). Bentonite: A Review of key properties, processes and issues for consideration in the UK context

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Summary

Research and development programmes conducted in the UK and overseas have led to much technical knowledge being accumulated over the last three decades on the properties and factors influencing the performance of bentonite barriers in radioactive waste disposal. However, the factors influencing bentonite performance within the context of the UK programme have received little attention. As a result, the Nuclear Decommissioning Authority (NDA), Radioactive Waste Management Directorate (RWMD) has commissioned this document, which is targeted at reviewing some of the key issues and processes associated with bentonite that are likely to be of greatest importance for the selection of an appropriate disposal concept and the development of the safety case. Topics not considered here have, in general, either been considered in other recent review work for RWMD or are the topics of ongoing work being carried out in parallel with this study. The following themes are included:

- Temperature dependence of bentonite performance;
- Effect of radiation on bentonite performance;
- Effect of bentonite on porewater evolution, and subsequent effects on glass evolution, wasteforms and canister corrosion;
- Effects of groundwater and waste compositions on bentonite stability and swelling;
- Effect of canister corrosion products on bentonite;
- Bentonite erosion and piping;
- The influence of bentonite composition on performance.

The key issues discussed in the review, and their relevance in the UK context, are summarised as a table at the end of the document. The key points that should be taken from this review are that:

- The evolution of bentonite under the conditions expected in a Geological Disposal Facility (GDF) is complex, and the processes affecting it are coupled, perhaps strongly.
- Most aspects of bentonite performance are likely to be specific to both the site (both groundwater flow rate and composition) and the particular bentonite that will be used.

- The use of bentonite imposes constraints on a number of aspects of GDF design, such as maximum allowable temperatures and the choice of other barrier materials.

- Issues associated with the performance of bentonite are of international concern, and, as a result, a great deal of work has been carried out and a significant knowledge base exists, which the UK can draw on.

The profile of any R&D work to understand the controls on the performance of bentonite in the UK programme will depend crucially on the choices of site and disposal concept. The current state of knowledge of bentonite properties and behaviour is sufficient to define the challenges that need to be considered when considering the merits of different disposal concepts in various geological environments. Work to understand how bentonite will perform in a disposal environment is continuing internationally, and as the UK programme develops, there are likely to be UK-specific topics for further research that are additional to the issues being considered by these international projects.

PREFACE

This report has been prepared by Quintessa Limited under contract to the NDA. The report has been reviewed by NDA, but the views expressed and conclusions drawn are those of the authors and do not necessarily represent those of NDA.

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Contents

1 Introduction

In the context of its mission to develop a Geological Disposal Facility (GDF) in the UK for higher activity radioactive wastes, the NDA's Radioactive Waste Management Directorate (RWMD) is currently carrying out generic studies to support the Managing Radioactive Waste Safely (MRWS) site selection process. These studies are intended to ensure that there is a sound and appropriate body of knowledge to underpin the advice that will be provided to Government concerning the identification of a candidate site or sites for further investigation.

Many of the disposal concepts being considered by RWMD for the disposal of High Level Waste (HLW), Spent Fuel (SF), highly enriched uranium (HEU) and plutonium (Pu) include a compacted bentonite buffer or a bentonite-rich backfill (Baldwin et al., 2008). If a disposal concept that uses bentonite is eventually selected, a thorough understanding of the processes that will occur in the bentonite under *in situ* conditions will be needed to support the design of the Geological Disposal Facility (GDF), and the development of a safety case for it. However, RWMD's current need is to understand the controls on the performance of bentonite at a more generic level to underpin site and concept selection, and in particular, to understand whether there are any factors that need to be taken which are specific to the UK programme.

UK-specific factors that might influence bentonite barrier performance and requirements have received relatively limited attention to date (because until relatively recently, the UK was not carrying out R&D to support the disposal of HLW/SF/HEU/Pu). As a result, it is envisaged that future UK R&D programmes are likely to include investigations into buffer properties and stability under hydrogeological and geochemical conditions associated with potentially suitable disposal sites in England and Wales. NDA RWMD has recognised the need to consider the potential evolution of bentonite buffer and backfill materials in a GDF (NDA, 2010) and has commissioned this document prior to the start of significant site-specific R&D and options studies to provide the necessary background information to underpin the generic studies and to guide the development of the R&D programme.

Compacted bentonite has been identified by a number of nations as being an important potential component of engineered barrier system (EBS) design for disposal systems for high level waste (HLW) and spent fuel (SF). It possesses the many favourable physico-chemical properties, including:

- an extremely low permeability (diffusion-dominated contaminant transport);
- a swelling pressure that is sufficiently high to establish and sustain good contact between the bentonite buffer and the host rock and canister;
- smectite ion exchange and amphoteric surface complexation sites for the adsorption of radionuclides and chemotoxic substances (and to contribute to pH buffering); and
- small pore sizes (and reduced water activity) which may suppress microbial activity and colloid migration.

The primary safety function apportioned to bentonite in the EBS depends on the role that it is designated to perform, namely:

- protection of a disposal canister by acting as a buffer to the host rock and remainder of the disposal system. In this role, the primary safety function of the bentonite is to protect and isolate the canister geochemically and physically through high confinement stresses, low free porosities and by being largely impermeable to advective porous medium water transport. Note that in this role bentonite is not expected to act as a significant radionuclide transport barrier, rather its primary role is to maintain the integrity of a disposal canister and retardation of radionuclides released from a failed canister is a secondary function;
- as an engineered seal in the wider disposal system, with the primary safety function being to mitigate fluid migration typically as part of gallery, shaft or adit sealing (including potentially to limit interaction between co-located disposal areas); and
- as a constituent part of bulk tunnel backfill (sand-bentonite mix for example) where the primary safety function is to modify the hydraulic properties of bulk materials to be more suitable for the engineering design. This typically involves reductions in permeability and porosity and as well as creating moderate swelling stresses to create better seals in otherwise non-swelling materials.

Radioactive waste management organisations have carried out extensive research on clay-based buffers and backfills, which have led to much technical knowledge being accumulated over the last three decades. This work is continuing, both as part of national programmes and as part of international projects such as the Äspö Task Force.

1.1 Objectives and Structure

As noted above, a large amount of information on the performance of bentonite under different conditions already exists. The objectives of this document are to build on this existing body of work in order to:

- provide a description of the current status with regard to the key issues and processes that will need to be considered in the UK programme;
- summarise relevant experimental and theoretical data; and
- set the information in the appropriate context for disposal in England / Wales.

The focus of the document is on the use of compacted bentonite as a buffer material in a disposal facility for HLW, SF, HEU and Pu. Many of the processes discussed and conclusions drawn may also be relevant when considering the use of a clay backfill in an ILW disposal concept. However, differences in clay composition and emplacement density and the safety functions assigned to the clay barrier will need to be taken into account, meaning that the conclusions may not be directly transferable.

Section 2 provides some necessary background concerning bentonite mineralogy. As requested by NDA RWMD the review presented in this document focuses on the following aspects of bentonite performance (Sections 2.3 to 10):

- Temperature dependence of bentonite performance (Section 2.3);
- The effect of radiation on bentonite performance (Section 4);
- Effect of bentonite on porewater evolution, and subsequent effects on glass evolution, wasteforms and canister corrosion (Section 5);
- Effects of groundwater and waste compositions on bentonite stability and swelling (Section 6);
- Effect of canister corrosion products on bentonite (Section 7);
- Cement-bentonite interactions (Section 8);
- Bentonite erosion and piping (Section 9); and
- The influence of bentonite composition on performance (Section 10).

Sections 2.3 to 10 comprise the 'current status' review. Section 11 focuses on those issues and processes that appear to be of the greatest importance for the UK programme at the current time. The review does not specifically focus on the potential impact of microbial processes because these have recently been reviewed elsewhere (e.g. Humphreys et al., 2010). Similarly, detailed consideration of the way in which gas might migrate through a buffer constructed from compacted bentonite may be found elsewhere.

The behaviour of bentonite under GDF conditions is an extremely broad subject and the constraints of this review did not allow for a comprehensive treatment of several aspects of bentonite behaviour where UK conditions are unlikely to be 'special'. These areas include the resaturation process and the associated homogenisation (or not) of the buffer with time, which is touched on in Sections 2.3 and 9, and the transport of gas through a bentonite buffer, which is touched on in Section 10.

The profile of any R&D work undertaken in order to understand the controls on the performance of bentonite in the UK programme will depend crucially on the choices of site and disposal concept as these will determine the required safety functions and their relative importance. One of the roles of this report is provide an input into RWMD's assessment of whether the current state of knowledge of bentonite properties and behaviour is sufficient to define the challenges that need to be considered when considering the merits of different disposal concepts in various geological environments. This assessment will be an important input into defining both current research needs while the programme is in a generic phase and future research needs once disposal concepts have been selected and sites are being investigated. As the UK programme develops, there are likely to be both UK-specific topics for further research as well as topics that have a general applicability for understanding the evolution of disposal systems that include bentonite. In the latter case, international projects such as the Äspö Task Force and Forge (Wendling, 2010) are working to improve fundamental understanding of key topics such as bentonite resaturation and transport properties and to understand how to translate the results of laboratory experiments and numerical models to full scale. Research by individual waste management organisations into issues of relevance to their programmes also continues.

Many of the terms used in the report are necessarily technical. Therefore, a glossary of mineralogical terms is provided in Appendix A.

The remainder of this section (Section 1.2) describes typical uses of bentonite in radioactive waste disposal systems.

1.2 The Role of Bentonite in the Geological Disposal of Radioactive Waste

The most common use of bentonite is as a buffer surrounding the waste canister or as a backfilling material (usually mixed with another material). It may also be an important component of low permeability seals. The main functions of a buffer are to:

- ▲ protect the waste canister from the physical and chemical processes occurring in the surrounding rock by:
  - retaining the waste canister in the position in which it was emplaced;
  - protecting the waste canister from external disruptive events such as earthquakes;
  - limiting groundwater flow around the waste canister;
  - conditioning the chemical environment around the waste canister;
  - limiting the transport of potentially harmful chemical (e.g. canister corrodants) and microbial species;
- ▲ limit the rate of transport of radionuclides that are released from the waste canister by:
  - ensuring that flow velocities are sufficiently slow that solute transport is dominated by diffusion; and
  - providing a large surface area for sorption.

The role that the bentonite buffer or backfill plays in providing long-term safety and the reliance placed on its performance in the post-closure safety case depends on a range of factors including:

- ▲ the wasteform and inventory;
- ▲ the overall design concept that underpins the disposal system, which defines the safety functions that must be fulfilled by the bentonite components;
- ▲ the design, material and manufacturing quality of the disposal canister;
- ▲ the properties of the host rock, including permeability, groundwater composition and mechanical properties;
- ▲ wider aspects of the host geological environment including the nature of the overlying strata and the likely response of the geosphere to long-term environmental change.

The following subsections describe three disposal concepts for HLW/SF that include bentonite as a buffer and a backfill material. The safety functions assigned to the bentonite buffer, and consequently the performance requirements specified for the bentonite component vary between disposal concepts, as described below. For a more detailed overview of disposal concepts, the reader is referred to Baldwin et al. (2008).

1.2.1 GDF Example 1: SKB's 'KBS-3' concept

The first example is the Swedish/Finnish KBS-3 design. Figure 1.1 illustrates the KBS-3V concept. A variant design, the KBS-3H concept has also been developed in which the disposal canisters are placed in horizontal tunnels. In the KBS-3 concept, the waste is sealed inside a copper disposal canister, which has a cast iron insert to provide mechanical strength. The disposal canisters are placed in vertical deposition holes and surrounded by a compacted bentonite buffer. The access tunnel is then backfilled with a bentonite or bentonite-based backfill material.

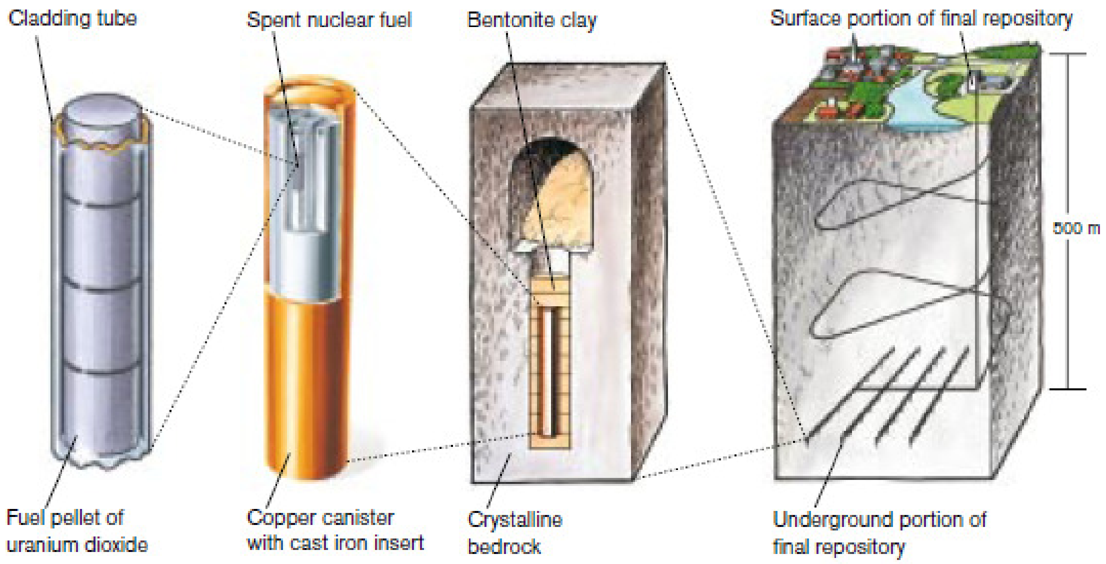


Figure 1.1: KBS-3 concept, with bentonite buffer and copper canisters (SKB, 2006b).

In general terms, the main safety functions of the bentonite buffer are (SKB, 2006b):

- To protect the waste disposal containers by providing physical protection (e.g., against mechanical shearing).
- To provide a hydraulic barrier that limits the transport of water and dissolved corrosive agents to the waste, and retards the transport of radionuclides released from the waste containers in dissolved or colloidal form.

SKB (2006a) suggests that to in order to prevent advective transport, the hydraulic conductivity of the buffer in the Swedish KBS-3 disposal system should be less than 10^{-12} m s^{-1}. Additionally, in order to ensure that the buffer is sufficiently homogeneous, the bentonite should develop a swelling pressure of at least 1 MPa at all locations within the buffer.

The main requirements of bentonite and bentonite-based tunnel backfills are that they:

- provide sufficient confinement, through swelling pressure and/or mechanical strength; and
- ensure the buffer functions properly and have a sufficiently low hydraulic conductivity to ensure that the backfill should not be a preferred pathway for radionuclide transport.

For these requirements to be fulfilled, the backfill should have a certain swelling pressure to assure tightness (swelling pressure > 0.1 MPa) and a limited hydraulic conductivity (< 10^{-10} m s^{-1}).

The hydraulic conductivity of a bentonite barrier (which can be thought of as one measure of its performance) is strongly related to the density of the clay, the identity of smectite interlayer cations (such as Na^+, Ca^{2+}), and to the ionic strength of the surrounding groundwater (SKB 2006a). It is important, therefore, to be able to emplace the bentonite with an appropriate density in order that the desired swelling pressure and hydraulic conductivity are achieved (or fall within the desired ranges). Safety function indicators and criteria that have been proposed for the KBS-3 buffer (SKB 2006a) include a constraint that the emplaced density of the buffer should be greater than 1650 kg m^{-3} (with the aim of filtering any colloids and promoting non-viability of bacteria), but less than 2050 kg m^{-3} in order to protect the canister from rock movements, particularly rock shear.

The KBS-3 concepts are intended to provide complete containment of the inventory within the disposal canister until the radioactivity has decayed to levels similar to those in an ore deposit. The geosphere is relatively less important than the EBS as a barrier and its main role in ensuring long-term safety is to protect the EBS. The copper canister is expected to be extremely durable if it properly protected by the buffer so the bentonite buffer plays a crucial role in ensuring long-term containment. The buffer also retards the transport of radionuclides from the small fraction of canisters that may fail. The performance of the bentonite buffer is therefore key to long-term safety, and its importance is reflected in the amount of work that has been carried out by SKB and Posiva to understand its properties and likely performance. Past work focused largely on MX-80 bentonite but more recent work is exploring the performance of a range of bentonites under a range of conditions.

1.2.2 GDF Example 2: Nagra's 'Opalinus Clay' Concept

In contrast to the crystalline host rock concept adopted by SKB (Section 0), Nagra (2002) describes a disposal facility design for Spent Fuel (SF), vitrified high-level waste (HLW) and long-lived intermediate-level waste (ILW), sited in the Opalinus Clay of the Zürcher Weinland in northern Switzerland (Figure 1.2).

The SF/HLW near field includes wasteforms, steel containers, and a bentonite buffer. The SF wasteform consists of uranium oxide pellets contained in a zirconium alloy (Zircaloy) cladding, along with other structural materials such as steel alloys. HLW is incorporated into borosilicate glass. The SF/HLW waste forms are emplaced in steel canisters, which are surrounded by bentonite. The ILW is embedded within cement or, in some cases, a bitumen solidification matrix in steel drums. Low-permeability seals will be placed between the two disposal areas to isolate the clay-based and cementitous disposal systems from each other.

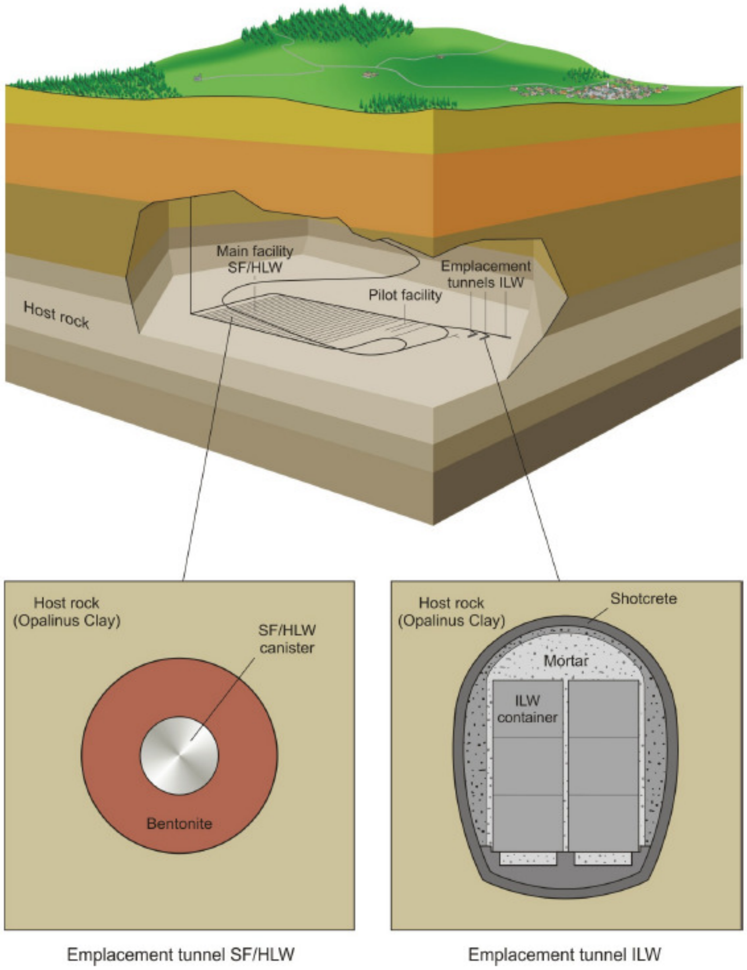


Figure 1.2: Possible layout for a deep geological repository for SF / HLW / ILW in Opalinus Clay (Nagra 2002).

For this concept, Nagra (2002) state that the features of the HLW/SF barrier system that are crucial in providing the safety functions are:

- The deep underground location of the repository, in a setting that is unlikely to attract human intrusion and is not prone to disruptive geological events.
- A low hydraulic conductivity host rock, with a homogeneous pore structure and a self-sealing capacity, thus providing a strong barrier to radionuclide transport and a suitable environment for the engineered barrier system.

- A chemical environment that provides a range of geochemical immobilisation and retardation processes, favours the long-term stability of the engineered barriers, and is itself stable due to a range of chemical buffering reactions.
- The bentonite buffer (for SF and HLW) that ensures that the effects of the presence of the emplacement tunnels and the heat-producing waste on the host rock are minimal, and that provides a strong barrier to radionuclide transport and a suitable environment for the canisters and the waste forms.
- SF and HLW waste forms that are stable in the expected environment.
- SF and HLW canisters that are mechanically strong and corrosion resistant.

Nagra (2002) state that the bentonite buffer in their concept has the following functions:

- Promotes confinement of radionuclides due to long re-saturation time and plasticity (giving rise to self-sealing properties after physical disturbance).
- Promotes attenuation of radionuclide release: transport will be dominated by diffusion, clay minerals may be sorbent and radionuclides should have low solubilities in pore water.

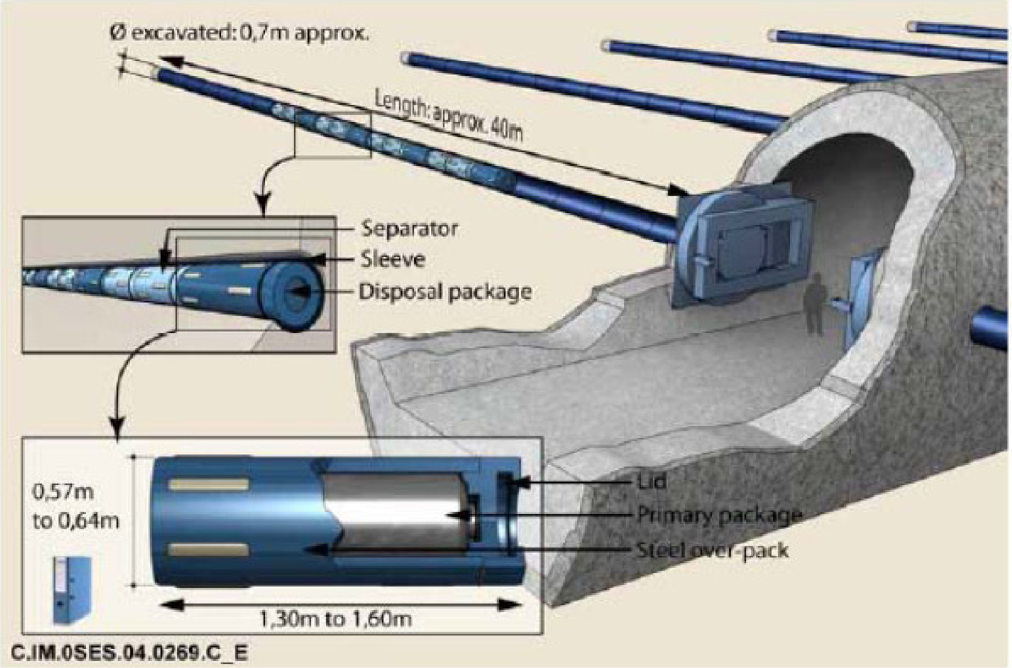
In this concept, the very low permeability host rock and the stable geochemical environment it provides are very important barriers to the release of radionuclides as the EBS. Therefore, while the bentonite buffer is an important component of the disposal system, ultimately it is one of many features that contribute to long-term safety.

1.2.3 GDF Example 3: Andra's Callovo-Oxfordian Clay Concept

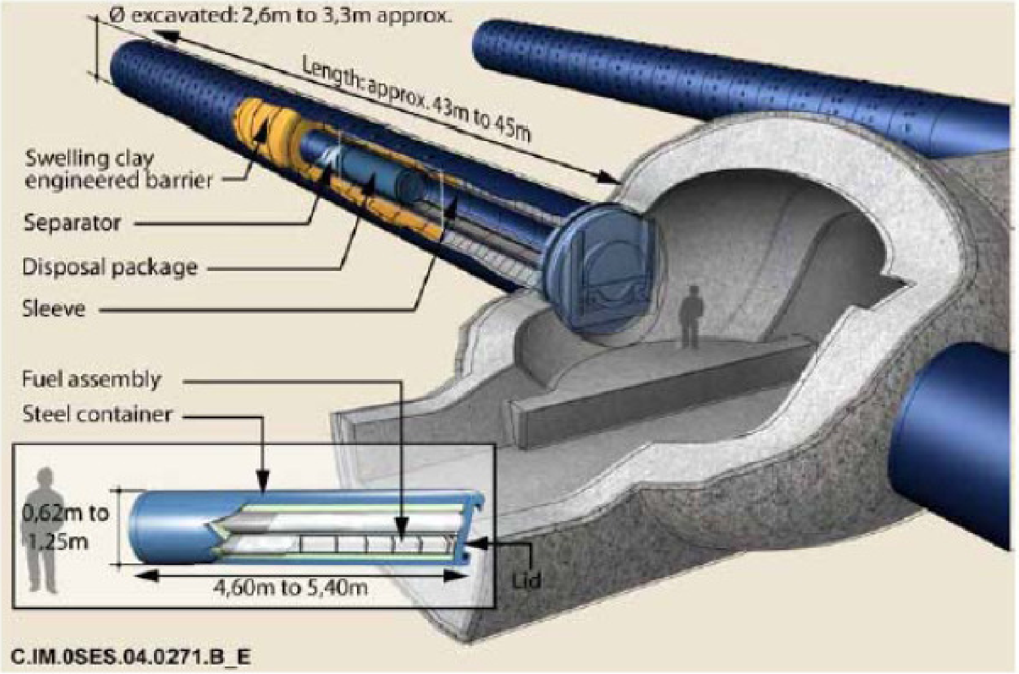
In this concept, HLW and SF are encased in unalloyed steel overpacks. The waste packages are then emplaced in steel-lined horizontal or near-horizontal boreholes, drilled in the walls on both sides of the disposal tunnels (Baldwin et al., 2008). The intended disposal concept is for a clay host rock. The Callovo-Oxfordian clay formation in the in the Meuse/Haute-Marne area of the Parisian Basin, at Bure has been considered as a potential host. HLW/SF, using the concept described below, and ILW/LLW, using a cementitious disposal concept, will be disposed in separate areas of a single facility.

The disposal boreholes have a perforated steel liner to assist with emplacement of the waste. In the SF disposal boreholes, rings of bentonite will be emplaced between this outer liner and a second inner axial unalloyed steel lining, or sleeve (Andra, 2002a-d; Baldwin et al., 2008) (Figure 1.3). The aim of the SF bentonite buffer in this concept is to form a continuous, low-permeability medium around the packages (post saturation) that limits the corrosion rate of the steel overpack and the transport of any dissolved radionuclides (Andra 2005c). Boreholes for the disposal of HLW have a smaller diameter and there is no bentonite buffer.

As in the Nagra concept, the low permeability host rock is a significant barrier to radionuclide release. The bentonite buffer is an important component of the disposal system, but, as demonstrated by the fact that it is not considered to be necessary for HLW, it is not the key barrier.



C (HLW) waste disposal tunnel. *(Images courtesy of Andra, France).*



Spent fuel disposal tunnel. *(Images courtesy of Andra, France).*

Figure 1.3: Illustration of Andra's HLW/SF disposal concept (from Baldwin et al., 2008).

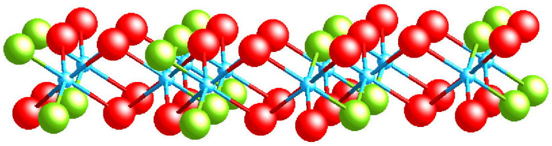
2 Bentonite Mineralogy

2.1 Bentonite Definition

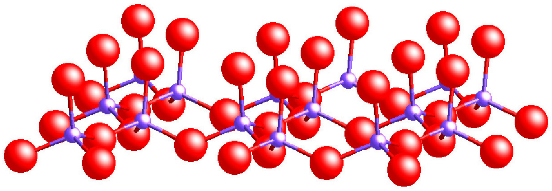
The term 'bentonite' was first applied by Knight (1898) to highly colloidal, plastic clay in Cretaceous beds of Wyoming (Grim, 1968). The term was redefined by Ross and Shannon (1926) as clays produced by the *in-situ* alteration of volcanic ash producing mainly smectite. More recently, the term 'bentonite' has been used to refer to smectite rich material regardless of origin (Grim, 1968). This is the definition that has been widely adopted in the radioactive waste community. The bentonite that is typically specified in EBS designs consists primarily of montmorillonite (a smectite group clay mineral), with interlayer calcium or sodium and minor amounts of quartz, feldspar, kaolinite, carbonates, sulphides, sulphates and organic matter (Apted et al., 1995).

2.2 Smectite Mineralogy

Two atomic structural units can be defined from which most clay minerals (including smectites), are formed (Grim, 1968). The first is an 'octahedral' sheet, consisting of aluminium, iron or magnesium surrounded by oxygen and hydroxyls in an octahedral configuration. The second is a sheet consisting of predominantly silicate tetrahedrons (Grim, 1968, Figure 2.1). Hydrous phyllosilicate minerals are classified on the basis of the nature of the linkages of octahedral to tetrahedral sheets (to give the categories '1:1', '2:1' and 'modulated' layers), with further sub-divisions into groups depending on the charge deficit across the 2:1 layer structure, the occupancy of the octahedral sheet, the nature of the interlayer region and chemical composition (Bailey, 1988). Smectite is a swelling clay mineral that consists of parallel stacks of '2:1' layers (Figure 2.2). Minerals from the mica and chlorite groups along with those from the talc-pyrophyllite group also have atomic structures based on 2:1 layers (Bailey 1984; Bailey 1988). Idealised and measured half-unit cell formulas of 2:1 minerals are written to include cations per $O_{10}(OH)_2$.



octahedral sheet fragment from a 1Tc pyrophyllite structure



tetrahedral sheet fragment from a 1Tc pyrophyllite structure

Figure 2.1: Structural units of clay minerals. Sheet fragments are shown which were extracted from a single layer triclinic (1Tc) pyrophyllite using CrystalMaker (atomic coordinates from Lee and Guggenheim, 1981). Silicon atoms are shown in dark blue, aluminium atoms in light blue, oxygen atoms in red and hydroxyls in green (from Wilson, 2003).

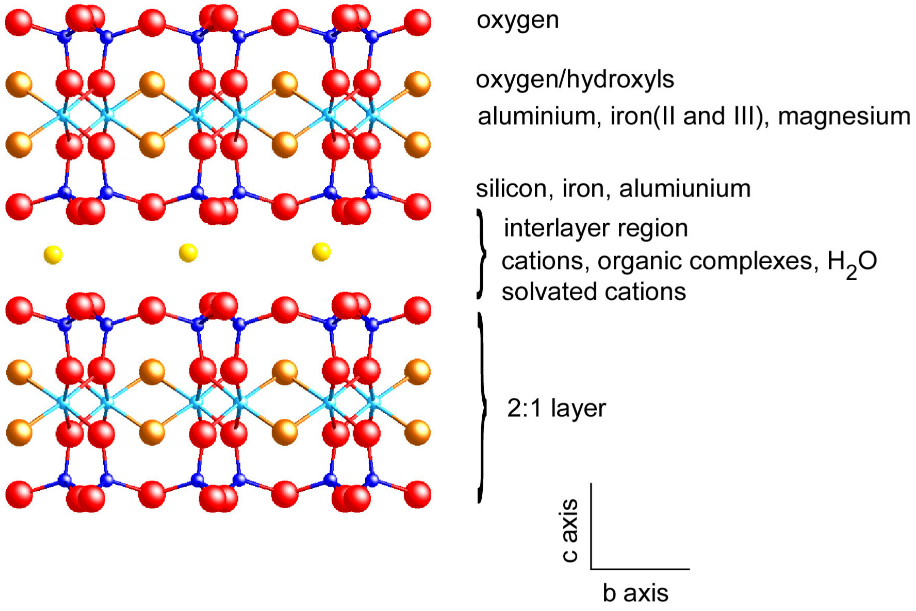


Figure 2.2: Simplified atomic model of an idealised C2/m smectite structure (based on cystallographic data from Tsirpursky and Drits, 1984). Two parallel 2:1 layers are shown with vacant trans-octahedra (in reality, the stacking is irregular). Aluminium (light blue) is present in the octahedral sheet; magnesium and iron are also commonly found (from Wilson, 2003).

The cations in octahedral co-ordination are generally magnesium, iron (II)/(III), and aluminium, although other medium-sized cations such as Li, Cr, and Zn may also be found (Bailey, 1980). The smallest structural unit of the octahedral sheet of non-modulated clay minerals (including smectite) contains three octahedra (Bailey, 1988). If all three octahedra are occupied, the sheet is classified as being trioctahedral, if only two of the possible three are occupied, it is classified as dioctahedral (Bailey, 1980). However, most natural clay mineral samples do not contain exactly 3.0 or 2.0 octahedral cations per formula unit (Bailey, 1988).

The 2:1 layers in smectite may be stacked in a 'turbostratic' orientation (Güven. 1988). Some smectite minerals may exhibit stacking which is more regular in nature with zero degree rotations between the successive layers or 'semi-random' stacking with random n x 60° rotations (Méring, 1975). Smectite is often associated with mixed-layer clays, where there are alternating stacks of unit cells of the different end-member layer silicates (Środoń, 1999). Mixed-layer phases are seen at the Earth's surface and under low-grade metamorphic and hydrothermal conditions.

The dioctahedral aluminous smectites typically present in bentonite are represented by the montmorillonite-beidellite series according to the structural formula (Güven, 1988):

$$(Al_{2-y}Mg_y^{2+})\ (Si_{4-x}Al_x)O_{10}(OH)_2\ E^+_{x+y} \cdot n\ H_2O$$

where E^+ represents the interlayer cation, x and y are the octahedral and tetrahedral substitutions respectively. The smectites with $y > x$ are referred to as montmorillonite, and those with $y < x$ are referred to as beidellite.

Typical aluminous smectite compositions associated with bentonite are given in Table 2.1. Examples of various bentonites (and their accessory mineral contents) considered either as EBS candidate materials or for research purposes by radioactive waste management agencies are given in Table 2.2.

Table 2.1: Typical smectite (montmorillonite) compositions included in envisaged HLW-EBS designs. The half unit cell formulae include (from left to right), interlayer cations, octahedral sheet cations and tetrahedral sheet cations.

Mineral	Half Unit Cell Formula [i.e. per $O_{10}(OH)_2\ n\ H_2O$]	Reference
Kunipia-F	$(Na_{0.48}Ca_{0.03}K_{0.01}\ Mg_{0.002})\ (Al_{1.54}Mg_{0.33}Fe^{3+}_{0.09}\ Fe^{2+}_{0.02})\ (Si_{3.87}Al_{0.13})$	Wilson et al. (2004)
MX-80	$(Na_{0.3})\ (Al_{1.55}Mg_{0.24}Fe^{3+}_{0.\ 20}Fe^{2+}_{0.01})\ (Si_{3.96}Al_{0.04})$	Madsen (1998)
Montigel	$Ca,Mg_{0.28}(Al_{1.36}Mg_{0.35}Fe^{3+}_{0.31}Fe^{2+}_{0.01})\ (Si_{4.00})$	Madsen (1998)

Table 2.2: Mineral compositions (wt.%) of various types of potential clay barrier materials (from Hicks et al., 2009).

	MX-80	Avonseal	Kunigel VI	Kunipia F	Montigel	Kyungju	Deponit CA-N	Deponit CA-N	FEBEX	S-2	Friedland
Montmorillonite	87	79	46-49	98-99	66	69.5	81	81.4	89-95*	88-96*	30
Quartz / Chalcedony	3	5	29-38	<1	8.3	1.4	1	0.4	1-3	1-3	20.2
Cristobalite	2					6.9	1	0.6	1-3	1-3	0.1
Feldspar	3	1.5	2.7-5.5		2-4	22.2	2	0.5	1-3	2-5	1.1
Calcite / Siderite			2.1-2.6	<1			10	5.6	0.6	0-2	0.5
Dolomite			2.0-2.8				3	1.3			
Analcite			3.0-3.5								
Pyrite	0.25		0.5-0.7				0.5	1.1	0.02		1.2
Mica	4				12-15			1.4			7.2
Illite	1[6]	9.5			2			4.6			26
Gypsum	0.7	2			1.8			0.4	0.14		0.7
Rutile / Anatase	0.2[6]							0.4			0.6
Organic Matter	0.2	0.3	0.31-0.34		0.03		0.2		~0.3		
Other					2-3				0.8		10.7 (Kaolin)

2.3 Smectite-water Interactions

The smectite component of bentonite gives it the capacity to swell. As reviewed by Savage (2005), there are two fundamental swelling processes: innercrystalline swelling (caused by the hydration of interlayer cations between 2:1 layers); and osmotic swelling, that results from gradients in ion concentrations between clay surfaces and porewater.

Innercrystalline swelling occurs due to the charge deficit across smectite 2:1 layers which is neutralised by the inclusion of an 'interlayer' system that may include exchangeable cations, hydrated cations and organic molecules (Bailey, 1980). The total layer charge in smectites generally ranges from ~0.2 to 0.6 units per $O_{10}(OH)_2$ (Güven. 1988). The incorporation of different hydrated cations and water molecules around the 2:1 layers of smectite enable the mineral to possess variable *d*(001) values that vary as a function of relative humidity, generally in a step-wise fashion (MacEwan and Wilson 1980; Wilson et al., 2004 *inter alia*).

3 Temperature Dependence of Bentonite Performance

3.1 Introduction

The use of bentonite as a buffer surrounding the disposal container in many of the HLW/SF disposal concepts means there is a natural focus on the impact of transient heat fluxes on the bentonite itself and on dependent processes in the context of bentonite safety functions. This section will provide an overview of the critical thermal properties of bentonite, followed by an assessment of the impact of heat directly on bentonite performance during the heating and initial resaturation phase. There is then a brief summary of the issues associated with the process understanding for water resaturation in bentonite in general and the longer-term impacts of thermal load on bentonite are then discussed. This overview is concluded by a summary of thermal limits that have been applied to bentonite as a buffer material in a range of radioactive waste disposal concepts.

3.2 Thermal Properties of Bentonite

The thermal properties of most interest are the bulk heat capacity, bulk thermal conductivity, and under radiative conditions (such as one could obtain with a gap between buffer and canister and buffer and host rock), the emissivity.

Bentonite is usually treated as a porous medium, and as such, thermal properties are heavily influenced by the properties of the fluid occupying what can be considered void-space. In order to calculate the bulk heat capacity and thermal conductivity in most porous media, this would simply involve treating the body as a simple mixture of the rock grains, water, and water vapour, and hence performing a mass or volume (as appropriate) averaging between the experimentally derived values of these properties for each of the known end member properties. The presence of water has a very large effect on the bulk thermal conductivity because fully saturated bentonite is approximately 1/3 water by mass. However, the strong interaction between water and bentonite, particularly the uptake of water into bentonite interlayers, means that bentonite tends to deviate from this simple mixing line, especially with regards to thermal conductivity.

Hicks et al. (2009) give a range of experimental data for thermal conductivity for bentonite. The function below summarises the results of Borgesson et al. (1994) (Figure 3.1).

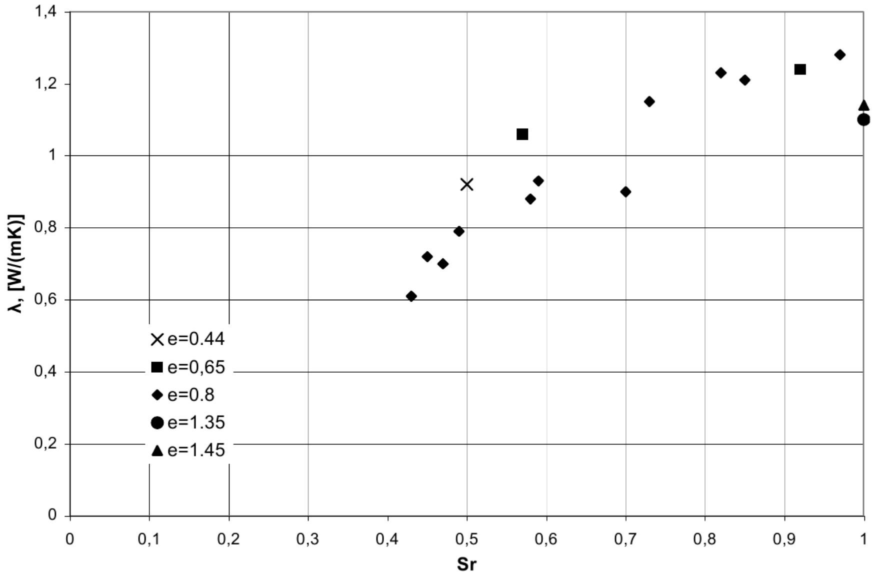


Figure 3.1: Thermal conductivity of bentonite with water saturation (Sr) for different void ratios (Borgesson et al. 1994, from Hicks et al., 2009).

$$c = \frac{A1 - A2}{(1 + e^{(S_w - x_0)/dx})} + A2 \qquad 3.1$$

where c is the thermal conductivity (W m^{-1} K^{-1}), S_w is water saturation (-), $A1$ = 0.6 (W m^{-1} K^{-1}), $A2$ = 1.28 (W m^{-1} K^{-1}), x_0 = 0.65 and dx = 0.1.

According to SKB (2006b), the specific heat capacity can be estimated using a simple mass weighting. Table 3.1 gives representative values of the specific het capacity for the various components (note that air is typically neglected as it has a comparably negligible heat capacity).

Table 3.1: Representative values for specific heat capacity in estimating bulk specific heat capacity for partially water-saturated bentonite.

Material	Value (J/kg/K)
Water	4183
Water Vapour	1850
Bentonite	800

The emissivity of a body is the measure of the degree to which a body behaves as a true black body. SKB (2006b) use a value of 0.88, which is typical for a dark, rough natural material.

3.3 Physical and Chemical Processes Associated with Short-term Re-saturation.

The typical assumption applied to bentonite re-saturation, is that ground water will be available in the host rock, and due to the high chemical suctions for water in partially saturated bentonite (SKB, 2006b), water will tend to be drawn in from the surrounding host rock into the bentonite. Clearly, the rate at which re-saturation can occur will be heavily controlled by the intrinsic permeability and water saturation state of the surrounding host rock. Typical estimates using standard multi-phase flow process models estimate complete re-saturation times of the order of 3-4 years in a permeable, fully saturated host rock (Rutqvist and Tsang, 2008).

The application of a thermal load on the inner (and nominally 'dry') side of a bentonite buffer has a significant impact in terms of accelerating the generation and diffusion of water vapour. In partially saturated porous media, the degree to which water vapour is present in the pores is usually described using Kelvin's Law (Claesson and Sällfors, 2005) and the suction pressure of the water phase, which, in turn, allows a vapour density in the gas phase to be calculated. This function is strongly dependent on the ambient temperature, such that high buffer temperatures will cause the generation of significant quantities of water vapour. The migration of this water vapour in bentonite can be described by a diffusion model utilising the vapour density as the driving potential (Claesson and Sällfors, 2005). Diffusivities for water vapour in bentonite are typically quite large (in the order of 5 10^{-6} m^2 s^{-1}) and orders of magnitude higher than equivalent hydraulic diffusivities for migration of liquid water under fluid pressure differentials. The water vapour flux in kg s^{-1} can be calculated as:

$$g_{vap} = -AD_v(S)\nabla\rho_v . \qquad 3.2$$

where A is the area (m^2), D_v is the vapour diffusion coefficient (m^2 s^{-1}) and ρ_v is the vapour density (kg m^{-3}). The diffusion coefficient is related to the unsaturated value, $D_v(0)$, by a scaling based on the water saturation, S_w:

$$D_v(S) = D_v(0)(1 - S_w) . \qquad 3.3$$

The water vapour density is given by

$$\rho_v = h\,\rho_{vS}\,. \tag{3.4}$$

where ρ_{vS} is the saturated water vapour density (kg m^{-3}) and h (-) is the relative humidity.

The saturated water vapour density, ρ_{vS}, is given by the empirical formula:

$$\rho_{vS} = 10^{-3}\exp\left(19.891 - \frac{4975.9K}{T}\right). \tag{3.5}$$

The relative humidity is defined using the following relationship (Engel et al. 2003):

$$h = \exp\left(\frac{-\Psi M_{vapour}}{\rho_w RT}\right). \tag{3.6}$$

where Ψ is the suction pressure, M_{vapour} is the molar mass of vapour, ρ_w is the water density, R is the gas constant and T is the water temperature (K).

It should be noted that because the water vapour migration is implicitly related to the water suction and both vapour and liquid water are driven in proportion to the suction pressure, under isothermal conditions only is it possible to combine these two processes into a single water migration function. It is also the case that as the temperature rises towards 100 °C, this formulation becomes considerably less reliable, and constraining experimental data become scarcer.

The net result, therefore, is to mobilise water vapour at the canister boundary and drive water away from the canister (Figure 3.2). Moving away from the heat source, some of this vapour will return to a liquid state and tend to migrate back towards the low-water saturation, high-suction inner surface, creating a local water circulation pattern. Given a sufficiently low water ingress rate from the host rock, large scale desaturation of the bentonite buffer is possible with the consequent potential for the desiccation of the inner volume of the bentonite. The loss of water from the inner volume has the secondary effect of reducing thermal conductivity and specific heat capacity of the desaturated bentonite, which in turn, will tend to cause the bentonite to heat further.

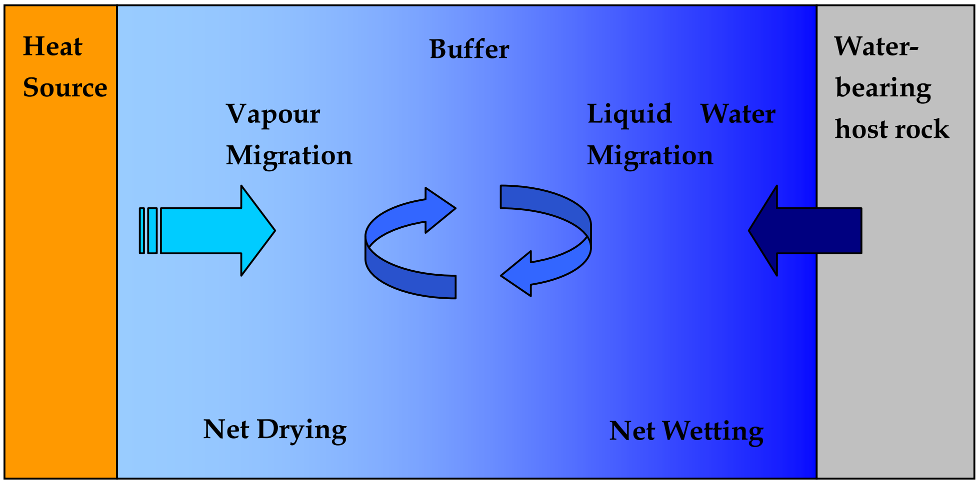


Figure 3.2: Schematic illustration of the drying and resaturation process of a clay buffer between a heat generating canister and the host rock.

The expectation for normal evolution of a bentonite buffer in a permeable host rock would therefore be some initial drying of the inner portion of the buffer at early times, driving water towards the outer annulus of the bentonite. This drying would eventually be overwhelmed by water ingress from the host rock saturating the outer portion of the bentonite and the expected reduction in heat power output from the canister, reducing the potential for heat induced water vapour migration (SKB 2006b). However, if the availability of water from the host rock is low, or the heat source is relatively large, then it is possible to dry large sections of the bentonite, and induce relatively high temperatures in the inner annulus. Intense desiccation causing microstructural collapse can occur in the warmest part, leading to contraction of the stacks of ordered smectite lamellae, so that spontaneous expansion may be only partial when water finally enters. The affected part of the buffer may permanently lose some of its expandability and self-healing capacity and be fine-fissured. Hence maintaining largely de-saturated portions of bentonite has a potentially serious impact on the swelling pressure that the buffer can maintain, with consequent second-order impacts on buffer safety functions, including the limitation of microbial activity and maintaining the mechanical stability of the canister.

In addition, these physical fluid processes will also tend to lead to an accumulation of solid chloride and sulphate salts near the hot canister surface (Figure 3.3), whilst driving away dissolved silica, so that canister corrosion may be encouraged, and variation in clay density in a radial direction may be incurred.

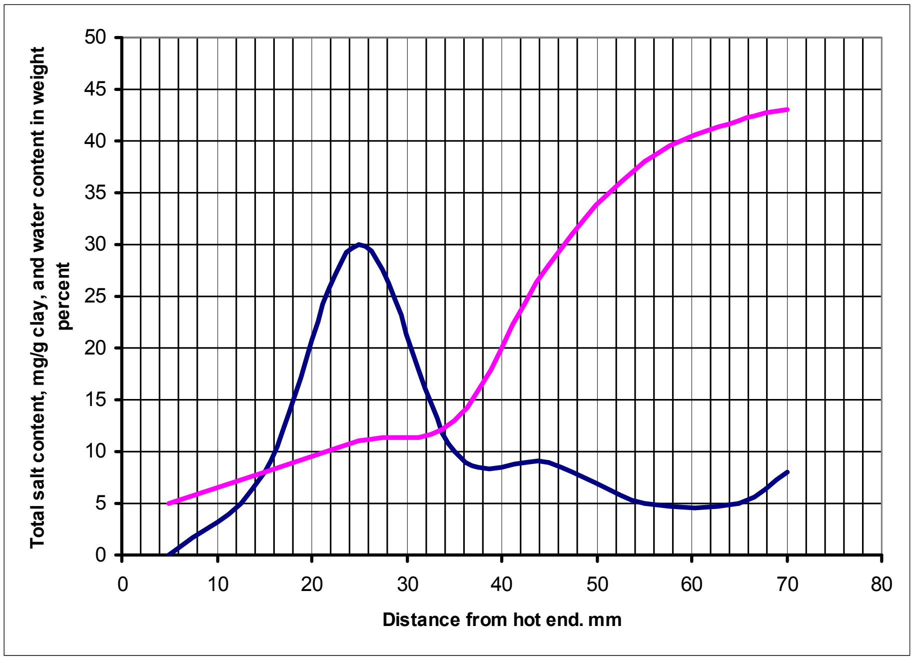


Figure 3.3: Wetting of the clay from the cold end (steadily rising curve) and accumulation of salt at the wetting front (curve with peak) in a laboratory experiment (Pusch, 2008).

If heating is sufficient, the build-up of steam can also have a direct impact on the bentonite. Experiments reported by Couture (1985) showed that the reaction of Na bentonite with liquid water at temperatures ranging between 100 and 200 °C causes limited loss in swelling capacity, reaction with water vapour at 150 to 250 °C (i.e. steam) results in rapid irreversible loss of most of the expandability. Later experiments have confirmed Couture's test results and indicate that the reason for the obvious deterioration of the buffer is precipitation of cementing siliceous material such as quartz and cristobalite (Pusch and Yong, 2006).

These thermal interactions close to the canister mean that it is often beneficial for a small portion of the bentonite immediately adjacent to the canister to be considered 'sacrificial' in the sense that physical and chemical changes caused by the presence of steam and high temperatures do not compromise the broader safety functions. Clearly the size of such a zone needs to be the subject of careful investigation (c.f. Hicks et. al. 2009), and it may be the case that any desiccation or cracking of bentonite adjacent to the canister may be intolerable simply because the prevention of significant microbial colonies adjacent to the canister becomes impossible.

3.4 Issues Associated with Water Resaturation in Bentonite.

As discussed above, the thermal pulse arising from emplacement of HLW/SF can potentially have a negative impact on the rapid resaturation of the buffer. For the KBS-3V concept rapid re-saturation is assumed as part of the anticipated engineering performance (SKB, 2006b), although for low permeability host rocks this cannot and should not be assumed. Given a sufficiently homogenous source of groundwater, such rapid resaturation behaviour has been observed under laboratory conditions. However, the response under field conditions has been much less convincing. The most recent and, arguably, best-instrumented example of this is the Canister Retrieval Test (CRT) conducted at the Aspö underground facility in Sweden (see Figure 3.4). In this case, a full canister disposal was simulated using an analogue canister containing heating elements to replicate the thermal effects of the waste. Water was supplied homogenously to the outer edge of the buffer, between the clay and the host rock to represent conditions expected during the resaturation period.

The thermal and water pressure conditions were varied over a five-year period to represent the expected evolution of the broader system. With regard to the re-saturation of the bentonite buffer by water, two key observations were made. Firstly, the rate at which water entered the buffer was not consistent with the expectations of the high suctions present in the buffer (and hence a consistent high driving force of water into the clay even as re-saturation progressed). Instead, following an initial re-saturation period of just over a year, the rate of water ingress dropped to zero until the water pressure was raised. Similarly, at the end of the experiment when the applied water pressure was reduced to atmospheric at the top of the cylinder, water ingress effectively ceased (see Figure 3.5). From this result, it was apparent that some form of hydraulic self-sealing was occurring once a confining stress had been developed. This observation was borne out by the sampled water contents of the buffer measured at various points, which showed high water saturations around the outer annulus, which then dropped rapidly back to just above initial conditions towards the centre of the bentonite above the canister. Such behaviour is not consistent with the porous medium process models typically used to model bentonite where complete re-saturation times of less than five years are often predicted (Bond et al., 2009).

This is not an isolated result at the field-scale, as a similar lack of complete re-saturation, despite plentiful water being available, has been observed for the FEBEX (Villar and Lloert, 2007) and AECL experiments (Dixon et al, 2005). Clearly, this could have impacts on the successful use of bentonite as a buffer, with the heating of the buffer potentially making such limited re-saturation even more prevalent.

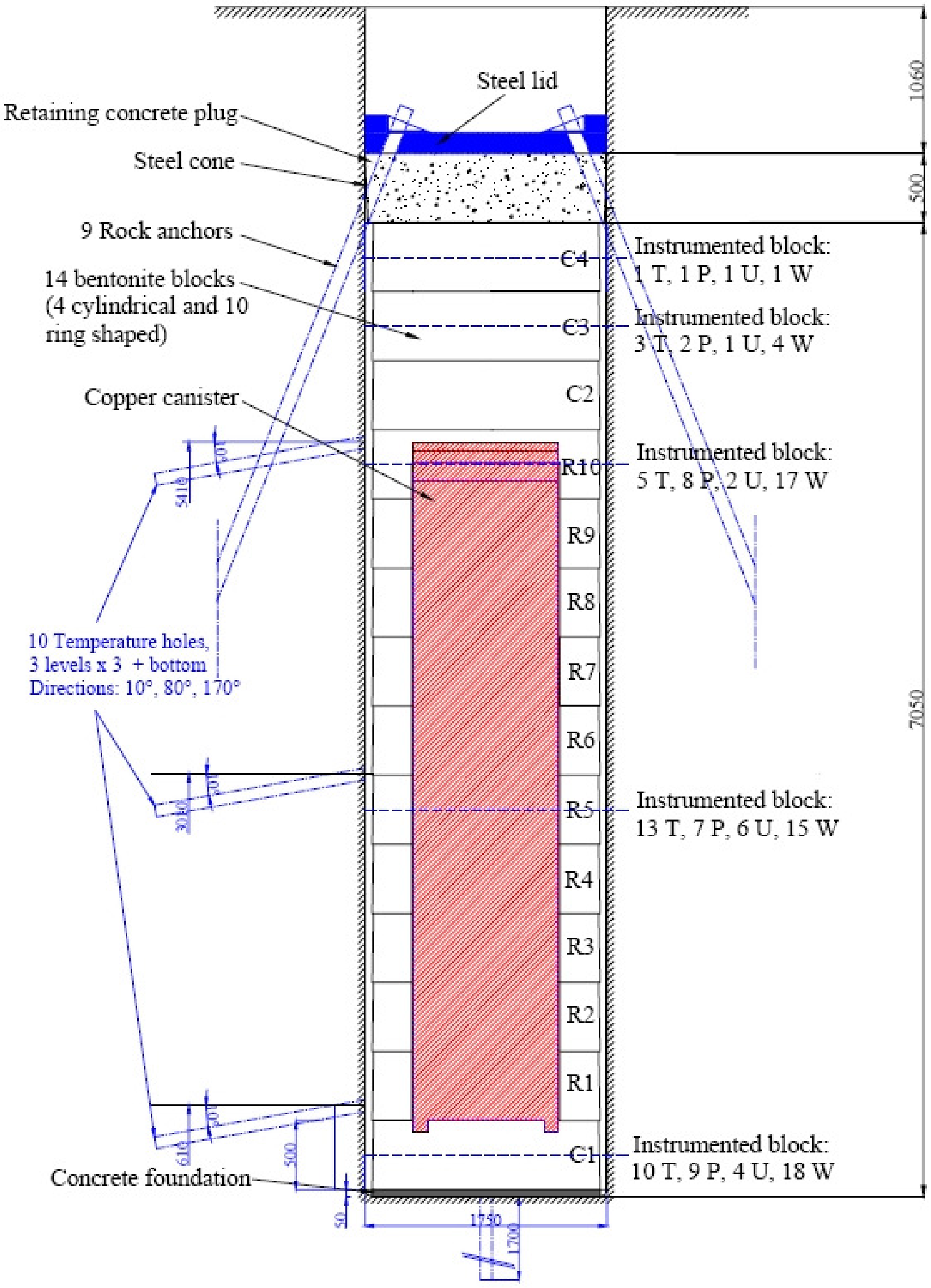


Figure 3.4: Canister Retrieval Test (CRT) Experimental Layout with Sensor Locations (from THERESA, 2008).

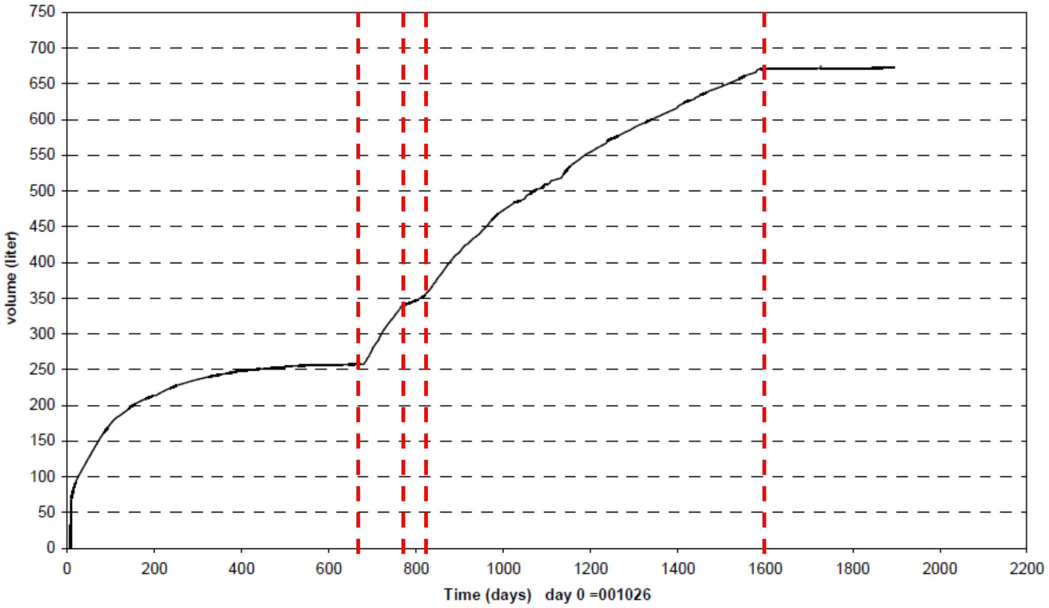


Figure 3.5: Water inflow rates to the CRT as a function of time. Major applied water pressure changes are marked with vertical red lines (from Bond et. al., 2009).

3.5 Long-term Chemical Behaviour of Bentonite

3.5.1 Natural Analogues

The long-term effects of high temperatures on bentonite (ignoring interactions with other materials such as steel and cement) may be assessed through natural analogues. The most thoroughly examined is the Ordovician 'Kinnekulle bentonite' that has a pressure/heat history similar to that envisaged for the proposed Swedish SF repository (Pusch and Madsen, 1995). The 400+ million years old bentonite beds were part of a sedimentary series formed in a marine environment and subsequently loaded by 2 km of Devonian sediments. Magma intruded parallel to the bedding planes about 90 m above the bentonite beds in Permian time. Numerical back-calculation of the temperature evolution and identification of temperature-sensitive conodont fossils have shown that the bentonite beds were thereby heated to 120-140 °C in the first 500 years after the magma intrusion, followed by a successive drop to about 90 °C after 1000 years. The average thermal gradient across the bed was 0.02 °C cm^{-1} in the first hundreds of years, which is only about one hundredth of that in deposition holes. The present content of montmorillonite in expandable form (mixed-layer smectite/illite) in the major bentonite bed is about 25 %, while illite makes up about 50 %. The rest was chlorite/kaolinite, carbonates, quartz, and feldspars.

An essential observation is that the bentonites are silicified and samples do not disintegrate spontaneously when submerged in water but do so only by ultrasonic treatment (Mueller VonMoos, 1990).

3.5.2 Experimental Evidence of the Chemical Evolution of Buffer

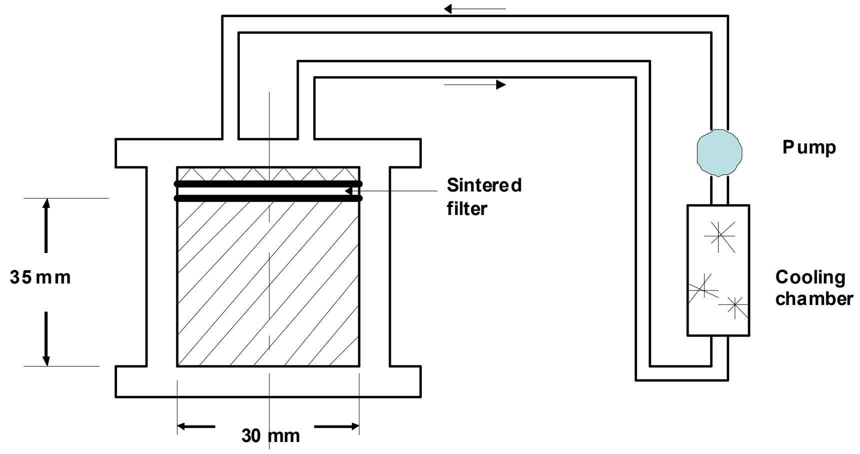
Full-scale hydrothermal tests using natural bentonite clay as the follow-up of numerous laboratory and half-scale scale experiments have contributed to the understanding of the thermally driven chemical processes and mineralogical changes. The CRT experiment provided the following chemical results (Pusch and Yong, 2006):

- The clay next to the canister surface with 90 °C temperature had undergone substitution of Al by Fe(III) in the octahedral layer, causing higher lattice stresses because of the larger ion radius of Fe(III) than of Al, thereby reducing the resistance to dissolution of the montmorillonite.

- Montmorillonite was the dominant mineral phase in both initial and final clays, but mineralogical changes induced by the hydrothermal conditions resulted in changes in smectite layer frequency, hence indicating dissolution/neoformation.

- The lower interlayer charge of the most altered clay means, according to classical double layer theory, that it should have a higher swelling pressure than the original, which was verified by measurements.

A further investigation of thermal behaviour of MX-80 is provided by a series of laboratory hydrothermal experiments using a test set-up shown in Figure 3.6 (Pusch, 2008). The temperature gradient of slightly less than 15 °C cm^{-1} clay was maintained throughout the saturation period, which lasted for about 3 weeks, after which the cells were kept at room temperature for 8 weeks. A 3.5 wt.% $CaCl_2$ solution was continuously percolated through the filter at the cold end. XRD analysis of specimens cut from the clay sample at the termination of the experiment showed that part of the montmorillonite component had collapsed in the hot region to 10Å spacing, while that in the colder parts remained in its original form. There was a weak tendency of the silica concentration to have increased in the central and colder parts, which was concluded to have emanated primarily from dissolution, causing precipitation of silica. Copper had dissolved and entered the clay to a significant extent in the hot part. The concentration gradient indicates that the migration was diffusive and curve fitting gave an approximate diffusion coefficient of 10^{-12} m^2 s^{-1}.



Cell with bottom part of copper metal and the other parts of acid-proof stainless steel. The copper was kept at 95°C throughout the test

Figure 3.6: Schematic of hydrothermal experimental apparatus (Pusch, 2008).

After the hydrothermal treatment, the samples were extruded into oedometers for determination of swelling pressure and hydraulic conductivity. Compared to unaltered MX-80, the swelling pressure had decreased to a small fraction and the hydraulic conductivity increased by 100 times in the hot part, while the central and cold parts retained their expandability. However, their hydraulic conductivity had also increased significantly. While all these experiments indicated only limited mineralogical changes, the rheological properties of the warmer part of the buffer were significantly changed. This was observed by shear testing of samples extracted after termination of hydrothermal tests in the laboratory as demonstrated by Figure 3.7, which shows that heating to 130 °C for one year gave a shear strain that was only about one third of that of a sample heated to 90 °C (Pusch et al, 1993a). The reason for the stiffening is believed to be the same as in the Kinnekulle case, i.e. precipitation of silica that acts as a cementing agent.

The nature of the silica precipitates is illustrated by the STEM micrograph in Figure 3.8 of almost pure montmorillonite (SWY-1) autoclaved in distilled water at 150 °C and 20 MPa pressure. The practical importance of silicification is obvious, the clay stiffens and shear displacement along fractures in the rock across deposition holes will be transferred to the canisters and generate high shear stresses in them (Figure 3.9).

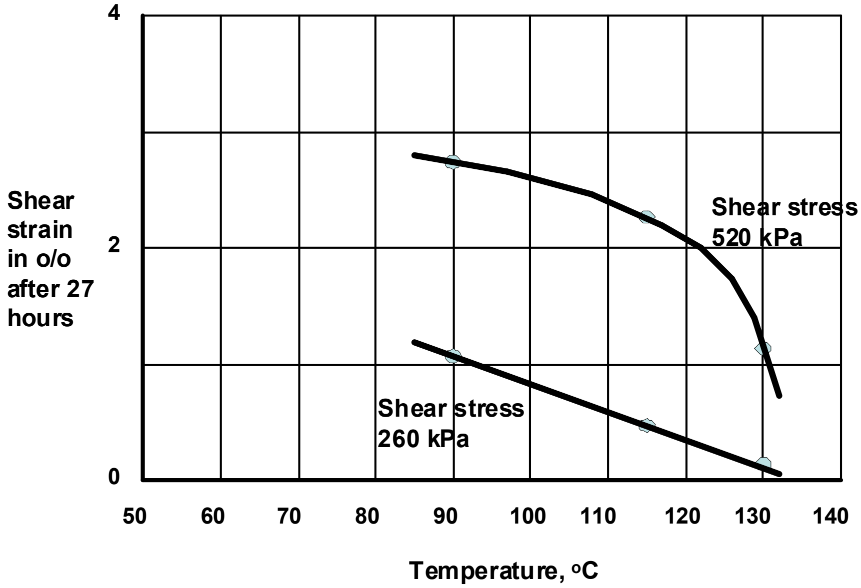


Figure 3.7: Shear box testing of MX-80 clay from hydrothermal experiment (normal stress 6 MPa). The accumulated strain was 2E-4 to 27E-4 in 27 hours (Pusch, 2008).

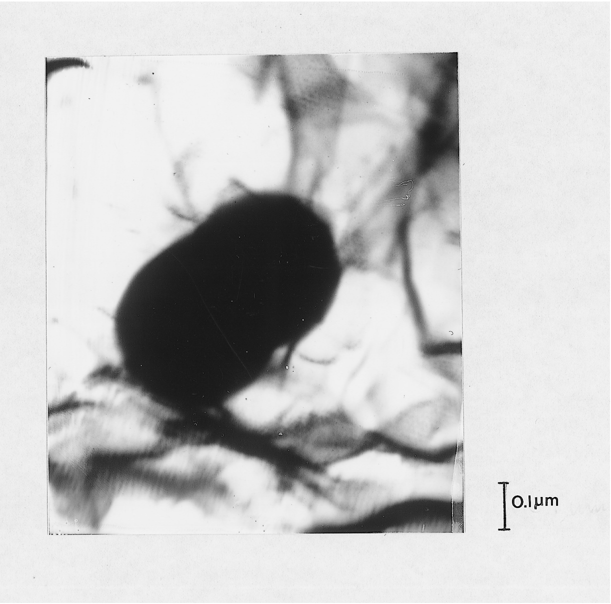


Figure 3.8: Electron micrograph of an example silica nodule in smectite clay (MX-80) autoclaved at 150 °C for 3 months.

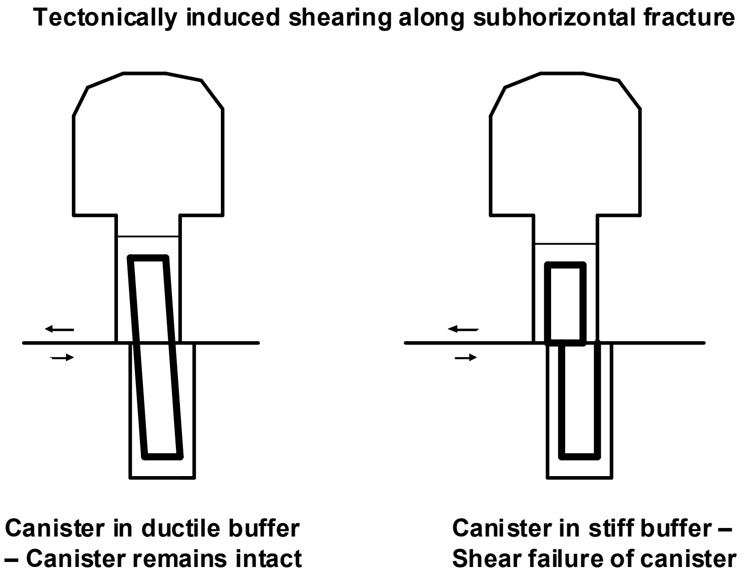


Figure 3.9: Importance of ductile performance of the buffer.

3.6 Implied thermal constraints on bentonite

Hicks et al. (2009) provide a comprehensive summary of the different thermal constraints applied by different waste management organisations and the reasoning behind those thermal constraints. For those organisations considering a bentonite buffer, the temperature constraints are tabulated in Table 3.2.

Table 3.2: Limiting temperatures for bentonite buffers and the justification for the limitation for different world-wide waste management organisations. Information taken from Hicks et al. (2009).

Organisation	**Limiting Temperature**	**Justification**
Canada (AECL)	100 °C	Limitation of chemical alteration of smectite to illite in the bentonite buffer. Limitation on corrosion of the titanium container.
Finland (Posiva)	100 °C	Prevent boiling of groundwater and excessive water vapour generation in the buffer and limit solute deposition at the canister surface with consequent potential for corrosion of the canister. Limit chemical alteration of the bentonite to less favourable physical properties.
France (ANDRA)	50 °C * (80 °C – 90 °C maximum given various uncertainties)	Limit mineralogical alteration of the bentonite and argillaceous host rock to less favourable physical and chemical properties.
Korea	100 °C	Limit chemical alteration of the bentonite Limit deposition of corrosion enhancing solutes at the canister surface.
Japan (JNC)	100 °C	Limit chemical alteration of the bentonite (transformation of smectite to illite)
Sweden (SKB)	100 °C	To avoid the need to include boiling water in the thermal modelling of the waste packages. To avoid excessive drying of the bentonite. To limit the corrosion rate of the copper canister. Limit deposition of corrosion enhancing solutes at the canister surface. Limit illitisation of the bentonite.
Switzerland (Nagra)	No temperature limit specified	Any limit is implicitly included in the requirements on other properties such as swelling pressure.

* It is not clear whether this is the average temperature within the buffer or the temperature at the buffer/inner liner interface.

3.7 Key Points

- Thermal effects can add further complication to an already complex set of coupled processes associated with the re-saturation of bentonite, which is usually required in order for the bentonite to perform as required by the safety case.
- The impact of temperature-induced precipitation of cementing agents (silica, sulphates, carbonates and iron precipitates) on the stress/strain properties of clay buffers may be significant. This matter is of fundamental importance particularly if buffer temperatures higher than 100 °C (or the boiling point of water at *in situ* pressures) are considered. Steam may also result in deleterious effects on bentonite properties (the 'Couture' effect).
- The impact of temperature gradients on the accumulation and dissolution of salts in the vicinity of canisters embedded in clay buffer needs to be assessed through experiments and modelling. This matter and the role of different clay minerals in the buffer are of vital importance for prediction of corrosion of canisters irrespective of the type of canister metal, especially if the groundwater has a high salinity.
- Assessment of clay materials with respect to coupled THMCB (T)hermal/(H)ydraulic/(M)echanical/(C)hemical/(B)iological behaviour, including gas conductivity and ion diffusivity needs to be made in order to obtain a basis for optimal selection of one specific candidate material. These matters may jeopardize the long-term isolating function of clay buffers.
- Field-based experiments of buffer re-saturation suggest that the re-saturation process may be self-limiting, and in some cases may never achieve completion. The low hydraulic conductivity of those parts of the buffer that have already re-saturated and the associated reduction in the driving forces for re-saturation in the outer part of the buffer causes the re-saturation process to stall. The presence of a disposal canister with elevated temperatures at its surface and associated thermal processes may further contribute to this effect.

4 Effect of Radiation on Bentonite Performance

4.1 Introduction

The impact of radiation on the buffer has been considered in the design and performance assessment (PA) of clay buffers since the formulation of the first design concept. Two major effects are considered: (1) radiolysis of porewater in the buffer and; (2) breakdown of the molecular structure of clay minerals.

4.2 Radiolysis

Radiolysis of porewater produces H-bearing radicals and oxygen compounds (including ozone and hydrogen peroxide). Radiolysis products may take part in chemical reactions affecting pH and oxidising canister metals. Oxygen compounds (in gaseous form) may occupy wider voids and can delay or inhibit water saturation and contribute to the heat-induced desiccation of the buffer adjacent to the hot canisters. This is expected to have a particularly deleterious impact on the buffer in very tight repository host media, such as argillaceous rock and very fracture-poor crystalline rock. Relatively little attention seems to have been given to the impact of gases formed through radiolysis on overall gas pressure. Given that most disposal canisters are thick-walled and so provide substantial shielding, it is likely that the amount of gas produced by radiolysis will be small compared with the amount that will be produced as a result of corrosion of steel containers or cast iron inserts. Radiolysis on its own is unlikely to result in a significant build-up of pressure.

4.3 Impact of Alpha Radiation on Clay Mineral Structure

The impact of alpha radiation on clay minerals (such as smectite) is related to changes in microstructural features and can be understood by considering the mechanisms for cation diffusion. Alpha radiation is expected to cause structural disintegration along the migration paths. For example, experiments have shown that montmorillonite that has been saturated with either of these elements, yielding around $5\ 10^{18}\ \alpha\ g^{-1}$, is completely destroyed and converted to an amorphous, siliceous mass (Beall, 1984).

Grauer (1986) reported that an alpha dose of around 4 10^{18} α g^{-1} is required to completely destroy the crystal structure of montmorillonite. For the HLW disposal concept developed by Nagra in the Gewähr Project, the extent of such α-damage was considered to be insignificant, affecting only a small fraction of the total amount of bentonite backfill. SKB (2006a) cite the RN-calculations for SR 97, where it was found that the total concentration of α-emitters in the buffer closest to the canister would give a total dose of 8 10^{15} α g^{-1} of bentonite for the first million years with the assumption of an early canister failure and state that this is less than 1% of the dose required to destroy the material closest to the failed canister. SKB (2006a) also stress that in most parts of the buffer the α-dose will much less because the α-emitters are strongly absorbed and will stay in the vicinity of the canister so that only very small part of the bentonite buffer will be affected (and even then this would not be substantial). However, if water flow takes place only through a few channels, they may well transport significant amounts of americium and similar radionuclides through the buffer to the surrounding rock, thereby increasing the potential for deleterious effects on clay mineral structure.

4.4 Impact of Gamma Radiation on Clay Mineral Structure and Properties

Early research showed that the crystal structure of the clay mineral kaolinite undergoes destabilization when exposed to gamma radiation (Jacobsson and Pusch, 1977), causing reduction of the size of the crystallites and a related increase in specific surface area. This effect may be similar or possibly more prevalent in smectite because of the large number of fragile hydrated layers that make up crystallites.

Experiments have been conducted, whereby confined samples of montmorillonite (Wyoming bentonite, MX-80) saturated with electrolyte-poor water were exposed to a radiation dose of about 3 10^7 Gy at one end (sealed by an iron plate) while the opposite end was in contact with weakly brackish water with Na as dominant cation (Pusch et al., 1993b). The radiated end was heated to 130 °C during the 1 year experiments and that opposite to 90 °C (thermal gradient of ~6 °C cm^{-1}). The solution was pressurised at 1.5 MPa. The adsorbed radiation dose was 3972 Gy h^{-1} at the hottest contact, around 700 Gy h^{-1} at half length of the sample, and 456 Gy h^{-1} at the coldest end. The analyses showed that the montmorillonite content was slightly reduced where the temperature had exceeded 115 °C, while the quartz and chlorite contents had increased. A small amount of illite appeared in the hottest parts despite the negligible potassium concentration in the solution. Comparison of MX-80 clay with and without radiation in otherwise equal, one year long tests showed that there were almost no differences in mineral and chemical composition except that Fe had migrated quicker from the iron plate into the clay under radiation.

Grauer (1986) found that a gamma dose of 3 10^8 Gy from ^{60}Co caused no structural alteration in bentonite. However, carbon dioxide and hydrogen gas were evolved during irradiation. Grauer (1986) also reported that gamma radiation and accelerated electrons can increase the cation exchange capacity (CEC) of montmorillonite. Moreover, γ-irradiation with ^{60}Co up to 9.5 10^7 Gy had no significant effect on the water permeability of compacted bentonite (Grauer, 1986).

As outlined in the review by Allard and Calas (2009), in contrast with 'heavy ions', ionizing radiation (such as gamma rays and beta rays) do not modify the crystallinity of clay minerals within a dose range reaching several GGy. However, structure breakdown can potentially result from radiolytic damage due to a severe ionizing irradiation and clay minerals can be amorphised under electron or ion beams (Allard and Calas, 2009).

In their review article, Allard and Calas (2009) note that although several properties of clay mineral (such as solubility, specific surface area, and exchange capacity) can be altered by local damage produced by radiation, the effects on properties appear significant only for high doses and remain relatively limited. However, they consider that research effort is still required to obtain a consistent and comprehensive understanding concerning the evolution of specific surface area and CEC with the radiation dose.

4.5 Key Points

- High doses of alpha radiation can have some impact through degradation of the clay mineral structure should certain radionuclides migrate through the bentonite, especially if the migration paths are narrow. Gamma radiation is less likely to result in damage to smectite crystallites.

- SKB has considered the effect of α-damage on a bentonite buffer (SR-Can assessment, KBS-3 disposal facility, SKB 2006a) assuming early canister failure, and concluded that only a small part of the buffer would be affected (and that this would not be substantial). Nagra has also considered the possibility of α-damage and concluded that deleterious effects were unlikely.

- Several clay mineral properties such as solubility, specific surface area, and exchange capacity can be altered by local damage produced by radiation, but the effects on properties appear significant only for high doses and remain relatively limited.

5 Bentonite Porewater Evolution, and Subsequent Effects on Wasteform Behaviour and Canister Corrosion

5.1 Bentonite Porewater Evolution

Although the bentonite pore water composition is generally not used directly in performance assessment (PA) calculations, a 'reference bentonite pore water composition' (e.g. McKinley and Savage, 1996) is usually defined to determine, amongst other things, canister corrosion rates, the dissolution rate of the waste matrix, and the solubilities and transport properties (diffusion, sorption) of radionuclides. A robust estimate of the bentonite porewater composition and its likely evolution with time is therefore an important component of the development of the safety case.

Key parameters in the definition of this reference pore water are pH and Eh, which have major effects on canister corrosion and radionuclide solubility and migration, and concentrations (activities) of aqueous species that may accelerate metal corrosion, and/or enhance radionuclide solubilities/mobilities. Species in this category would include HS^-, HCO_3^-, and of course, Cl^-. An important aspect of this evaluation is not only to define a (starting) pore water composition, but also to gain insight into controlling processes and mechanisms, such that changes in pore water composition can be predicted when the system is subject to internal (e.g. waste thermal output) and external (e.g. glacial cycling) perturbations. Until relatively recently, models were essential because of the difficulties in establishing a true pore water composition experimentally in compacted bentonite.

Redox is generally assumed to be controlled by equilibria involving dissolved iron species and iron minerals (such as magnetite or siderite) (Wilson et al., 2006a, SKB, 2006a *inter alia*). Reactions involving reduced sulphur species are generally deemed to be of lesser importance because of the assumed non-viability of sulphate-reducing bacteria in compacted bentonite. To a certain extent, the precise controlling reactions are a site-specific issue, in that the concentrations of redox-sensitive species may be dominated by the composition of the ambient groundwater at a site. In UK groundwaters, the amounts of sulphate may be quite high (such as in, or adjacent to, Permo-Triassic sedimentary basins) and thus may be critical in this regard.

The pH of bentonite-equilibrated groundwaters is assumed to be determined through the interaction of a number of factors, such as: ion exchange on clay; protonation-deprotonation reactions at clay edge sites; dissolution-precipitation reactions of trace carbonate minerals (calcite, siderite, dolomite); dissolution-precipitation reactions of the major clay mineral component (montmorillonite) of the bentonite; the concentration of conservative anions (usually Cl^-) in the ambient groundwater; and the assumed PCO_2 of the system[1]. Different assessments/authors place different emphasis on each of the above factors, but the consensus is that the clay fraction principally acts as a cation exchanger, with the silicate exchanger being essentially inert and pH being determined by the contribution from the trace carbonate mineral concentration, and the ambient PCO_2/chloride activity (e.g. SKB, 2006a, Nagra, 2002). However, there are question marks concerning not only the thermodynamic validity of ion exchange-based models for clay (Stumm and Morgan, 1981) but also the plausibility of ion exchange models to predict long-term clay behaviour, so that a more rigorous approach employing a solid-solution model for montmorillonite hydrolysis has been advocated (Arthur and Wang, 2000). Recent models of bentonite porewater evolution (especially with regard to pH) have included considerations of ion-exchange, surface reactions and minerals hydrolysis (Savage et al., 2010c). In addition, Kaufhold et al. (2008) have investigated the effect of exchangable cations on pH.

Ironically, the end-result of the current modelling approach is that although bentonite is part of the 'engineered' barrier system, to all intents and purposes, adoption of an ion exchange-based model generally necessitates that pH is fixed by the ambient geochemical conditions (PCO_2, Cl^-) at a site, rather than by the essential mineral component (montmorillonite) of the bentonite itself. A more 'holistic' model incorporating the effects of clay mineral hydrolysis has been advocated by Savage et al. (in press) in an attempt to avoid the current widespread practice of the use of different models for different processes in the bentonite such as swelling, pore fluid evolution and clay alteration.

In the UK, it will be necessary to apply pore water evolution models to the range of groundwaters expected at candidate disposal sites to produce 'reference near-field pore waters' for solubility calculations, canister corrosion tests etc. Moreover, experimental techniques developed through the NF-PRO project to measure pore water compositions directly in compacted bentonite (Muurinen and Carlsson, 2007) will also need to be pursued with UK groundwater compositions.

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[1] PCO_2 is usually fixed externally in the geosphere and may be relatively high in sedimentary basins (0.001 to 0.01 bars), but often much lower in higher-strength rocks (typically < 0.00001 bars) (Savage et al., 1997).

5.2 Effects of Bentonite on Wasteform Behaviour

For the most part, interactions between glass and clay have been considered to be deleterious to waste isolation. Experiments to investigate the interaction of waste glasses with clay have been reported by a number of authors (e.g. Grambow et al., 1986; Godon et al., 1989; Godon and Vernaz, 1990; Vernaz and Godon, 1991). There have also been a number of modelling studies to interpret these experimental investigations (Grambow et al., 1986; Curti and Smith, 1991; Curti et al., 1993). Harrison et al. (2009) summarise recent work in this field.

Grambow et al. (1986) carried out experiments with a Japanese waste glass, both with, and without, bentonite. Experimental results revealed greater dissolution of the glass in the presence of bentonite. This enhanced dissolution was interpreted to be a result of greater solubility of silica in the presence of bentonite due to pH being buffered at relatively higher levels than without bentonite. Modelling carried out by this author focussed principally upon changes in pH and silica solubility as the controlling factors in waste glass dissolution.

Glass-clay interactions have been a particular focus for French researchers (Godon et al., 1989; Godon and Vernaz, 1990; Vernaz and Godon, 1991). For example, Godon et al. (1989) conducted a suite of experiments reacting the French nuclear waste glass 'R7T7' with a variety of clays, sand and granite. They noted little difference in reaction of the glass with granite, sand and one clay (a bentonite 'activated' with Na), but greater alteration of the glass with all other clays. The amount of dissolution and thickness of alteration layer on the glass varied with clay type. The highest alteration was associated with K-Mg-rich, Na-Si-poor clays, suggesting that cations other than Si were important in defining the rate of reaction. However, Godon et al. (1989) attributed this enhancement of glass dissolution to a 'removal' of silica from aqueous solution, principally by a mechanism of silica sorption on clay.

The SCK-CEN CORALUS *in situ* test (Valcke et al., 2006) has increased confidence in many of the results from small-scale and modelling work. Inactive and doped SON-68 glasses were placed in contact with three different clay-based materials (Boom Clay, Ca bentonite mixed with sands and graphite, and Ca bentonite mixed with powdered SON-68 glass) under *in situ* conditions for durations of up to 10 years. A key result from the point of view of this study is that the addition of powdered glass to the clay material decreased the alteration rate of the glass significantly (up to two orders of magnitude), although it must be noted that even this long-term experiment is only measuring the short-term dissolution rate of the glass. This result is consistent with observations that a high silica content in the bentonite decreases the glass dissolution rate.

In terms of evidence from natural systems, Techer et al. (2001) studied the corrosion behaviour of a natural basaltic glass preserved in clay in the Salagou dike intruded into a Permian argillaceous formation about 1.4 Ma ago, as a means of assessing the long-term behaviour of nuclear waste glass in a clay-based GDF. The alteration rates estimated from palagonite thickness and age of this glass are comparable to those measured on natural glasses altered in non-clay media. The occurrence did not result in long-term alteration kinetics significantly different from those measured in simple glass/water systems. In this case, it seems that the clay forms a protective covering to the glass, rather than acting as a 'catalyst' to enhance dissolution as suggested by other workers.

In conclusion, clay may have a deleterious effect on glass, by the extent to which glass is affected strongly depends upon its chemical composition and the composition of the bentonite (and pore water) with which it comes into contact with.

With regard to wasteforms other than glass, the presence of bentonite is not known to accelerate spent fuel or PuO_2 dissolution (Lemmens et al., 2008).

5.3 Effects of Bentonite on Canister Corrosion

A study recently reported by SKB (2009b) that examined bentonite-copper interactions found that when copper in contact with bentonite undergoes corrosion, some of the copper appeared to penetrate into bentonite. The corrosion rate is likely to be influenced by the geochemical conditions in the buffer (e.g. pore water composition).

In experiments carried out through the NF-PRO project, corrosion rates of iron/steel were generally slightly lower in experiments without compacted bentonite, than in comparable tests with solid bentonite present (Figure 5.1). This suggests that the presence of the clay influences the corrosion reactions (such as the dissolution rate of the corrosion product film) occurring on the surface of the steel.

However, there is also experimental evidence that bentonite can act to inhibit the growth of steel corrosion products. Smart et al. (2004) and Carlson et al. (2007) describe experiments where both carbon steel wires and coupons of cast iron and carbon steel were reacted with compacted MX-80 bentonite and artificial groundwater (sodium chloride and carbonate) at 30 and 50 °C for several hundred days. The experiments showed that the layer of corrosion product on bentonite was thinner than in aqueous solution alone. These experiments suggest that bentonite could act as a 'pump' for metal corrosion and influence factors such as the dissolution rate of the corrosion product film that occurs on the surface of steel canisters. It is likely that the release of Fe under anaerobic conditions will result in Fe-rich clay minerals such as berthierine forming at the iron-bentonite interface (see Section 7.1).

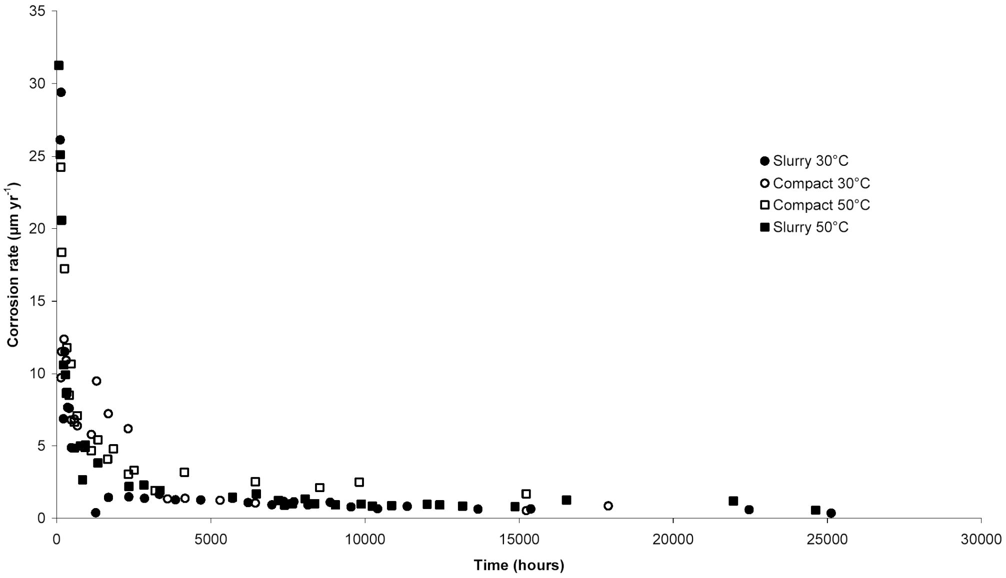


Figure 5.1: Example of results from anaerobic corrosion experiments on steel in bentonite slurry and compacted bentonite at 30 °C and 50 °C (from Carlson et al. (2007).

5.4 Key Points

- ▲ It will be necessary to apply pore water evolution models to groundwaters at candidate disposal sites to produce 'reference near-field pore waters' for a number of aspects of safety case development (such as radionuclide solubility calculations and to consider canister corrosion rates). Application of direct measurement techniques for geochemical parameters in samples of compacted bentonite saturated with UK groundwaters should also be carried out.

- ▲ For the most part, interactions between glass and clay have been considered to be deleterious to waste isolation. However, the composition of the clay strongly influences the extent to which glass may react.

- ▲ With regard to copper, some corrosion of the copper has been observed to occur and the rate of corrosion will probably be influenced by the pore water chemistry of the bentonite.

- ▲ Experiments suggest that compacted bentonite could act as a 'pump' thus increasing iron/steel corrosion and influence factors such as the dissolution rate of the corrosion product film that occurs on the surface of the steel canisters. However, there is also evidence that bentonite inhibits the growth of steel corrosion products.

6 Effects of Groundwater and Waste Compositions on Bentonite Stability and Swelling

6.1 Groundwater

The properties and long-term behaviour of bentonite can be perturbed by the presence of certain groundwater compositions in the GDF environment. There are essentially two issues to consider:

- Long-term clay mineral transformations (such as illitisation) whereby the desirable properties of swelling clays are degraded.
- Effects of bentonite-groundwater interaction on swelling pressure.

6.1.1 Mineral Transformations (including illitisation)

Consideration of this issue has tended to be focused towards illitisation of the montmorillonite component of the bentonite, but other reactions can also be important.

Illite is a common K-bearing, aluminous, non-swelling 2:1 layer silicate. The K^+ is essentially fixed in position between 2:1 layers, which have a higher layer charge deficit than smectites. Illite may exist as discrete (non-swelling) particles, or may be intercalated with other clay layer types to form 'mixed layer' minerals (with restricted ability to swell). Of particular relevance is mixed layer illite/smectite which forms as smectite is gradually altered to illite.

In natural systems, illitisation is often observed in sediments undergoing burial diagenesis (e.g. Burst 1959; Powers 1967; Hower et al. 1976). This process is therefore strongly dependent on both temperature and time. The process of illitisation broadly involves 2:1 layer charges increasing (Al is substituted for Si in tetrahedral sheets), uptake of K into interlayer regions, and the release of silica. As noted by Karnland and Birgersson (2006), there has been much discussion in the literature as to the precise reaction mechanisms of smectite illitisation and understanding of the illitisation process is far from being well-understood. In fact, smectite illitisation is one of the most discussed phenomena in the field of clay mineralogy.

Karnland and Birgersson (2006) evaluated a number of models for illitisation and chose that described by Huang et al. (1993) to apply to the Swedish KBS-3 disposal concept. Huang et al. (1993) suggest the following second order rate law:

$$-\frac{dS}{dt} = A \cdot \exp(-Ea / RT) \cdot [K^{+}] \cdot S^{2} \qquad (6.1)$$

where S is smectite fraction, A is frequency factor (8.08 10^{-4} s^{-1}), exp = exponential function, t is time (s), Ea is activation energy (28 kcal mol^{-1} or 117.15 kJ mol^{-1}), R is the gas constant, K^{+} is expressed as a concentration (mol L^{-1}).

In addition to this function, the availability of dissolved K^{+} needs to be considered when considering the potential for illitisation of bentonite. This is discussed by Karnland and Birgersson (2006), who calculate that if the montmorillonite content in the bentonite is a minimum of 75 %, then potassium mass corresponding to at least 5 % of the bentonite mass is required in order to fully convert the montmorillonite in the buffer. In the KBS-3 concept, each canister is surrounded by approximately 10.5 m^3 bentonite buffer. The buffer density of 2.0 10^3 kg m^{-3}, after saturation with water, gives a total bentonite mass of ~$1.7 \cdot 10^4$ kg per deposition hole. Consequently, total illitisation (complete loss of swelling) requires approximately 850 kg of potassium per deposition hole (Karnland and Birgersson, 2006). If the Äspö granodiorite is assumed to be the host rock, in order to completely transform the buffer in one deposition hole, all of the potassium in 9 m^3 of the rock has to be used. Therefore, the total amount of potassium in the vicinity of the buffer is likely to be sufficient for a total transformation of the buffer if this potassium is mobile. Therefore, the availability of K^{+} is a crucial factor for considering illitisation potential (Karnland and Birgersson, 2006).

Karnland and Birgersson (2006) review possible K^{+} concentrations and identify typical concentrations associated with two mineral assemblages: illite (or muscovite), kaolinite, and quartz showing a lower K^{+} concentration in the solution (e.g. ~ 10 ppm at pH 6.5, 40 °C); and a second group containing illite (muscovite), K-feldspar (microcline), and quartz showing a higher K^{+} concentration in the solution (e.g. ~ 900 ppm at pH 6.5, 40 °C) and conclude that: the illitisation rate will theoretically be higher in the warmer inner parts of the buffer at constant potassium concentration; the initial potassium present will be consumed; and diffusive transport of potassium will be initiated, which will slow down the transfer of K^{+} and illitisation. Therefore, calculations using kinetic models such as that suggest by Huang et al. (1993) will overestimate the degree of illitisation because a constant potassium concentration is used and the transport restriction in fractures and buffer is not taken into account (Karnland and Birgersson, 2006).

The model of illitisation produced by Karnland and Birgersson (2006) using the data and rate law suggested by Huang et al. (1993) is given in Figure 6.1 The model demonstrates the importance of temperature on the rate and therefore degree of illitisation over time. This is one of the most important constraints on near-field temperatures (and hence layout and design) for the KBS-3 concept (SKB, 2006b).

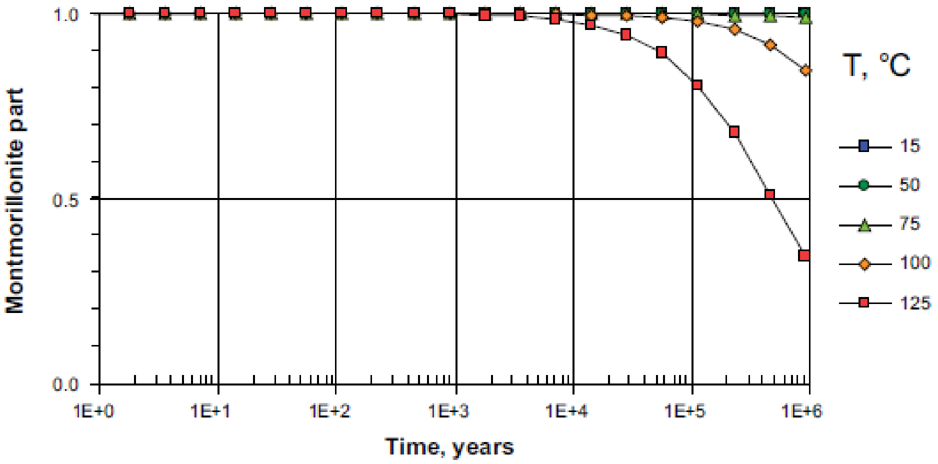


Figure 6.1: Model of smectite illitisation, showing remaining montmorillonite part for different temperatures with [K^+] = 0.002 molar (80 ppm) according to the Huang et al. (1993) kinetic model (from Karnland and Birgersson, 2006) (E_a = 28 kcal mol^{-1} and A = 8.1 $10^4 s^{-1}$ mol^{-1}).

Given that the maximum temperature in the proposed Swedish repository is calculated to be below 50 °C after 1,000 years, below 25 °C after 10 000 years and less than one degree above the unaffected rock temperature after 100 000 years, calculated montmorillonite illitisation is insignificant for the actual KBS-3 conditions (Karnland and Birgersson, 2006).

Karnland and Birgersson (2006) discuss the uncertainties associated with the modelling, which include: uncertainties in predicting K^+ concentrations; the extrapolation of higher temperature measured reaction rates to lower temperatures; possible differences in behaviour of silica concentrations; reaction mechanisms and rates under different conditions are not particularly well understood, solid/fluid ratios and the pH of pore fluids will have a strong influence (e.g. Eberl et al. 1993 showed in laboratory experiments that illite may be formed from smectite under hyperalkaline conditions at temperatures as low as 35°C). However, as noted by Karnland and Birgersson (2006), when pH values are not hyperalkaline, the extreme K^+ concentration of 3000 ppm (~80 mM) found in the Salton Trough geothermal area (Huang et al. 1993) increases the illitisation rate by a factor of 40, which still gives insignificant illitisation in the disposal facility.

Karnland and Birgersson (2006) consider the potential effects that illitisation may have upon bentonite safety functions. They report that the KBS-3 design criterion for minimum swelling pressure is 1 MPa, which corresponds to a calculated maximum acceptable montmorillonite illitisation of 30 % (the effect of illitisation on swelling pressure is shown in Figure 6.2).

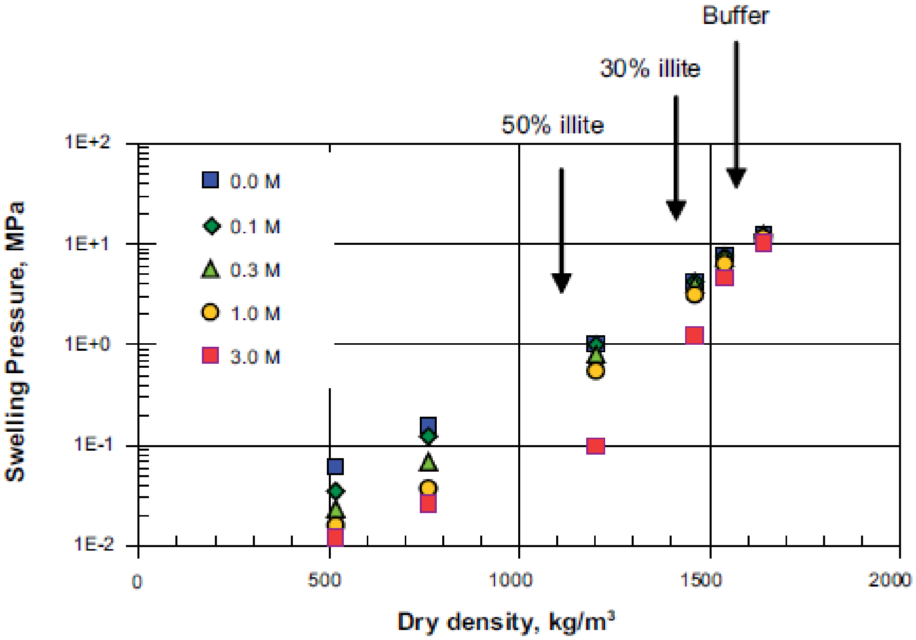


Figure 6.2: Swelling pressure of MX-80 material in contact with pure water and NaCl solutions. Dots show measured values. Buffer indicates the swelling pressure of unaltered buffer material at KBS-3 target density, 30 % illite indicates the pressure at maximum acceptable transformation, and 50 % illite illustrates the pressure at a 50 % illitisation (Karnland and Birgersson, 2006).

Therefore, the modelling suggests (with certain caveats such as pH not becoming hyperalkaline and that the smectite is aluminous) that there should be insignificant transformation of the montmorillonite during the lifetime of the KBS-3 disposal concept when emplaced in a granitic host rock (unless the rock is saturated with a K-rich brine).

Three generic groundwater compositions are considered in current UK work: DET6, DET 8 groundwaters from Sellafield (higher strength rock, Nirex, 1994); and Callovo-Oxfordian (clay – lower strength sedimentary rock) (Bath, 2007). The K^+ concentrations associated with DET6 and DET8 are 1.48 mg L^{-1} (3.8 10^{-5} mol L^{-1}) and 9.43 mg L^{-1} (2.4 10^{-4} mol L-1) respectively, whereas for the Callovo-Oxfordian, it is 278 mg L^{-1} (7.1 10^{-3} mol L^{-1}). Therefore, if these water compositions reacted with the KBS-3 EBS, the model reported by Karnland and Birgesson (2006) could be interpreted as showing that illitisation and associated effects on swelling pressure are likely to be insignificant. However, this is dependent upon pre-existing assumptions concerning prevailing temperatures and supply of K^+ that would need to be considered should an EBS similar to KBS-3 be adopted in the UK. For example, research conducted by SKB and elsewhere (e.g. Pusch and Kasbohm, 2002) suggests that the long-term effects of montmorillonite degradation in saline groundwater could include the formation of beidellite or kaolinite, rather than illite.

As mentioned in the review by Savage (2005), Pérez del Villar et al. (2005) and Fernández et al. (2005) investigated analogue evidence for the long-term stability of bentonite, by studying the Spanish Cala de Tomate and Archidona bentonite deposits both of which have been invaded by seawater during their geological history. Pérez del Villar et al. (2005) noted changes in exchangeable cations, BET-specific surface area and dispersibility, as a result of interaction of the Cala de Tomate deposit with saline waters, but no mineral transformations were reported. The Archidona bentonite has been invaded by seawater and meteoric water at different stages of its past history, but shows no sign of mineral alteration as a result of these processes (Fernández et al., 2005).

6.1.2 Effects on Swelling Pressure

The smectite component of bentonite gives it the capacity to swell. As reviewed by Savage (2005), two fundamental swelling processes operate: innercrystalline swelling (caused by the hydration of interlayer cations between 2:1 layers); and osmotic swelling that results from gradients in ion concentrations between clay surfaces and porewater. As outlined by Savage (2005), a number of models have been suggested for the prediction of swelling pressure (these are extensively reviewed by Grauer, 1986; and Karnland, 1997). In brief, these include: empirical models; diffuse double layer models; DLVO theory (based on considering interaction between charged surfaces in aqueous solutions due to van der Waal's forces); and thermodynamic models (which generally consider only the macroscopic properties of clay-water systems).

In Sweden, SKB has adopted an interpretation of clay buffer swelling pressure in which clay particles are considered as macro-ions and the entire clay-water system may be viewed as a 'polyelectrolyte' (Figure 6.3) (Savage 2005). SKB has used the thermodynamic model of Low and Anderson (1958), with modifications using 'Donnan' relationships for saline systems (Savage 2005).

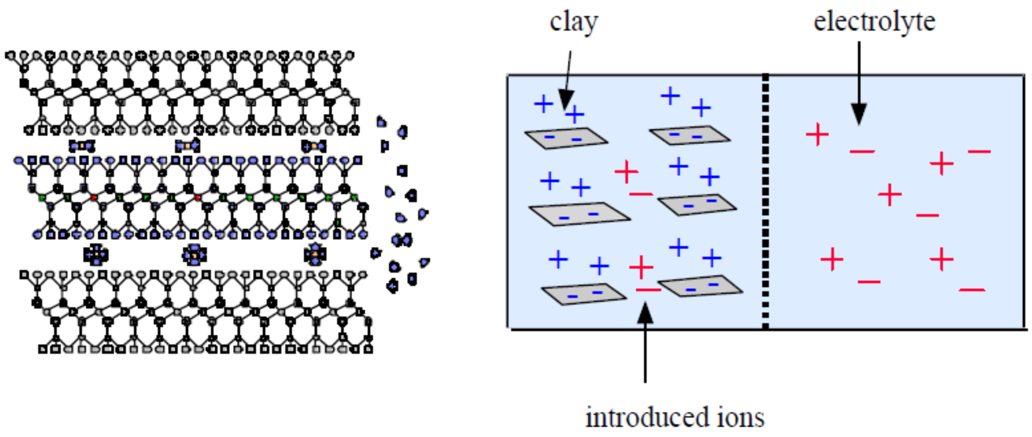


Figure 6.3: SKB's polyelectrolyte interpretation of the clay-electrolyte system. The clay is seen as a 'soluble polyelectrolyte', contributing positively and negatively charge ions to the clay-water system. An osmotic equilibrium is set up between the clay and external electrolyte, involving diffusion of water molecules and ionic species. The osmotic pressure created reduces bentonite swelling in saline solutions (from Karnland et al. (2007).

SKB broadly consider that the chemical potential or molar Gibbs energy of the clay-water system may be represented by (Karnland et al., 2002):

$$\mu_w = \mu_0 + RT\ln\frac{P_c}{P_0} + RT\ln\frac{P_e}{P_0} + m_w gh + \overline{V}_w \cdot P + zFE + \ldots \qquad (6.2)$$

where μ_0 is the chemical potential of free water, the second and third terms represent the energy contribution from the clay and electrolyte respectively, P_c, P_0, and P_e represent the vapour pressure set by the clay, pure water, and an electrolyte, respectively. The fourth term represents the contribution from hydrostatic pressure, where g is the gravity constant and h is height. The fifth term represents water pressure of another origin, where V_w is the molar volume of water. The last term represents the contribution from electrostatic origin.

SKB has adapted the model of Low and Anderson (1958) by direct measurement of swelling pressure, water activity, and porewater concentrations in bentonite clays at different clay, salt, and water conditions. These measurements show that:

- There is an exponential relation between swelling pressure and mean basal interlamellar (c-axis) spacing of the clay.

- Ions from the external electrolyte solution enter the clay volume, leading to decreased water activity in the clay.

- Introduced ions enter the swelling pressure-inducing volume in the clay.
- Swelling pressure is systematically reduced at all clay densities by interaction with saline fluids.

Consideration of double layer effects implies that decreases in swelling pressure in bentonites contacted by saline solutions are accounted for by diffusion of water molecules alone (Savage, 2005). However, SKB measurements show that ionic species from external saline solutions are transported into the clay and these introduced ions are treated as 'an additional osmotic component' acting on the clay-water volume, such that the difference in concentration between external and introduced ions leads to a drop in swelling pressure (Savage, 2005).

Application of the thermodynamic relationship developed by Low and Anderson (1958) to experiments with high salt concentrations led to swelling pressures being underestimated due to the migration of ionic species from the external electrolyte into the clay-water system and the resulting reduction of partial molal free energy of water in the clay-water system. The model based on Low and Anderson (1958) therefore had to be modified (see Savage, 2005).

'Donnan exclusion' has been used by SKB to estimate the amount of ions introduced into the clay and hence the amount of reduced swelling pressure due to contact with a saline solution (Karnland, 1997; Karnland et al., 2002). Donnan exclusion refers to the restriction of the migration of anions through the narrow aqueous film surrounding clay platelets due to the repulsion by the negative charge on the clay platelets. In order for electrical neutrality to be maintained, cations remain with the anions so that their migration is also restricted (i.e. the measured concentration of cations and anions in the clay decreases with increasing compaction of the clay).

SKB have stated that that if the bentonite buffer density exceeds 1.9 Mg m^{-3}, the functional requirements for the swelling pressure to exceed 1 MPa will be fulfilled, with groundwater salinities up to 3 M NaCl (SKB, 2004). Similarly, the functional requirement for buffer hydraulic conductivity of 10^{-12} m s^{-1} will also be fulfilled if the buffer density is greater than 1.8 Mg m^{-3}, even for 3M NaCl equivalent salinity (SKB, 2004).

Karnland et al. (2005) have extended this work to consider the swelling properties of bentonites/clay deposits from Greece (Deponit-CaN), India (Kutch), Germany (Friedland Clay), the Czech Republic and Denmark. Experiments showed that the swelling behaviour of Ca-montmorillonite is very different from Na-montmorillonite because innercrystalline swelling is much less than the Na-variety.

For the SR-Can assessment, SKB considered that the swelling pressure of the buffer under fully-saturated conditions is a function of the cation exchange capacity of the clay, the clay density, and the ionic composition of the surrounding groundwater (Savage 2005).

The empirical relationship between swelling pressure and clay density for smectite-rich clay saturated with freshwater is (Hedin, 2004):

$$P_s^{fresh} = AT\left(\exp\left(B\frac{\rho_{solid}(\rho_{clay}-\rho_{water})}{\rho_{water}(\rho_{solid}-\rho_{clay})}\right)-1\right) \qquad (6.3)$$

where *A* and *B* are fitting parameters, *T* is temperature (K), and ρ_{clay}, ρ_{water} and ρ_{solid} are the densities of saturated clay, water, and solid clay particles, respectively. The equation is not valid for diagenetically altered smectite clays, such as hydrothermally treated montmorillonite-rich clay as exemplified by Pusch and Yong (2006).

For saline groundwater, Hedin (2004) considers that the swelling pressure will be reduced due to osmotic effects, leading to a Donnan equilibrium. Hedin (2004) gives the following relationship for the clay swelling pressure in an external NaCl concentration C [M] where Na^+ is the adsorbed cation on the clay:

$$P_s^{saline}\sqrt{(P_s^{fresh})^2 + (2RTC\alpha_d)^2} - 2RTC\alpha_d \qquad (6.4)$$

Where P_s is the swelling pressure (kPa), *R* is the gas constant, (Kmol) and α_d (dimensionless) is the degree of dissociation for the external NaCl solution of concentration C, which is given by:

$$\alpha_d \approx 10^{\frac{-0.34\sqrt{C}}{1+1.83\sqrt{C}}} + 0.03C \qquad (6.5)$$

Models used by SKB to calculate bentonite swelling pressure in solutions of different salinity require testing in fluids more complex than NaCl. For example, groundwaters in the UK may be complex Na-Ca-Cl-SO_4 fluids, rather than a simple solution of NaCl. This will involve experimental studies of the type described by Karnland et al. (2002) and further development of predictive models.

6.2 Effect of High Mg and Al in Wastes on Porewater Evolution and Bentonite Stability

6.2.1 Introduction

Much of the UK's HLW glass stock is derived from reprocessing of Magnox spent fuel has a much higher Mg and Al content than the glasses studied by other waste management organisations (e.g. Andra). Further, it may not be possible to reprocess all of the UK's stock of Magnox spent fuel, meaning that it may be necessary to dispose of small quantities of Magnox spent fuel in the GDF. As a result, NDA RWMD is interested in the effect of the high Mg and Al contents of such wastes on bentonite porewater and evolution (assuming waste canisters degrade and fail).

With regard to the issue of high Al content, it seems likely that significant amounts of Al would be available for reacting with bentonite only when prevailing pH conditions become extremely acid or extremely alkaline (Figure 6.4). With regard to pH evolution in an EBS, extreme values are generally only associated with hyperalkaline cement pore water which (as outlined in Section 8) can result in the dissolution of smectite and the formation of non-swelling zeolite/feldspathoid minerals. Therefore, in this section focuses on the possible reactions between Mg-bearing waste, groundwater and smectite.

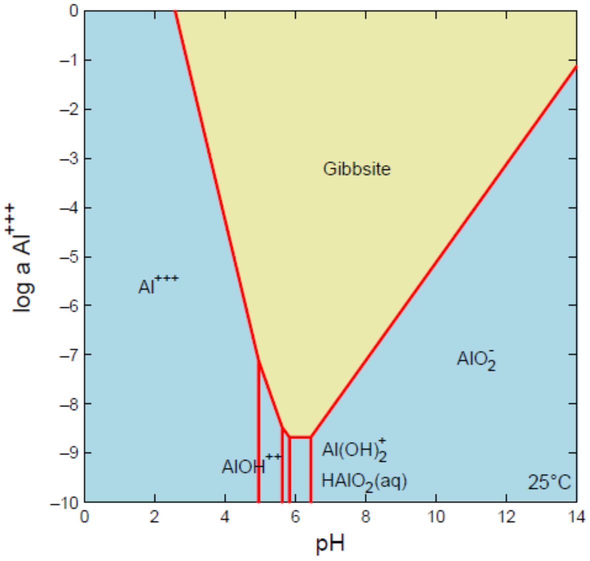


Figure 6.4: Predominance diagram showing solubility of gibbsite ($Al(OH)_3$) as a function of pH in pure H_2O (T = 25°C, P = 1 bar) showing minimisation of Al solubility at circum-neutral pH. All thermodynamic models in this section were produced using Geochemist's Workbench (Bethke, 2008) and the database 'thermo.com.v8.r6+.dat.'

6.2.2 Interaction of Bentonite with Mg-rich Waste.

If there is a high availability of dissolved Mg for bentonite porewater, ion exchange processes (which operate over short timescales) would need to be considered. It could be the case that an initial reaction would be ion exchange, with interlayer Na^+ being replaced by Mg^{2+}. As with replacement with other cations (such as Ca^{2+}), this could affect physical properties of the bentonite (such as swelling pressure). Over longer time periods (possibly hundreds to many thousands of years), montmorillonite could undergo alteration to other clays rich in Mg. Thermodynamic models have been produced in order to demonstrate the possible evolution of smectite chemistry in high Mg^{2+} solutions that could arise as a result of the dissolution/corrosion of Mg-bearing wastes or alloys. The generic groundwater compositions considered are 'DET6' and 'DET8' (Nirex, 1994) and the French Callovo-Oxfordian (Bath, 2007). These water compositions (Table 6.1) were subjected to aqueous speciation calculations using Geochemist's Workbench (Bethke, 2008) and calculated cation activities were plotted an a logarithmic activity diagram, also constructed using GWB (Figure 6.5).

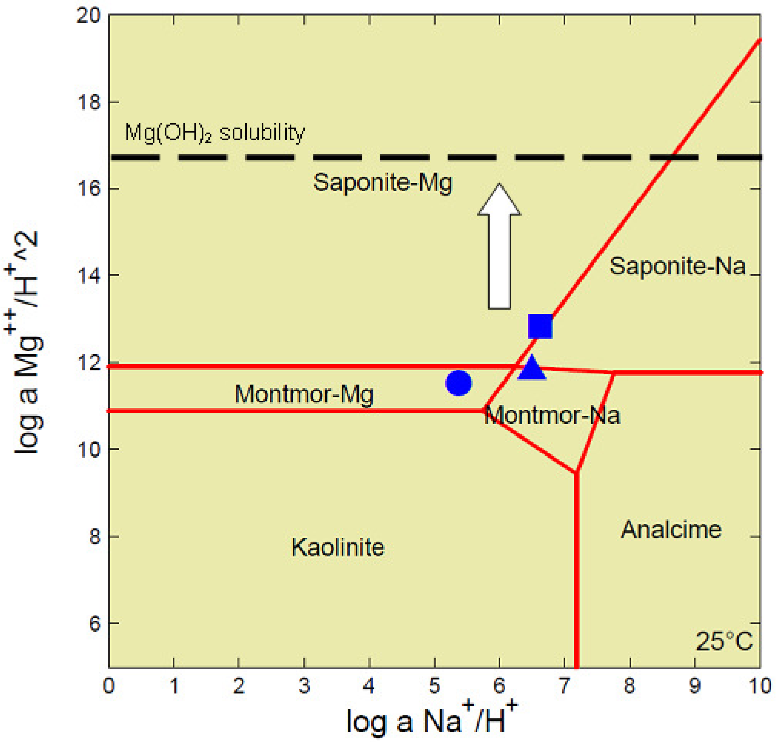


Figure 6.5: Logarithmic activity diagram with plot of activity ratios calculated for DET6 (square), DET8 (triangle) and Callo-Oxfordian (sphere) groundwaters (T = 25 °C; P = 1 bar; $SiO_{2(aq)}$ activity buffered by chalcedony). The diagram shows the possible evolution of water compositions due to reaction with Mg-rich wastes (illustrative solubility limit for $Mg(OH)_2$).

In order to consider possible evolution of Mg^{2+} activities due to groundwater/Mg-waste and bentonite pore water/Mg waste interactions, log *a* $Mg^{2+}/(H^{+})^2$ values were computed (Table 6.2). These calculations assumed that Mg^{2+} concentrations could be buffered by phases such as brucite ($Mg(OH)_2$) or a hydrated magnesium-silicate mineral, such as sepiolite for example.

Table 6.1: Generic groundwater compositions ('DET6', 'DET8', and C-OX 'Callovo-Oxfordian) (values from Nirex, 2004 and Bath, 2007).

	DET6	**DET8**	**C-OX**
pH	8.75	7.73	7.00
Eh (V)	-0.132	-0.078	-0.156
log *f* $CO_{2(g)}$	-3.56	-3.94	-1.96
	Conc. (M)	Conc. (M)	Conc. (M)
Na	8.16E-03	8.03E-02	3.20E-02
K	3.79E-05	2.41E-04	7.10E-03
Ca	2.07E-04	4.71E-02	1.50E-02
Mg	3.52E-05	6.66E-04	1.40E-02
Fe	9.37E-06	3.47E-05	3.30E-04
$SiO_{2(aq)}$	2.28E-04	1.59E-04	9.40E-05
Al	7.32E-07	6.26E-06	6.90E-09
Cl	5.27E-03	1.53E-01	3.00E-02
SO_4	2.73E-04	6.24E-03	3.40E-02
HCO_3	2.80E-03	1.73E-04	2.90E-03

Table 6.2: Magnesium activity buffers and values of log *a* $Mg^{2+}/(H+)^2$ (calculated using Geochemist's Workbench (Bethke, 2008).

Mineral	Solubility limiting reaction	log *a* $Mg^{2+}/(H^+)^2$ (T=25°C)*	Log *a* $Mg^{2+}/(H^+)^2$ (T=100°C)
Brucite	$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$	16.30	12.45
Periclase	$MgO + 2H^+ = Mg^{2+} + H_2O$	21.34	16.08
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{:}6H_2O + 8H^+ = 11\ H_2O + 4Mg^{2+} + 6SiO_{2(aq)}$	13.20	10.27

* $P = P_{sat}$

The solubility diagram given in Figure 6.5 suggests that as pore water becomes increasingly rich in dissolved Mg, aluminous smectites such as montmorillionite will become less stable than Mg-saponite. Like montmorillonite, saponite is a smectite mineral that shows variation in layer spacing as a function of relative humidity and therefore, has the ability to undergo innercrystalline swelling, and thus has been considered as an alternative candidate buffer material (Section 10). Therefore, it may be the case that the alteration of montmorillonite would, at least in theory, not be particularly detrimental to bentonite buffer function. However, given that many silicate minerals have complete solid solution between and Fe(II) and Mg end-members, and that clay mineral alteration mechanisms are complex, it is arguably the case that the potential for alteration of smectite to non-swelling magnesian layer silicates warrants consideration when Mg is present in high concentrations. Experiments whereby bentonite was reacted with saline solutions suggest that eventually there may be some degree of alteration to non-swelling layer silicates (e.g. (Herbert et al., 2004).

Another process that should be considered in the development of the safety case is the possibility of montmorillonite undergoing only partial alteration to Mg-rich layers. If the mechanisms of alteration included the partial dissolution of tetrahedral sheets, or changes/disruption to the distribution of layer charges in clay crystallites, the rheological and swelling properties of the bentonite could change. This was noted by Wilson et al., (2006b) who found that montmorillonite reacted with Fe powder and NaCl solution at 250°C showed alteration of the montmorillonite to an Fe-rich smectite with reduced capacity to expand after ethylene-glycol solvation (the diagnostic test used for the identification of swelling clay by powder X-ray diffraction). This appeared to be due to the partial loss of tetrahedral Si units and an increase in H-bonding in clay crystallites (Wilson et al., 2006b).

In addition to the potential for long-term mineralogical alteration, experiments have shown that bentonite properties may be altered by reaction with saline Mg solutions. For example, Hofmann et al. (2004) reacted two industrial bentonites, IBECO SEAL-80 and TIXOTON TE with saturated salt brine ($MgCl_2$) at 25 °C over the time period of 150 days and found that sorption capacity and swelling were reduced during contact with the salt brine, but could be reversed by removing the salt after treatment (Hofmann et al., 2004).

Suzuki et al. (2008) report experiments in which a crude bentonite (Kunigel V1) was reacted with simulated seawater (Mg concentrations up to 55 millimolar), at temperatures of either 60 or 90 °C over 6000 h (250 days). Magnesium was taken up by the bentonite during the experiments at levels over the cation exchange capacity (CEC; 0.78 meq g^{-1} for the original bentonite) at 90 °C. The excess Mg was not replaced by ammonium ions, leading Suzuki et al. (2008) to suggest that a Mg solid (Mg-hydroxide) formed in the bentonite. In addition, the CEC decreased from 0.78 to 0.45 meq g^{-1} as the amount of accumulated Mg increased; the distribution coefficient (K_d) for Cs in the altered bentonite was half of that in the original bentonite; and potential swelling capacity (measured as swelling power) was reduced.

6.3 Key Points

- Non-swelling illite is the most likely long-term product of interaction of bentonite with groundwater, but calculations carried out by other waste agencies suggest that this transformation is unlikely to be extensive enough to reduce the swelling capacity of bentonite significantly at temperatures of less than 100 °C and with typical abundances of potassium in the geosphere. However, these calculations will need to be repeated for UK conditions (temperature, local groundwater compositions). The degree of potential bentonite illitisation is one of the prime criteria for temperature limits in the KBS-3 concept.

- Models have been developed that predict the effect of salinity on bentonite swelling pressure. However, many (such as those by considered by SKB) require testing in fluids more complex than NaCl because groundwaters in the UK may be complex Na-Ca-Cl-SO_4 fluids. It is likely that this will require experimental studies of the type described by Karnland et al. (Karnland et al., 2002), and possibly further development of predictive models.

- Preliminary thermodynamic models suggest that if there is a high availability of dissolved Mg from waste, it could be the case that interlayer Na^+ is replaced by Mg^{2+}. As with replacement with other cations such as Ca^{2+}, this could affect physical properties of the bentonite such as swelling pressures and warrants consideration.

- ▲ Little research has been undertaken on the capacity for smectite to be altered from aluminous to magnesian compositions, although it may be a possibility. In addition, bentonite that has come into contact with Mg brines has been observed to lose some sorption capacity.

7 Effect of Canister Corrosion Products on Bentonite

7.1 Iron/steel-bentonite Interactions

There are a number of physico-chemical processes that could occur should steel / iron waste containers be used in an EBS along with bentonite. Steel is likely to corrode and react with the smectite component of the bentonite. Depending on dissolved carbonate, chloride and sulphide concentrations and redox, possible steel corrosion products under low oxygen conditions include magnetite (which may form via metastable $Fe(OH)_2$ or 'green rust' compounds), iron carbonates (such as siderite), iron sulphides and iron (oxy)hydroxides (e.g. Tamaura et al., 1984; Antunes et al., 2003; Refait et al. 2003; Wersin et al., 2003; King, 2008).

In general, magnetite has been the most commonly observed corrosion product in the experiments on iron-bentonite reactions that are discussed here. Possible processes that may result in an EBS as a result of iron-bentonite interactions have been examined using natural analogues, experimental data and geochemical modelling. A number of radioactive waste management-related organisations have undertaken, or commissioned, work on iron-bentonite interactions, including: Nagra (Grauer, 1986); SKB and Posiva (e.g. Carlson et al., 2007; Wersin and Snellman, 2008; Wersin et al., 2008); CEA Cadarache (e.g. Bildstein et al., 2006); JNC (and now JAEA, e.g. Wilson et al., 2006a, 2006b); ANDRA (e.g. Marty et al., 2010). Bentonite–steel interaction is of particular concern to the Nagra and Andra concepts and to the KBS-3H concept, where a steel supercontainer is employed. Concerns regarding the potential for large-scale transformation of bentonite to non-swelling clay through interactions with steel have led SKB and Posiva to consider much more chemically inert metals (e.g. Ni, Ti) for the supercontainer (Wersin et al., 2010).

The interaction of iron with bentonite has few, if any, natural analogues due to the lack of native Fe in the Earth's crust (Wilson, 2003; Wilson et al., 2006a). There are very few examples of natural analogues that have resulted due to anthropogenic activities. One is the study by Kamei et al. (1999) who observed green-coloured bentonite in the vicinity of an iron component of a bentonite mine. The smectite present in this bentonite contained significant amounts of iron, which apparently had entered smectite interlayer regions.

However, where iron is present in an EBS, two potential alteration pathways may be envisaged for an iron waste canister or supercontainer and a clay buffer/backfill (Wilson, 2006a):

1. the alteration of montmorillonite to Fe-rich smectite;
2. the replacement of smectite with non-swelling phyllosilicates, such as chamosite (iron-rich chlorite) or berthierine/odinite (1:1 iron-rich minerals).

Chlorite (non-swelling layer silicate) formation appears to be kinetically inhibited and may occur through an Ostwald step process via odinite, cronstedtite, and/or berthierine precursors. Older specimens of odinite tend to have greater proportions of interstratified 14 Å layers than younger specimens, and this is taken to indicate that unstable odinite transforms to a more chlorite-like mineral upon shallow burial (Bailey, 1988). This sequence odinite–berthierine–chlorite has been recorded (or inferred) for sequences in the Jurassic Sundance Formation Wyoming (Ryan and Hillier, 2002), the Tuscaloosa Formation sandstone, U.S. Gulf Coast (Ryan and Reynolds, 1996), and the sandstones of the Lower Vicksburg Formation, south Texas (Grigsby, 2001). Berthierine is generally deemed to be a metastable precursor to chlorite, (Ahn and Peacor, 1985), with berthierine itself often ‘cannibalising’ odinite, a mixed ferrous-ferric silicate (Huggett and Hesselbo, 2003).

A number of experiments investigating the stability of smectite in the presence of iron have recently been described in the literature (e.g. Guillaume et al, 2003, 2004; Lantenois et al., 2005; Charpentier et al., 2006; Wilson et al., 2006b; Carlson et al., 2007; Perronnet et al., 2007, 2008). In general these experiments include bentonite and iron present as native Fe powder, Fe plate, magnetite (a likely steel corrosion product) and aqueous solutions. The experimental temperatures generally range from 80 to 300 °C, with experimental durations generally being up to ~9 months.

However, the results of these experiments do not give an unequivocal indication of the most likely reaction pathway that may occur in an engineered backfill system, largely due to the short-term nature of the experiments (with many workers adopting the approach of applying elevated temperatures to combat slow reaction kinetics) and issues associated with mineral metastabilities and differences between experimental parameters that will affect reaction kinetics (such as temperature, fluid to solid ratios, run time, fluid/solid compositions, type of iron compound). In general, the higher temperature experiments (>250 ºC) resulted in chlorite formation (Guillaume et al., 2003), whereas lower temperature experiments tend not to show significant alterations, or result in the formation of a 1:1 mineral or an altered iron-rich saponite-type smectite (e.g. Lantenois et al., 2005; Wilson et al., 2006b).

Lantenois et al. (2005) suggested a conceptual model for smectite destabilisation, whereby Me-Fe-(III)OH groups are preferentially deprotonated with Fe(0) acting as a proton acceptor, the adsorption of Fe^{2+} on clay edge sites induces the reduction of structural Fe(III) and migration into interlayers prior to the migration into octahedral sheets due to a large layer-charge deficit. Lantenois et al. (2005) suggest that the presence of di and tri-octahedral domains thereby results in destabilisation. However, Perronnet et al. (2007) cite other experimental data, which they state are not concordant with the observations made by Lantenois et al. (2005). Perronnet et al. (2007) suggest that destabilisation of smectite in the presence of Fe can be described by three mechanisms: (1) the reduction of structural Fe(III), resulting in layer charge increase and uptake H^+ or other cations into interlayer space; (2) destabilisation of smectite into Si-Al-Fe disordered regions; (3) incorporation of Fe^{2+} from native Fe oxidation and maturation into 7 or 14Å minerals. Perronnet et al. (2007) consider particle properties and suggest that smectite stability in the presence of iron depends on the energetic heterogeneity of smectite edge faces.

It will be realised from this discussion that laboratory experimental data are equivocal and that the precise reaction mechanisms and kinetics of smectite alteration to 1:1 and Fe-rich smectite/vermiculite are not well understood. However, it appears to be the case that Fe(II) produced from Fe(0) oxidation reacts with smectite which may lose tetrahedral units to form disordered smectite/gel regions with recrystallisation occurring to produce either Fe-rich smectite / 1:1 minerals (e.g. berthierine, odinite, cronstedtite). These minerals are probably metastable with respect to Fe-rich chlorite, that is observed to form under higher temperature conditions. Further experimental work is underway, funded principally by Andra.

A number of papers have been published on the modelling of bentonite in contact with steel under typical HLW-EBS conditions (e.g. Bildstein et al., 2006; Wersin et al., 2008; Marty et al., 2010, Savage et al., 2010a). It should be noted that a number of thermodynamic properties required for modelling iron-bentonite interactions have not been measured for a number of relevant minerals, resulting in estimated values being used (e.g. Wilson et al., 2006a). This introduces a significant degree of uncertainty into models used to calculate mineral solubilities. However, these models suggest that there is the potential for montmorillonite to be altered to non-swelling Fe-rich clay minerals at the bentonite-steel interface over timescales relevant to PA.

There is arguably much scope for further work on models of iron/steel-bentonite interactions, including (but not limited to): further or more detailed considerations of mineral growth kinetics; the role of cation exchange; the effect of intruding groundwater composition; the effect of using different models of bentonite porosity and solute transport (most models developed to date do not explicitly consider that much of the water present in compacted bentonite is present in smectite interlayers/sorbed to smectite surfaces).

One possible reaction pathway that has received relatively little attention is that whereby bentonite porewater at the bentonite-steel interface has an increasingly high pH due to the reaction:

$$Fe_{(metal)} + 2H_2O = Fe^{2+} + 2OH^- + H_{2(g)} \qquad (7.1)$$

This development of relatively high pH (>10) may accelerate montmorillonite dissolution and may encourage the growth of non-swelling phases such as zeolites and feldspathoids (analcime and clinoptilolite for example, Savage et al., 2007).

Another factor that may need to be considered (depending upon the composition of smectite included in EBS design) is the production of $H_{2(g)}$ and the reducing conditions set up by steel corrosion. Some smectites (such as that present in the Kutch bentonite) contain Fe(III) and it has been noted that if smectite with high Fe(III) content is present in an EBS, there could potentially be reduction of Fe(III) resulting in changes in the clay structure and properties (Anastácio et al., 2008). Studies suggest that Fe(III) reduction in smectite octahedral sheets results in a reduction of swelling and an increase in cation exchange capacity (e.g. Stucki, et al., 1984; Chen et al., 1987; Lear and Stucki, 1989; Khaled and Stucki, 1991).

7.2 Copper

Copper has been considered as a canister material by a number of radioactive waste management organisations (in Sweden, Finland, and Canada, for example).

Diffusion of copper into bentonite is a slow process. It has been suggested that it could result in an increase in hydraulic conductivity (2-5 times), but given the extremely low hydraulic conductivity of compacted bentonite prior to any alteration, it may be considered to be insignificant (Pusch, 1982).

More recent work also suggests that truly detrimental effects due to copper-bentonite interactions on physicochemical properties have not been noted and that it is unlikely there will be any deleterious effect (this is the case for all alloys/metals with low corrosion rates (e.g. Karnland et al., 2000; SKB, 2006b). Experimental work reported by Carlsson (2008) also suggests little changes to bentonite due to interaction with copper. Although Cu^{2+} may exchange for interlayer Na^+, exchange constants indicate that this is likely to be minor (Zhang and Sparks, 1996). There is also some limited evidence that copper may move into bentonite (SKB, 2009b). However the alteration of 2:1 smectite layers due to the presence of copper is not envisaged.

7.3 Key Points

- ▲ It is unlikely that the interaction of copper (and other corrosion-resistant metals) with bentonite will result in any significant alteration of 2:1 smectite layers.

- ▲ The dissolution of iron and steel corrosion products could plausibly result in the alteration of the smectite component of bentonite, to non-swelling iron-rich minerals, especially at steel-bentonite interfaces. The significant alteration of smectite to non-swelling iron-rich phases may be deleterious to the performance of an EBS. However, some possible reactions pathways include the formation of iron-rich smectite/vermiculite which may retain some (limited) ability to swell. The precise mechanisms and kinetics of alteration of smectite such as montmorillonite to iron-rich silicates is not particularly well-understood.

- ▲ An increase in bentonite porewater pH at the bentonite-steel interface could occur as corrosion progresses, resulting in the alteration of smectite to non-swelling feldspathoids (e.g. analcime) or zeolite minerals.

- ▲ Other iron-bentonite interactions could potentially occur that may be deemed undesirable, such as competition between Fe(II) and radionuclides for sorption sites and possible cementation effects due to the growth of corrosion products.

- ▲ If bentonite barriers are used which include a significant amount of Fe(III)-smectite, steel corrosion could result in Fe reduction and changes in the crystal structure and physical properties of the clay.

- ▲ There is much room for further work on iron-bentonite interactions, including:
  - Experiments to measure rates of alteration and to verify mechanisms by which smectite may be altered to different iron-rich minerals (this would enable geochemical reactive transport models to be improved).
  - Experiments to measure thermodynamic properties of iron-rich clay minerals (this would reduce uncertainty associated with geochemical modelling).
  - Reactive transport models could be further developed in order to include systematic considerations of the effect of pore water chemistry, cation exchange and porosity models on predicted bentonite alteration.
  - Natural analogue studies.

8 Cement-Bentonite Interactions

8.1 Processes and Effects

Concerns about the potential deleterious interactions between cement/concrete and clay in HLW/SF waste package buffers and tunnel backfills have recently led to most, if not all, waste management agencies (e.g. SKB, Posiva, Nagra, JAEA, Andra) to consider so-called 'low-pH cements' for all uses where cementitious materials are deemed to be required in geological repositories (e.g. fracture grouting, shotcrete, tunnel plugs). Moreover, most agencies have active programmes to limit and account for all uses of cement and concrete in the GDF environment (e.g. Hagros, 2007).

Because of these concerns, cement-clay interactions have been studied extensively in the last ten years, through laboratory experiments (e.g. Johnston and Miller, 1984; Madsen, 1998; Ichige et al., 1998; Kubo et al., 1998; Fujiwara et al., 1998; Vigil de la Villa et al., 2001; Ramírez et al., 2002; Nakayama et al., 2004; Yamaguchi 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 relevant analogue investigations (e.g. Tinseau et al., 2006; Arcilla et al., 2009; Honrado et al., 2009; Savage et al., 2010b). However, it should be noted that most, if not all these studies, have considered the interaction of OPC-type cement with bentonite, and not formulations of low pH cements, which are currently being considered in many programmes as being the preferred material for fracture grouts, shotcrete, and tunnel plugs in repositories for HLW/SF. The fundamental principle in the production of low pH cement is that the amount of cement is reduced by substitution of materials such as fly ash, blast furnace slag, silica fume, and/or non-pozzolanic silica flour. The lower cement content reduces the heat of hydration through removal of the portlandite component of the cement. The lack of free portlandite ensures that the pH of entrained pore fluid is also reduced, from greater than 12.5 to less than 11. Because low pH cement has little, or no, free portlandite, the cement consists predominantly of calcium silicate hydrate (C-S-H) gel. However, there are actually very few published works on low pH cement (e.g. Savage and Benbow, 2007), especially review or 'consensus' documents from which an overall perspective on their properties and applicability can be drawn.

There are also some useful reviews extant, especially from a PA perspective (e.g. Takase, 2004; Gaucher and Blanc, 2006; Savage et al., 2007; Alexander and Neall, 2007; Savage and Benbow, 2007; Gribi et al., 2008). Taking the lead from these reviews, most authors agree that the most important processes in defining the spatial and temporal extent of cement-clay interaction and consequent changes in bentonite properties are:

- Diffusive transport of cement pore fluids into bentonite/clay, with mixing and reaction with the clay pore fluids. Sharp gradients in pH (and PCO_2) across the interface encourage the rapid precipitation of solid carbonates, such as aragonite and calcite, and hydroxides such as brucite ($Mg(OH)_2$), leading to a decrease in porosity.

- Fast exchange of cations in cement pore fluids (principally K, Na, and Ca) for cations (mainly Na^+ in bentonite) in interlayer sites in montmorillonite, leading to a decrease of swelling pressure. These exchange reactions advance in front of dissolution-precipitation reactions (e.g. Fernández et al., 2009).

- Fast protonation-deprotonation reactions at clay edge sites. Typically, such sites can neutralise 55 moles of hydroxyl ions per cubic metre of MX-80 bentonite (at 2000 kg m^{-3} water-saturated compaction density).

- Slow dissolution of montmorillonite and other minerals present, such as quartz, feldspars, pyrite, and gypsum. At elevated pH, such reactions consume hydroxyl ions, thus chemically neutralising the advancing cement pore fluids. These reactions lead to an increase in porosity and may decrease clay swelling pressure due to mass loss.

- Precipitation of secondary minerals such as clays, hydroxides, carbonates, calcium silicate hydrates, and aluminosilicates, such as zeolites and feldspars (e.g. Savage et al., 2007). These minerals may form in a zonal fashion, with relatively more siliceous zeolites (clinoptilolite, phillipsite) more likely to form at lower pH (distal regions of migrating cement pore fluids), whereas C(A)SH, illite, feldspars, and the more aluminous phases (analcime, heulandite) are more likely to form at higher pH and hence, the more proximal regions of migrating cement pore fluids (e.g. Figure 8.1).

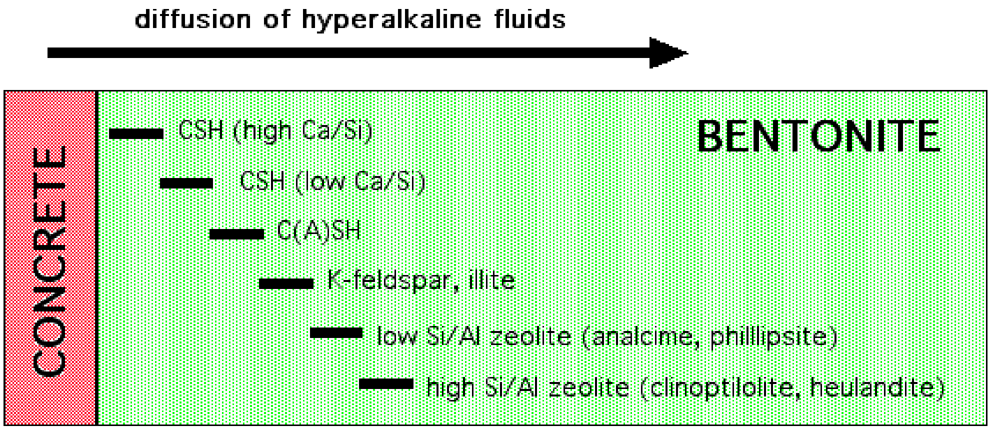


Figure 8.1: Schematic diagram of the potential sequence of secondary minerals due to the migration of hyperalkaline pore fluids through bentonite. As the composition of cement pore fluids evolves with time, sodi-potassic phases will be replaced by more calcic varieties. From Savage et al. (2007).

These reactions can result in the following changes to bentonite properties.

▲ Porosity: a recent review of laboratory experimental and analogue data of cement-clay interfaces (Savage, in press) noted that systems dominated by diffusion produce porosity decreases in clay, regardless of pore fluid type (e.g. Fernández et al., 2009; Tinseau et al., 2008). Moreover, reaction-transport simulations of clay with calcic cement pore fluids (i.e. those typical of low-pH cements) all show decreasing porosity with time such that porosity decreases to zero at some distance/time within the simulation. Typically, this time is a few hundred or a thousand years.

▲ Hydraulic conductivity: Hydraulic conductivity is not calculated in reaction-transport simulations of cement-clay interactions, and where it has been measured in laboratory experiments, the measurements have been carried out under unrealistic conditions (e.g. with circulation of high pH fluids under advective conditions - Savage, in press). Since porosity is predicted to decrease with time due to cement-clay reactions in diffusive transport conditions, similar changes to hydraulic conductivity are to be expected.

▲ Swelling pressure: A reduced swelling pressure in bentonite (30-80 % lower than initial) has been measured due to exchange of Ca for Na in smectite interlayers in laboratory experiments where compacted bentonite has been contacted with cement or cement pore fluids (e.g. Karnland, 1997; Sugiyama and Tsuji, 2008). Ion exchange fronts generally move in advance of fronts of mineralogical alteration by a few centimetres, depending upon time and transport properties (e.g. Fernández et al., 2009; Tinseau et al., 2006).

▲ Mineralogical composition: Data from model simulations show similar mineral alteration sequences (e.g. Figure 8.1). This sequence of alteration has not been confirmed by laboratory experiments, but this may be a function of their relatively short duration and hence the small scale of alteration. Evidence from a 125 year-old industrial analogue of clay-cement (OPC) interaction at Tournemire shows a sequence of calcite, gypsum, Na-zeolites, and K-feldspar with increasing distance across a 2-3 cm zone of claystone adjacent to a cement contact (Tinseau et al., 2006). However, this interface is notable for the absence of CSH-type minerals. Simulations with pore fluids with pH ≥ 13 contain appreciable proportions of Na/K-bearing minerals such as analcime, K-feldspar, Na/K-zeolites, and illite (e.g. Savage et al., 2002).

Previous studies have highlighted that cement-bentonite interactions are strongly non-linear, with a complex interplay between fluid transport, clay ion exchange and dissolution, secondary mineral growth, and consequent changes in physical properties (porosity, permeability, and swelling pressure) of the bentonite (Figure 8.2).

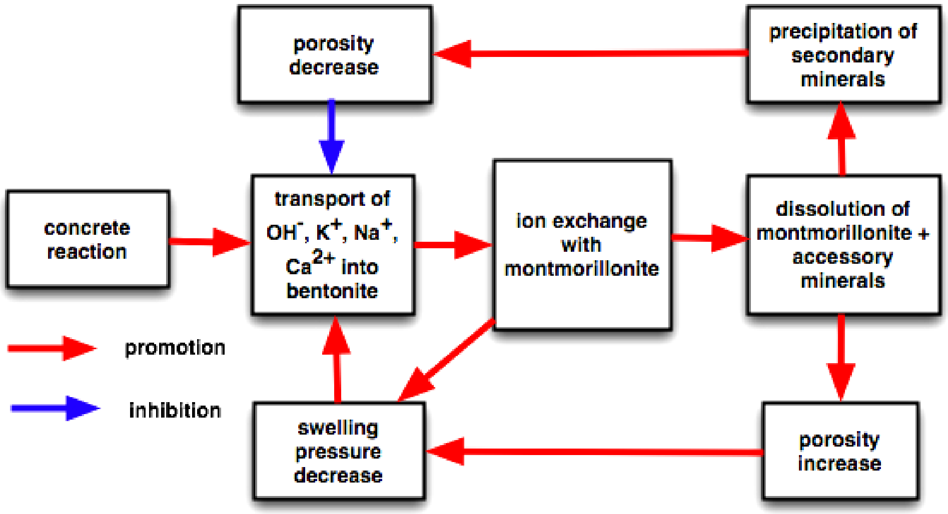


Figure 8.2: Cement-bentonite interaction as a coupled non-linear system. After Takase (Takase, 2004).

This behaviour means that it is difficult to predict long-term behaviour and materials properties from short-term experimental data. Potential impacts upon long-term properties of clay through interaction with cement have thus been assessed previously either by using simple bounding assumptions, such as limitation by mass balance, kinetics, and/or mass transport, or by coupled modelling of reaction and transport processes. These bounding assumptions are considered below.

8.2 Mass Balance Considerations

The dissolution of montmorillonite in a hyperalkaline solution (pH > 10) can be formulated as follows (e.g. Savage et al., 2007; Gribi et al., 2008):

$$\begin{aligned}&\mathrm{Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 2H_2O + 4.68OH^- \Rightarrow}\\&\qquad \mathrm{0.33Na^+ + 0.33Mg^{2+} + 1.67Al(OH)_4^- + 4HSiO_3^-}\end{aligned} \tag{8.1}$$

It thus takes 4.68 moles of OH^- to dissolve one mole of montmorillonite, assuming no other hydroxide-consuming or generating reactions occur (e.g. through the dissolution of accessory minerals in bentonite, or the precipitation of secondary minerals), and that no dilution of OH^- in groundwater takes place. Consequently, the mass of dissolved montmorillonite (kg) can be calculated as follows (e.g. Gribi et al., 2008):

$$\text{dissolved montmorillonite} = \frac{\text{mass of concrete} \times n\mathrm{OH^-} \times M}{4.68} \tag{8.2}$$

with $n\mathrm{OH^-}$ being the amount of OH^- released per kg of concrete and M being the molar mass of montmorillonite ($M = 0.367$ kg mol^{-1}).

Using the above formula, Gribi et al. (2008) in an assessment of cement-clay interactions for the KBS-3H concept, calculate maximum amounts of hydroxide a degrading cement grout is able to generate and the amount of montmorillonite it is subsequently able to dissolve per disposal drift. Consequently, if the total amount of cement in a drift is 2630–3950 kg, 15052 moles of OH^- can be generated (at most) by this amount of low pH cement. These OH^- ions are potentially capable of dissolving 1185–1780 kg of montmorillonite, which is equivalent to 1475–2224 kg of bentonite (assuming 80 wt % of montmorillonite in bentonite). The total amount of bentonite in a drift (not even taking into account the backfilled sections) is about 1 055 000 kg, so the dissolved bentonite represents 0.1–0.2 % of the total bentonite inventory.

8.3 Kinetic Considerations

Montmorillonite dissolution is a slow reaction, such that its rate could provide a constraint on how much clay could be dissolved in contact with cement/concrete. The dissolution rates of most aluminosilicate minerals are accelerated by increasing OH^- concentrations at pH > 8 (e.g. Lasaga, 1984). A number of studies of montmorillonite dissolution at alkaline pH under far-from-equilibrium conditions have been carried out in recent years. The results of studies carried out at or near room temperature are summarised in Figure 8.3. These data were all acquired in experimental systems with small amounts of clay contacting large amounts of pH buffer solutions.

Although the data in Figure show considerable variation (across three orders of magnitude at equivalent pH), reaction rates are slow, being in the order of 10^{-14} to 10^{-11} mol m^{-2} s^{-1}. It may be seen that there is a significant dependence upon pH (OH^-), broadly described by rate being proportional to $[H^+]^{-0.3}$. This implies that the rate of dissolution of montmorillonite is a factor of 8 greater at pH 11 than at pH 8 (ambient pH of bentonite pore fluids) and a factor of 4 greater at pH 13 than at pH 11.

However, this is a pessimistic scenario, i.e. that dissolution of montmorillonite occurs under far-from-equilibrium conditions at large fluid/solid ratios. In reality, the rate of dissolution would be slowed orders of magnitude by rapid approach to equilibrium in the compacted state (i.e. very low fluid/solid ratio), although the precise mechanism of montmorillonite dissolution close to equilibrium is uncertain. For example, Cama et al. (2000) identified both transition-state theory (TST) and empirical Si-inhibition mechanisms for montmorillonite dissolution which could describe their experimental data near equilibrium. Montmorillonite dissolution could be further inhibited by Al dissolved in the pore fluid, as shown for other clay minerals such as kaolinite (Oelkers, 2001), but this issue remains uninvestigated for montmorillonite.

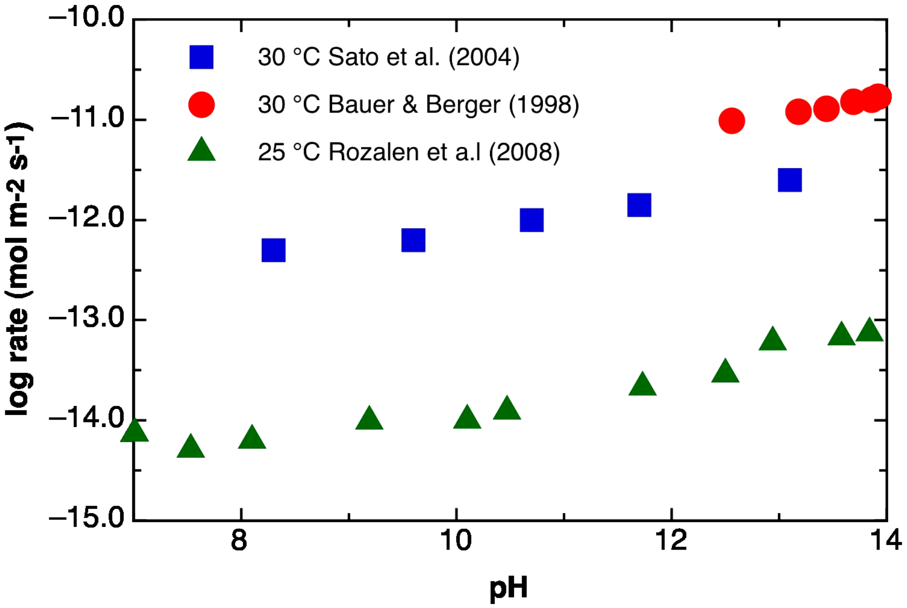


Figure 8.3: Summary of near-room temperature experimental studies of montmorillonite dissolution at alkaline pH and under far-from-equilibrium conditions at high water/clay ratios. Data are from Bauer and Berger (1998), Rozalén et al. (2008) and Sato et al. (2004).

As a contrast to the studies of montmorillonite dissolution in dispersed, high water/clay systems, Yamaguchi et al. (2007) studied the alteration of clay in compacted bentonite-sand mixes at alkaline pH and variable temperature (Yamaguchi et al., 2007). Cylindrical discs consisting of 70 % bentonite and 30 % quartz sand were compacted to a density of 1600 kg m^{-3} and reacted with NaCl-NaOH solutions of variable pH at 50 to 170°C. Extrapolating these data to pH 10 at 25 °C results in a rate of ~10^{-18} mol m^{-2} s^{-1} (i.e. approximately 50 000 times less than the rate in dispersed systems), such that 10 % alteration of the clay buffer would imply a duration of 6 million years.

8.4 Mass Transport Considerations

The dissolution of montmorillonite reaction will be limited by slow diffusive transfer of hydroxyl ions into the bentonite. Effective diffusion coefficients for solute transport through bentonite are very low, and generally less than 10^{-10} m^{-2} s^{-1}. Mass transport by diffusion will thus inhibit alkaline alteration of bentonite.

Consideration of Fick's first law demonstrates that the magnitude of mass transfer by diffusion is dependent upon the concentration difference across the medium concerned:

$$F = -D\frac{dC}{dx} \qquad (8.3)$$

where F = mass flux (mass of solute per unit area per unit time); D is the diffusion coefficient (m^2 s^{-1}); and dC/dx is the concentration gradient.

The use of low-pH cements with entrained fluids of pH ≤ 11 could thus decrease diffusive transport of hydroxyl ions by two orders of magnitude in comparison with fluids leached from OPC cement and concrete (pH ~13) because of the relative differences in hydroxyl ion concentrations in pore fluids associated with the two types of cement. This assumes immediate consumption of OH^- by dissolution reactions in the buffer/seal.

Dissolution of montmorillonite constrained by the transport of OH^- ions in and around the buffer material can be simulated by combining mass transport equations with a number of reactions, including montmorillonite dissolution, and the growth of secondary minerals in reaction-transport computer codes.

Table 8.1 summarises modelling studies carried out over the last ten years to investigate cement-clay reactions. Although the systems studied range from pure bentonite, bentonite-sand mixes, to claystones, and each was carried out with different boundary conditions (e.g. some with reaction kinetics, some without; some with a discrete cement phase included, some without, etc), there is a consistency of some aspects of the results, such as porosity closure after a few hundred to one thousand years or so, and alteration thicknesses of less than 20 cm, especially where reaction kinetics have been included, and where the initial pH is 11 or less.

Table 8.1: Summary of some cement-clay reaction-transport simulations (at 25°C) carried out over the last ten years.

Solid	Initial pH	Kinetics?	Products	Alteration depth (m)	Porosity (%)	Ref
Bentonite + sand	11.3	Yes	CSH minerals, Ca-zeolite, celadonite, calcite	0.1 @ 3.2 ka	40 -> 0 @ 3.2 ka	[1]
Claystone	13.2	No	CSH minerals, sepiolite, Ca-zeolite, illite	0.6 @ 10 ka	15 -> 0 @ 2.5 ka	[2]
MX-80 (1800 kg m^{-3})	12.5	No	Illite, zeolites, CSH minerals, saponite, chlorite	0.2 @ 100 ka	?	[3]
Opalinus Clay	13.5	Yes	Illite, calcite, CSH minerals, zeolites, sepiolite	0.1 @ 50 ka	11 -> 0 @ 0.1 ka	[4]
Bure clay	13.2	No	Illite, analcime, Ca-zeolites	0.15 m @ 25 ka	15 -> 2 @ 25 ka	[5]
Bentonite + sand	11	Yes	Calcite, CSH minerals, Ca-zeolites	0.01 @ 10 ka	40 -> 0 @ 10 ka	[6]
Bentonite + sand	10, 10.5, 11, 11.5	Yes	Calcite, celadonite, Ca-zeolites, CSH minerals	0.015 @ 1 ka (pH 11)	40 -> 0 @ 1 ka (pH 11)	[7]
Claystone	12.5	Yes	Calcite, muscovite, Ca-zeolite	< 0.02 @ 0.015 ka	Porosity decrease	[8]
Bure clay	12.5	Yes	CSH minerals, calcite, Ca-zeolites, illite, saponite, hydrotalcite	0.01 @ 0.1 ka	15 -> 0 @ 0.1 ka	[9]
Generic clay	12.5	No	CSH minerals, calcite, gibbsite	0.001 @ 0.07 ka	10 -> 0 @ 0.07 ka	[10]

[1] Savage et al. (2002). [2] De Windt et al. (2004). [3] Gaucher et al. (2004). [4] Michau (2005) and Traber and Mäder (2006). [5] Trotignon et al. (2007). [6] Ueda et al. (2007). [7] Watson et al. (2007). [8] De Windt et al. (2008). [9] Marty et al. (2009). [10] Kosakowski et al. (2009).

8.5 Key Points

- ▲ Other international agencies have now adopted (or are in the process of adopting) low pH cement/concrete as their preferred material for fracture grouts, shotcrete, and tunnel plugs in repositories for HLW/SF. Moreover, disposal facility designs aim to reduce the amounts of cement/concrete left in the system at closure (e.g. SKB/Posiva intend to remove concrete roadways and shotcrete before closure).

- ▲ The main reactions due to the interaction of hyperalkaline pore fluid (pH 10-13.5) and aluminosilicate minerals (in bentonite or rock) include cation exchange, smectite dissolution, precipitation of secondary minerals (Savage, 1997). Such reactions may result in changes in bentonite porosity, swelling pressure, hydraulic conductivity, and sorption capacity. Bentonite-cement interactions include complex, non-linear processes, making it difficult to extrapolate the results of laboratory experiments to the timescales of interest for the safety case.

- ▲ Reactive transport models may be used to predict the evolution of mineral assemblages in bentonite, but there are many uncertainties associated with the data available for such modelling, such as the growth rates of alteration products.

- ▲ Low pH cements may result in less aggressive chemical conditions, however, it is still possible that smectite alteration may occur in alkaline environments (pH 9-10), albeit much more slowly than at pH 13.

- ▲ There is much room for further research into cement-bentonite interactions, including:
  - Experimental work to reduce uncertainties concerning smectite alteration rates and bentonite degradation rates under hyperalkaline conditions.
  - Further experimental and modelling work that considers the nature and possible extent of smectite alteration at low pH cement-bentonite interfaces.
  - Simple scoping calculations for UK-specific GDF designs and conditions.

9 Bentonite Piping and Erosion

9.1 Introduction

As outlined in Section 1, the main safety functions of the bentonite buffer (in general terms) are:

- To protect the waste disposal containers by providing physical protection (against mechanical shearing for example).
- To provide a hydraulic barrier that limits the transport of water and dissolved corrosive agents to the waste, and retards the transport of radionuclides released from the waste containers in dissolved or colloidal form.

'Piping' refers to the erosion of clay along a linear feature and will take place if the following conditions are fulfilled:

- The water pressure in a fracture is higher than the total pressure in the clay and the clay's shear resistance.
- The hydraulic conductivity of the clay is low enough that water flow into the clay ceases to counteract the water pressure in the fracture.

Piping occurs before full saturation of the buffer.

'Erosion' is a different process, which takes place if drag forces on clay particles from water movement are higher than the sum of frictional and attractional forces between the particle and the clay structure. Erosion could occur as a consequence of piping, but also in the long-term (i.e. after GDF closure) at the interface between water-bearing fractures and the bentonite. Erosion will therefore affect clay gel that has penetrated these fractures during swelling. Clearly, for buffer functions to be maintained in the long-term, it is essential that buffer swelling closes any channel opened by piping. This will be the case if mass transfer by buffer swelling is greater than the erosion/piping rate and that piping does not re-occur (SKB, 2004).

Bentonite piping and erosion are processes that are primarily of interest for rocks in which groundwater flow is predominantly through fractures (i.e. higher strength rocks). However, they could occur at any point where there is a focused flow of water, for example where the backfill or buffer is in contact with a fracture or flow channel in a concrete lining that channels flow from behind the lining or if a particularly transmissive bedding plane or interbed is present in a sedimentary rock.

If transmissive features in the excavation walls are not adequately sealed, water inflows have the potential cause piping and erosion of the emplaced bentonite materials. These processes have the potential to cause significant removal of the bentonite materials and thereby, hamper barrier emplacement during GDF operation and subsequently influence the performance of the engineered barrier system. Measures commonly taken to reduce the potential for piping and erosion include grouting of inflow features, noting the potential for cementitious grouts to result in degraded performance of bentonite, and not emplacing waste packages in close proximity to identified 'major' flowing fractures, whether grouted or not. For example, SKB does not plan to make use of disposal holes that intersect fractures with a significant potential to flow.

The following text describes bentonite piping and erosion in more detail and summarises the experimental evidence for their occurrence. The potential impacts of the processes are discussed and suggestions made regarding the possible need for further research and assessment.

9.2 Bentonite Piping

Piping takes place when a critically high hydraulic gradient is built up or when the pore pressure is sufficiently high to result in hydraulic fracturing (Pusch, 2008). Bentonite materials are likely to be emplaced in repositories as pellets or as pre-compacted blocks, or in some combination of the two. The bentonite materials emplaced will only be partially saturated with water. After emplacement, as water flows into the GDF from the surrounding rocks, the bentonite will sorb more water and swell. During this phase of hydration, increasing saturation and swelling, the bentonite will exist in the form of a gel that is not physically strong. The density and strength of the bentonite will gradually increase as its water saturation increases and full swelling pressure is developed.

If water inflow to GDF tunnels and waste deposition holes is localised in fractures that carry more water than the swelling bentonite can sorb, the water pressure will act on the emplaced bentonite. Where the gel is too soft to stop the water inflow, piping will occur in the bentonite and lead to the formation of channels (e.g. Figure 9.1). In more detail, piping will occur when the water pressure in the fracture exceeds the sum of the counteracting total pressure from the clay and the shear resistance of the clay. The channels formed during piping have a strong effect on focusing water flow and this focussed flow may facilitate erosion of the bentonite.

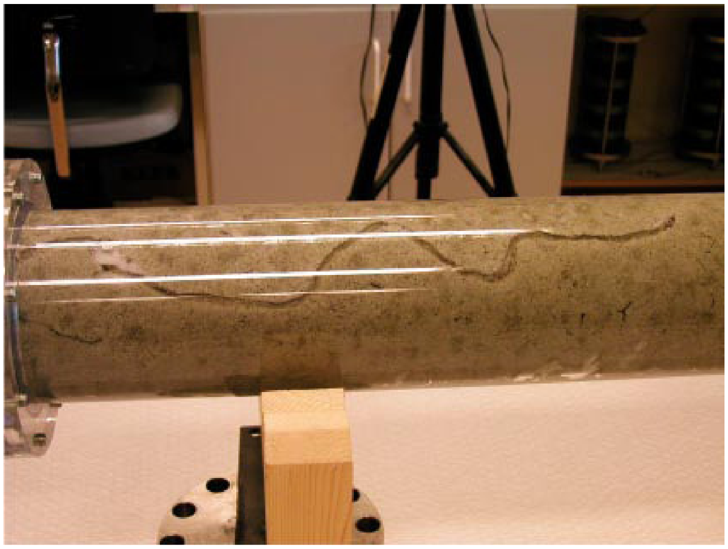


Figure 9.1: Photograph of a channel formed by piping during a test in which a 1% salt solution was passed at a flow rate of 0.1 l/min through bentonite pellets in a Plexiglas tube (Figure A13.4 of R-06-72, Börgesson and Sandén 2008).

Evidence showing the occurrence of piping has been reported by Börgesson and Sandén (2006; 2008) who undertook various small-scale laboratory tests, and by Jonsson (2008) who described some half-scale and full-scale backfilling trials that were carried out as part of SKB and Posiva's BACLO Project. Piping has also been observed in two 'field' tests conducted in the Äspö Underground Research Laboratory (URL); the LOT test (Karnland et al. 2000) and the Large Scale Gas Injection Test (LASGIT) (European Commission 2008). In addition, SKB (2006a) notes that one of the deposition holes in the Prototype Repository test at Äspö has a rather large water inflow which could be related to piping and erosion.

Börgesson and Sandén (2006; 2008) describe tests that involved placing MX-80 pellets in tubes and in artificial slots, and similar tests with tubes involving 30/70 mixtures of bentonite and crushed rock (Figures 9.2 to 9.5). These tests were designed to study the behaviour of bentonite backfill materials when exposed to different water flow rates and water salinities. One experiment was also conducted with the aim of examining the ability of a bentonite-crushed rock mixture to self-seal by swelling after piping had occurred.

Figure 9.2: Photographs of bentonite pellets in a Plexiglas tube being filled with water (left) and of a channel later formed by piping (right) (Figure A14.4 of R-06-72, Börgesson and Sandén 2008).

Figure 9.3: Photographs of bentonite pellets in a Plexiglas tube being filled with water (left) and of channels later formed by piping (left and right) (Figure A16.4 of R-06-72, Börgesson and Sandén 2008).

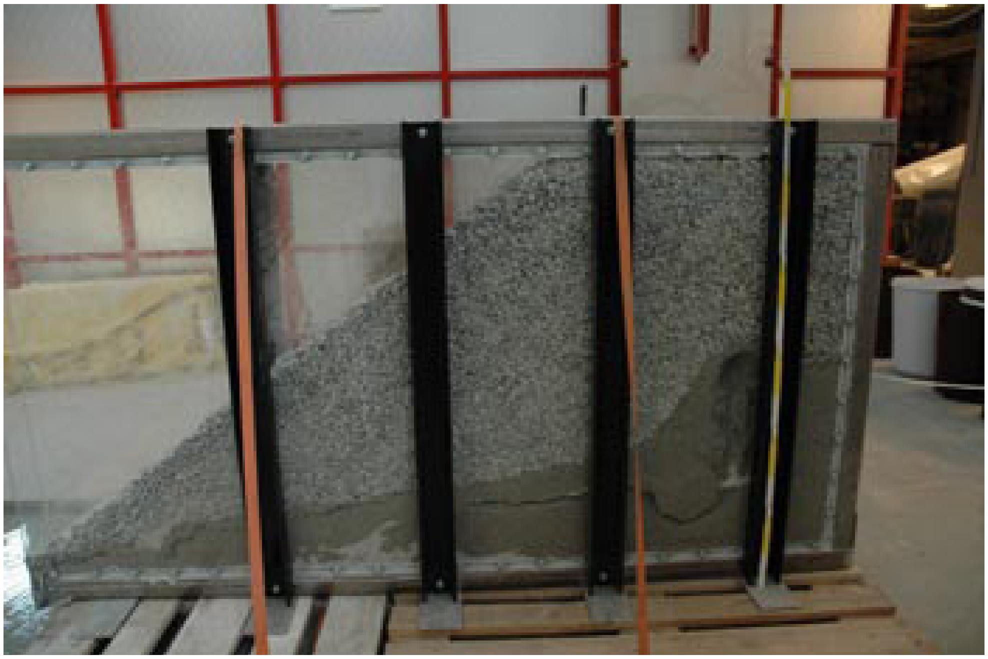


Figure 9.4: Photograph of bentonite pellets placed in an artificial Plexiglas fracture being filled with water. Note the localisation of wetting and the formation of a channel by piping (Figure A27.1 of R-06-72, Börgesson and Sandén 2008).

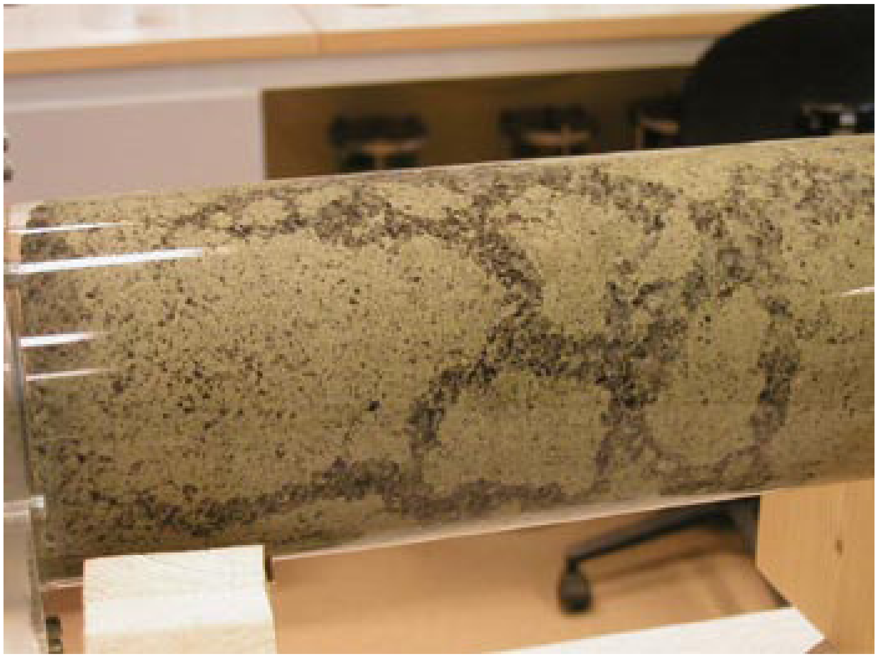


Figure 9.5: Photograph of channelled water flow through a mixture of MX-80 bentonite and crushed rock in a Plexiglas tube (Figure A20.3 of R-06-72, Börgesson and Sandén 2008). In the channels the bentonite was washed out leaving behind the crushed rock.

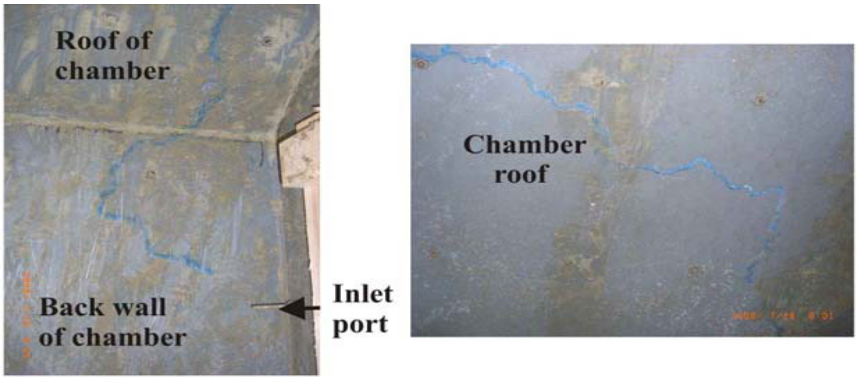
Piping and strongly channelled flow were observed in six of the eight tests that involved placing MX-80 pellets in the Plexiglass tubes. In the other two of these tests, the swelling of the bentonite was sufficiently fast to seal off any flow paths and prevent piping. These latter tests involved the lowest water flow rates (0.001 L min^{-1}) and a test with a low flow rate (0.01 L min^{-1}) and salt water (3.5%).

In the strict sense, piping was not observed in the tests with 30/70 mixture of bentonite and crushed rock, but in one case channelled flow occurred where the bentonite had been partially eroded out of the tube leaving behind flow paths containing only crushed rock (Figure 9.5). Börgesson and Sandén (2008) report that the ability of the bentonite-crushed rock mixture to heal such channels as the remaining clay expands was very low.

Jonsson (2008) described results from tests performed in the surface-based Clay Laboratory at Äspö. Half-scale and full-scale mock-ups of tunnels were backfilled using a combination of pre-compacted bentonite blocks and bentonite pellets. Water was then injected at various locations on the outer surface of the backfilled volume to represent the flow of groundwater inwards from the surrounding host rock. In some of the tests a blue dye was used to leave a visible record of the water flow paths.

Various observations were made during the tests, including significant channelled rapid flows of water through the backfill material. The backfill material had a very low resistance to incoming water. Water entering the tunnel tended to move along the contact between the backfill and the tunnel wall, rather than moving towards the central areas of the backfilled tunnel.

Dye was seen to arrive at the front surface of the test very quickly after injection, and after partial dismantling, the dye provided evidence of channelled flow (Figure 9.6). Most of the water flowed in a single channel. However, in this period when the bentonite had not reached full water saturation, only small amounts of bentonite were eroded away.



(a) Test 11 showing flow path along back wall and roof of chamber

(b) Test 12 showing flow path along wall of chamber

Figure 9.6: Photographs of the inner surface of the bentonite backfill after partial dismantling of a half-scale tunnel mock up. Blue dye shows evidence of channelled flow (Jonsson 2008).

9.3 Bentonite Erosion

9.3.1 Introduction

In the context of this report, the process of bentonite erosion may be thought of as the removal of bentonite from an engineered barrier in groundwater. Bentonite may be eroded in the form of colloids or larger particles.

Bentonite erosion may be caused by various physical and chemical processes. For example, bentonite may be eroded as a result of chemical processes that lead to bentonite swelling and the formation and dispersion of colloids at the bentonite-water interface, or as a result of shearing by flowing water (if flows are fast enough). Bentonite erosion is dependent on the composition of the clay and the salinity and composition of the aqueous phase.

Over the last few years, very significant research programmes have been running in Scandinavia to investigate bentonite erosion (e.g. Neretnieks et al. 2009). The following sections outline some of this research and summarise key points.

9.3.2 Experimental Studies

Expansion of bentonite and colloid formation

When bentonite is placed in contact with water it has a tendency to swell. Figure 9.7 shows how different bentonites (smectites containing particular counter ions) swell in deionised water. Smectite containing monovalent Na^+ or K^+ ions swell considerably, whereas smectites containing divalent ions (Ca^{2+}, Mg^{2+}) swell much less.

If bentonite is contacted by dilute water, salts initially in the bentonite pore water may diffuse out into the surrounding water and be dispersed. The ion concentration at the bentonite-water interface may then decrease and a stable colloidal suspension of clay can form due to repulsive forces between the clay particles (Neretnieks et al., 2009).

Figure 9.8 shows results that illustrate the formation of a colloidal suspension of bentonite. The tests involved placing 0.2 g of bentonite at the bottom of a test tube and contacting this with 10 ml of deionised water. The clay was allowed to swell and expand into the water giving a smectite volume fraction of 0.7 %. A thin, very fine filter with nominal pore size of 10 μm, was then fastened in the tube at the top of the gel/sol. The tubes were then filled to the top with water of different compositions. After one day the tube was turned upside-down. The response was easy to observe visually within 5 minutes. Either the clay dispersed and started to fall through the net or else it stayed above the net.

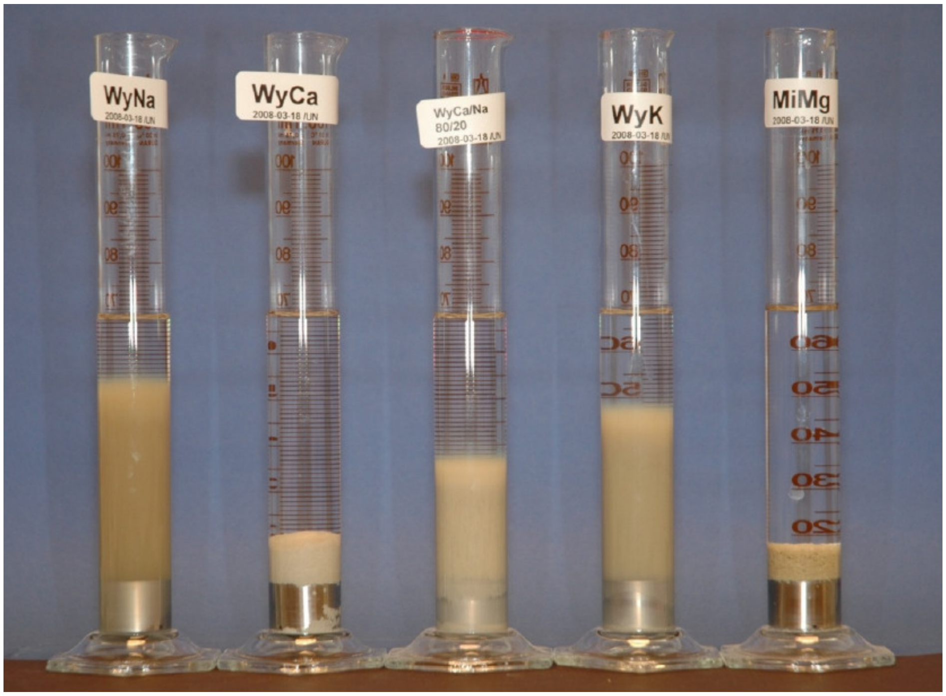


Figure 9.7: Free swelling tests with pure montmorillonites with only Na^+ as counter ion (left), only Ca^{2+} as counter ion (second from left), with a Ca^{2+}/Na^+ ratio of 80/20 (middle), with only K^+ as counter ion (second from right), and with only Mg^{2+} as counter ion (right) (Neretnieks et al., 2009).

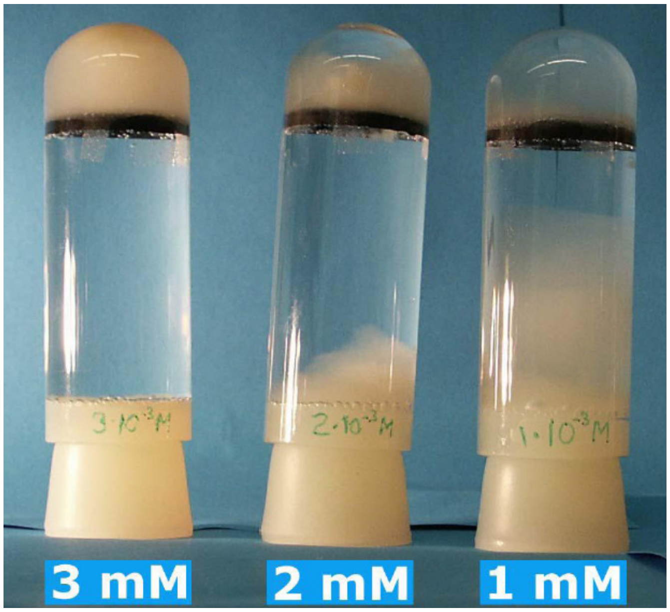


Figure 9.8: The influence of dissolved calcium concentration on the formation and stability of sodium smectite colloids (Neretnieks et al., 2009).

The various tests performed show that stable suspensions of bentonite colloids can form, and that the stability of the colloids in these suspensions depends in a complex way on the concentrations of ions in the aqueous phase.

In colloid science it is common to define a Critical Coagulation Concentration (CCC) in terms of the concentration of a key dissolved ion (e.g. Ca^{2+}) below which colloids are stable in solution, and above which colloids tend to agglomerate into larger particles that then settle under the influence of gravity. Research on bentonite colloids suggests that a simple formulation of the CCC may not be sufficient and that, instead, the stability of bentonite colloids may need to be described in terms of several factors.

Figure 9.9 is a diagram developed by Clay Technology that illustrates the possible stability limits of colloidal suspensions (sols) of Kutch type montmorillonite in sodium-calcium systems (Birgersson et al., 2009). The development of such phase-type diagrams of bentonite colloid stability is new, and further research is likely to be needed to more fully understand the effects of various groundwater constituents and the behaviour of other bentonite types.

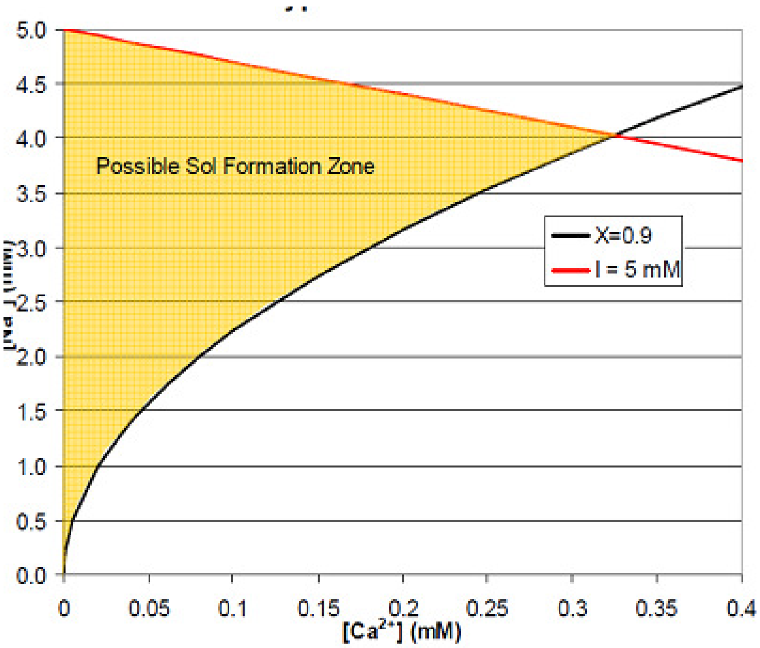


Figure 9.9: Limitations of a possible sol formation zone for Kutch type montmorillonite in equilibrium with an external Ca/Na-solution and monovalent anions (e.g. Cl^-). X indicates the mole fraction of Na-montmorillonite in the initial clay (here 0.9) and I is the ionic strength of the coexisting fluid (from Birgersson et al., 2009).

In summary, under certain chemical conditions bentonite can disperse to form stable colloidal solutions. According to Neretnieks et al. (2009), the formation of stable suspensions of bentonite colloids could lead to considerable amounts of clay being eroded away from a bentonite barrier in a repository if groundwater flow rates are high enough and groundwater salinities are low for long periods of time. Such stable colloidal suspensions could conceivably be carried very long distances without being filtered or clogging the fracture network (Neretnieks et al., 2009).

Erosion of bentonite in fractures

This section evaluates some recent experimental work performed in Sweden by SKB and its contractors to investigate buffer erosion, with the focus on if and how bentonite from the KBS-3 buffer moves into and subsequently behaves in fractures in the host rock.

Key experiments that have sought to investigate this area include:

- Glass Slit Tests (Neretnieks, 2009).
- Artificial Fracture Tests (Jansson, 2009).
- Erosion Tests (Birgersson et al., 2009).

Neretnieks (2009) investigated the behaviour of four different bentonites in a water-filled artificial fracture formed using two vertical glass plates (Figure 9.10). The glass plates were 180 by 130 mm in size and the fracture formed between the two plates had an aperture of 1.3 mm.

The bentonite was initially added as a layer at the bottom of the fracture. This was allowed to settle and swell, and then the fracture was inverted so that the bentonite layer was at the top of the fracture (Figure).

The four clay materials used in the experiments were:

- MX-80.
- MX-80 that had been washed to remove gypsum[2].
- Na-MX-80 with no accessory minerals.
- Ca-MX-80 with no accessory minerals.

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[2] The washing treatment process actually removes gypsum and clay, and so yields a material with a relatively high concentration of accessory minerals.

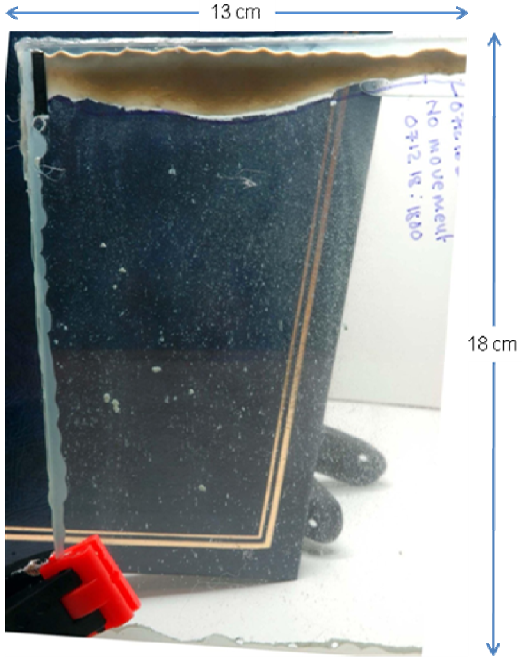

Figure 9.10: Artificial water-filled fracture formed from two glass plates with a layer of brown bentonite between the plates at the top (Neretnieks, 2009).

Observations made for the untreated MX-80 system included (Neretnieks 2009):

- In dilute waters, bentonite gel can be pulled apart by gravity to form blobs with enclosed accessory minerals, which sediment down through the fracture.
- Large blobs, which span the aperture of the fracture, are retarded by friction on the walls; small blobs (above colloidal size) sediment rapidly.
- The dimensions of the fracture influence gel formation and sedimentation.

Observations on washed MX-80 were (Neretnieks, 2009):

- The washed material does not rapidly disintegrate into a stable sol, even if the porewater concentration is below the CCC.
- Gel can be pulled apart by gravity and sediment downwards (Figure 9.11).
- *'The outer rim of the swollen gel can separate into a clear, thin gel and a more concentrated gel containing the detritus material'* (Figure 9.12).

It was also suggested that *'a tentative interpretation is that as the gel expanded upwards the detritus material expands with it, but near the edge where the gel density had decreased the smectite particles could move independently of the detritus leaving it behind. In this case, half a mm thick region of more concentrated detritus remained forming a potential filter cake.'*

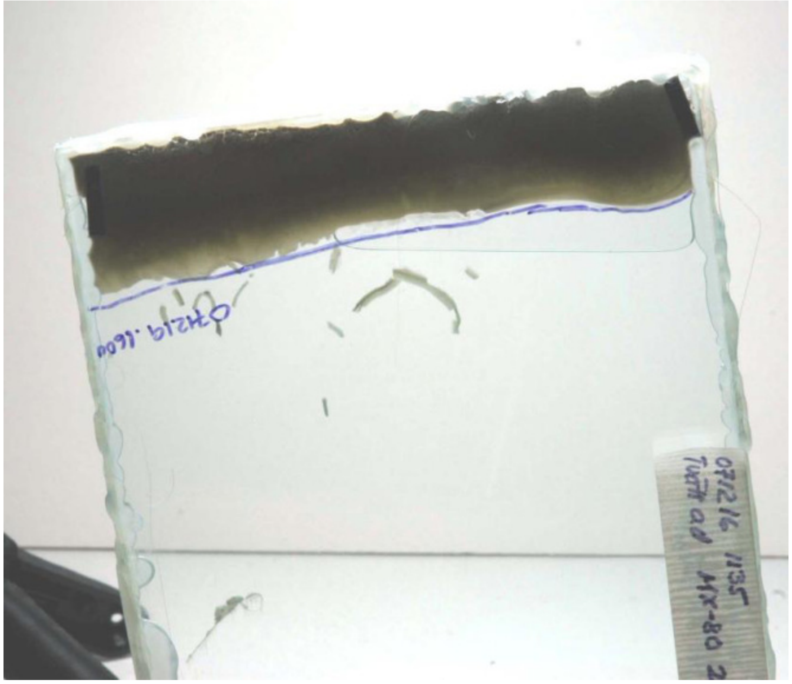

Figure 9.11: Artificial water-filled fracture formed from two glass plates with brown bentonite between the plates at the top, showing the formation and settlement of blobs and worms of bentonite (Neretnieks, 2009).

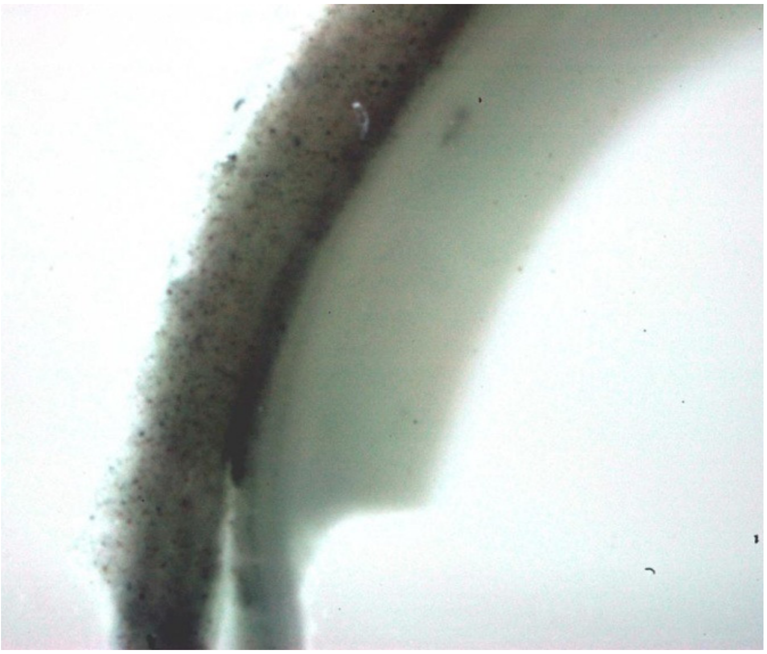

Figure 9.12: Close up of the bentonite gel worm showing variation in the amount of dark accessory minerals (Neretnieks, 2009). Note Neretnieks calls the structure a gel but arguably it could be termed a sol.

While the experiments illustrate the effects of gravity on clay gels and demonstrate settling of relatively large clay particles (well above the colloidal size range), the glass plates do not provide a good representation of a real fracture of the type and dimensions likely to be found in a GDF host rock. In particular, the aperture of the artificial fracture used in the experiments was rather large and the results of the experiments may have been influenced by the experimental set-up. Neretnieks (2009) suggests that the accessory minerals in the bentonite material could slow the expansion of smectite towards the bentonite gel/water interface. However, the evidence presented for this is not clear, and the interpretation of the experiments as showing the formation of a potential filter cake is not conclusive.

The experiments on the system with Na-MX-80 and no accessory minerals failed because of leaks and air bubbles. Also some anomalously high Ca concentrations were observed that were hard to explain given that the bentonite was a Na-type.

Observations made in experiments on the system with Ca-MX-80 and no accessory minerals showed aggregation and settling of clay aggregates in waters of ~1 mM Ca, which SKB assumes to be close to the effective CCC for this particular system.

Jansson (2009) described some more elaborate experiments, this time with an experimental set-up designed to represent bentonite swelling and erosion in a horizontal fracture (Figure 9.13). Bentonite that had been washed to remove gypsum was compacted to a density of 1,000 kg m^{-3} in a container attached on one side of a 0.1 to 1.0 mm wide fracture, through which distilled water was pumped (Figure). The bentonite container had a separate water supply, which was used to saturate the bentonite. Two experiments were conducted; the first with a truly horizontal fracture and the second with the fracture inclined by 2 to 3 degrees down towards the inlet in order to try to allow some air bubbles that had formed to escape to the outlet.

Photographs of the experiments are shown in Figure 9.14 and Figure 9.15, which have been annotated to highlight key aspects. The photographs are taken from above the horizontal fracture and are oriented so that the water flow through the fracture appears to be down the page and the bentonite appears to be swelling out of its container into the fracture from the right hand side of the page.

The first experiment (Figure 9.14) shows the erosion of bentonite and the dispersion of bentonite colloids and particles, described by Jansson (2009) as a sol, into the water flowing in the fracture. Also seen in this experiment is the development of a discontinuous layer of darker and relatively feldspar-rich material close to the bentonite gel/sol interface.

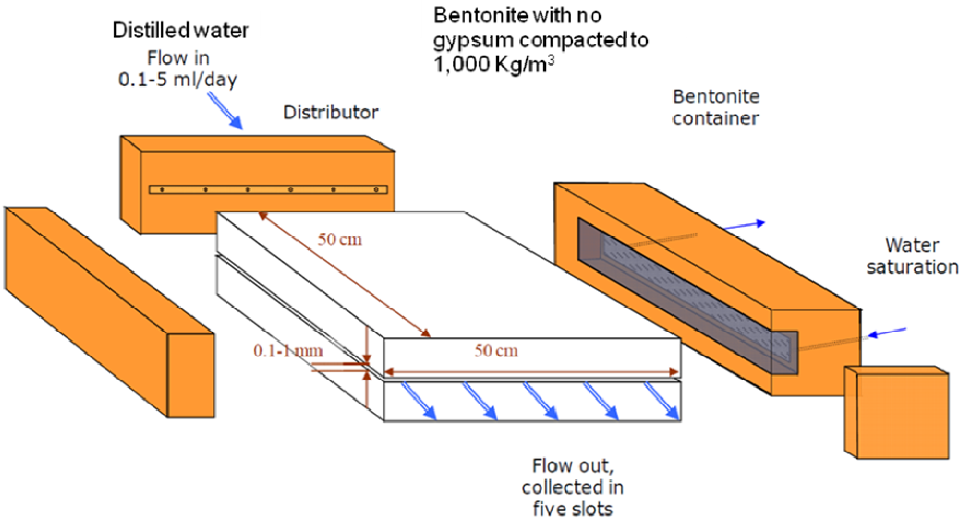

Figure 9.13: Diagram of the experimental set-up for the artificial fracture tests of Jansson (2009).

The second experiment, having a slightly inclined fracture, illustrated some further processes in addition to those observed during the first experiment. As well as bentonite swelling, bentonite erosion and the formation of a discontinuous layer of darker and relatively feldspar-rich material close to the bentonite gel/sol interface, dispersed bentonite was seen to move within the fracture towards the flow-inlet side of the fracture under the influence of gravity (Figure 9.15). The dispersed bentonite affected the water flow pattern, which became channelled, as shown by the use of blue dye (Figure 9.15).

The concentration of colloids at the fracture outlet is quoted as being < 0.18 g L^{-1}, and the colloids reaching the outlet were measured as < 200 nm in size and mostly < 100 nm in size (Jansson 2009).

As noted above in respect of the scoping experiments of Neretnieks (2009), this experimental set-up still does not provide a good representation of a real fracture of the type and dimensions likely to be found in the GDF host rock, but nonetheless these experiments have produced some interesting observations on the processes that can occur as bentonite swells and is eroded in a fracture. The observations of potentially complex, time varying water flow patterns through fracture areas that contain dispersed bentonite are important, and various similar effects (e.g. fingering) might be envisaged.

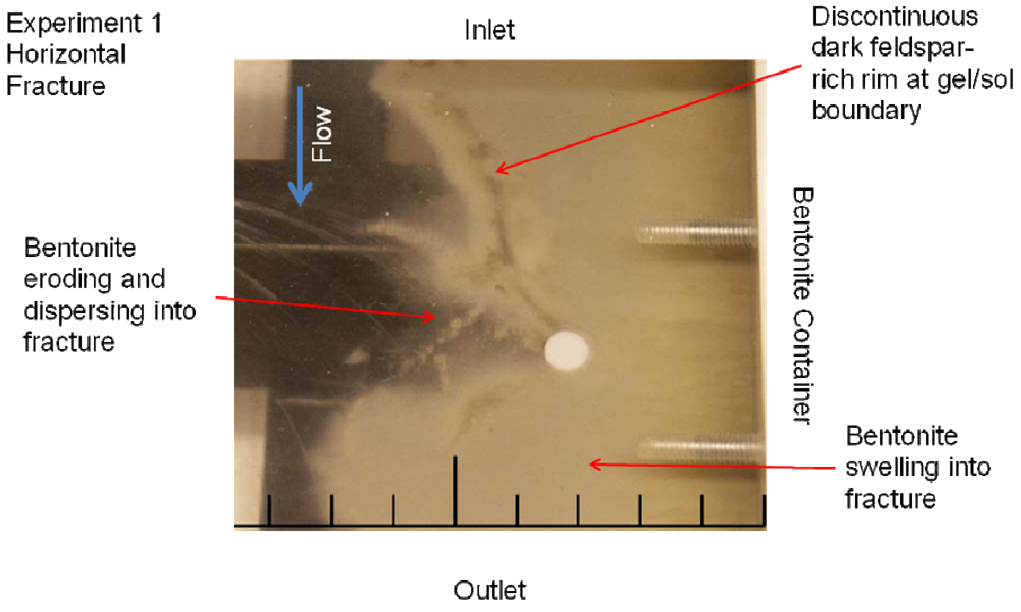

Figure 9.14: Annotated photograph of the first the artificial fracture tests of Jansson (2009).

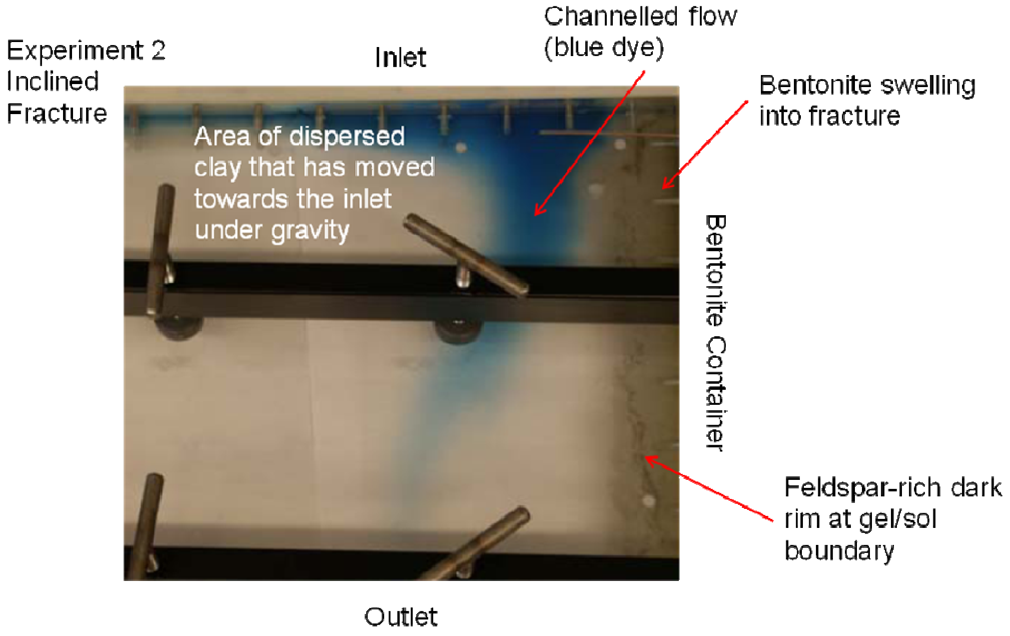

Figure 9.15: Annotated photograph of the second the artificial fracture tests of Jansson (2009).

In more detail, the density of the bentonite in the experiments was lower than is planned for the waste deposition holes in the Swedish KBS-3 repository, and so in this respect the experiments may give the impression of less bentonite swelling (and possibly less bentonite erosion) than may occur in the repository system. However, the experiments were conducted with distilled water and the experiments may, therefore, give the impression that bentonite erosion is more likely and extensive than may actually occur in a real system containing saline, or slightly saline, groundwater.

A further uncertainty is that the experiments were conducted with atmospheric levels of CO_2, which will have influenced the solubility of calcite, the concentrations of Ca^{2+} in the waters, and possibly had an effect on the stability of the bentonite colloids. Finally, there is evidence that in two-phase aqueous systems, colloids may adhere to, or collect at, the gas-water interface (e.g., Bennett et al., 1998) and so it will be important to consider the possible influence of gas on bentonite colloids.

Birgersson et al. (2009) described some experiments focussed directly on measuring the erosion of bentonite. In these experiments, various ionic solutions were circulated past bentonite clay samples and the swelling pressures exerted and the turbidity of the circulating solutions measured. Changes were made to the composition and salinity of the solutions during the experiments, and bentonite erosion was evidenced by a decrease in swelling pressure and an increase in solution turbidity. Unfortunately, however, it is not clear the observed changes in swelling pressure resulted solely from erosion, or whether some of the changes were due to changes in solution chemistry.

The clay materials used in the experiments were:

- Pure Na-montmorillonite.
- MX-80 that had been washed to remove gypsum.

The solutions used in the experiments were:

- $CaCl_2$.
- Mixtures of $CaCl_2$ and NaCl.
- $CaSO_4$.
- $CaCO_3$.
- Pure water.

Example results from these experiments are shown in Figure 9.16.

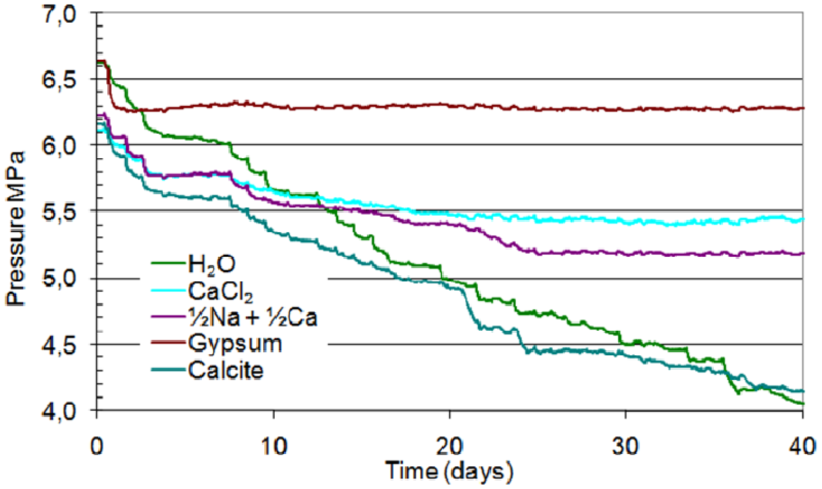

Figure 9.16: Swelling pressures measured on Na-montmorillonite samples exposed to different circulating waters (Birgersson et al., 2009).

The results indicate that (Birgersson et al., 2009):

- Erosion does not occur in the presence of gypsum, presumably because gypsum causes the solubility of Ca^{+2} in the circulating solution to be above the effective CCC in this system. Measured concentrations of Ca^{+2} in these solutions are ~16 mM.

- Erosion of Na-rich montmorillonite stopped when a solution of 5mM NaCl and < 2.5 mM $CaCl_2$ was circulated.

- Erosion of MX-80 with no gypsum stopped when a solution of 0.7 mM NaCl and 0.2 mM $CaCl_2$ was circulated.

These experiments have provided some point observations on specific chemical conditions that may prevent bentonite erosion. However, because of the experimental set-up in which the bentonite samples were physically held in the apparatus beneath a metal gauze or filter, they have not really provided information on physical erosion of bentonite.

9.4 Bentonite Piping: Key Points

- Although relatively few experiments on bentonite piping have been conducted to-date, consistent results have been obtained at a range of scales, including laboratory, URL and 'field' test scales, and these results show that bentonite piping is likely to occur, particularly for disposal facilities with bentonite barriers constructed in fractured host rocks with active groundwater flow systems. It is unlikely to be a problem in clay- or mudstone-hosted disposal facilities.

- Bentonite piping is primarily driven by fluid pressure gradients. Water pressure gradients that could cause piping are most likely to occur early in the history of a GDF (i.e., during construction, operation, and in the period before re-saturation is complete), particularly in fractured host rocks where water flows will tend to be focussed. Such fluid pressure gradients will tend to decline over time as the GDF re-saturates.

- Bentonite piping is influenced by water flow rates, the properties of the bentonite or bentonite-based materials used, and by water salinities and compositions.

- SKB (2006) argues that for their host rock and design, piping will not occur after repository is fully re-saturated because pressure gradients will have reduced.

- The potential effects of gas production as a possible cause of bentonite piping (because gas production may influence repository saturation and fluid pressure gradients) are currently uncertain and, depending on the disposal concept(s), these issues may need to be investigated.

- Once the system has re-saturated, there is a question as to how well the remaining bentonite will re-homogenise and achieve uniform hydrogeological and mechanical properties. The degree of re-homogenisation and sealing of any former channels will depend on various factors, principally including the swelling of bentonite that has not been eroded away but remains around the channels. Almost no data are available on bentonite re-homogenisation following piping or erosion, but the planned excavation of the Prototype Repository facility at the Äspö HRL may provide some data of this type.

- The likely occurrence of bentonite piping would need to be taken into account when designing the engineered barrier system and planning its installation. A key concern is that piping (should it occur) must not prevent the achievement of sufficient tunnel backfill densities. Significant loss of mass through piping will mean that the backfill cannot fulfil its long-term hydrogeological barrier functions. Another concern is that appropriate backfill emplacement procedures would need to be developed and followed so that piping does not unduly hinder GDF operations – the procedures will need to manage the effects of piping, for example in causing localised water flows, inhomogeneous wetting of the backfill, and backfill erosion into the GDF excavations.

- The likely occurrence of bentonite piping is one of several technical arguments related to the KBS-3 design in favour of backfilling and closing sections of the repository in which waste has been emplaced as soon as possible.
- Research and development work on bentonite piping is continuing within Scandinavia. If bentonite barriers form part of design concepts selected for the UK GDF, then further research and development work is likely to be needed here to take account of the particular disposal concepts, engineered barrier materials and designs selected, and to take account of environmental conditions that might occur in the disposal system.

9.5 Bentonite Erosion: Key Points

- In very general terms, bentonite erosion is more likely to occur in fractured host rocks with active groundwater flow systems that contain dilute, sodium-dominated groundwaters, than in systems with less groundwater flow (e.g., in un-fractured rocks) and with more saline, calcium-dominated waters. Bentonite erosion is not an issue in diffusion-dominated systems (e.g. in clay and mudstone host rocks).
- A range of experiments has been performed (by SKB and Posiva) to investigate various aspects of bentonite swelling, erosion and dispersion. The range of experiments conducted to date is limited, understanding is incomplete, and only some areas of the issue have been addressed.
- There are questions over how relevant the experiments performed are to a real disposal system. For example, real fractures will be rough, will have various orientations, intersections and asperities, and on average may be considerably narrower than considered in the experiments. This issue of physical scale is also potentially important as none of the experiments has been conducted over length scales greater than a few centimetres.

- The occurrence and significance of bentonite erosion will depend on the disposal concept, the design of the engineered barrier system, the particular bentonite materials used (e.g. composition and emplaced density), the pattern and rates of groundwater flows within the host rock and the engineering disturbed zone, and on the chemistry of the clays and groundwaters.

- In terms of the potential significance, the uncertainties associated with bentonite erosion are considerable. If large amounts of buffer material are eroded away from the buffer, significant advective flow of groundwater could occur within a deposition hole and this might lead to much more rapid waste container corrosion. In a KBS-3 type disposal system developed in fractured rocks, the consequences of bentonite erosion could be significant to safety because the safety functions of both the container and the buffer might, therefore, be compromised.

- Further work may be needed in several areas, including:
  - To understand the role of water chemistry on bentonite colloid formation, stability and dispersion, particularly the role of dissolved Ca^{2+} in possibly preventing erosion of Na-rich clays.
  - To take account of processes not accounted for in current conceptual models (e.g., the effects of chemistry and diffusion at the bentonite/water interface during erosion, the effects of friction between bentonite swelling into a fracture and the rock, the effects of dispersed bentonite on water flow).
  - To resolve differences of view related to filtration processes. Some authors (Neretnieks, 2009) have suggested that the accessory minerals in natural bentonite materials or mineral additives (e.g., quartz) might play a role in filtering bentonite colloids and thereby in limiting their migration through fractures. There is, however, no clear evidence that supports the postulated formation of 'filter cakes' from these materials during bentonite erosion. In addition, the impacts on feasibility and on the properties of the buffer caused by adding such mineral additives have not been assessed.
  - To investigate the properties and behaviour of candidate bentonites or bentonite-based materials considered for use in the GDF.
  - To investigate site-specific groundwater flows and chemistries once a potential site or sites have been identified.

10 Influence of Composition on Performance

In this section the impact of different bentonite compositions on buffer and backfill performance are considered.

10.1 Buffer

10.1.1 Introduction

The buffer material should be chosen to ensure that there is confidence that it will perform the safety functions required as part of the KBS-3 concept:

- limit advective transport;
- resist mineralogical transformations;
- eliminate microbes;
- prevent canister sinking;
- damp rock shear movements;
- avoid liquefaction;
- others, including allowance of gas escape, minimisation of source of potential canister corrodants (e.g. pyrite, oxygen).

In theory, a number of different types of bentonite buffer could meet these requirements.

10.1.2 Compositional Options

There are essentially two main options:

1. to use raw bentonite which is compacted under high pressure to produce dense blocks; or
2. mix granulated or powdered smectite with an ‘aggregate’.

Currently, most waste management agencies have adopted option (1) above (blocks of compacted pure bentonite) as their preferred choice, with Japan being one of the few countries to have remained with a bentonite-sand (70:30) mix as their reference design for HLW/SF, primarily owing to the greater thermal conductivity of the latter (JNC, 2000).

Bentonite-aggregate mixtures

This option (proposed in the early days of buffer design primarily due to cost considerations), involves the preparation of mixtures in which the voids between coarser (aggregate) grains are filled by clay particles (thus imparting a sealing capacity). The 'skeletal' structure does not allow much swelling because of the structural strength of the 'skeleton' and the relatively small fraction of clay, which results in a strong reduction in density and expandability of the clay component. The proportion of clay in the mixture is very important for ensuring that the voids between the larger aggregate grains are suitably filled. Ideally the aggregate should have a 'Fuller' type of grain size distribution (Pusch and Yong, 2006). If the clay component consists of very dense particle aggregates and the mixture is effectively compacted, the bulk density will be high and the hydraulic conductivity and compressibility low (Pusch and Yong, 2006). However, the bulk conductivity will be higher than for pure, unmixed bentonite because the clay particles do not fit the shape of the voids exactly meaning that the density of the fully swollen clay component will be relatively low (about 1600 kg m^{-3} at maximum).

The aggregate material can consist of mixed fractions of silt, sand, and gravel, or crushed rock, which automatically gives a Fuller-type granulometr. In the latter case, problems can arise as the crushing process, the rock fragments become coated by a thin layer of very fine rock debris which raises the hydraulic conductivity of the mixture and lowers the strength. Effective flushing with water before mixing the aggregate with the bentonite is therefore required if crushed rock is used. Special attention should be paid to the fine tail of the grain size curve. It has been shown that D5 (the maximum particle size of the fifth percentile of the grain size curve), should be less than 10 µm (Pusch and Yong, 2006).

Because of the sensitivity to mechanical disturbance, mixed buffer materials with low clay contents cannot be prefabricated in the form of stable coherent blocks, but instead require *in situ* placement and compaction. This cannot be done with the canisters already in place; instead, compaction around a temporary metal former is required. This former is then is removed to allow insertion of the canister and subsequent filling of the gap between canister and compacted buffer with quartz sand. It has been shown in AECL's underground laboratory that such an approach is feasible for mixtures of

40/60 smectite clay and uniformly graded sand placed and compacted in 50 mm layers to dry densities of up to 1800 kg m^{-3}, which corresponds to slightly more than 2100 kg m^{-3} at complete water saturation (Dixon et al, 2002). Effective compaction of mixtures with this relatively high amount of clay is difficult and clay contents in the interval 20 - 30% may be optimal with respect to density, hydraulic conductivity and resistance to compression (Pusch and Yong, 2006). Lower clay contents (<~20%) could make the buffer more sensitive to early chemically induced degradation and clay contents higher than ~40 wt.% would make *in situ* compaction ineffective. Preparation of blocks with higher clay content than about 40 % may be more attractive in terms of construction and cost.

However, there are positive aspects of constructing mixed buffers by on-site compaction compared with the block option; the placement and compaction are simpler and cheaper. Also, the tight contact between rock and buffer that is established during the construction phase is valuable because it means that insignificant radial displacements in the buffer occur in the maturation (resaturation) phase, and hence there is less requirement for a high expandability (swelling) during resaturation to fill voids. Negative aspects include the lower saturated density that may allow microbial growth in the buffer, the higher hydraulic conductivity, and the lower swelling pressure and self-sealing potential. Since SKB and POSIVA have consistently considered only crystalline rock as a host medium, the expected inflow of water in the deposition holes led these organisations to abandon bentonite-aggregate mixtures and instead focus on the block option. However, if the host rock is 'dry', *in situ* compaction may be worth considering further.

Pure bentonite

Around 30 years ago, the first studies were made on bentonite with respect to use as buffer material in a disposal facility for spent nuclear fuel. A few commercial high quality bentonites from, *inter alia*, Bavaria in Germany and Wyoming in the USA were studied. 'Wyoming bentonite' was used for studies in several countries, and a material from the American Colloid Company with the brand name MX-80 was chosen for many of these studies. The material turned out to be very suitable and much important early laboratory work on MX-80 was carried out, especially by Nagra in Switzerland, and by SKB in Sweden. Several other countries have more recently studied the properties of other swelling clays, frequently using MX-80 as a reference. Large-scale field tests in the Stripa mine and, currently, at the Äspö hard rock laboratory in Sweden have used MX-80 as the buffer material and as an admixture in tunnel backfill material.

MX-80 is not the sole source of bentonite worldwide. SKB has carried out a large amount of research recently to examine alternatives sources and compositions (e.g. Karnland et al., 2006). A conclusion from these studies by SKB is that the sealing properties vary strongly between available materials, mainly because of different contents of swelling 2:1 clay minerals, but also as a function of the type of charge compensating cations and the concentration of the test solutions.

However, at high densities, only those materials with relatively lower contents of swelling 2:1 minerals have sealing properties that would make them inappropriate as buffer material.

The large majority of the hydrothermal stability experiments have been performed on montmorillonite-rich bentonite, which is also the original major clay mineral in the Kinnekulle natural analogue. This smectite species would therefore be a natural choice and SKB has selected it for most sealing purposes in the KBS-3V concept.

SKB has defined required buffer properties, which are listed in Table 10.1.

Table 10.1: Some design requirements for bentonite buffer in KBS-3V (SKB, 2009a).

Density at water saturation, kg m^{-3}	Hydraulic conductivity (m^{s-1})	Swelling pressure, (MPa)	Montmorillonite content in % of solid mass	S-bearing minerals in ppm of solid mass*	Organic substance in ppm of solid mass*
1950-2150	<1E-12	$0.1<p_s<7$	>75	2000	2000

*Applied to the MLW repository at Forsmark (SFR) but not yet defined for HLW disposal.

SKB is considering the use of montmorillonite-rich clays of MX-80 type represented by commercially available candidate materials from North America and Mediterranean countries and from the Far East. It became obvious during analyses by SKB that natural smectite-rich clays, mostly bentonites, contain accessory minerals that can be detrimental to the long-term performance of copper and steel canisters. This led to specification of maximum allowed concentrations of sulphur-bearing and carbonate minerals as well as of organics.

Although the criteria in Table 10.1 are useful, they are, arguably, incomplete. For example, while the density is certainly an indicator of many physical properties it does not determine the stress/strain behaviour or the chemical interaction of buffer and canister.

SKB has considered other candidate materials (Pusch, 1999), including:

- Saponite (magnesium-rich trioctahedral smectite);
- Mixed-layer clay with interlayered mica/illite/montmorillonite;
- Kaolinite; and
- Palygorskite.

Saponite is one of ENRESA's candidate buffer materials and has been considered in SKB buffer research work on the grounds that clays of this type had been found to be more chemically stable in deep drillings than montmorillonite-rich smectites (Gueven et al, 1987). Mixed-layer clays may be less expandable than pure smectites but they are widely used for isolating chemical waste because of the relatively small impact of high salt contents on their performance. Kaolinite seems to resist higher temperatures, as indicated by the Stripa experiment with Fo-Ca7 bentonite (mixed layer smectite/kaolinite with kaolinite) and it has a low hydraulic conductivity and compressibility (Pusch et al, 1993a). However, unlike smectite, kaolinite layers lack the capacity for significant expansion.

Palygorskite has the ability (almost as high as that of MX-80, Pusch, 1999) to swell (although not via the same mechanism associated with smectites). However, the relationship between bulk density and swelling pressure for this material (a very steep positive correlation) would require specific attention in the design of the disposal system in which it is to be used (see Pusch, 1999).

A consideration of the overall properties of these material candidates has led to the conclusion that the most suitable buffer materials are clays rich in montmorillonite and saponite (Pusch, 1999). However, most research and development has focused on bentonites that have montmorillonite as the predominant smectite component.

One of the advantages of using pre-compacted buffer in the form of dense clay blocks is that preparation and installation in the deposition holes are relatively simpler. However, measures have to be taken to isolate the blocks from water and moist air. The pressure required to reach the desired high density of buffer blocks by uniaxial compression is on the order of 100 to 200 MPa provided that the degree of water saturation of the granular or powdered clay to be compressed does not exceed ~70 % (Pusch, 2002). Since the KBS-3V concept implies that the clay blocks ultimately expand to establish contact with rock and canister, the density of the initially only partly water saturated blocks is determined by the requirement that the saturated buffer must ultimately reach the required value, which for KBS-3V is 1950 - 2050 kg m^{-3} (SKB, 2009a), after expansion to fill these voids. Depending on the estimated risk of erosion and loss of clay material, quartz fines may have to be added to the smectite-rich buffer material prior to compaction. The coarse grains will tend to accumulate at the fracture openings and clog them (Figure 10.1), thus reducing the erosion potential.

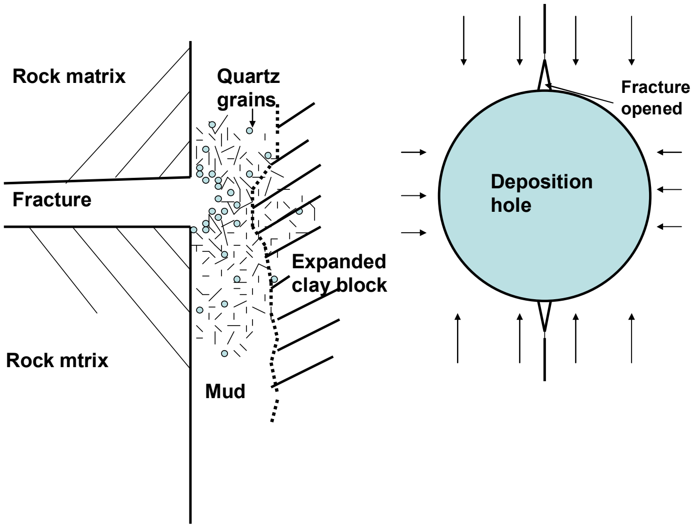

Figure 10.1: Clogging of fractures by quartz grains forming arches. Right: Deposition hole in rock with strongly anisotropic stress field that causes widening of a steep intersecting fracture into which the buffer clay can move (Pusch, 2008).

The time taken for complete hydration and maturation to occur (i.e. internal displacements occurring to even out stress differences and anomalies), depends strongly on the capacity of the host rock to provide water. In low-permeability rocks such as clay/mudstone, complete re-saturation and maturation may take many decades or centuries, while in normally fractured crystalline rock, it is estimated to take less than a century. In certain fracture-poor granites, such as the Forsmark rock proposed to host the Swedish repository, complete hydration and maturation may be as slow as in 'tight' sedimentary rock. The option of *in situ* placement and compaction of buffer with 20 - 30 % clay minerals implies different hydration and maturation rates compared with equally dense, pure clay. Since the major hydrating force is effectively the suction of the strongly hydrophilic smectite minerals (which is lower for mixed buffer), the wetting is slower in the early stage than for the dense, smectite rich option (Pusch and Yong, 2006).

10.1.3 Physical Properties

The most important physical properties of bentonite for the development of the safety case include hydraulic and gas conductivities and the canister-bearing capacity. The hydraulic conductivity is determined by the microstructure, which can be considered to be largely homogeneous for dense, smectite-rich clay and heterogeneous for mixed buffers. Table 10.2 summarises typical data of hydraulic conductivity and swelling pressure of a number of mixed buffers. The smectite content is the key parameter, followed by density.

Table 10.2: Physical data for MX-80 and mixtures of crushed rock and montmorillonite-rich clay (MX-80 and Italian GEKO bentonite) (Pusch and Cederström, 1984; Pusch 2002).

Buffer **% Clay**	**Density (at water saturation)** **(kg m^{-3})**	**Hydraulic conductivity** **(dist. water)** **(m s^{-1})**	**Hydraulic conductivity** **(Forsmark**)** **(m s^{-1})**	**Swelling Pressure** **(dist. water)** **(MPa)**	**Swelling Pressure** **(Forsmark)** **(MPa)**
100 % MX-80	2000	4E-13	2E-12	7.3	4.7
50 % MX-80	2100	1E-12	1E-11	2.0	1.0
30 % GEKO/QI	2200	1E-12	1E-11	0.9	0.5
30 % MX-80	1950	1E-11	<1E-10	0.2	0.1
10 % GEKO/QI	2350*	<1E-11	1.1E-10	0.2	0.1
10 % GEKO/QI	2200	<1E-10	3.4E-10	0.1	0.02

* The bottom clay bed for the 60000 t silo in the SFR repository for LLW/ILW waste has this density, obtained by heavy vibratory rollers.
** Forsmark brackish water composition.

The selection of a suitable buffer mixture depends on the criteria set for the performance. SKB's present criterion for maximum hydraulic conductivity ($1\ 10^{-12}$ m s^{-1}) of the buffer would only be fulfilled by 100 % clay of MX-80 type with density at water saturation of more than 2000 kg m^{-3} for the salt water case. In contrast, AECL's criterion implies a conductivity of not more than $1\ 10^{-11}$ m s^{-1}, making mixtures with 30 % smectite clay and a density of 2200 kg m^{-3} more acceptable for water compositions of a higher salinity (Pusch and Yong, 2006).

The ability of gas to escape through the buffer at pressures lower than the swelling pressure is essential. Gas bubbles with very high pressure can otherwise grow at the contact between canister and buffer and consolidate the buffer to the extent that it becomes unacceptably stiff, potentially even damaging the host rock. Gas, primarily hydrogen (H_2), will be formed by the anaerobic corrosion of metals, such as steel or iron canisters and the iron core of SKB canisters (once copper canisters have failed). Water vapour (steam) generated at the buffer/canister contact in the hydration phase may also have a degrading impact on smectite in the buffer.

The mechanisms by which gas is transported in clay buffers determine the potential for the release of gases generated at the buffer/canister interface. Gases tend to follow discrete paths and the pressure required for a pathway to become established is the key parameter, not the gas conductivity. This is obvious from experiments on different scales using smectite clay. These have shown that an amount of only 0.02 to 0.2 % of the total porewater volume is displaced before gas passes through the clay (Figure 10.2). The tests demonstrated that there is a threshold pressure for gas breakthrough that it is of the same order of magnitude as the swelling pressure (Pusch, 2008). The LASGIT experiment at the Äspö URL is a full-scale experiment that is currently investigating the transport of gas generated at the canister surface through a bentonite buffer.

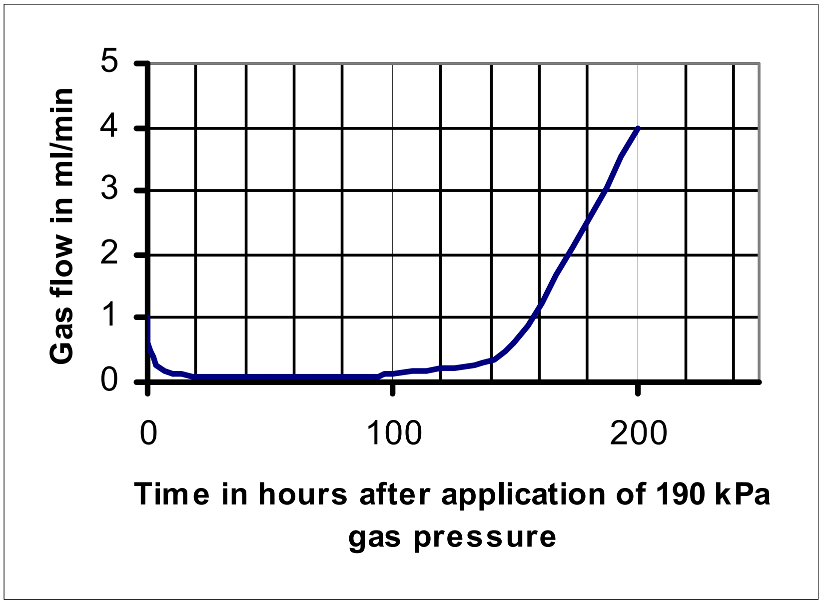

Figure 10.2: Nitrogen gas movement at the critical gas pressure 190 kPa in montmorillonite-rich clay (MX-80) with 1680 kg m^{-3} density at saturation with seawater (Pusch, 2008).

However, it is not known if a low gas pressure can result in breakthrough, and whether stepwise pressure increase gives the same results as more rapid pressurising, or whether consolidation of the buffer under slowly built up gas pressure can cause the threshold pressure to become so high that the surrounding rock might be damaged. Modelling based on microscopy has led to Figure 10.3, which implies that channels consisting of hydraulically interacting voids filled with clay gels emanate from the expanded clay powder grains that remain after hydration of the buffer (Pusch et al., 2001). The gels may stay intact at slowly increased gas pressure or be displaced and cause clogging of channels and voids. In case of *in situ* placement and compaction of buffer with 30 % clay minerals, the swelling pressure is lower and the critical gas pressure is therefore lower as illustrated in Figure 10.4 (Pusch and Yong, 2006). Further research is required specifically with respect to how gas that has escaped from the buffer in the deposition holes will migrate in very tight host rock.

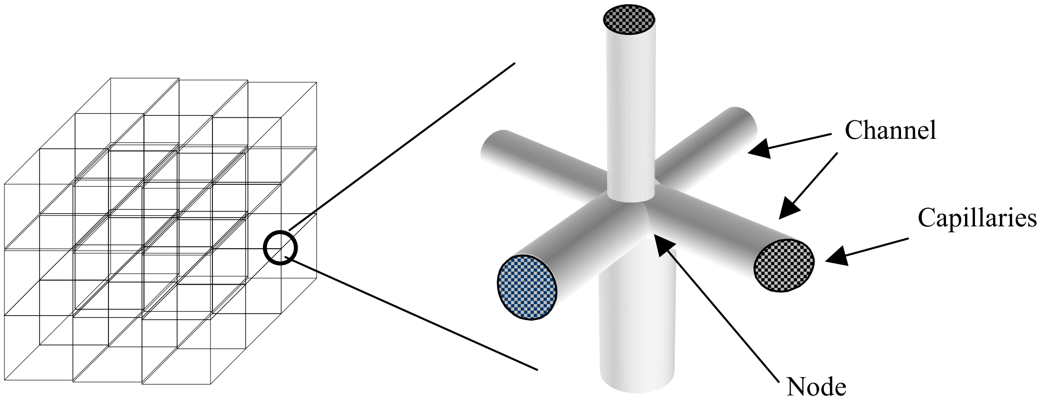

Figure 10.3: Schematic view of the 3D model concept with the channel network mapped as a cubic grid with channels intersecting at a node in the grid. The channels have varying cross section and represent continuous voids filled with clay gels exfoliated from the initially dense buffer grain (Pusch and Yong, 2006).

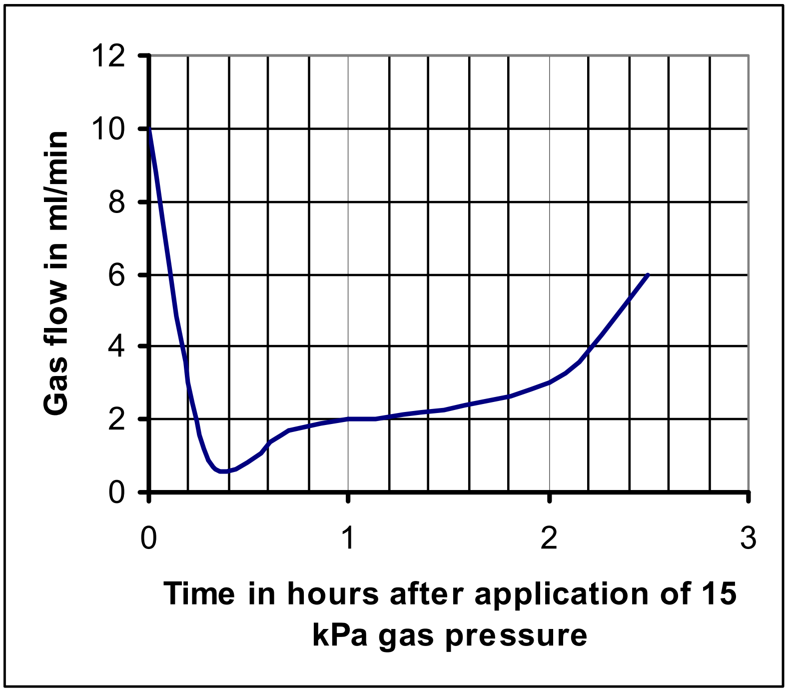

Figure 10.4: Example of gas penetration at the critical pressure 15 kPa in a 10/90 mixture of montmorillonite-rich clay (MX-80) and Fuller-graded aggregate. Density at saturation with seawater 2200 kg m^3 (Pusch, 2008).

The bearing capacity of the buffer is essential because it determines the ability to carry the heavy canisters without yielding or undergoing long term settlement by creep. This capacity is related to the compressibility of the buffer and to its expandability, of which the swelling pressure is a measure. While dense smectite-rich buffer has a bearing capacity that is more than sufficient, its expandability means that the overlying backfill in the drifts of a KBS-3V disposal facility will be displaced upwards, generating tension stress in the canisters which are firmly held at the base (Figure 10.5).

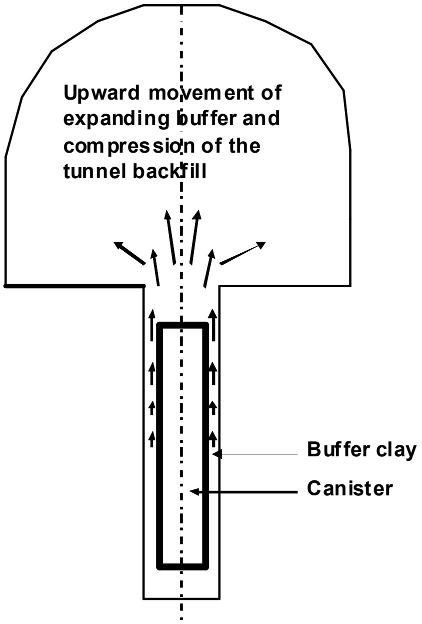

Figure 10.5: Axial tension of canister by upward expansion of the buffer clay at its upper part in conjunction with compression of the tunnel backfill. The lower and central part of the canister is firmly held by the clay (Pusch, 2008).

Mixed buffers with 20 – 30 % smectite and a density of 2200 kg m^3 or more have a much lower swelling pressure but their bearing capacity is still sufficient (as concluded from the experience from foundation engineering in areas with smectitic moraines and application of current soil mechanical theory; Sutton, 1993).

10.1.4 Thermal Properties

Thermal conductivity is one of the physical properties that is important for system performance, but for which no criteria have been explicitly specified by SKB. High temperatures delay water saturation of the buffer and can cause desiccation resulting in permanent microstructural collapse (Section 2.3). Attempts have been made to minimise the impact by mixing quartz grains and graphite into the buffer to increase the thermal conductivity (e.g. Pusch and Yong, 2006; Pusch, 2008). Quartz has a heat conductivity (8 W $m^{-1}K^{-1}$) that is 2-3 times higher than that of most other minerals and more than 300 times higher than of air. Graphite has even higher heat conductivity, although the value strongly depends on the degree of crystallinity. The volumetric proportions of quartz, graphite, other minerals and air-filled voids are therefore of great importance for the heat transferring capacity of the buffer. Graphite has been used by the Czech organization responsible for developing HLW disposal and by its Belgian equivalent. However, it has been ruled out by SKB because it cannot be guaranteed that it will not contribute to the proliferation of microbes despite its crystalline nature (Fred Carlsson, SKB - pers. comm.). The thermal conductivity of a freshly installed buffer consisting of montmorillonite-rich clay of MX-80 type with a dry density of 1600 kg m^3 and a water content of 10 %, corresponding to about 50 % degree of water saturation, is about 0.7 $Wm^{-1}K^{-1}$ and it rises to about 1.1 $Wm^{-1}K^{-1}$ at complete water saturation. The required thermal properties of the buffer are not specified by SKB and POSIVA, because they are implicitly defined for a given thermal power of the disposal canister by the maximum allowed buffer temperature.

In assessing the performance of different buffers from the viewpoint of thermal conductivity, *in situ* compacted buffer with 20-30 % smectite content is deemed advantageous to very dense smectite-rich buffer provided that the 'aggregate' is 100 % quartz material.

10.1.5 Chemical Interaction of Different Buffer Components

The most important interaction of different buffer components concerns the long-term stability of the smectite component. Amongst the processes that could take place are illitisation (Section 6) and cementation (Section 2.3). Experiments and natural analogues suggest that temperature and temperature gradients determine the rate of conversion of smectites to illite and that neoformation of illite can take place relatively early depending on the temperature conditions and access to potassium. Smectites exploited for preparing buffers should be poor in potassium-bearing accessory minerals such as K-feldspars and muscovite and it has been suggested that tunnels adjacent to deposition holes should be backfilled with material containing no more than a minimum of these minerals (Pusch and Yong, 2006).

Mixed buffers with low clay contents are of course more vulnerable than materials rich in clay. Ideally, the aggregate component of the mixed material should consist of pure quartz and quartzite, which is very stable, physically and chemically. These constituents would also give high thermal conductivity. The risk of cementation is not greatly increased because the contribution to the formation of free silica by decomposition of accessory minerals has been largely eliminated.

10.1.6 Microbial Impacts

The impact of microbes on the performance of radioactive waste disposal systems has been considered by numerous agencies, including NDA RWMD and these are reviewed in detail elsewhere (Humphreys et al., 2010). In brief, there is a concern that if microbes are active in the bentonite they could enhance canister corrosion and radionuclide transport. However, there is still considerable debate about the viability of microbes in compacted bentonite and at what precise density they may (or may not) be active (e.g. Stroes-Gascoyne et al., 2007; Masurat et al., 2007). The problem has been studied from different viewpoints, one of which is the microstructural constitution of the clay, and the possibility for microbes to survive and migrate within this type of system. The present belief is that smectite clays with densities at water saturation lower than 1200 kg m^{-3} have sufficiently large voids to host large amounts of bacteria and allow them to multiply and migrate by breaking gel bonds, although hydrogen bonding puts limits to their mobility (Pusch and Yong, 2006). The frequency of relatively large voids in smectite-rich buffer clay with a bulk density of about 1800 kg m^{-3} may be sufficient to host bacteria like the *Desulfotomaculum nigrificans*, which plays a role in the degradation of copper canisters (Pusch, 2008). However, at higher bulk densities, bacteria are not able to move in the clay because of the limited space and the mechanical strength of the clay. They will ultimately lose their potential for producing spores and will die, as has been documented experimentally.

In assessing the performance of different buffers from the viewpoint of survival and migration of microbes, dense smectite-rich buffer is superior to *in situ* compacted buffer in which interconnected voids may offer better possibilities for microbes to survive, multiply, and be mobile.

10.1.7 Preparation and Homogeneity of Buffers

The homogeneity of the buffer material to be compacted has to be checked through a specified quality assurance process. This process is less demanding for smectite-rich buffers than for mixtures with 20-30 % smectite content (Dixon et al., 1992). The homogeneity of the maturing buffer can be predicted by applying THMC material models (Pusch and Yong, 2006). Application of models of this type predicts that the constitution of smectite-rich buffer will vary significantly with the time after closure of the deposition holes. However, such models are currently not able to include formation of discontinuities such as the steep desiccation fractures, which are known to be formed radially in the buffer from the canister surface to about 1/3 of the buffer radius before self-sealing ultimately begins. The whole matter of homogenization with time by redistribution of porewater and creep strain in the particle network is poorly understood and the degree of homogeneity of the ultimately formed buffer needs further investigation for allowing accurate performance analyses.

10.2 Tunnel Backfill

SKB and Posiva are the principal waste management organisations that have researched the design, performance, and testing of tunnel backfills for repositories for HLW/SF.

In the KBS-3 concept, buffer swelling will cause an upward expansion with a resulting compression of the tunnel backfill. This needs to be counteracted by the backfill in order to keep the buffer density within the desired limits. The concentration of canister-corroding agents in the backfill should also be low. As for the buffer, a certain amount of initially entrapped oxygen is unavoidable in the backfill, and the pyrite concentration could pose a long-term problem. There is, however, no specific constraint placed on this concentration by SKB and Posiva.

Tunnel backfill design and testing are areas of rapidly-moving development in the programmes of SKB and Posiva, due principally to the inability of their original reference design to meet design criteria during testing reported for the 'Backfill and Plug Test' carried out at the Äspö Hard Rock Laboratory (Gunnarsson et al., 2001, 2004). During the last five years, SKB/Posiva has looked at the following tunnel backfill compositions through their 'BACLO' research programme (Gunnarsson et al., 2006; Sandén and Börgesson, 2006; Sandén et al., 2008; Wimelius and Pusch, 2008; Keto et al., 2009):

▲ A 70:30 mixture of MX-80 bentonite and crushed rock. This granular mixture was designed to be emplaced in sloping layers across the tunnel width. This design was discarded after testing in the 'Backfill and Plug Test' when measured permeabilities exceeded design criteria (Gunnarsson et al., 2004).

▲ Pre-compacted blocks made of a mixture of bentonite of buffer quality and crushed rock with a weight ratio of 30/70. The gaps between the rock and the blocks are filled with bentonite pellets. The maximum grain size for the ballast material (the crushed rock) was assumed to be 5 mm. Again, this has been discarded, post-SR-Can.

▲ Pre-compacted blocks of a natural swelling clay (not necessarily a bentonite). Friedland clay was used as an example of such a material in the SR-Can assessment. The whole tunnel is filled with pre-compacted blocks. The gaps between the rock and the blocks are filled with pellets of the same material. This design is currently being taken forward with further testing of installation and performance being ongoing.

The current status of SKB/Posiva's backfill programme is reported by Keto et al. (2009). The backfill concept currently is a block concept based on filling the majority of the tunnel with pre-compacted backfill blocks and the remaining volume with bentonite pellets. Investigations in the BACLO programme concern three alternative block materials: Asha 230 bentonite (bentonite sourced from India), Friedland clay, and a mixture of bentonite and crushed rock (30:70). The pellet materials used to fill the remaining spaces between the blocks and the surrounding rock consist either of pure

Ca- or Na-bentonite (with varying granule size distributions) or of Friedland clay fragments (granules). It is also assumed that pellets/granules are used both in the void between the blocks and the rock wall/roof, and also underneath the blocks to provide a low-permeability foundation layer for the block assemblage. Results showed that (Keto et al., 2009):

- ▲ Asha 230 bentonite blocks (with estimated smectite content between 60 and 80 %) and bentonite pellets seems to be able fulfil all the requirements set for backfilling at block filling degrees of 70, 80, and 90 % if the geometry of backfill components is also taken into account in the backfill design (upward swelling of the buffer). This material also has the potential to fulfil the requirements for backfill at even lower block filling degrees (< 70 %), but factors such as homogenisation and compressibility has to be investigated further.

- ▲ For Friedland clay backfill (with ~30 % swelling clay mineral content), the situation concerning the proportion and geometry of the pellet fill is similar to that encountered for all backfill materials considered, (i.e. the buffer-backfill interaction requires further evaluation with updated backfill geometry before it can be judged to be a suitable material). However, based on self-sealing tests, as a first estimate, it is recommended that the block filling degree should not be very much less than 70 % for this material.

- ▲ For a 30 % bentonite/70 % aggregate mixture, it was determined that the block filling degree should be > 80–90 %. This is based on theoretical calculations of average backfilled tunnel densities achieved as compared to the density criteria needed to exhibit adequate hydraulic and mechanical performance. However, even at this degree of backfilling, the material does not seem to have sufficient self-sealing capacity and is at risk for development of permanent hydraulic piping features. Therefore, it remains to be determined what bentonite/aggregate ratio would be able to provided adequate performance as a backfill.

A continuing concern for SKB/Posiva regarding the selection of a reference tunnel backfill concept is continuing issues arising during installation (Keto et al., 2009):

- ▲ Piping (Section 9.2) can develop in backfill and under high point inflow rates and erosion of backfill (Section 9.3) can be substantial.

- ▲ The backfill cannot be counted on to act as a substantial sink for inflowing water. In particular, the pellet materials do not initially saturate uniformly and water can move rapidly from the point of inflow to the working face, particularly under high inflow conditions.

- ▲ Under conditions where the volume of pellet fill is limited, water can move into the block-filled volume and generate preferential flow paths along the block boundaries potentially resulting in development of erosive features.

- ▲ Piping through backfilled volumes tends to occur along existing interfaces, with preference to flow along the pellet-rock boundaries. Under moderate point inflow conditions, the piping features do not result in extensive erosion of the backfill. Water tends to move rapidly along the piping feature to the downstream face of the backfill, meaning that it will be necessary to deal with the inflow almost as rapidly as it enters the tunnel.

- ▲ Due to the rapid movement of the water through the backfill it will be necessary to ensure that backfill operations do not cease for longer than a few days or up to one week in order to avoid problems with the installation process.

In view of the submission of the SR-Site licence application to the authorities in Sweden towards the end of 2010, it can be envisaged that SKB/Posiva will need to try and resolve some of these issues in a timely manner.

10.3 Summary of Key Points

Bentonite emplaced in compacted block form is the preferred option for the clay buffer for most waste management organisations. Only Japan and Canada have opted for a clay-aggregate mixture for this EBS component. A clay-aggregate mixture uses less bentonite and may have better thermal conductivity properties, but also has a higher hydraulic conductivity. The key issues are summarised below.

- ▲ Buffer properties are strongly dependent upon the amount and type of swelling 2:1 clay content in the bentonite.

- ▲ The option of bentonite-aggregate mixtures proposed in the early days of buffer design (primarily due to cost considerations), involves the preparation of mixtures such that the voids between coarser (aggregate) grains become occupied by clay particles (thus imparting a sealing capacity). The suitability of the material properties produced by such an approach would depend on safety requirements and would need to be carefully considered.

- ▲ SKB has considered materials other than montmorillonite-rich bentonite, such as saponite, mixed layer clays, kaolinite and palygorskite, for use as a buffer.

A consideration of the overall properties of these material candidates has led to the conclusion that the most suitable buffer materials are clays rich in montmorillonite and saponite.

- ▲ The most important physical properties of bentonite for the development of the safety case include hydraulic conductivity and the canister bearing capacity. The hydraulic conductivity is determined by the microstructure, which can be considered to be largely homogeneous for dense, smectite-rich clay and heterogeneous for mixed buffers. The smectite content is the key parameter, followed by density. The bearing capacity of the buffer is essential since it determines the ability to carry the heavy canisters without yielding or undergoing long term settlement by creep. It is also essential that gas can escape through the buffer at pressures lower than the swelling pressure and that the bentonite reseals when the gas pressure drops so that it continues to provide a hydraulic barrier. The pressure required for a pathway to become established, rather than the gas conductivity is the key parameter.

- ▲ The choice of buffer material should consider potential reactions between buffer components. The most important interaction of different buffer components concerns the long-term stability of the smectite component. Therefore, buffer material should have a low K content to minimise the potential for illitisation.

- ▲ In assessing the performance of different buffers from the viewpoint of survival and migration of microbes, dense smectite-rich buffer is superior to *in situ* compacted buffer in which interconnected voids may offer better possibilities for microbes to survive, multiply and be mobile.

- ▲ Only SKB and Posiva have investigated the design and performance of tunnel backfill in any detail. There have been considerable difficulties in arriving at a design/composition that can be installed effectively whilst retaining desirable performance capabilities. SKB/Posiva has dropped their original preferred design (a clay-granite mix) and are currently testing a compacted clay block-pellet design. Work is ongoing to arrive at a preferred design.

11 Summary of Key Issues

Much of the material presented in this document is quite detailed and includes information on both the physical and chemical properties of bentonite and the processes that may influence them (within the context of the use of bentonite in HLW/SF EBS designs). A key point to note is that, although for simplicity the reactions and processes have been discussed as individual topics, many of the processes discussed in Sections 2.3 to 10 will be strongly coupled and cannot be considered, or optimised, in isolation.

Key points were highlighted at the ends of Sections 2.3 to 10. Table 11.1 summarises the most important of these issues from the perspective of the current state of the UK programme. It also identifies issues where it may not be straightforward to apply knowledge and data gathered by other programmes directly to the UK case because of differences in groundwater compositions and/or waste characteristics. Table 11.1 also lists possible implications for the UK radioactive waste management programme and suggestions for future work.

The key points that should be taken from this review are that:

- The evolution of bentonite under the conditions expected in a GDF is complex and the processes affecting it are coupled, perhaps strongly.
- Most aspects of bentonite performance are likely to be specific to both the site (both groundwater flow rate and composition) and the particular bentonite that will be used.
- Issues associated with the performance of bentonite are of international concern, and, as a result, a great deal of work has been carried out and a significant knowledge base exists, which the UK can draw on.

However, conclusions drawn by others on the basis of a particular combination of groundwater and bentonite compositions need to be evaluated carefully and critically before being applied to the UK case. In particular, groundwaters and potentially suitable sites in England and Wales are likely to be both more complex chemically and more saline than the waters that are found at disposal sites currently being considered in Scandinavia and Europe. It is important that a realistic range of compositions is considered in future work.

SKB/Posiva have to date carried out a large fraction of the work to understand the controls on bentonite performance, and this work has been carried out in the context of Scandinavian groundwater compositions and MX-80 bentonite (although increasingly other compositions are being considered). These are not necessarily representative of UK conditions. The very high profile of this research in their programmes reflects the key role that the bentonite buffer plays in ensuring long-term safety in the KBS-3 concepts. Although research into the performance of bentonite is important in other programmes such as those of Nagra and Andra, there is arguably a somewhat lesser emphasis on buffer stability in these programmes.

The profile of any R&D work to understand the controls on the performance of bentonite in the UK programme will depend crucially on the choices of site and disposal concept. The current state of knowledge of bentonite properties and behaviour is sufficient to define the challenges that need to be considered when considering the merits of different disposal concepts in various geological environments. As the UK programme develops, there are likely to be both UK-specific topics for further research as well as topics that have a general applicability for understanding the evolution of disposal systems that include bentonite. In the latter case, international projects such as the Äspö Task Force are working to improve fundamental understanding of key topics such as bentonite resaturation and transport properties and to understand how to translate the results of laboratory experiments and numerical models to full scale.

Table 11.1: Summary of key issues, their scope from a UK perspective and the type of further work that could be undertaken.

Issue	Understanding	UK scope	Possible Further Work
Temperature effects on bentonite	The impact of temperature-induced precipitation of cementing agents (silica and iron complexes) on the stress/strain properties of clay buffers may be significant. This matter is of fundamental importance particularly if buffer temperatures higher than 100 °C are considered. Steam may also result in deleterious effects on bentonite properties. Extensive drying may have a deleterious effect. Further complicates uncertainties regarding resaturation (see below)	Thermal effects on bentonite will need to be carefully considered in the design and the development of the safety case. The impact of temperature gradients on the accumulation and dissolution of salts in the vicinity of canisters embedded in clay buffer need to be assessed Assessment of clay materials with respect to coupled THMCB (T)hermal/(H)ydraulic/(M)echanical/(C)hemical/(B)iologicalbehaviour, including gas conductivity and ion diffusivity needs to be made in order to obtain a basis for optimal selection of one specific candidate material.	Thermal modelling of waste heat output and GDF temperatures for UK waste compositions. Consideration of calculated temperatures on bentonite function. Modelling of coupled THMCB processes. Participation in collaborative studies on bentonite resaturation, for example Task 8 of the Äspö project

Re-saturation	Large-scale experiments suggest that the theory and laboratory-based understanding of bentonite resaturation may not be a good description of the process at full scale. Resaturation times may be significantly longer than previously predicted, and full re-saturation may not occur in some cases.	A potentially crucial topic because of the need for the bentonite to re-saturate fully to fulfil its safety functions and the dependence of thermal properties on saturation.	Continuation of work being carried out in projects such as THERESA. Participation in collaborative studies on bentonite re-saturation, for example Task 8 of the Äspö project.
Radiation effects on bentonite	The effects of alpha and gamma radiation on the breakdown of clay layers is reasonably understood.	Needs to be considered in the development of the safety case but is unlikely to have a major impact on design etc. Other considerations with respect to radiation doses are likely to be more important (corrosion rates, gas generation by radiolysis, operational considerations).	UK-specific calculations of radiation dose to bentonite and comparison with experimental data will ultimately be required as part of demonstrating confidence in the safety case.
Bentonite pore water composition.	Reasonably well-understood, but data mostly based on modelling rather than direct measurement.	Will need to be addressed for specific groundwaters from candidate sites to establish controls on safety case-relevant parameters such pH, redox.	Geochemical modelling, direct laboratory measurements.
Effect of bentonite on waste glass	Glass dissolution may be increased in contact with some clays, but mechanisms are poorly understood.	Potential issue if vitrified waste not emplaced in containers. UK glass has not been studied.	Site-specific modelling/experiments required if disposal concepts with very short-lived canisters are considered.

Effect of bentonite on steel/iron corrosion	Bentonite may increase corrosion to some extent due to prohibition of corrosion product growth, thereby acting as a 'pump' for corrosion.	Needs to be considered in development of safety case if steel/iron is present with bentonite (especially at interfaces). Of particular importance if UK disposal concept uses steel/iron canister and relies on very long period of absolute containment within the canister to provide long-term safety.	Reactive transport modelling, further experiments with site-specific groundwater and bentonite compositions.
Bentonite illitisation	Bentonite may react with K^+ to form non-swelling illite. Unlikely to be significant at $T < 100$ °C. Increased by availability of K-rich groundwaters/brines.	Groundwaters at candidate sites may differ significantly from those studied in other programmes so results may not be directly transferable. Will need to be considered in UK programme for site-specific chemical conditions and predicted temperatures.	Application of existing kinetic models to site-specific groundwater compositions and near-field temperatures.
Effect of saline groundwater on bentonite	Salinity affects swelling pressure by an osmotic process. Models are available for simple (NaCl) brines.	Groundwaters at candidate sites are both more complex and likely to be more saline than those considered in other programmes, so the results may not be directly transferable. Will need to be considered in UK programme for specific chemical conditions.	Experiments required with complex site-specific groundwaters to establish validity of currently-available models.

Effect of Mg on bentonite	Mg present in waste could react with bentonite, and result in changes to swelling pressure via interlayer exchange, some loss of swelling due to cementation effects, or alteration of montmorillonite to other minerals. The understanding of this issue is rather limited. However, one of the minerals, saponite, that is likely to be formed has been considered as an alternative to montmorillonite and the major clay mineral in the bentonite.	Issue less relevant if: (1) Mg wastes do not come into contact with bentonite; (2) Mg-rich brine formation is avoided.	Experimental/modelling work required to increase understanding if bentonite is to be exposed to unusually high Mg concentrations (i.e. Mg-rich brine).
Effect of Fe on bentonite	Steel/iron corrosion product could react with bentonite to produce reduced swelling or non swelling minerals, thereby causing changes in swelling pressure, bentonite cementation, and loss of sorption sites. The kinetics of smectite alteration to iron-rich minerals is not well understood.	Will be relevant if UK adopt EBS design that includes carbon steel components, especially if they come into direct contact with bentonite. Will be of key importance if the UK disposal concept combines a carbon steel canister with a requirement for the buffer to ensure a very long canister lifetime.	Much scope for further work, including both experimental studies and geochemical modelling.

Effect of cement on bentonite	Cement pore fluids will react with bentonite via cation exchange, smectite dissolution, and precipitation of new minerals, resulting in changes in bentonite porosity, swelling pressure, hydraulic conductivity, and sorption capacity. These interactions are complex, non-linear processes, making it difficult to extrapolate the results of lab experiments to the timescales of interest for the safety case. Other international agencies have now adopted low pH cement/concrete as their preferred material for fracture grouts, shotcrete, and tunnel plugs in repositories for HLW/SF.	Although potential cement-bentonite interactions are often ignored in PA, they are of relevance to waste co-location and should be considered, in particular if a higher strength host rock is selected. Simple scoping calculations for specific designs and conditions are required, even if more complex further work was undertaken.	Experimental work to (1) reduce uncertainties concerning smectite alteration rates and bentonite degradation rates under highly alkaline conditions; (2) consider the nature and possible extent of smectite alteration at low pH cement-bentonite interfaces. The experimental work could be supported by modelling.
Bentonite Piping	Piping may occur in fractured rocks during buffer/backfill installation.	The likely occurrence of bentonite piping would need to be taken into account when designing the EBS and planning its installation.	Further research and development work is likely to be needed for specific conditions.

Bentonite Erosion	Erosion is of concern post-closure in fractured rocks and may be caused by various physical and chemical processes and is dependent on the composition of the clay and the salinity and composition of the aqueous phase. If large amounts of buffer material are eroded away from the buffer, significant advective flow of groundwater could occur around the buffer and this might lead to much more rapid waste container corrosion, with the safety functions of both the container and the buffer being compromised.	The occurrence and significance of bentonite erosion will depend on the disposal concept, the design of the engineered barrier system, the particular bentonite materials used, the pattern and rates of groundwater flows within the host rock and the engineering disturbed zone, and on the chemistry of the clays and groundwaters. All of these factors would need to be considered in the context of the selected site.	Further research and development work is likely to be needed, especially for specific conditions.
Composition effects (1): bentonite and bentonite aggregate mixtures	Most countries have opted for a compacted bentonite blocks as the buffer material of choice, mainly due to hydraulic conductivity requirements. However, designs exist that employ clay-aggregate mixtures. These are cheaper, but perform less well hydraulically than pure bentonite.	Performance requirements for a buffer in candidate geological environments need to be defined to aid buffer/backfill selection process, i.e. if hydraulic conductivity needs to be $< 10^{-12}$ m s^{-1}, then a pure bentonite needs to be selected.	Scoping system calculations need to be performed to establish design requirements.

Composition effects (2) alternative clay type	SKB have identified clays other than montmorillonite that could form the basis of a buffer. However, these are less well researched in the context of radioactive waste disposal. Compared to montmorillonite based materials, the behaviour of possible alternative clay minerals under GDF conditions is less well understood.	If montmorillonite based bentonite was rejected as a buffer, there would need to be a programme of research to determine its suitability in a disposal facility.	Laboratory and geochemical models of ‘alternative’ material would be required.

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Appendix A Glossary of Mineralogical Terms

Analcime/Analcite:	an aluminous, hydrous framework silicate mineral, with the idealised composition $NaAlSi_2O_6 \bullet H_2O$. *Sensu-stricto* is part of the feldspathoid group of minerals. However, it is sometimes discussed with reference to zeolite.
Beidellite:	a dioctahedral member of the smectite group of clay minerals which includes mainly aluminium in the octahedral sheets and some aluminium in the tetrahedral sheets. An idealised Na-dominated composition (half unit cell) is $Na_{0.33}Al_2Si_{3.66}Al_{0.33}O_{10}(OH)_2 \bullet nH_2O$ (where n is function of relative humidity/water activity).
Bentonite:	a rock type that has a significant proportion of smectite.
Berthierine:	a trioctahedral iron-rich '1:1' (non-swelling) clay mineral. A typical idealised half unit cell composition is $(Fe_2Al)(SiAl)O_5(OH)_4$.
Brucite:	a crystalline magnesium hydroxide ($Mg(OH)_2$) mineral.
Calcite:	a crystalline calcium carbonate ($CaCO_3$) mineral.
Celadonite:	a member of the mica group of layer silicate minerals with the composition $K(Mg,FeII)(FeIII,Al)[Si_4O_{10}](OH)_2$.
Chamosite:	an iron-rich chlorite mineral with the idealised half unit cell formula of $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$.
Chlorite:	a group of layer silicate minerals comprised of 2:1 (tetrahedral-octahedral-tetrahedral) layers between which there is a hydroxide sheet.
Clinochlore:	magnesium-rich chlorite mineral with the idealised half unit cell formula of $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$.
Clinoptilolite:	see **Zeolite.**
C-(A)-S-H:	Calcium-(Aluminium)-Silicate-Hydrate (gel). A common constituent of cement. Minerals composed of calcium, (aluminium) silicate and water may be referred to as C(A)SH minerals.

Chalcedony:	a cryptocrystalline form of silica (SiO_2).
Cronstedtite:	an Fe(II)/Fe(III) 1:1 layer silicate mineral with a typical idealised half unit cell formula of $Fe(II)_2Fe(III)_2SiO_5(OH)_4$.
Feldspar:	a group framework silicate minerals (solid solutions between end member compositions $KAlSi_3O_8$ - $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$).
Gibbsite:	a crystalline aluminium hydroxide ($Al(OH)_3$) mineral.
Greenalite:	a trioctahedral 1:1 layer silicate mineral with the idealised half unit cell formula of $Fe_3Si_4O_5(OH)_4$.
Heulandite:	see **Zeolite.**
Hydrotalcite:	a hydrous layered hydroxide with the idealised formula $Mg_6Al_2(CO_3)(OH)_{16} \bullet 4(H_2O)$.
Illite:	a potassium-bearing 2:1 layer silicate mineral with variable chemical composition represented by the half unit cell formula of $K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$.
Kaolinite:	a dioctahedral 1:1 layer silicate mineral with the idealised half unit cell formula of $Al_2Si_2O_5(OH)_4$.
Phillipsite:	see **Zeolite.**
Mica:	group of (non-swelling) 2:1 layer silicate minerals with strong cleavage appearing parallel to 2:1 layers.
Mixed-layer:	mixed layer clays have either irregular or regular interstratifications of different layer types (structure and/or composition). Examples include illite/smectite, kaolinite/smectite and chlorite/smectite.
Montmorillonite:	a dioctahedral aluminous smectite clay mineral that includes magnesium in the octahedral sheet (leading a layer charge deficit that is satisfied by hydrated interlayer cations). A typical idealised half unit cell formula for Na-saturated montmorillonite is $Na_{0.33}Al_{1.66}Mg_{0.33}Si_4O_{10}(OH)_2 \bullet nH_2O$.
Muscovite:	potassic mica mineral, with an idealised half unit cell formula formula: $KAl_3Si_3O_{10}(OH)_2$.

Odinite:	complex, iron-bearing 1:1 layer silicate with the composition $(FeIII,Mg,Al,FeII,Ti,Mn)_{2.5}(Si,Al)_2O_5(OH)_4$.
Palygorskite:	a magnesium aluminium clay mineral (with a ribbon-like 'modified' molecular structure). A typical half unit cell composition is represented by $(Mg,Al)_2Si_4O_{10}(OH)\bullet 4H_2O$.
Portlandite:	crystalline calcium hydroxide ($Ca(OH)_2$) – a common Portland cement constituent.
Pyrophyllite:	aluminous dioctahedral 2:1 mineral with a half unit cell formula of $Al_2Si_4O_{10}(OH)_2$.
Quartz:	a commonly occurring crystalline silica (SiO_2) mineral.
Saponite:	a trioctahedral smectite mineral, generally with Mg and Fe as the predominant octahedral sheet cations. A typical idealised half unit cell formula (Na interlayer) is $Na_{0.33}(Fe(II),Mg)_3Si_{3.66}Al_{0.33}O_{10}(OH)_2\bullet nH_2O$.
Sepiolite:	Mg-rich layer silicate mineral (modulated structure) with the idealised composition $Mg_4Si_6O_{15}(OH)_2\bullet 6H_2O$.
Smectite:	group of swelling clay minerals comprised of three sheets; two tetrahedral sheets between which there is an octahedral sheet (a '2:1' layer). A charge deficit across these sheets results in positively charged ions and water being present within 'interlayer' regions. The spacing between 2:1 layers varies as a function of chemical composition and relative humidity.
Talc:	magnesian trioctahedral 2:1 layer silicate. Half unit cell formula is $Mg_3Si_4O_{10}(OH)_2$.
Vermiculite:	a 2:1 layer silicate mineral with a half unit cell formula represented by $(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2\bullet 4H_2O$.
Zeolite:	a microporous aluminosilicate mineral. The porous structure can accommodate a wide range of ion/molecules and as such, they are used commercially as sorbents, catalysts and ion exchangers. Typical composition include: $(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\bullet 12H_2O$ (phillipsite); $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\bullet 12H_2O$ (clinoptilolite); $(Ca,Na)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\bullet 12H_2O$ (heulandite).