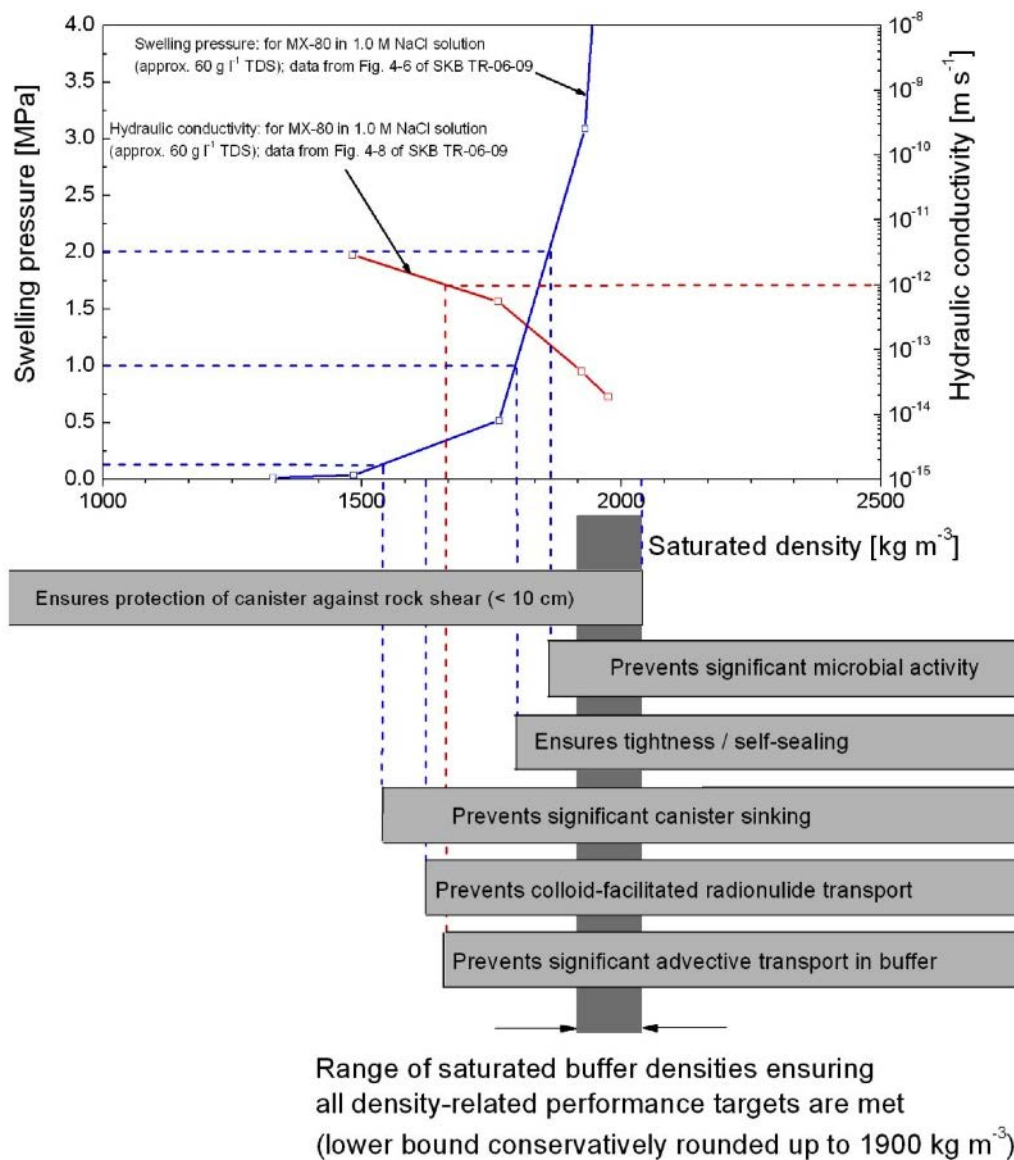
An example of the relation between long-term safety requirements and performance targets is illustrated in Figure 21, where it can be seen that target values are defined in terms of hydraulic conductivity, swelling pressure and saturated density (Posiva, 2010). In this case, the curves representing changes in swelling pressure or hydraulic conductivity as a function of saturated density are based on measurements at room temperature in an experimental system containing MX-80 bentonite saturated with a 1 M NaCl solution (SKB, 2006). It should be noted that temperature above ambient would lead to a shift of the blue line downwards and narrow the applicable density window.

An objective and safety-relevant criterion for exchangeability suggested by Figure 21 is that any alternative bentonite subjected to the same experimental conditions should generate similar curves as shown in the figure such that the respective performance targets are met over a range of saturated densities that are achievable in practice. Such a criterion would be inherently empirical in nature because there is no reliable conceptual basis

for predicting target values based on initial-state properties such as mineralogy, mineral chemistry, water content, water chemistry and dry density. The design-basis requirement that bentonite contain at least 75 wt% montmorillonite, for example, is not based on theoretical predictions but rather on a large body of experimental evidence indicating that this is an adequate amount of montmorillonite to achieve swelling pressures between 2 and 10 MPa and hydraulic conductivities  $< 10^{-12} \text{ m s}^{-1}$  if the saturated density is between 1950 and 2050  $\text{kg m}^{-3}$  and if groundwater salinities are within a range of values expected at Olkiluoto.

Should Posiva use such empirical performance-target criteria as a basis for justifying the exchange-

ability of alternative bentonites, then a question that should be considered is whether the range of experimental conditions supporting such justifications has been determined in a manner that is both scientifically defensible and adequately bounding with respect to expected conditions in the repository and with respect to the different bentonite types being considered. For example, most swelling pressure tests on MX-80, Milos Deponit CaN and other bentonite types (e.g., Karnland, 1997a; Pusch, 1999; Karnland et al., 2006; Carlson and Keto, 2006) have used pure water or simple NaCl or  $\text{CaCl}_2$  solutions to represent ranges in the chemistry of groundwaters that could exist in KBS-3 repositories in Finland or Sweden (e.g., Pastina and Hellä, 2006).



**Figure 21.** Diagram illustrating relations among various performance targets for the buffer as a function of saturated density (Posiva, 2010). The reference to SKBTR-06-09 is for SKB (2006).

While this approach may be reasonably bounding with respect to the effects of salinity and  $\text{Na}^+$  and  $\text{Ca}^{2+}$  concentrations on swelling pressure it leaves open the question whether other solution properties, such as pH or the concentrations of other solutes such as  $\text{Mg}^{2+}$  and  $\text{K}^+$ , could significantly affect the swelling pressure. Although such effects may be unlikely, it is difficult to rule them out completely given the empirical basis of current understanding concerning the effects of water chemistry and other properties on swelling pressure (Hedin, 2004). In such cases a limited number of confirmatory tests could help answer such questions and would enhance confidence that the respective performance targets are relevant to Okiluoto conditions.

### 8.3 Exchangeability in relation to the target state

Justifications for the exchangeability of different bentonite types should consider potential impacts on performance targets and safety functions that could result as the buffer evolves from its initial state to the target state. As noted earlier, this evolution will occur during a transient period lasting hundreds to thousands of years. The buffer will become fully saturated with groundwater during this time and will experience relatively high temperatures and steep temperature gradients as heat dissipates into the host rock. A bentonite having a relatively low thermal conductivity and high concentration of accessory minerals such as anhydrite, for example, might be more susceptible to the effects of cementation during this transition period than the reference MX-80 material. If so, justification for the use of such a bentonite should include an analysis of why the effects of any cementation that could occur would not be sufficient to jeopardize the safety functions of the buffer.

To evaluate the exchangeability of bentonites from the perspective of changes that might occur to the buffer as the target state evolves from the initial state may be difficult for several reasons. Experimental support for such evaluations from studies such as the ABM and LOT tests can realistically cover only a very small fraction of the total transition time. The evolution of the buffer during this time will likely be controlled by complex and possibly strongly coupled thermal, mass-transport, chemical/mineralogical and mechanical processes

that may be difficult to adequately account for using numerical models. It may be difficult to verify that model predictions are reliable given the experimental limitations noted above and possible difficulties in interpreting initial and boundary conditions in studies of analogous natural systems. Even if such models were to prove useful in reliably predicting temporal and spatial changes in bentonite mineralogy, it may be difficult to relate the effects of such changes to the buffer's safety-relevant physical, thermal and rheological properties. These potential complications suggest that an integrated approach using the results of well-qualified experimental, modelling and natural-systems studies may be needed to evaluate the exchangeability of bentonites in relation to the target state of the buffer and its evolution from the initial state.

### 8.4 Exchangeability in relation to potentially adverse near-field conditions

The response of different bentonite types to environmental conditions that could pose a threat to buffer performance should be considered in evaluations of bentonite exchangeability. Bentonites with montmorillonite predominantly in the Ca rather than Na form, for example, may be less susceptible to the effects of sol formation and erosion if the buffer were to come into contact with dilute groundwaters. Should such erosion occur and result in a partial loss of density, certain bentonites may be able to sustain some, if not all, of their performance targets over a broader range of subsequently evolving groundwater salinities than others. Different bentonites may also be less susceptible than others to interactions involving cementitious materials or Fe-bearing repository components depending on the types, amounts and reactive surface areas of the smectite clays and accessory minerals. From this perspective differences rather than similarities in bentonite types may be the most important attributes concerning their exchangeability.

Evaluations of the exchangeability of bentonites from the perspective of potentially adverse conditions in the near field may require consideration of experimental evidence and the results of modelling studies. General concerns related to such studies discussed in the preceding sections are also applicable here.

**Table 11.** Synthesis of summary comments from previous sections.

Property	Summary	Comments
<b>Composition &amp; sources</b>	<ul style="list-style-type: none"> <li>• Only MX-80, Deponit CaN, Kutch 'Basic Star' meet &gt; 75 % smectite criterion.</li> <li>• Different bentonites contain different amounts of potentially safety-relevant contaminants.</li> <li>• Kutch bentonites have high contents of Fe<sup>3+</sup> which may be detrimental to swelling in the long-term.</li> <li>• MX-80 is consistent in composition of major minerals, but minor minerals show considerable variation.</li> <li>• Wyoming and Greek bentonites have CEC ~1 eq kg<sup>-1</sup>, but have different charge compensating cations.</li> <li>• Some bentonites have layer charge mainly in the octahedral layers (MX-80, Deponit CaN), whereas others (Indian type) have charge mainly in the octahedral layers.</li> <li>• Backfill designs that include Friedland Clay or clay/ballast mixes require greater precision regarding emplacement density than those using Milos Bentonite.</li> </ul>	It is clear that there is a wide range in minor mineral content of bentonites with consequent potential implications for properties and behaviour.
<b>Hydraulic behaviour</b>	<ul style="list-style-type: none"> <li>• There are few datasets describing the hydraulic behaviour of Ca-bentonites.</li> <li>• Ca-bentonite has a fundamentally different pore structure than Na-bentonite.</li> </ul>	Additional data on the hydraulic properties of Ca-bentonite are desirable. Nevertheless, there are fundamental differences between the hydraulic properties of Na- and Ca-bentonites.
<b>Mechanical behaviour</b>	<ul style="list-style-type: none"> <li>• Ca-bentonite has greater strength and swelling pressure than Na-bentonite.</li> <li>• For tunnel backfill, clay-ballast mixtures have the greatest demands in terms of required density.</li> </ul>	Design requirements for mechanical behaviour have (conservatively) been chosen by Posiva/SKB to be those defined by Ca-bentonites.
<b>Long-term alteration</b>	<ul style="list-style-type: none"> <li>• Interaction of bentonite with groundwater is likely to lead to the dominance of Ca on the cation exchange site, regardless of the initial composition.</li> <li>• Ca-bentonite may be more resistant to long-term alteration than Na-bentonite.</li> <li>• There are few experimental data, if any, for the alteration of Ca-bentonite by cement pore fluids (especially the low-pH variety) or by iron container materials.</li> </ul>	More experimental data for cement- and iron-clay interactions are desirable. Ca-bentonite may be more resistant to long-term alteration than Na-bentonite.
<b>Colloidal properties</b>	<ul style="list-style-type: none"> <li>• Ca-bentonites with Ca/Na &gt; 90/10 are much more resistant to colloid formation than Na-bentonites</li> <li>• Ca-bentonites could become more sodic with time due to interaction with ambient groundwater.</li> </ul>	Bentonites with Ca/Na > 90/10 may be less susceptible to colloid formation, but long-term cation exchange with groundwater could be a problem.
<b>Swelling behaviour</b>	<ul style="list-style-type: none"> <li>• Many different types of bentonite can achieve performance targets for swelling pressure, but there is a lack of experimental data for behaviour in mixed electrolyte solutions.</li> <li>• Mechanistic models are not currently available.</li> </ul>	Further experimental work with mixed electrolyte solutions is desirable along with further effort to develop a more mechanistic understanding of swelling behaviour.

## 8.5 Summary

Summary comments from previous sections of this report are synthesised in Table 11. It may be seen from this Table that:

- There are some fundamental differences between Ca- and Na-bentonites such as colloidal behaviour, 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 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.



Posiva's view that assessments of the exchangeability of different bentonite types as buffer materials should be based on performance requirements for this engineered barrier seems reasonable, but the level of understanding needed to adequately support such assessments is not clear and would seem to depend on the types of requirements being considered. Assessments addressing long-term safety requirements may be the most challenging because these requirements relate to a target state of the buffer that will not be attained until hundreds or thousands of years have elapsed since the initial state, and to subsequent interactions involving the buffer with continuously evolving near-field conditions. Should such assessments be based in

whole or in part on experimental testing, then it is important to consider whether the experimental conditions are appropriate and defensibly bounding with respect to conditions expected in the near field over long periods of time. Assessments based on modelling should consider whether the models adequately represent thermal, mass-transport, chemical/mineralogical and mechanical processes controlling bentonite-water interactions, whether the reliability of the models has been verified to the extent possible in relation to relevant experimental and natural systems studies, and whether model results can be sensibly related to safety-relevant physical, thermal and rheological properties of the buffer.

## 9 References

- Aagaard, P., and Helgeson, H. C., Activity/composition relations among silicates and aqueous solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites, and mixed-layer clays. *Clays and Clay Minerals* 31: 207–217, 1983.
- Adamson, A. W., *Physical Chemistry of Surfaces*, Interscience Publishing, John Wiley & Sons, New York, 1967.
- Agus, S. S., and Schanz, T., A method for predicting swelling pressure of compacted bentonites. *Acta Geotechnica* 3: 125–137, 2008.
- Ahonen, L., Korkeakoski, P., Tiljander, M., Kivikoski, H., and Laaksonen, R., Quality assurance of the bentonite material, Posiva Working Report 2008-33, Posiva Oy, Olkiluoto, Finland, 2008.
- Allen, C. C., and Wood, M. I., Bentonite in nuclear waste disposal: a review of research in support of the Basalt Waste Isolation Project. *Applied Clay Science* 3: 11–30, 1988.
- Apted, M., Arthur, R., Bennett, D., Savage, D., Sällfors, G., and Wennerström, H., Buffer erosion: An overview of concepts and potential safety consequences, SSM Report 2010:31, Swedish Radiation Safety Authority, Stockholm, Sweden, 2010.
- Arcilla, C. A., Pascua, C. S., Vargas, E., Honrado, M. L. L., Alexander, W. R., Namiki, K., Fuji, N., Yamakawa, M., Sato, T., and McKinley, I. G., Reaction pathways for rising hyperalkaline groundwater in a bentonite mine in the Philippines. *Geochimica et Cosmochimica Acta Goldschmidt Conference Abstracts*: A50, 2009.
- 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.
- Arthur, R. C., and Wang, J., Claystone constraints on models of the long-term chemical evolution of buffer porewaters. *Scientific Basis for Nuclear Waste Management* (R. W. Smith and D. W. Shoesmith, eds.) 608: 551–556, 2000.
- Bennett, D., The feasibility of backfilling a repository of spent fuel: an assessment of recent developments by SKB, SSM Report 2010:38, Swedish Radiation Safety Authority, Stockholm, Sweden, 2010.
- Bildstein, O., Trotignon, L., Perronnet, M., and Julien, M., Modelling iron-clay interactions in deep geological disposal. *Physics and Chemistry of the Earth* 31: 618–625, 2006.
- Birgersson, M., Börgesson, L., Hedström, M., Karnland, O., and Nilsson, U., Bentonite erosion. Final report, Technical Report TR-09-34, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2009.
- Birgersson, M., Karnland, O., and Nilsson, U., Freezing in saturated bentonite – A thermodynamic approach. *Physics and Chemistry of the Earth* 33: S527–S530, 2008.

- Birgersson, M., Karnland, O., and Nilsson, U., Freezing of bentonite: Experimental studies and theoretical considerations, SKB Report TR-10-40, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Börgesson, L., Dueck, A., and Johannesson, L.-E., Material model for shear of the buffer – evaluation of laboratory test results, SKB Report R-10-31, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Börgesson, L., and Hernelind, J., Earthquake induced rock shear through a deposition hole. Influence of shear plane inclination and location as well as buffer properties on the damage caused to the canister, SKB Report TR-06-43, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Börgesson, L., and Hernelind, J., Earthquake induced rock shear through a deposition hole. Modelling of three model tests scaled 1:10. Verification of the bentonite material model and the calculation technique, SKB Report TR-10-33, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2010.
- Carlson, L., Karnland, O., Oversby, V. M., Rance, A., Smart, N., Snellman, M., Vähänen, M., and Werme, L. O., Experimental studies of the interactions between anaerobically corroding iron and bentonite. *Physics and Chemistry of the Earth* 32: 334–345, 2007.
- Carlson, L., and Keto, P., Verification of substitution of bentonites by montmorillonitic clays, Posiva Working Report 2006-62, Posiva Oy, Olkiluoto, Finland, 2006.
- Cathelineau, M., Guillaume, D., Mosser-Ruck, R., Dubessy, J., Charpentier, D., Villiéras, F., and Michau, N.: Dissolution–crystallization processes affecting di-octahedral smectite in presence of iron metal: implication on mineral distribution in clay barriers. In *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement*, Tours, France, pp. 35.
- Cuevas, J., Vigil de la Villa, R., Ramirez, S., Sanchez, L., Fernández, R., and Leguey, S., The alkaline reaction of FEBEX bentonite: a contribution to the study of the performance of bentonite/concrete engineered barrier systems. *Journal of Iberian Geology* 32: 151–174, 2006.
- De Windt, L., van der Lee, J., and Pellegrini, D.: Reactive transport modelling of pH controlling processes in cement/clay systems. In *Tenth International Symposium on Water-Rock Interaction*, Villasimius, Italy, pp. 1315–1318.
- Dixon, D. A., Porewater salinity and the development of swelling pressure in bentonite-based buffer and backfill materials, POSIVA 2000-04, Posiva Oy, Helsinki, Finland, 2000.
- 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.
- 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.
- Eng, A., Nilsson, U., and Svensson, D., Äspö Hard Rock Laboratory. Alternative Buffer Material installation report, International Progress Report IPR-07-15, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2007.
- Fritz, B., Multicomponent solid solution and computer modelling of weathering processes, In (J. I. Drever eds) *The Chemistry of Weathering*, Reidel Publishing Corporation, 1985.
- Fujiwara, A., Takegahara, T., Chiba, T., Ikeda, T., Takase, H., Savage, D., and Metcalfe, R.: Kinetic controls on cement porefluid-bentonite interactions in engineered barriers: new insights from experimental and numerical simulations. In *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement*, Reims, France, pp. 25–26.

- Gaucher, E., Blanc, P., Matray, J. M., and Michau, N., Modeling diffusion of an alkaline plume in a clay barrier. *Applied Geochemistry* 19: 1505–1515, 2004.
- 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, Wetingen, 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.
- Hagros, A., Estimated quantities of residual materials in a KBS-3H repository at Olkiluoto, SKB Report R-08-33, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2007.
- Hansen, J., Korkiala-Tanttu, L., Keski-Kuha, E., and Keto, P., Deposition tunnel backfill design for a KBS-3V repository, Posiva Report 2009-129, Posiva Oy, Olkiluoto, Finland, 2009.
- 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.
- Herbert, H.-J., Kasbohm, J., Moog, H. C., and Henning, K.-H., Long-term behaviour of the Wyoming bentonite MX-80 in high saline solutions. *Applied Clay Science* 26: 275–291, 2004.
- Herbert, H.-J., and Moog, H. C., Cation exchange, interlayer spacing, and water content of MX-80 bentonite in high molar saline solutions. *Engineering Geology* 54: 55–65, 1999.
- Herbert, H.-J., and Moog, H. C.: Modeling of saturation and swelling effects in clays under different saline conditions. In Eurosafe, Cologne, Germany.
- Hermansson, H.-P., The stability of magnetite and its significance as a passivating film in the repository environment, SKI Report 2004:07, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 2004.
- Honrado, M. L. L., Pascua, C. S., Vargas, E., Arcilla, C. A., Alexander, W. R., Namiki, K., Fuji, N., Yamakawa, M., Sato, T., and McKinley, I. G., Smectite and zeolite formation from the pyroclastic deposits of the Aksitero Formation, Philippines. *Geochimica et Cosmochimica Acta Goldschmidt Conference Abstracts: A547*, 2009.
- 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.
- Ichige, S., Mihara, M., and Ito, M.: Alteration of compacted bentonite in alkaline solution. In Annual Spring Meeting, pp. 611.
- Inoue, A., Potassium fixation by clay minerals during hydrothermal treatment. *Clays and Clay Minerals* 31: 81–91, 1983.
- Johannesson, L.-E., Backfilling and closure of the deep repository, Phase 3 – pilot tests to verify engineering feasibility. Geotechnical investigations made on unsaturated backfill materials SKB Report R-08-131, Swedish Nuclear Power and Waste Management Company, Stockholm, Sweden, 2008.
- Johannesson, L.-E., and Nilsson, U., Deep repository – engineered barrier systems. Geotechnical behaviour of candidate backfill materials. Laboratory tests and calculations for determining performance of the backfill, SKB Report R-06-73, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- Johnson, L. H., Marschall, P., Wersin, P., and Gribi, P., HMCBG processes related to the steel components in the KBS-3H disposal concept, SKB Report R-08-25, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.

- Johnston, R. G., Strope, M. B., and Anantatmula, R. P., X-ray diffraction/electron microprobe analysis of surface films formed on alloys during hydrothermal reaction with geologic materials, In (C. S. Barrett, P. K. Perdecki, and D. C. Leyden eds) *Advances in X-Ray Analysis*, Plenum Press, New York, USA, 1985.
- Juvankoski, M., Description of basic design for buffer, Posiva Working Report 2009-131, Posiva Oy, Olkiluoto, Finland, 2010.
- Juvankoski, M., and Marcos, N., Design basis for buffer components, Posiva Working Report 2009-132, Posiva Oy, Olkiluoto, Finland, 2009.
- 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., Muurinen, A., and Karlsson, F.: Bentonite swelling pressure in NaCl solutions - experimentally determined data and model calculations. In *Symposium on Large-Scale Field Tests in Granite*, Sitges, Spain.
- 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.
- Keto, P., Dixon, D. A., Gunnarsson, D., Jonsson, E., Börgesson, L., and Hansen, J., Assessment of backfill design for KBS-3V repository, Posiva Working Report 2009-115, Posiva Oy, Olkiluoto, Finland, 2009.
- Kjellander, R., Marcelja, S., and Quirk, J. P., Attractive double-layer interactions between calcium clay particles. *Journal of Colloid and Interface Science* 126: 194–211, 1988.
- Komine, H., and Ogata, N., Experimental study on swelling characteristics of compacted bentonite. *Canadian Geotechnical Journal* 31: 478–490, 1994.
- Komine, H., and Ogata, N., Prediction for swelling characteristics of compacted bentonite. *Canadian Geotechnical Journal* 33: 11-22, 1996.
- Korkiala-Tanttu, L., Finite element modelling of deformation of unsaturated backfill due to swelling of the buffer, Posiva Working Report 2008-88, Posiva Oy, Olkiluoto, Finland, 2008.
- Kozłowski, T., Some factors affecting supercooling and the equilibrium freezing point in soil–water systems. *Cold Regions Science and Technology* 59: 25–53, 2009.
- Kruyt, H. R.: *Colloid Science*, Elsevier, New York, 1952.

- Kubo, H., Kuroki, Y., and Mihara, M., The basic research of the long term degeneration of bentonite by concrete pore water. *Geotechnology Bulletin* 46 (10), 1998.
- 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.
- Kuula-Väisänen, P., Leppänen, M., and Kolisoja, P., Hydraulic properties of backfill materials, Posiva Working Report 2008-90, Posiva Oy, Olkiluoto, Finland, 2008.
- Laaksonen, R., MANU - Purchase of bentonite process description, Posiva Working Report 2009-64, Posiva Oy, Olkiluoto, Finland, 2010.
- Laine, H., and Karttunen, P., Long-term stability of bentonite: a literature review, Posiva Report 2010-53, Posiva Oy, Olkiluoto, Finland, 2010.
- Lantenois, S., Lanson, B., Muller, F., Bauer, A., Jullien, M., and Plançon, A., Experimental study of smectite interaction with metal Fe at low temperature: 1. Smectite destabilization. *Clays and Clay Minerals* 53: 597–612, 2005.
- Lehikoinen, J., Bentonite-cement interaction – Preliminary results from model calculations, Posiva Working Report WR 2009-37, Posiva Oy, Olkiluoto, Finland, 2009.
- Likos, W. J., and Wayllace, A., Porosity evolution of free and confined bentonites during interlayer hydration. *Clays and Clay Minerals* 58: 399–414, 2010.
- Lippmann, F.: The thermodynamic status of clay minerals. In *Seventh International Clay Conference*, pp. 475.
- Low, P. F., The swelling of clay. I: Basic concepts and empirical equations. *Soil Science Society of America Journal* 43: 473–484, 1979.
- Low, P. F., The swelling of clay. II: montmorillonites. *Soil Science Society of America Journal* 44: 667-676, 1980.
- Low, P. F., Structural component of the swelling pressure of clays. *Langmuir* 3: 18, 1987.
- Madsen, F. T., Clay mineralogical investigations related to nuclear waste disposal. *Clay Minerals* 33: 109-129, 1998.
- Marcos, N., Bentonite-iron interactions in natural occurrences and in laboratory – the effects of the interaction on the properties of bentonite: a literature survey, Posiva Working Report 2003-55, Posiva Oy, Olkiluoto, Finland, 2003.
- Marty, N., Claret, F., Gaboreau, S., Cochepin, B., Munier, I., Michau, N., Gaucher, E. C., and Burnol, A.: Dual alteration of bentonite by iron corrosion and concrete interaction under high temperature conditions. In *Clays in Natural and Engineered Barriers for Radioactive Waste Confinement*, Nantes, France, pp. 473–474.
- Marty, N. C. M., Tournassat, C., Burnol, A., Giffaut, E., and Gaucher, E. C., Influence of reaction kinetics and mesh refinement on the numerical modelling of concrete/clay interactions. *Journal of Hydrology* 364: 58–72, 2009.
- May, H. M., Kinniburgh, D. G., Helmke, P. A., and Jackson, M. L., Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate minerals: kaolinite and smectites. *Geochimica et Cosmochimica Acta* 50: 1667–1677, 1986.
- Meunier, A., and Velde, B., *Illite*, Springer-Verlag, Berlin, Heidelberg, 2004.
- Milodowski, A. E., Cave, M. R., Kemp, S. J., Taylor, H., Vickers, B., Green, K., Williams, C. L., and Shaw, R. A., Mineralogical Investigations of the Interaction between Iron Corrosion Products and Bentonite from the NF-PRO experiments (Phase 1), BGS Report CR/07/116, British Geological Survey, Keyworth, UK, 2007.

- Milodowski, A. E., Cave, M. R., Kemp, S. J., Taylor, H., Vickers, B., Green, K., Williams, C. L., and Shaw, R. A., Mineralogical investigations of the interaction between iron corrosion products and bentonite from the NF-PRO Experiments (Phase 1), SKB Technical Report TR-09-02, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2009.
- Montes-H, G., Fritz, B., Clement, A., and Michau, N., Modeling of transport and reaction in an engineered barrier for radioactive waste confinement. *Applied Clay Science* 29: 155–171, 2005.
- Moreno, L., Neretnieks, I., and Liu, L., Modelling of erosion of bentonite gel by gel/sol flow, SKB Report TR-10-64, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2011.
- Muurinen, A., Studies on the chemical conditions and microstructure in the reference bentonites of Alternative Buffer Materials Project (ABM) in A<sup>?</sup>spo, Posiva Working Report 2009-42, Posiva Oy, Olkiluoto, Finland, 2009.
- Muurinen, A., and Lehtikoinen, J., Porewater chemistry in compacted bentonite. *Engineering Geology* 54: 207–214, 1999.
- Nadeau, P. H., and Reynolds, R. C., Burial and contact metamorphism in the Mancos Shale. *Clays and Clay Minerals* 29: 249, 1981.
- Nakayama, S., Sakamoto, Y., Yamaguchi, T., Akai, M., Tanaka, T., Sato, T., and Iida, Y., Dissolution of montmorillonite in compacted bentonite by highly-alkaline aqueous solutions and diffusivity of hydroxide ions. *Applied Clay Science* 27: 53–65, 2004.
- 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.
- Pastina, B., and Hellä, P., Expected evolution of a spent nuclear fuel repository at Olkiluoto, Posiva Report 2006-05, Posiva Oy, Olkiluoto, Finland, 2006.
- Pegado, L., Jönsson, B., and Wennerström, H., Ion correlation attraction in a molecular solvent. *Journal of Chemical Physics* 129: 184503-1-9, 2008.
- Perronnet, M., Jullien, M., Villiéras, F., Raynal, J., Bonnin, D., and Bruno, G., Evidence of critical content in Fe(0) on FoCa7 bentonite reactivity at 80°C. *Clay Science*, 2007.
- Posiva, TKS-2009. Nuclear Waste Management at Olkiluoto and Loviisa Power Plants. Review of Current Status and Future Plans for 2010–2012, Posiva Report TKS 2009, Posiva Oy, Olkiluoto, Finland, 2010.
- Pusch, R., Swelling pressure of highly compacted bentonite, SKB Report TR 80-13, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1980.
- 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., Börgesson, L., and Erlström, M., Alteration of isolating properties of dense smectite clay in repository environments as examples by seven pre-Quaternary clays, SKB Report TR-87-29, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1987.
- 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.

- Ramírez, S., Cuevas, J., Vigil, R., and Leguey, S., Hydrothermal alteration of "La Serrata" bentonite (Almeria, Spain) by alkaline solutions. *Applied Clay Science* 21: 257–269, 2002.
- Ransom, B., and Helgeson, H. C., A chemical and thermodynamic model of aluminous dioctahedral 2, 1 layer clay minerals in diagenetic processes, regular solution representation of interlayer dehydration in smectite. *American Journal of Science* 294: 449–484, 1994.
- Ransom, B., and Helgeson, H. C., A chemical and thermodynamic model of dioctahedral 2, 1 layer clay and minerals in diagenetic processes, dehydration of smectite as a function of temperature and depth in sedimentary basins. *American Journal of Science* 295: 245–281, 1995.
- Roberson, H. E., and Lahann, R. W., Smectite to illite conversion rates: effect of solution chemistry. *Clays and Clay Minerals* 29: 129, 1981.
- Rotenberg, B., Morel, J.-P., Marry, V., Turq, P., and Morel-Desrosiers, N., On the driving force of cation exchange in clays: Insights from combined microcalorimetry experiments and molecular simulation. *Geochimica et Cosmochimica Acta* 73: 4034–4044, 2009.
- Savage, D., The effects of high salinity groundwater on the performance of clay barriers, SKI Report 2005:54, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 2005.
- 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., Geochemical constraints on buffer pore water evolution and implications for erosion. In: 'Copper Corrosion and Buffer Erosion'. Synthesis and Extended Abstracts from a Workshop in Stockholm, Sweden, September 15–17, 2010, SSM Report 2011:08, Swedish Radiation Safety Authority, Stockholm, Sweden, 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, 2010a.
- Savage, D., Noy, D. J., and Mihara, M., Modelling the interaction of bentonite with hyperalkaline fluids. *Applied Geochemistry* 17: 207–223, 2002.
- Savage, D., Watson, C., Benbow, S., and Wilson, J., Modelling iron-bentonite interactions. *Applied Clay Science* 47: 91–98, 2010b.
- Schatz, T., and Martikainen, J., Laboratory studies on the effect of freezing and thawing exposure on bentonite buffer performance: Closed-system tests, Posiva Report 2010-06, Posiva Oy, Olkiluoto, Finland, 2010.
- SKB, Long-term safety for KBS-3 repositories at Forsmark and Laxemar - a first evaluation. Main report of the SR-Can project, SKB Technical Report TR-06-09, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2006.
- 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, 2010.
- 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.
- Skipper, N. T., Lock, P. A., Titiloye, J. O., Swenson, J., Mirza, Z. A., Howells, W. S., and Fernandez-Alonso, F., The structure and dynamics of 2-dimensional fluids in swelling clays. *Chemical Geology* 230: 182–196, 2006.
- 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.



- Smith, P. A., Neall, F., Snellman, M., Pastina, B., Nordman, H., Johnson, L. H., and Hjerpe, T., Safety assessment for a KBS-3H spent nuclear fuel repository at Olkiluoto: Summary report, SKB Report R-08-39, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.
- Sridaharan, A., Prediction for swelling characteristics of compacted bentonite: Discussion. *Canadian Geotechnical Journal* 34: 1004, 1997.
- Tinseau, E., Bartier, D., Hassouta, L., Devol-Brown, I., and Stammose, D., Mineralogical characterization of the Tournemire argillite after in situ reaction with concretes. *Waste Management* 26: 789–800, 2006.
- Van Loon, L., and Glaus, M. A., Mechanical compaction of smectite clays increases ion exchange selectivity for cesium. *Environmental Science and Technology* 42: 1600–1604, 2008.
- Vidal, O., and Dubacq, B., Thermodynamic modelling of clay dehydration, stability and compositional evolution with temperature, pressure and  $H_2O$  activity. *Geochimica et Cosmochimica Acta* 73: 6544–6564, 2009.
- Vigil de la Villa, R., Cuevas, J., Ramirez, S., and Leguey, S., Zeolite formation during the alkaline reaction of bentonite. *European Journal of Mineralogy* 13: 635–644, 2001.
- Villar, M. V., and Lloret, A., Influence of temperature on the hydro-mechanical behaviour of a compacted bentonite. *Applied Clay Science* 26: 337–350, 2004.
- Wang, Y., Bryan, C., Xu, H., and Gao, H., Nano-geochemistry: geochemical reactions and mass transfers in nanopores. *Geology* 31: 387–390, 2003.
- 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.
- Watson, C., Hane, K., Savage, D., Benbow, S., Cuevas, J., and Fernandez, R., Reaction and diffusion of cementitious water in bentonite: results of 'blind' modelling. *Applied Clay Science* 45: 54–69, 2009.
- Wersin, P., Birgersson, M., Olsson, S., Karnland, O., and Snellman, M., Impact of corrosion-derived iron on the bentonite buffer within the KBS-3H disposal concept: the Olkiluoto site as case study, SKB Report R-08-34, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.
- Wersin, P., and Snellman, M., Impact of iron on the performance of clay barriers in waste disposal systems: Report on the status of research and development, SKB Report R-08-45, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 2008.
- Wilson, J., Cressey, G., Cressey, B., Cuadros, J., Ragnarsdóttir, K. V., Savage, D., and Shibata, M., The effect of iron on montmorillonite stability. (II) Experimental investigation. *Geochimica et Cosmochimica Acta* 70: 323–336, 2006.
- Yamaguchi, T., Sakamoto, Y., Akai, M., Takazawa, M., Iida, Y., Tanaka, T., and Nakayama, S., Experimental and modeling study on long-term alteration of compacted bentonite with alkaline groundwater. *Physics and Chemistry of the Earth* 32: 298–310, 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.
- Yong, R. N., Mohamed, A. M. O., and Warkentin, B. P., *Principles of Contaminant Transport in Soils*, Elsevier, Amsterdam, 1992.