

Proceedings of the International Workshop on Bentonite-Cement Interaction in Repository Environments

14-16 April 2004, Tokyo, Japan

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October 2004

Nuclear Waste Management Organization of Japan (NUMO)

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Executive Summary

This report describes an international workshop on bentonite-cement interactions in possible future repositories for High Level Waste (HLW) and/or Spent Fuel (SF). The meeting was hosted by NUMO and POSIVA from 14th - 16th April 2004 in Tokyo, Japan and aimed to overview comprehensively the present knowledge about these interactions. A goal was to identify key uncertainties and how these might be reduced by modelling and laboratory tests, including tests in Underground Research Laboratories (URLs).

The document reports 20 presentations covering various aspects of cement-bentonite interactions, which were given during five sessions:

- Session I: Repository concepts and the uses of cement;
- Session II: Mineralogy during bentonite-cement interaction;
- Session III: Barrier performance and functions during bentonite-cement interaction;
- Session IV: Modelling - detailed research models versus Performance Assessment (PA) models;
- Session V: Concluding discussions.

Discussions related to the presentations are also reported and associated abstracts are given in an appendix.

The various proposed uses of cement and bentonite are overviewed. In many repository designs, bentonite would be used in engineered barrier systems, to retard radionuclide migration and/or to control groundwater flow. Cement-based materials could also form an important component of the barrier system and/or be needed during repository construction. Depending upon the design, cement could physically contact the bentonite, or be sufficiently close that alkaline pore fluid from the cement may interact with the bentonite.

The workshop highlighted that a lot of data about cement-bentonite interactions have been acquired and the main processes have been identified. Consequently, priorities for future experimental, field and theoretical work can be suggested and a Performance Assessment (PA) framework can be proposed.

Important statements from the workshop are:

- Mass transfer (both ions and neutral species) can occur in both directions over an interface of highly compacted bentonite and concrete (transport of Mg, Ca, OH⁻ etc in and out).
- Mass transfer rates as a function of time at the bentonite-cement interface, as well as at different depths in both materials, should be recorded in experiments and simulations, whenever possible.

- The effects of cement on bentonite are mainly governed by the concentration and rate at which OH^- ions enter the bentonite.
- From the point of view of buffer performance, the contribution of cations entering the buffer (e.g. Ca^{2+} , Na^+) to the chemical potential of species in the clay pore water is important, and at least partly governs the buffer's physical properties.
- Two important and inter-related effects of a high pH plume on montmorillonite and accessory minerals in highly compacted bentonite, which may affect the buffer functions are:
 - mineralogical alteration of bentonite components, which will consume the chemical buffering capacity of the bentonite and affect the pore water chemistry;
 - osmotic effects (e.g. differences between the activities of ions in the external solution and the activities of ions in the inter-lamellar water solution), which are a function of the external pH and influence the temporal sequence of mineral dissolution and precipitation.
- Experimental studies should focus on determining dissolution rates under alkaline conditions.
- Non-compacted bentonite and highly compacted bentonite are structurally quite different materials, and therefore experimental results are not directly transferable. However, experiments using non-compacted materials may give thermodynamic data and useful information about reaction rates and reaction mechanisms.
- The pH buffering capacity of highly compacted bentonite is a key parameter. There is a fast (surface hydroxyl sites) and a slow (montmorillonite crystal lattice) component in the buffering capacity. The maximum total buffering capacity of bentonite with a montmorillonite content of 75 wt% is approximately 9.5 moles of OH^- ions per kg of clay.
- It is important to thoroughly understand the relative propagation rates of diffusing OH^- ions and the reaction front of the alteration processes in highly compacted bentonite. Over timescales relevant to PA, significant propagation of a high pH plume in the buffer seems to be possible, but the potential overall consequences depend on the disposal concept.
- There is a risk of cementation of the bentonite buffer affected by a plume of high pH. With some exceptions (i.e. calcite, gypsum) all the accessory minerals will transform to secondary minerals upon reaction with high alkaline solutions. Since neo-formed precipitates often have larger molar volumes than the reactants, cementation may be accompanied by a porosity decrease.
- The mechanical (e.g. swelling pressure, plasticity) and transport-related (e.g. diffusivity) properties of highly compacted bentonite altered by a high pH plume have not been investigated thoroughly.
- There is conflicting experimental evidence as to whether the transport of a high pH plume

originating from NaOH solution would be significantly faster than that of a high pH plume originating from $\text{Ca}(\text{OH})_2$ solution. Some experiments suggest that the rates would be faster, whereas others imply no difference.

- Where massive cement or concrete surrounds or neighbours bentonite such as thick tunnel liner around the buffer, the formerly dry bentonite will be saturated by cement pore water. Initially this saturation process will lead to reaction of hydroxide with the bentonite. As long as mass transport through the concrete is dominated by diffusion, these phenomena are relatively easy to model. Potential consequences can be reduced by taking care of mass balances (thickness of the buffer vs. thickness of the concrete layer).

In summary, varied mineral dissolution, precipitation and alteration reactions will cause inter-related temporal changes in porosity, permeability and mechanical properties of bentonite. A holistic understanding of these changes is needed to evaluate the overall safety implications. Additional work should focus on developing integrated interpretations using presently available data and improved coupled models of bentonite alteration should be developed.

A need for a more unified approach to identifying and implementing potential solutions to problems with using cement and bentonite in barrier systems was identified. In particular it would be desirable to improve communication between management, researchers investigating cement-bentonite interactions, and engineers and workers in the construction industry who will design and implement the barrier systems. It was also pointed out that regulatory frameworks usually lag behind technological innovations that may constrain the use of materials other than cement, when account is taken of the timescales of repository projects.

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1 INTRODUCTION

This report summarises an international workshop on bentonite-cement interactions in repository environments that was hosted by NUMO and POSIVA from 14th - 16th April 2004 in Tokyo, Japan. The workshop's purpose was to overview comprehensively the present knowledge about these interactions. It was aimed to identify key uncertainties and how these might be reduced by modelling and laboratory tests, including tests in Underground Research Laboratories (URLs).

The host organisations are seeking to construct deep geological repositories for High Level Waste (HLW)/Spent Fuel (SF). It was expected that the workshop would lead to a clearer definition of key issues that should be considered in the design and Performance Assessment (PA) of such repositories. However, many of the conclusions ought also to be applicable to geological repositories intended for other kinds of waste. Designs proposed for repositories of Low Level Waste (LLW) and Intermediate Level Waste (ILW, here considered to include TRU wastes which contain significant quantities of long-lived transuranic nuclides) were also considered.

The need for the workshop arose because bentonite and cement are components of many designs proposed for underground repositories. In many cases bentonite would be used in the systems of engineered barriers to radionuclide migration, to retard radionuclide migration and/or to control the flow of groundwater. Cement could also form an important component of the barrier systems. Even designs in which cement has no barrier function usually envisage that cement-based materials will be needed during the construction stage.

The fact that cementitious materials will be far from equilibrium with the natural groundwater conditions and with any bentonite component of a barrier system needs to be taken into account when designing a repository. The use of Ordinary Portland Cement (OPC) may cause formation of a high-pH groundwater plume that could in turn cause problematic chemical reactions. From the point of view of long-term safety it might perhaps be most prudent to avoid OPC completely close to the areas of waste emplacement in a HLW or SF repository and in such areas seek to replace it by other materials. With this goal in mind low-pH substitutes are being developed and tested for some repository applications. However, it is not clear whether such materials will be available within the time frames of many on-going repository programmes. Therefore, there is a continuing need to assess the implications of using cement-based materials.

During the workshop various aspects of cement-bentonite interactions were addressed by 20 presentations that were given during five sessions:

- Session I: Repository concepts and the uses of cement;
- Session II: Mineralogy during bentonite-cement interaction;
- Session III: Barrier performance and functions during bentonite-cement interaction;
- Session IV: Modelling; detailed research models versus PA models;
- Session V: Concluding Discussions.

Extended abstracts containing supporting information were also prepared by all the contributors.

The present document aims to summarise objectively the research results presented during these sessions and in the supporting extended abstracts, together with details of the associated discussions. To highlight the major issues identified during the meeting, each of the following sections juxtaposes key findings and arguments that were presented during several contributions. The extended abstracts themselves and other supporting literature are then presented in the appendix.

2 PROPOSED USES OF CEMENT AND BENTONITE IN REPOSITORIES

2.1 Types of radioactive waste and disposal concepts

Internationally different types of radioactive waste are being, or are planned to be, disposed of in different kinds of geological repository. The detailed design of such repositories reflects the specific characteristics of the wastes.

Different countries classify radioactive waste differently, according to varying criteria. The kinds of waste referred to in the workshop are:

- LLW is produced mainly by routine operations of nuclear facilities, and by certain laboratories and medical facilities. Such waste will also be produced during decommissioning. It is primarily contaminated by low concentrations of beta- and gamma- emitting radionuclides, though some material contaminated by alpha-emitting nuclides may be present. It does not usually require special handling, unless alpha-emitting.
- ILW contains higher concentrations of beta/gamma contamination and sometimes alpha emitters. These wastes usually require remote handling, but produce little heat. Such waste originates from routine power station maintenance operations, such as ion exchange resins. The waste is sub-divided into short-lived (usually with radionuclides having half lives of less than 30 years) and long-lived wastes.
- ‘TRU waste’ is defined as a separate category of waste in some countries and consists of waste containing a significant component of alpha-emitting transuranic nuclides. In some countries these wastes are included in the classification of ILW.
- HLW usually comprises spent fuel and highly active by-products from fuel reprocessing (if re-processing is part of the fuel cycle). The waste contains high concentrations of beta/gamma emitting fission products and alpha emitting actinides. HLW is a long-lived waste type that produces significant heat and requires remote handling.

The classification of wastes adopted in Japan is illustrated schematically in Figure 1. The corresponding kinds of adopted or proposed geological disposal facilities are given in Figure 2. Generally the depth of any geological disposal facility depends on:

- the radio activity of the wastes;

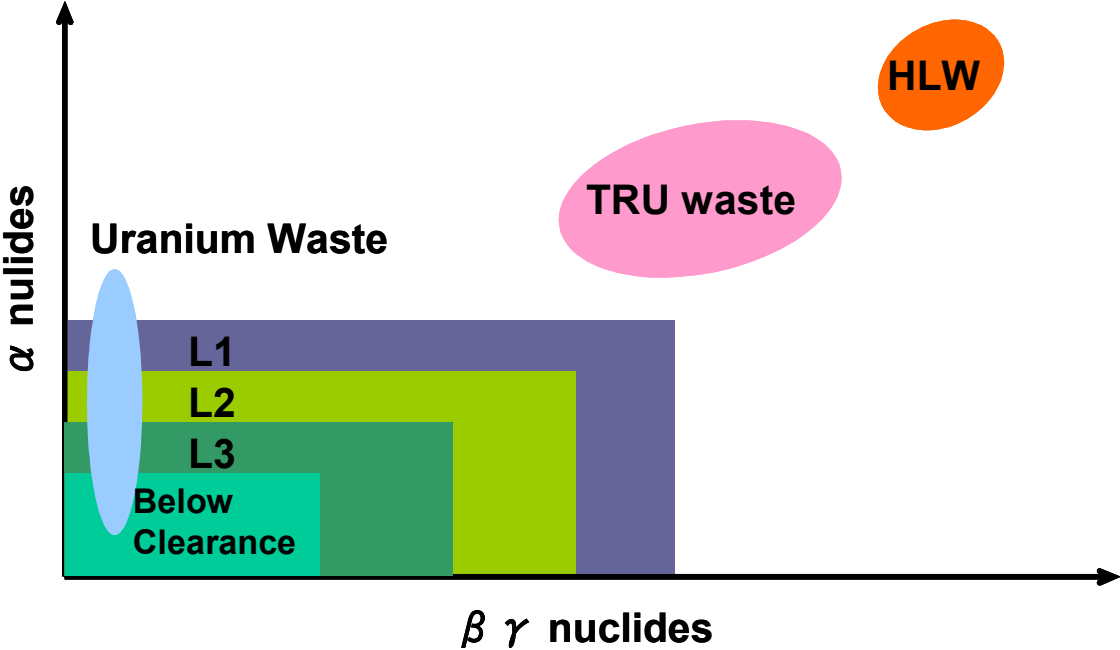


Figure 1: Summary of radioactive waste classification in Japan (after Kitayama et al). L1, L2 and L3 wastes are all LLW consisting of materials such as insides of cores and channel boxes (L1), liquid condensate and concentrated metal (L2), and concrete blocks (L3).

- the half-lives of the nuclides present in the waste;
- bedrock conditions at the disposal site.

Generally, the higher the overall radioactivity of the waste and the longer the half-lives of the nuclides present, the deeper will be a geological repository (Figure 2).

However, a feature of the different disposal concepts is the reliance to a greater or lesser degree on a multi-barrier system comprising both engineered and natural barriers. The Engineered Barrier System (EBS) will comprise mainly cement based materials for LLW/ILW repositories and/or bentonite for HLW repositories while the natural barrier will be a carefully selected geological formation¹.

2.2 Proposed uses of cement in repositories

Cement-based materials will be used as a major component of most barriers in a LLW, ILW or TRU waste repository. Cement has properties that are well suited to containing radionuclides by both physical and chemical processes making it a very attractive material to use as the main component of the EBS. These properties include:

- Buffering capacity determines the long-term chemical conditioning provided by the cement in its ability to buffer the pH of invading groundwaters to values ≥ 12.5 . Most radionuclides have a very low solubility under these high pH conditions. Microbial activity will also be suppressed.
- Mechanical strength affects the ability of the cement to prevent structural collapse of excavated cavities.
- Permeability affects the rate of groundwater flow into and out of the repository, lower permeability favouring the slowing of any potential release of the radionuclide inventory.
- Sorption on CSH gel phases which are the major components of hydrated cements will retard the migration of radionuclides.

Cement will therefore be used as the material for walls and floors, for encapsulating the waste, to backfill gaps between waste packages, and as a sealant for tunnels and shafts. A design of a LLW waste repository illustrating these uses is given in Figure 3.

In the case of a HLW repository, cement is not considered part of the barrier system. Instead only its physical properties in adding mechanical strength and impeding groundwater flow in the pre-closure phase are considered important. Functions and requirements of cement within the EBS depend on waste/repository type and whether pre- or post- closure, summarized in Table 1.

These components are represented in a schematic tunnel section of a HLW repository in Figure 4.

¹e.g. a mudrock such as the Opalinus Shale in Switzerland (McKinley et al.) or a crystalline rock such as the migmatitic mica gneiss that has been chosen in Finland (Hansen).

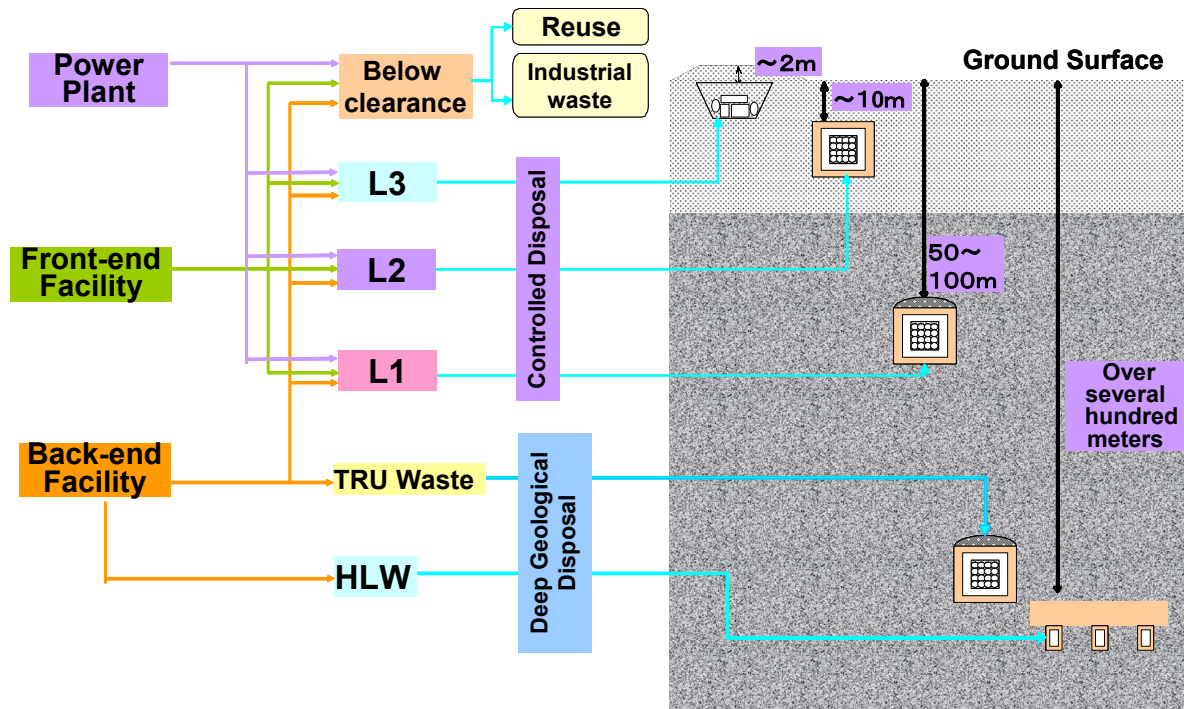


Figure 2: Outline of kinds of geological disposal proposed or adopted for the disposal of different sorts of radioactive wastes in Japan (after Kitayama et al).

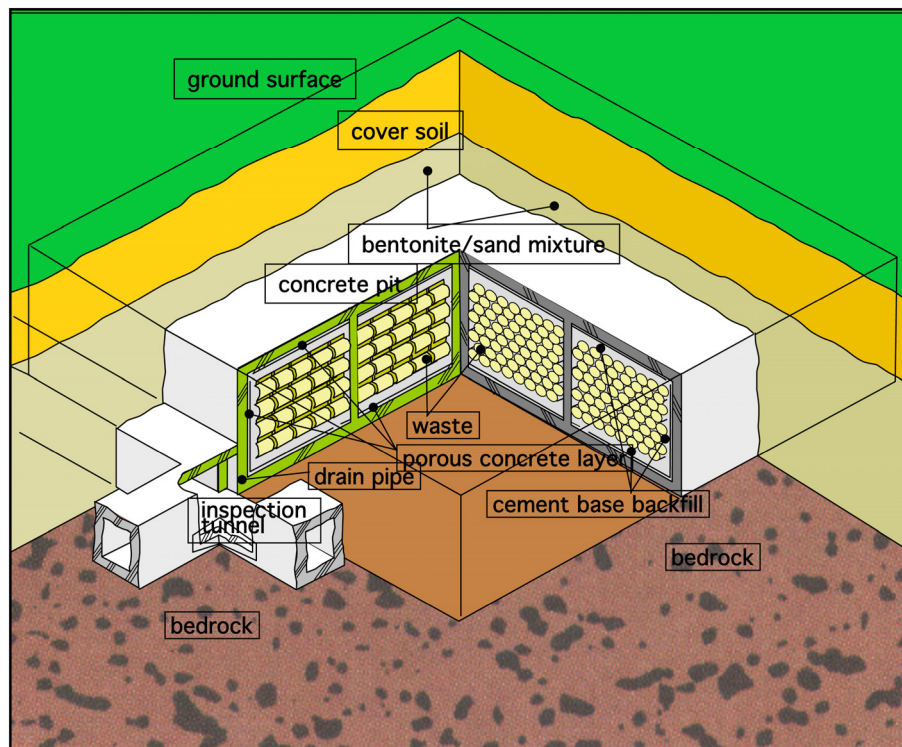


Figure 3: A view of the LLW repository at Rokkasho, Japan (Kitayama et al.). Cement - based materials form a major component of most of the barriers, surrounding the waste packages, the backfill material, liners and floors.

Table 1: Functions and requirements of the cement-based material components in a HLW repository.

Components	Functions	Pre-closure requirements	Post-closure requirements
Structural liner	Ensure mechanical stability of tunnels and shafts	Mechanical strength	No detrimental effects on other barriers
Grout – back wall	Provide contact between liner and host rock Suppress water inflow	Low permeability	No detrimental effects on other barriers
Cover grouting	Suppress water inflow through fractures	Low permeability	No detrimental effects on other barriers
Mechanical plug	Confine and mechanically support backfill material	Mechanical strength	No detrimental effects on other barriers

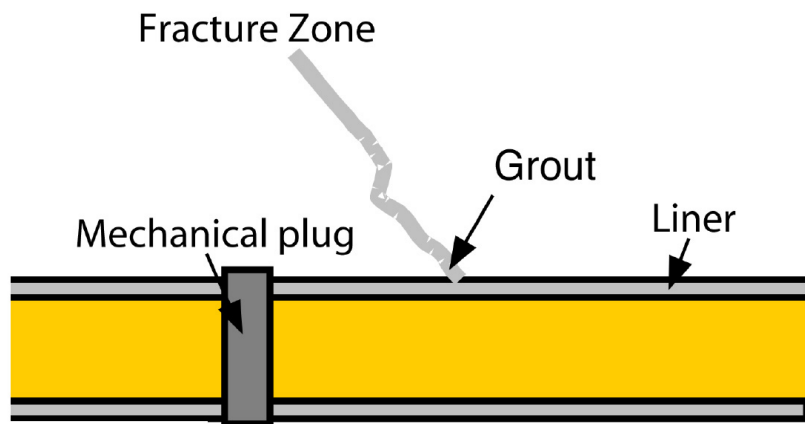


Figure 4: Examples of the use of cement in a tunnel section of a HLW repository concept (Kitayama et al.).

2.3 Proposed uses of bentonite in repositories

Highly compacted bentonite will be used as the buffer material around the waste package and as such, forms the bulk of the EBS. Water-saturated highly compacted bentonite is an ideal barrier material because of its physical and chemical properties (Arthur et al.). These properties include:

- diffusion barrier behaviour, which is due to the very low hydraulic conductivity that in turn causes the migration of any solutions through bentonite to be by diffusion only;
- low permeability, which should nevertheless be high enough to allow the passage of gases generated from the corrosion of metallic components in the EBS, without cracking or rupturing;
- colloid filtering behaviour, which is due to the very small grain size that effectively stops the migration of any colloid-sized particles;
- ability to prevent growth of microbes, which is due the low water activity (availability of free water) in the highly compacted bentonite;
- sorption capacity, which is very significant for adsorbing any radionuclides that may be released from a canister and that is a consequence of the very high surface area with abundant reactive sites and surfaces;
- thermal conductivity, which should be sufficiently high to ensure rapid dissipation of radiogenic heat and is particularly important in the safe disposal of HLW;
- swelling pressure, which should be sufficiently high to sustain good contact with the host rock and EBS, but not so high as to deform other components in the EBS or fracture the host rock;
- mechanical buffering/plasticity, which should be high enough to absorb rock movements, but not so high as to cause the position of EBS components to shift in their deposition holes or drifts.

Functions and requirements of bentonite within the EBS depend on waste and repository type.

Bentonite will only be used in LLW or TRU repositories as an outer layer between the cement barriers and the host rock to ensure near-field solute transport is diffusion dominated (Kitayama et al.).

In the case of a HLW repository, the EBS will comprise almost exclusively bentonite, though backfill may possibly also include crushed rock. In contrast cement is only to be used for structural purposes. The functions and requirements of bentonite in the HLW repository are summarized in Table 2.

The use of the bentonite buffer is shown in the conceptual design of the planned spent fuel repository at Olkiluoto in Finland in Figure 5 (Hansen).

Table 2: Functions and requirements of bentonite components of HLW disposal (based on Vieno, McKinley et al.).

Components	Main functions	Pre-closure requirements	Post-closure requirements
Buffer	Encase waste package and: <ul style="list-style-type: none"> ● Protect the canister against minor rock displacements ● Act as an impermeable barrier to the mass transport by ground water ● Provide geochemical buffering and retardation capacity ● Act as a colloid filter ● prevent growth of microbes ● Conduct heat from canister to rock 	<ul style="list-style-type: none"> ● Restrict mass transfer rates between the canister and host rock ● Have chemical and mechanical stability ● No harmful effects on the other barriers 	<ul style="list-style-type: none"> ● Restrict mass transfer rates between the canister and host rock ● Be sufficiently permeable to gases ● Have chemical and mechanical stability ● No harmful effects on the other barriers
Sealing plug	Confine backfill material and retard release of radionuclides	<ul style="list-style-type: none"> ● Restrict mass transfer rates along back-filled tunnels/shafts ● Have chemical and mechanical stability ● No harmful effects on the other barriers 	<ul style="list-style-type: none"> ● Restrict mass transfer rates along back-filled tunnels/shafts ● Have chemical and mechanical stability ● No harmful effects on the other barriers
Backfill	<ul style="list-style-type: none"> ● Have low permeability for ground water ● Keep the canister and the buffer in place ● Help keep the tunnel mechanically stable 	<ul style="list-style-type: none"> ● Restrict mass transfer rates along back-filled tunnels/shafts ● Be chemically and mechanically stable ● Have no harmful effect on other barriers 	<ul style="list-style-type: none"> ● Restrict mass transfer rates along back-filled tunnels/shafts ● Be chemically and mechanically stable ● Have no harmful effect on other barriers

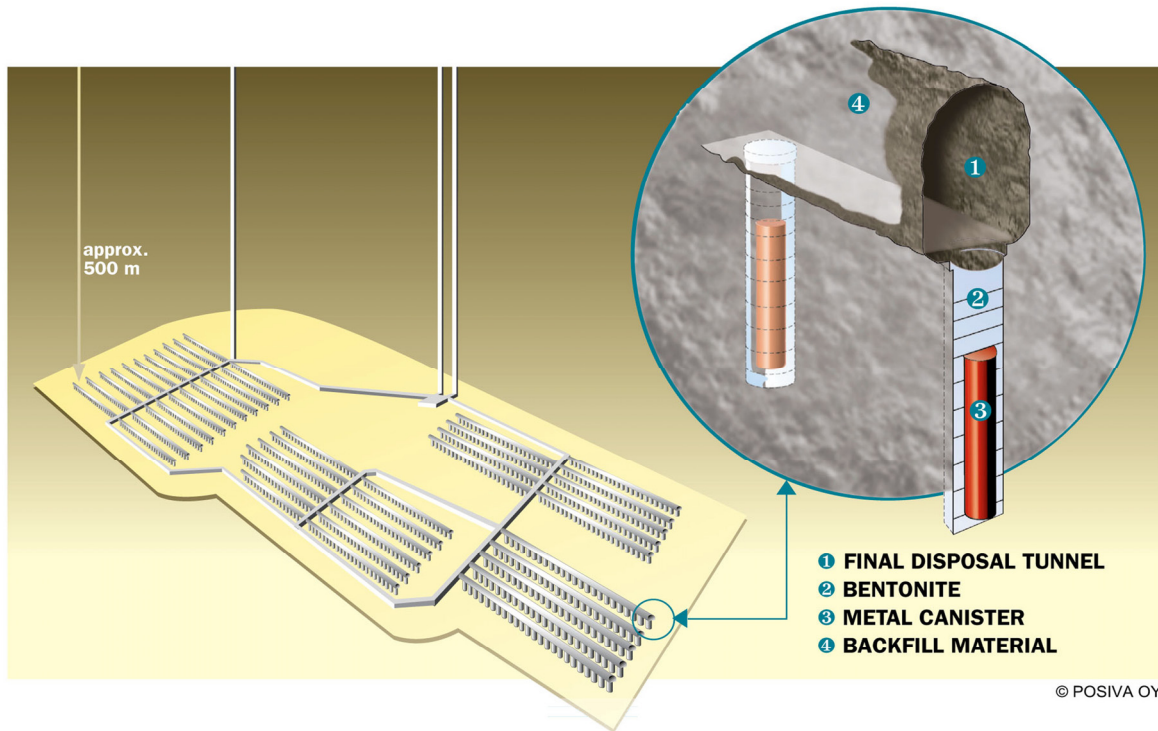


Figure 5 : Design and use of bentonite in the planned spent fuel repository in Finland (Hansen). Shown is the KBS-3V type design. The spent fuel assemblies will be packaged in copper-iron canisters, which are surrounded by a buffer of highly compacted bentonite in the deposition hole. The material for the tunnel backfill has not yet been determined.

2.4 Requirement for cement and bentonite to be used together in repositories

Most proposed repository concepts have cement-based materials and bentonite in close proximity. However, high pH cement-conditioned water has undesirable effects on the properties of bentonite, summarized in Table 3.

2.5 Alternative concepts

Strategies for avoiding cement/bentonite interaction have been suggested and include:

- Alternative materials could replace bentonite components in the cases of LLW and TRU waste repositories and cement in the case of HLW waste repositories.
- Alternative designs could avoid the close proximity of cement based materials and bentonite.
- Removal of cement used in pre-closure phases could be carried out before the final closure of a repository.
- Low-pH (less alkaline than conventional cements) could be developed.

A summary of these concepts is given in Table 4.

In practice, however, it may not be possible to avoid using cement-based materials and bentonite in close proximity in a repository environment. These reasons may include:

- Regulatory issues affecting alternative construction materials in a repository environment remain largely unaddressed. Cement, however, is a widely used construction material and its mechanical, physical and chemical properties have been identified (although not necessarily understood) and will therefore behave in a predictable manner.
- Scheduling may have been largely decided (as is the case in Finland) and could limit the scope for additional research into new materials and technologies and the development of new working repository concepts.

Table 3: Key roles of bentonite and their sensitivity to degradation by cement (McKinley et al.). Each key problem has been identified as a result of interaction with cement leachate and bentonite.

Bentonite role	Significance of cement leachate for bentonite role	Key potential problem
Diffusion barrier	Major	Cementation/ cracking, Montmorillonite dissolution
Colloid filter	Major	Cementation/ cracking, Montmorillonite dissolution
Radionuclide sorption	Some	Ion exchange, Montmorillonite dissolution
Plasticity (gas flow)	Major	Cementation, Montmorillonite dissolution
Thermal conductivity	None	Not Applicable
Mechanical buffer	Some	Cementation, Montmorillonite dissolution
Microbe barrier	Some	Cementation/ cracking, Montmorillonite dissolution

Table 4 : Alternative concepts in avoiding or minimizing the effects of cement/bentonite interaction. Many of the suggestions are known technologies in the construction industry, but have received little attention from the radioactive waste management industry (McKinley et al.).

Type	Component/ strategy used to minimise cement/bentonite interaction	Material	Advantages	Disadvantages
TRU	Hydraulic cage	Relatively high-permeability material such as gravel	<ul style="list-style-type: none"> ● Avoid advective flow driven by hydraulic gradients ● Minimises effects of cementation or cracking ● Avoids release of gas by acting as a macro-porous buffer. 	Long-term performance unknown
TRU	Colloid filter	<ul style="list-style-type: none"> ● Special plastic ● Self-healing concretes ● Zeolites 	Filters colloids that may bind with radionuclides	Long-term performance unknown
HLW	Repository design (e.g. aligning tunnels)	Not applicable	Reduces total amount of cement in repository	Long-term mechanical strength of repository may be compromised
HLW	Retrieving cement before closure	Not applicable	Reduces total amount of cement in repository	Long-term mechanical strength of repository may be compromised
HLW	Structural liner	<ul style="list-style-type: none"> ● Steel ● Ceramics ● Natural stone 	Reduces total amount of cement in repository	Long-term performance unknown
HLW	Cover grouting	<ul style="list-style-type: none"> ● Resin ● Clay ● Carbonate/silicate cements ● PEM (Pre-fabricated EBS Module)¹ 	Reduces total amount of cement in repository	Long-term performance unknown (organics should probably be avoided in HLW/SF repositories)
HLW	Mechanical plug	<ul style="list-style-type: none"> ● Natural stone ● Metals 	Reduces total amount of cement in repository	Long-term performance unknown
HLW	Floors	<ul style="list-style-type: none"> ● Gravel ● Natural stone paving 	Reduces total amount of cement in repository	

¹ a pre-fabricated module consisting of multiple barrier components such as bentonite inside a steel liner, surround by sacrificial material (crushed tuff, volcanic glass etc) and a concrete liner on the outside.

3 MINERALOGY AND GEOCHEMISTRY OF CEMENT-BENTONITE SYSTEMS

Cement/bentonite interaction is a key issue in the longevity of a TRU or HLW repository. The main problem is the degradation of the bentonite barrier as a result of groundwater that has been conditioned by the adjacent cement. Through experimentation, key chemical/geochemical processes have been identified.

3.1 *Experimental approaches*

A lot of detail regarding the cement/bentonite interaction has been obtained through experimental studies. Experimental approaches reported during the meeting included:

- Batch reactors:
 - Bentonite and crushed rock with synthetic saline waters
 - Cement in H₂O

- Flow through reactors:
 - Bentonite and crushed rock with synthetic saline waters
 - Bentonite with NaOH-NaCl, KOH-KCl and Ca(OH)₂-CaCl₂ solutions (most common approach)
 - OPC and H₂O

- Diffusion flow reactors:
 - Sand/bentonite mixture in synthetic cement/groundwater

Details of the experiments are given in Table 5.

Additionally, there was some discussion of studies of experiments that are reported in the published literature. It was highlighted that most published data are for experiments with mudrocks rather than isolated smectite. Furthermore, experiments have been carried out under a wide range of conditions and the results are difficult to compare in a meaningful fashion.

Similarly, when bentonite has been used in experiments, there is a question as to the purity of the smectite present.

It was noted that the solubility of NaOH and Ca(OH)₂ in pure water is of quite a different order: at 20°C, c.44 mol/L and c.0.04 mol/L, respectively. Hence experiments with NaOH solutions can reach much higher pH values/OH⁻ ion concentrations.

Table 5: Summary of experiments designed to investigate cement/bentonite interaction described during the workshop.

Contributor	Experiment design	Solids	Solutions	T (°C)	Duration	Main parameters tested	Main Purpose	Major types of information obtained				Comments	
								Reaction mechanisms	Kinetic	Thermodynamic	Mass balances		Transport parameters
Otsuki	Batch reactor	OPC	Deionized H ₂ O	25	c. 1 week	Cement chemistry and compressive strength	Test a model for leaching of calcium from cement	No	Yes	No	Yes	Yes	Experimental results were not used to derive a model, only to test it. No kinetic parameters or rate laws were deduced
	Accelerated batch reactor	OPC	Deionized H ₂ O (replaced every 24 hours)	25	c. 9 weeks	Cement chemistry and compressive strength	Test a model for leaching of calcium from cement	No	Yes	No	Yes	Yes	Experimental results were not used to derive a model, only to test it. No kinetic parameters or rate laws were deduced
Sato et al.	Flow-through cell	Na-montmorillonite	0.3M NaOH-NaCl or 0.3M KOH-KCl	30, 50, or 70	7 to 10 days	Solution composition over time	Determine dissolution rates and mechanism	Yes	Yes	No	No	No	A rate law and kinetic parameters were derived
	In situ within AFM chamber	Na-montmorillonite	0.3M NaOH	25	c. 1.5 hours and 2-8 days	Mineral particle size over time	Determine dissolution rates and mechanism	Yes	Yes	No	No	No	Particle sizes measured by AFM <i>during</i> reaction. Kinetic parameters were derived
	In situ within AFM chamber	Na-montmorillonite	1.0M NaOH - NaCl	25	< 1 day	Mineral particle size over time	Determine dissolution rates and mechanism	Yes	Yes	No	No	No	Particle sizes measured by AFM <i>during</i> reaction. Kinetic parameters were derived
	Batch reactor	Na-montmorillonite	0.3M NaOH	50	6 to 33 days	Starting and final mineral particle size	Determine dissolution rates and mechanism	Yes	Yes	No	No	No	Particle sizes measured by AFM <i>after</i> reaction. Kinetic parameters were derived
Karnland et al.	Titration	Na-montmorillonite	Acid added to pH = 4, Alkali added to pH = 10	30, 50, or 70	Not applicable	pH as a function of time	Determine dissolution mechanisms	Yes	No	No	No	No	
	Batch diffusion cell	Na-, K- or Ca-exchanged MX-80 bentonite (dominantly montmorillonite)	0.1, 0.3 or 1.0M NaOH, 1M KOH, 0.02M Ca(OH) ₂ (saturated), 1M NaCl and H ₂ O	Room	70 to 100 days	Cation Exchange Capacity (CEC), mineralogy, mineral and pore water compositions (including pH), and swelling pressure	Determine pH buffering capacity, changes in mineralogy, swelling pressure, CEC	Yes	Yes	No	Yes	No	No

Table 5. Continued.

Contributor	Experiment design	Solids	Solutions	T (°C)	Duration	Main parameters tested	Main purpose	Major types of information obtained					Comments
								Reaction mechanisms	Kinetic	Thermodynamic	Mass balances	Transport parameters	
Vuorinen et al.	Batch reactor	Crystalline rock from Olkiluoto or MX-80 montmorillonite	High pH synthetic Na-Ca-Cl waters (fresh and saline pH = 12.5; saline pH = 13.5)	c. 25	1 week to 1.5 years	Mineral and solution compositions	Determine secondary minerals, alteration reactions	Yes	No	Yes	No	No kinetic parameters or rate laws were deduced	
	Flow-through cell	Crystalline rock from Olkiluoto and MX-80 montmorillonite	Synthetic fresh ground water, Na-Ca-Cl water and high pH Na-Ca-Cl water (fresh + saline, pH = 8.8 and 8.3; saline pH = 12.5)	c. 25	1 year and 1.5 years	Mineral and solution compositions (out-flow and pore water), CEC	Determine secondary minerals, alteration reactions and propagation of an alkaline plume	Yes	No	Yes	Yes	No kinetic parameters or rate laws were deduced	
Yamaguchi et al.	Batch reactor	Compacted sand and Na-montmorillonite (Kunigel V1)	Na-Cl-OH water, 0.1, 0.3, 1 M NaOH	50 to 170	4 to 8 weeks	Mineralogy, remaining montmorillonite and Si, Al and Ca concentrations in solutions	Determine dissolution rates and mechanisms	Yes	No	Yes	No	Kinetic parameters were derived	
	Diffusion cell	Compacted sand and Na-montmorillonite (Kunigel V1)	0.5M and 10 ⁻² M NaOH	10 to 90	18 to 28 weeks	Dissolution rates	Determine diffusivity of alkali solutions in bentonite	Yes	No	Yes	Yes	Kinetic parameters were derived	
Ito et al.	Batch	OPC	Deionized H ₂ O	20	2 years	Hydraulic and mechanical properties	Determine chemical-mechanical-hydraulic properties	No	No	No	Yes	Leaching tests provided for material suitable for mechanical testing	
	Flow-through	OPC	Deionized H ₂ O or 1M NaNO ₃	20	2 years	Hydraulic and mechanical properties	Determine chemical-mechanical-hydraulic properties	No	No	No	Yes	Leaching tests provided for material suitable for mechanical testing	
Berner	Flow-through	OPC	Deionized H ₂ O	Room	To >3 years (3000 pore volumes)	Solution composition	Determine solution composition as a function of time	Yes	Yes	No	No	Only experiments described by Berner that were carried out at PSI are considered. No rate laws or parameters derived	

3.2 Processes

3.2.1 Cement degradation

Variations in the chemistry of pore water released from cement as a function of time are summarised in Figure 6. Cement dissolution releases mainly Na, K, OH (early), and Ca, OH (later).

The initial high Na and K concentrations are a consequence of the non-restricted solubility of NaOH and KOH present in freshly hydrated cement. The following increasing/high Ca concentration is a result of Ca(OH)₂ solubility. The peak in SiO₂ reflects SiO₂ release from CSH phases (Berner).

The effect on cement of releasing these components is to increase porosity and permeability and to lower compressive strength (Otsuki; Ito et al.). The last two effects have been found to be a function of the former. However, these effects are countered by cementation processes (e.g. carbonation/calcite precipitation), which can lower the effective porosity, and therefore the permeability, to almost zero (Berner).

Local groundwater flow and transport conditions have a major influence on the release and transport of cement and subsequently on the magnitude of the high pH plume (Vieno). Important controlling factors include:

- Sub-horizontal fracture zones divide the flow pattern into layered zones. It is unlikely that a significant amount of cement above or from major sub-horizontal zones would be transported into the sparsely fractured rock below the zones.
- The water leaving a grouted rock spot will not have the pH and other properties of cement pore water, but is diluted by the groundwater flowing around/through the grouted area. This source term dilution is enhanced by the fact that grouting is carried out at fracture zones and other locations where flow rates are highest.
- Further buffering and dilution take place during transport in the geosphere. In open fractures with a limited buffering capacity and a small WL/Q (half of the “flow wetted” surface divided by the flow rate), the leachate may, however, be transported over long distances.
- Transfer of OH⁻ ions from water-conducting fractures intersecting a deposition hole is limited by the boundary layer (film) resistance between the flowing groundwater and the stagnant pore water in the buffer. The fraction of OH⁻ ions entering the buffer decreases with an increasing flow rate of groundwater along the fractures.

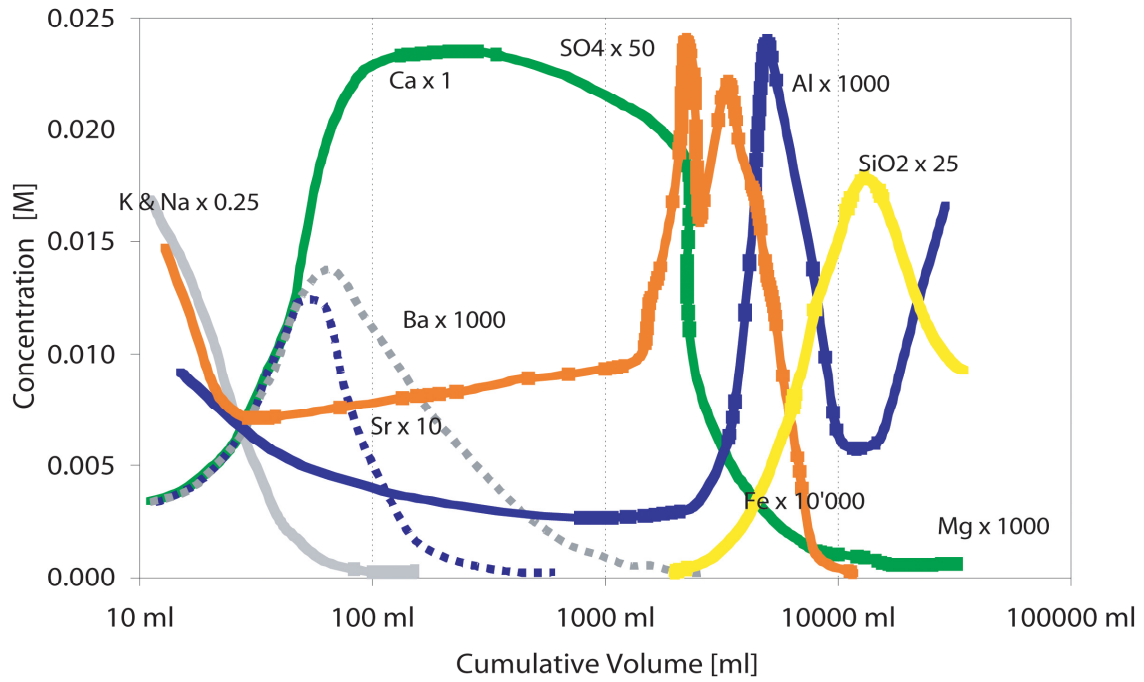


Figure 6: Schematic representation of ion release from degrading cement (10 ml of cumulative volume correspond to 1 sample pore volume) (Berner). The apparent double peak in the sulphate concentration represents an experimental failure.

3.2.2 Bentonite degradation

One of the most predictable changes is an increase in the pH of the buffer pore water (Gaucher). This increase influences significantly both the chemical and physical properties of the buffer including:

- The structure of montmorillonite consists of superimposed layers, each of which contains a plane of Al ions sandwiched between two inward pointing sheets of linked SiO₄ tetrahedra. These layers are separated by a cation exchange layer, shown in Figure 7 (Sato et al.; Ichikawa et al.).

Montmorillonite dissolves along the edge surface whereas the basal surface remains relatively un-reacted, apart from minor pitting (Sato et al.). A two-step mechanism for the dissolution of montmorillonite is shown in Figure 8.

Reaction between the hydroxyl groups in the cement leachate and bentonite gives a significant release of silicon (Karnland et al.). Initially silicon in solution is controlled by the dissolution of silica polymorphs (cristobalite and quartz) followed by the dissolution of montmorillonite (Karnland et al.).

The release of silicon from montmorillonite is shown to by some studies to be incongruent (silicon is released preferentially compared to the concentration of other components) and conditions move towards the stability field of beidellite (Karnland et al.). This behaviour is supported by the presence of beidellite in the results of Vuorinen et al. Conversely, Sato et al. suggest the dissolution of montmorillonite is congruent based on the concentrations of silicon and aluminium in both NaOH and KOH solutions corresponding to the stoichiometry of montmorillonite.

- Secondary minerals will form as a result of the interaction between cement leachate and bentonite. The types and abundances of secondary minerals will reflect the composition of the solution phase (pH, pe, cations etc). The important minerals associated with the degradation of bentonite are identified in Table 6.

Some of these phases are believed to be metastable on the timescales relevant to the safety assessment of a waste repository. Given enough time these solids could transform into other more stable phases under the prevailing local conditions (Oda et al.; Gaucher). Some potential reaction paths are:

Montmorillonite -> Illite -> Zeolites
 Montmorillonite -> Illite -> Saponite -> Clinochlore
 Montmorillonite -> Illite -> Phillipsite -> K-Feldspar

Problems still persist in predicting which of these secondary phases will be important because of the poor knowledge of possible reaction products (including some which may not yet have been identified), mineral dissolution rates and growth kinetics which are subject to considerable uncertainty (Lehikoinen).

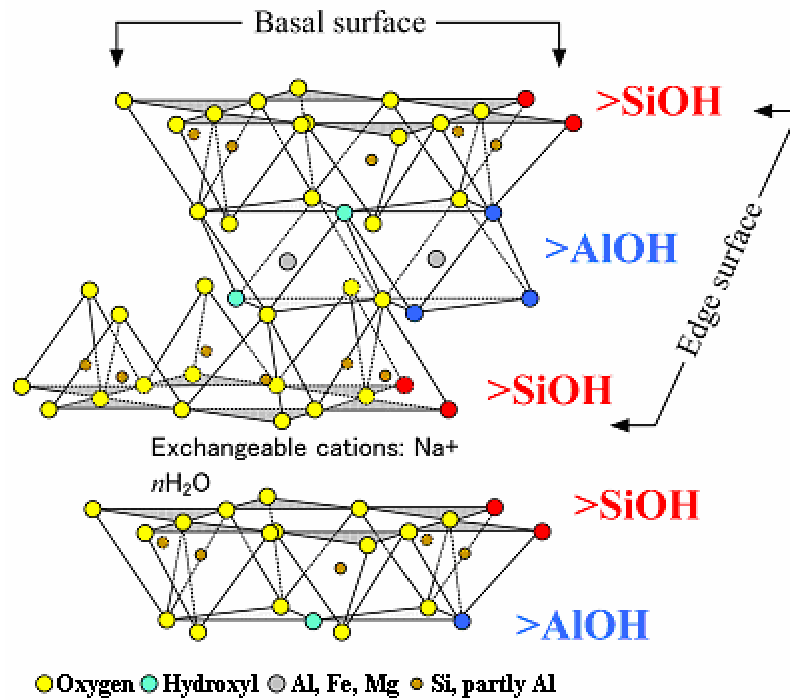


Figure 7: Layered structure of montmorillonite where Al ions are sandwiched between two inward pointing sheets of linked SiO₄ tetrahedra. The basal surface runs parallel to the silicate sheets whereas the edge surface is perpendicular to the sheets. The dissolution of montmorillonite is along the edge surface, reactive sites are shown in colour (Sato et al.; Ichikawa et al.).

Alkaline Condition

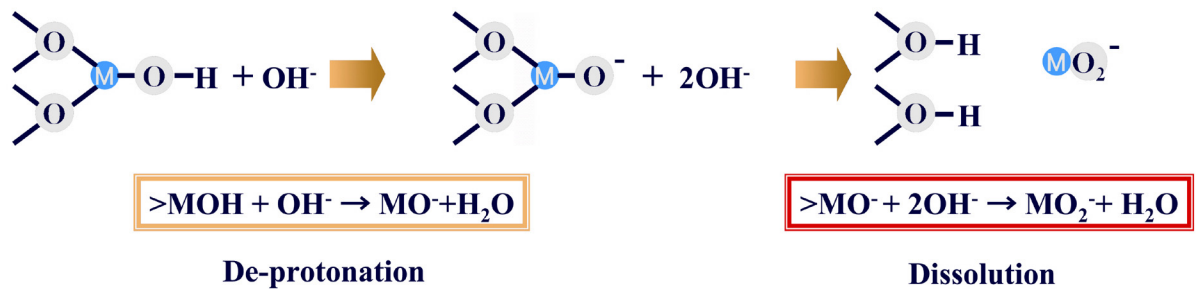


Figure 8: Proposed two step dissolution mechanism of montmorillonite under high pH conditions (Sato et al.).

Table 6: Mineral transformations as bentonite degrades under high pH conditions (Oda et al.; Gaucher; Lehtikoinen). Precipitating minerals have been tentatively assigned to different groundwater conditions, although differences may arise from those suggested here depending on local conditions.

Original minerals in bentonite	Dissolving minerals	Precipitating minerals (theoretical and observed)			
		NaOH dominant solution	KOH dominant solution	Ca(OH) ₂ dominant solution	Other
Na-montmorillonite	Na-montmorillonite	Na-Beidellite	Illite	Ca – Montmorillonite	Halite
Gypsum	Gypsum	Analcime	Phillipsite	CSH	Calcite
Albite	Albite		K-Feldspar	CAH	Chlorite
Silica polymorphs	Silica polymorphs		Muscovite	CASH	Quartz
Calcite					

- Cation exchange reactions may occur at the same time as the mineral transformations in Table 6. Notably, Mg-exchanged sites (MgX_2) in the unaltered bentonite will become Na-exchanged (NaX) in NaOH solutions, K-exchanged (KX) in KOH solutions and Ca-exchanged (CaX_2) in $Ca(OH)_2$ solutions.
- Cation Exchange Capacity (CEC) is significantly increased on exposure to strong NaOH solutions ($>0.3M$) (Karnland et al.) and synthetic high pH Na-Ca-Cl waters (molar ratios of Na/Ca $\sim 2.4, 24$ and 2330 ; Vuorinen et al.). In contrast, solutions exposed only to NaCl and $Ca(OH)_2$ saturated solutions show no significant change. Although replacement of Na in the montmorillonite by Ca was found for the experiments conducted in the $Ca(OH)_2$ saturated solutions (Karnland et al.) and controlled replacement could be achieved using a $CaCl_2$ solution (Ito et al.).
- Dissolution rates of minerals in bentonite are strongly dependent on pH and temperature. The dissolution rate increases with an increase in pH and/or temperature (Sato et al.).

The rate of dissolution at any time will also depend on the degree to which equilibrium is approached. Solids that are far from equilibrium with respect to a particular solution will dissolve much faster than solids that are close to equilibrium (Takase).

Similar rates are obtained from Si and Al concentrations, and NaOH and KOH experiments, showing no effects of interlayer cation on dissolution rates (Sato et al.).

A summary of the dissolution rate laws presented at the workshop is given in Table 7.

- The buffering capacity of unpurified bentonite may be controlled by silica polymorphs in the early stages of degradation because of their faster dissolution when compared to montmorillonite (Lehikoinen).

The buffering capacity of montmorillonite is the sum of two contributions:

- the edge surface hydroxyl sites (see Figure 7) which undergo very fast reactions;
- the montmorillonite structure itself, which tends to undergo slow reactions and will not buffer the pore fluid chemistry until the edge surface sites have been exhausted.

The interaction between the montmorillonite and hydroxide ions takes place according to:



or



Meaning one mole of Na-montmorillonite consumes 4.67 moles of OH^- , or 12.7 moles of OH^- are buffered per kilogram of clay. This is deemed acceptable to keep the pH below 11, by neutralizing at least 0.5 moles of OH^- per kg of clay (Lehikoinen).

Table 7: Rate laws governing the dissolution of montmorillonite, mentioned during the workshop.

Worker:	Yamaguchi et al.
Rate law:	$R_A = 0.8[\text{OH}^-]^{1.4} e^{-\frac{48000}{RT}}$
Source:	Experimentally derived
T (°C):	50 - 170
pH:	13 - 14
Comments:	Also used by Takazawa et al.
Worker:	Sato et al.
Rate law:	$R_A = \left(4.74 \cdot 10^{-6} \cdot e^{-396/RT} \cdot \frac{177 \cdot e^{204/RT} \cdot a_{\text{OH}^-}}{1 + 177 \cdot e^{204/RT} \cdot a_{\text{OH}^-}} + 1.70 \cdot e^{-69.7/RT} \cdot \frac{0.0297 \cdot e^{23.5/RT} \cdot a_{\text{OH}^-}}{1 + 0.0297 \cdot e^{23.5/RT} \cdot a_{\text{OH}^-}} \right) \cdot \left(1 - e^{(-610^{-10}) \cdot (\Delta G_f^{\circ}/RT)^6} \right)$
Source:	Experimentally derived
T (°C):	30, 50 and 70
pH:	8 - 13.5
Worker:	Lehikoinen
Rate law:	$R_A = 10^{-12.31} \cdot a_{\text{OH}^-}^{0.34}$
Source:	Huertas et al. (2001)
T (°C):	25
pH:	12.5
Worker:	Takase
Rate law (1):	$R_A = k \cdot A \cdot (a_{\text{H}^+})^{-0.34} \left[1 - \exp \left[-a \left(\log \frac{Q}{K} \right)^6 \right] \right]$
Rate law (2):	$R_A = k \cdot A \cdot (a_{\text{H}^+})^{-0.34} \left(1 - \frac{Q}{K} \right)$
Source:	Fujiwara et al. (2003)
T (°C):	
pH:	
Comments:	<p>$a = 6e-10$ and $\log K = -17.1$</p> <p>Rate law 1 is based on the empirical model suggested in Cama et al. (2000) and Rate law 2 is derived from transition state theory</p>

Where: R_A is the specific rate (usually $\text{molm}^{-2}\text{s}^{-1}$) k is the rate constant; a and A are constants; Q is the ion activity product for the montmorillonite; K is the equilibrium constant for the dissolution of montmorillonite; R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$); T is the absolute temperature.

In highly compacted bentonites, the pH buffering capacity is at a maximum because the solution migration is diffusion controlled (Lehikoinen).

- Solution modelling predicts that with the precipitation of zeolites, associated with the mineralogical changes, the pH of the cement leachate is neutralized, which in turn may inhibit further dissolution of the bentonite (Oda et al). Swelling pressure is reduced on exposure to high concentration NaOH and NaCl solutions (>0.3M). A major difference was that NaCl gave a rapid decrease to a new stable pressure value, while contact with the NaOH solution gave a gradual decrease (Karnland et al.). Low concentration NaOH solution and Ca(OH)₂ saturated solution had no effect on the swelling pressure (Karnland et al.).

Consolidation tests show that the greater the difference between the pre-consolidation stress (overburden pressure) and the current overburden pressure (i.e. unloading of overburden pressure due to adjacent cement dissolution) the greater the tendency for the material to swell (Ito et al.).

- Precipitation/cementation processes are difficult to evaluate. Depending on experimental set up (e.g. flow through reactors), some workers found that precipitation/cementation effects were not significant. However, this may not be truly representative of a real system where secondary minerals are likely to grow in situ (see precipitating minerals in Table 6).

Cementation may be a significant issue because of the increased chance of the bentonite barrier cracking and solution transport being advective as opposed to diffusive (McKinley et al.).

- Porosity has been described as either increasing or decreasing as a function of dissolution and precipitation rates of the primary and secondary minerals. In the long term this will depend on the stability of these secondary phases once formed (Arthur et al.). Where only dissolution of the bentonite is considered (e.g. Kato et al.), the porosity increases. If considering the growth of alteration products they are likely to form in situ (cementation) and so decrease the porosity (e.g. Berner; Gaucher).
- Permeability and porosity are strongly dependent on each other. Similarly, permeability will increase or decrease as a function of the dissolution and precipitation of the primary and secondary minerals.
- Hydraulic conductivity is related to the permeability and porosity of the bentonite. Predictive modelling has shown the hydraulic conductivity to generally increase with ongoing exposure to a high pH plume (Kato et al.). Similarly this is dependent on the dissolution and precipitation rates of the primary and secondary minerals.
- Diffusivity of bentonite has been predicted to decrease as a function of time (Kato et al.). This can be attributed to the decreasing difference in solution concentration across the EBS and the decrease in porosity due to cementation by secondary minerals.
- Sorption will be important and an intact bentonite has excellent sorption capability, one of the main criteria for using it. However, assessing the sorption capability of secondary

minerals is difficult and results in uncertainty as to the evolution of sorption capacity as a function of time.

- Shear strength (the ability to resist failure by a shear motion stress field) is independent of sodium replacement calcium in montmorillonite (Ito et al.).

Other relevant factors which were mentioned, but not addressed, include:

- density;
- settling;
- swelling of corrosion products;
- construction defects;
- microbial activity;
- gas generation.

3.3 Data

3.3.1 Thermodynamic data

There is a great need for better thermodynamic data to assess the significance of potential geochemical reactions under different scenarios pertinent to the needs of a particular country. General issues relevant to this problem, which apply to both cement and bentonite are given below.

- The mineralogy, structural formulae and crystallinity of secondary solids are not well defined.
- Thermodynamic properties of representative clay minerals, zeolites and CSH/CASH solids/gels are poorly known.
- Minerals formed initially tend to be metastable and may transform into other more stable phases over the timescales involved.
- Precipitates may be amorphous or poorly crystalline and may persist metastably with respect to their crystalline counterparts for a very long time.
- Crystalline solids are often complex solid solutions that exhibit a wide range of composition depending on the chemistry of the coexisting aqueous phase. Currently solid solution modelling is not employed in repository degradation models.
- Databases are of variable and often uncertain quality and notably:
 - data for a particular phase of importance for radioactive waste PA is often missing;

- databases often have internal inconsistencies;
 - peer-review of data entries is often lacking.
- There are poor data for aqueous species at high pH (especially Si- and Al- species).

A particular issue in the case of cement is that $\text{Ca}(\text{OH})_2(\text{s})$ solubility is not well known and depends on the method used for deriving activity coefficients. This is critical because the selection affects further high pH items in databases. (e.g. CaOH^+ reactions).

Some of these issues can be addressed by:

- using a peer reviewed database as a starting point, such as SPRONS.JNC, to which data are systematically added;
- using numerical approaches that allow reasonable estimates to be made and uncertainties to be assessed;
- carrying out additional experiments for key phases to support these estimations;
- estimating bounding parameter values;
- assigning the same bounding parameter values (e.g. equilibrium constants) to groups of similar minerals;
- deriving relevant data for all the different minerals which may form in the EBS system as a result of cement/bentonite interaction.

A key issue for consideration is the validity of estimation techniques. Is it realistic to rely on estimated thermodynamic quantities or should the focus remain on deriving the relevant data for all the different minerals (the approach adopted by Gaucher)?

3.3.2 Kinetic data

There is similarly a great need for more reliable kinetic data for relevant mineral phases, in the cases of both cement and bentonite.

Significant progress has been made in bounding rates and determining relative rates of reaction. An important issue is whether this progress is adequate for the needs of barrier design and ultimately PA.

However, compared to uncertainties associated with thermodynamic data, even greater uncertainties are associated with kinetic data.

Problems still persist in the derivation of reliable kinetic data, notably:

- It is particularly difficult to obtain reliable rates under high pH and temperature conditions, whether in the cases of bentonite or cement.
- In the cases of experiments aimed at understanding cement and/or bentonite alteration most workers tend to choose specific experimental conditions. This was partially

addressed by Sato et al. who conducted their experiments over a range of temperatures, from 30 - 90°C.

- Bentonite is a mixture of different minerals containing primarily montmorillonite, but also gypsum, silica polymorphs, albite and calcite. Purification of montmorillonite is particularly difficult and so experimental studies invariably investigate the dissolution of a mixture of these minerals.
- Dissolution of the primary minerals versus the growth of secondary minerals in bentonite is largely unknown. Combined with the variability in groundwater conditions (pH, p_e , temperature, species in solution, etc.) gives a large number of kinetic controlling factors which are poorly constrained.
- In the cases of minerals present in bentonite or cement, different rate laws can be derived from the same experiment depending on the fitting parameters and assumptions made.

As in the case of thermodynamic data, a potentially fruitful approach is to either estimate rates or obtain experimental rates for groups of chemically and crystallographically similar minerals.

4 EVALUATING THE PERFORMANCE OF CEMENT-BENTONITE BARRIER SYSTEMS

4.1 Numerical modelling

Numerical modelling provides a very useful tool in predicting mineral (both chemical and physical) and solution properties in the long term evolution of a HLW repository. The major available modelling approaches are equally applicable to both bentonite and cement alteration. However, though a multitude of these different approaches were discussed during the workshop, not all were applied to both bentonite and cement in Table 8.

In summary, the main modelling approaches are:

- forward modelling (equilibrium and kinetic);
- inverse modeling;
- coupled chemical/mass transport modelling (mostly using 1D transport codes);
- coupling handled by a single code;
- different aspects handled by different codes (e.g. PHREEQC handling chemistry and a separate 1D transport model);
- 2D coupled modelling showing calcite growth while treating diffusion;
- ion-migration models (dealing with the relationship between electrochemical potentials, transport and reaction);
- coupled chemical/mechanical/hydraulic (Finite Element Model, FEM) codes;

Table 8: Summary of numerical modelling approaches described during the workshop. Different approaches were taken to confirm experimental results and predict both chemical and physical changes in materials as they degrade.

Worker	Approach	Applied to	Mass transport		Computer codes
			Maximum dimension	Coupling of chemistry and transport?	
Oda et al.	Forward equilibrium modelling	Bentonite, Cement	1D	Yes, diffusion	PHREEQC
Vuorinen et al.	Forward and inverse equilibrium modelling	Combined bentonite and rock	3D (FEMLAB)	Yes (FEMLAB) advection and diffusion	PHREEQC, FEMLAB
Otsuki	Sequential calculation of transport - kinetic reaction - physical properties	Concrete/cement	1D	Yes, diffusion	Un-named numerical calculation
Takazawa et al.	Sequential calculation of transport - kinetic reaction - physical properties	Compacted bentonite/sand mixture	1D	Yes, advection and diffusion	Un-named numerical calculation (includes chemical speciation using PHREEQC)
Gaucher	Forward equilibrium modelling along a flow path, with overall reaction rate controlled by transport, calculation of mineralogy and porosity	MX-80 bentonite, Jurassic mudrock	1D	Yes, diffusion	PHREEQC
Ito et al.	Sequential calculation of stress – boundary conditions – chemistry - mechanical properties – deformation - physical properties	Bentonite, cement	2D	Yes, advection	MACBECE (developed by authors)
Lehikoinen	Sequential calculation of transport - kinetic reaction - physical properties	Montmorillonite	1D	Yes, diffusion	Un-named numerical calculation
Kato et al.	Sequential calculation of transport - kinetic reaction - physical properties	Kunigel V1 bentonite, cement	1D	Yes, advection and diffusion	Un-named numerical calculation
Ichikawa et al	Calculation of transport - physical properties - (MD/HA)	Kunipia-F bentonite	2D	Yes, advection and diffusion	Un-named code, developed by authors
Berner	Calculation of transport - kinetic reaction - physical properties	Cement	2D	Yes, diffusion	MCOTAC
Takase	Simultaneous calculation of transport - kinetic reaction- physical properties	Bentonite	1D	Yes, advection and diffusion	RAIDEN

- macro-properties estimated from micro-scale processes (Molecular Dynamics (MD)/Homogenization Analysis (HA)).

The capability of these models to accurately predict the performance of the components in an EBS as a function of time is limited by:

- appropriate mineral representation, especially the secondary minerals, including:
 - CSH-phases (there is still an on-going debate concerning the nature of appropriate analogous CSH phases);
 - zeolites;
 - smectites.
- formulation of key underlying models/laws/functions, especially:
 - solid solution models - these have yet to be incorporated into modelling of EBS;
 - activity coefficient models - using different methods provides different answers in terms of the activity of a species in solution;
 - rate laws - both dissolution and precipitation of relevant phases in the system;
 - hydrological constraints - including groundwater velocity, advection vs. diffusion, porosity, permeability, and hydraulic conductivity.
- differences between actual and modelled phases, notably:
 - chemical differences;
 - degree of crystallinity (which is very hard to determine as mineral phases may be present as gels, or be semi- or wholly- crystalline and different states of the same can have solubilities ranging over several orders of magnitude).

Several of the models were used to predict the depth of degradation as a function of time and are summarized in Table 9.

4.2 Towards PA modelling approaches

Additional work is needed before an adequate model for assessing the performance of cement-bentonite barrier systems can be produced. Notably it is necessary to:

- define an appropriate simplification of the cement-bentonite system;
- demonstrate appropriate levels of conservatism in the models.

However, considerable progress has been made so far and a general approach to developing such PA models can now be suggested.

Some of the important mechanisms controlling the degradation of the buffer by the cement leachate have been identified and investigated. These can be represented schematically as shown in Figure 9 (Takase).

Table 9: Summary of predictive models described during the workshop. These models assessed the depth of degradation of materials in the EBS as a function of time.

Worker	Material	Phenomena investigated	Timeframe (years)	Depth affected (cm)	Validation against real systems?
Otsuki	OPC	Porosity increase	10 100 1000	5 10 30	Yes
Lehikoinen	Na-montmorillonite	Porosity vs. secondary minerals	1,000	Porosity lost < 10 Reaction products >35	No
Gaucher	Na-montmorillonite	Secondary minerals	100,000	65	No
Takase	Na-montmorillonite	Secondary minerals	1,000,000	50 - 200	No

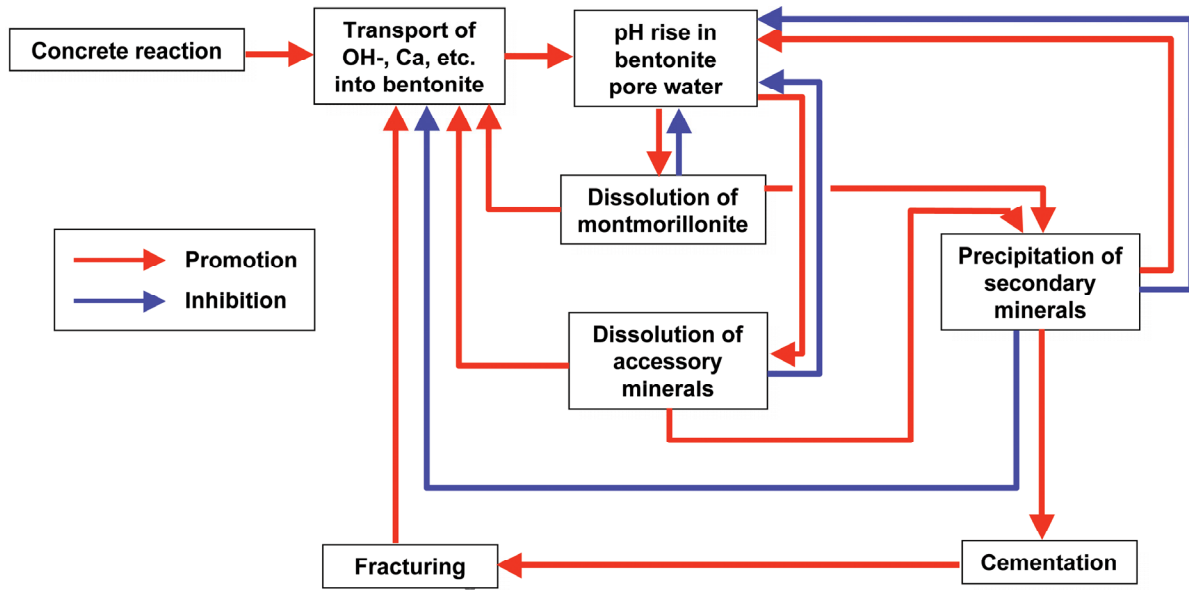


Figure 9: Cement/Bentonite interaction as a coupled non-linear dynamical system (Takase).

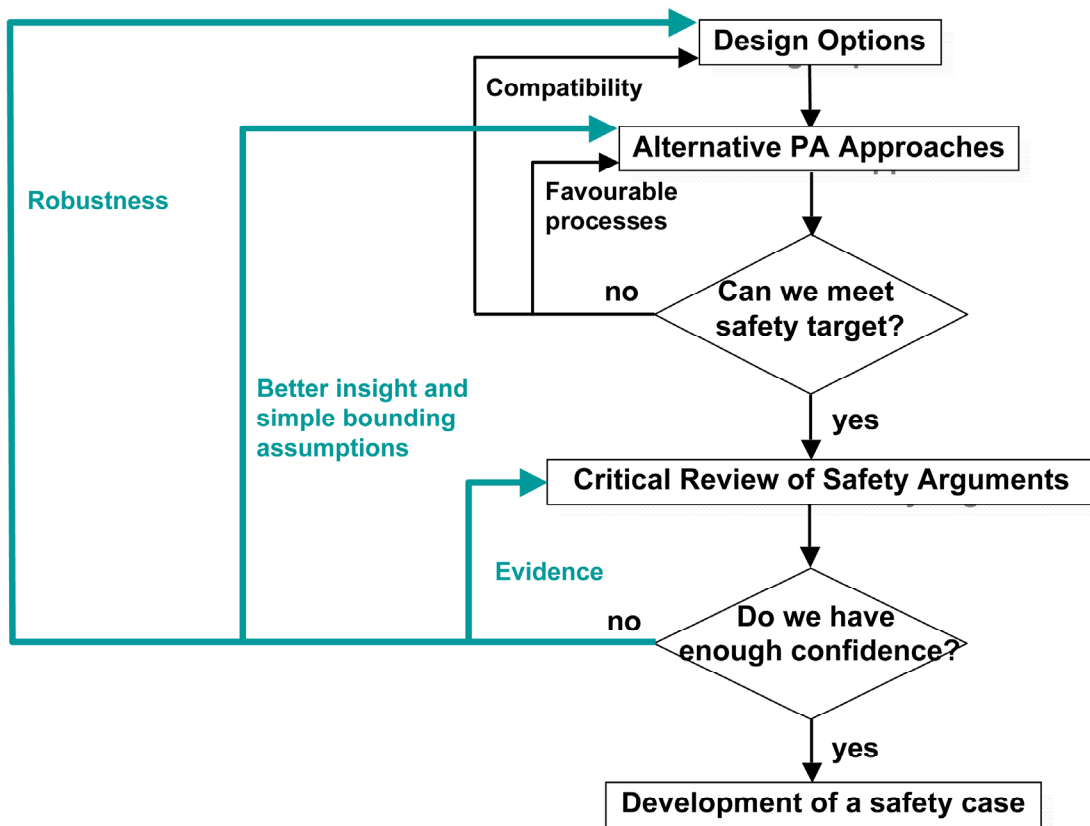


Figure 10: Preliminary PA model scheme (Takase).

Representing cement/bentonite interaction in this way has several advantages:

- Modifications to this diagram are simple to implement as more mechanisms and couplings are found.
- Magnitudes of the mechanisms can be indicated.
- The representation facilitates simplification of the system by visualizing mechanism interaction.
- Helps to define conservative models where all mechanisms can be considered in terms of their importance.

Alternative possible approaches consider the degradation of the buffer to be limited by three distinct controls:

- mass balance, whereby there is a sufficient amount of bentonite to buffer the pH of the cement leachate;
- mass transport, whereby not all OH⁻ released from the cement will necessarily react with the buffer because of the low diffusion rates in the buffer in comparison with advective transport around the tunnel;
- reaction kinetics, whereby the total amount of buffer left intact at a specific time is governed by its dissolution rate.

A final PA assessment of the EBS for HLW considering cement/bentonite interaction could follow the guidelines represented in Figure 10 (Takase).

4.3 Natural/anthropogenic analogues

Natural and anthropogenic analogues to the EBS system do exist and were mentioned, but they were not discussed in detail. This can be attributed largely to the subject matter of the workshop, where the focus was specifically on the interaction of cement and bentonite. However, using natural and anthropogenic analogues have potentially important benefits, notably:

- providing a better insight into key mechanisms;
- giving insights into the later stages of the time frames considered by the PA of a HLW repository;
- allowing for the evaluation of the extent of localized versus macro-scale hydrological mechanisms (e.g. diffusion versus advection).

Two natural analogues of particular interest, which were mentioned during the workshop and which provide information on cement-buffered hyperalkaline groundwaters are:

- Maqarin, Jordan;
- Khushaym Matruk, Jordan.

Although these sites have already been studied extensively, a re-examination may provide more confidence and further insights in assessing the mechanisms of cement leaching and alteration. However, little new information is likely to be provided about cement-bentonite interaction. It would be worthwhile to examine available information from actual underground investigation sites (URLs) where cement has been used during construction. Such evaluations may give useful information about the eventual formation of an alkaline plume and are presently being undertaken on some data from the Äspö Hard Rock Laboratory in Sweden.

5 ISSUES FOR CONSIDERATION IN DESIGN AND PERFORMANCE ASSESSMENT OF HLW/SF REPOSITORIES

5.1 Approach to presentation of major issues

Issues to be considered in the design and performance assessment of HLW/SF repositories are considered in two sub-sections. In the first part, issues that were discussed during the workshop are summarised, based on questions that were asked of each speaker, responses to those questions and comments that were made following each presentation. Since at different times similar questions were offered and similar answers were given, the issues discussed have been consolidated and are not presented on a presentation-by-presentation basis.

The issues have been classified generally according to the topics of the sessions in the workshop. However, the first and last sub-divisions of the topics discussed do not correspond to particular sessions but highlight research achievements and management issues respectively. Additionally, not all issues discussed in each session are presented together. This approach is necessitated by the fact that sometimes an issue raised in one session was more appropriate to the theme of another.

It is stressed that there was not necessarily a consensus concerning the accuracy of the statements that were made. However, these discussion points highlight the range of opinions that were expressed by the workshop participants.

The second subsection summarises the responses to a questionnaire. The section aims to highlight areas of agreement and areas of disagreement.

5.2 Issues discussed in the workshop

5.2.1 Achievements of research to date and priorities for future work

The discussions highlighted that a lot of data have been acquired and key processes have been identified. There was considerable discussion of the most appropriate uses of this information. Issues that were highlighted are:

- Priorities for future experimental, field and theoretical work can be suggested based upon the work completed already.
- A framework for PA can be suggested based on these data.
- Additional work should focus on developing integrated interpretations from the diverse data that are available already.
- Additional experiments to verify present understanding should be undertaken.
 - Additional information on the long-term evolution of cement-barrier systems would be desirable.
 - Consideration should be given to long-term experiments.
 - Analogues could yield useful information.
 - There are underground lab facilities, such as the Mol URL in Belgium, which have been operating for 20 to 30 years and could be used to give useful information on these time-scales.
- It is desirable for new materials to be considered in place of cement and to question ‘conventional wisdom’ which states that cement is the best material to use for construction and barrier functions in many circumstances.
- It is desirable to develop low pH cements ($\text{pH} \leq 11$, but not so low as to promote excessively rapid corrosion of steel materials) with particular properties for certain applications, such as grouting where water-rock interactions at higher pH would have detrimental effects
- It is important to identify which of the possible problems that have been highlighted by experimental and theoretical investigations would actually be encountered in real repository environments.
- There is a need to identify what research and development can and should be done within the available timescales.

5.2.2 Issues concerned with repository concepts and the uses of cement

The discussions highlighted that, since the roles of bentonite in different kinds of repository are quite different, interactions between bentonite and cement have different implications for safety.

Three general topics were considered by the discussions:

- To some extent the amount of cement used will be dependent on the disposal concept. For example, the KBS-3H concept would use less cement than the KBS-3V concept where the volume of excavations is large due to the deposition tunnels.
- The relative spatial distributions of cement and bentonite will be different in different disposal concepts. For example grout will be distributed heterogeneously through the rock mass, depending upon the characteristics of the fracture network in the host rock.

- At Olkiluoto the rock is more fractured nearer to the surface than at greater depths. More grout will be required in this upper fractured zone than in deeper rock.
 - Major inflows will be from major fracture zones, which will consequently be the features where most grout is used. At Olkiluoto, typically there will be 40 – 70 m between the water-conducting features (WCF) at the waste emplacement depth.
- If groundwater flows are high, there may need to be some low-permeability material or a hydraulic cage to ensure adequate longevity of any cement barrier system (this is an issue for TRU repositories). It is currently generally considered that bentonite is the most suitable low-permeability material, but consideration should be given to developing alternatives such as:
 - new concrete technologies, for example fibrous concretes;
 - low-permeability concrete surrounding a higher-permeability cement barrier;
 - special materials stable at high pH (e.g. zeolites).

An important implication of the second point for repository design is that the impact of grouting cement on bentonite used in a barrier system will not be uniform throughout the barrier, because of the heterogeneous distribution of grouted fractures.

When developing new concrete technologies, particularly low-permeability concretes, consideration also needs to be given to the possibility of fractures developing. If such fractures are heterogeneously distributed, one effect could be heterogeneous leaching of alkaline water from the concrete.

The practicality of grouting and alternatives to cement-based systems (e.g. resins, clays) are important issues.

5.2.3 Issues concerned with bentonite and cement mineralogy

A key theme of the discussions was the importance of the pH versus time relationship as a control on both the stability and sequence of mineral formation. It was highlighted that information is needed concerning the relationship between the concentration gradient of hydroxide across a bentonite barrier and the rate at which an alkaline plume migrates.

Strongly alkaline pore fluids would cause alteration of bentonite, but there is some doubt as to the relative importance of alteration of accessory minerals and montmorillonite for reducing swelling pressures at different stages of the evolution:

- Possibly, prior to breakthrough, swelling pressure could be a combination of swelling of unaltered material and a reduction in swelling due to alteration.
- There would be a change in swelling pressure across an alkaline front migrating through a bentonite barrier.

Aspects of the design of experiments to investigate these phenomena received considerable attention. Important issues that were mentioned are:

- When interpreting the results of experiments designed to investigate the alteration of

bentonite by alkaline pore fluids, it is important to recognize that CSH phases might precipitate.

- It is important to understand the dissolved carbonate system if the alteration of bentonite in alkaline pore fluids is to be understood. As a consequence, it would be valuable to impose a constant partial pressure of CO₂ on experimental bentonite-alkaline pore fluid alteration experiments.
- Care is needed to take into account the possibility that trace cristobalite and quartz may remain in purified smectite when using dissolved silica concentrations to conclude that incongruent dissolution of smectite has taken place.
- Extrapolation of the results of laboratory tests, for example cement leaching tests, or observations on old man-made cement, to timescales relevant to repository safety assessments is problematical.
- Techniques exist to accelerate processes such as leaching in the laboratory (e.g. by increasing diffusion rates using an electric field), but these techniques may be accompanied by a change in the mechanisms of chemical and/or migration processes. One approach to solving this problem is to combine the results of un-accelerated and accelerated laboratory tests.
- When experimental solutions are varied it is important to ensure that the ionic strength of the different solutions is constant in order that results can be compared.

There was little discussion of redox conditions, but the potential reduction of carbonate to methane was mentioned. It was pointed out that this process will not occur unless there is microbial activity, though it is difficult to assess whether microbial activity would occur or not.

Other topics that were discussed are as follows:

- Specific reactive surface areas change during reactions, but during the course of a laboratory experiment these effects are not always significant because reaction rates may be too slow.
- In experimental alteration of bentonite or bentonite-sand mixtures, rates of pH variations with respect to time may not be constant, suggesting that the reaction rates vary over time. Possible causes are:
 - formation of preferential migration pathways through a sample and/or
 - formation of inert mineral coatings on the surfaces of migration pathways.
- The potential corrosion of steel components in low-pH cement need not be a problem, if such components can be removed prior to repository closure.

5.2.4 Issues concerned with barrier performance and functions

Much of the discussion focused on the potential undesirability of using cement and bentonite together in barrier systems. Key issues for safety that were highlighted are:

- The evolution of porosity in bentonite is important.
 - The initial porosity is very high.
 - If cement-bentonite alteration results in porosity reduction that causes a permeability decrease there could be an adverse effect on safety since the potential for gas pressures to rise, leading to eventual cracking of the barrier, might be enhanced.
- It is unclear whether or not there would be an increase in the total volume of minerals and a corresponding decrease in pore space near to the boundary between cement and bentonite.
 - There is a need not only to consider relatively low-pH evolved cement pore fluids, but also original high-pH fluids rich in NaOH and KOH.
 - If there is insignificant K in the fluids, then illitization will not occur, but the general sequence of appearance of the other phases will be broadly similar.
- The different swelling properties of Ca-bentonite and Na-bentonite could cause a change in the mechanical characteristics and hydrogeological properties of a bentonite barrier system during interaction with cement.
- It is necessary to consider the possibility that alteration may lead to the formation of regions with high porosity next to regions with low porosity and cause mechanical instabilities.
- Gas migration could be affected significantly by bentonite-cement interactions.
 - Volumes of gas could be significant in TRU repositories and will need to escape.
 - If bentonite is used and cementation occurs during alteration then fracturing could occur.

Although the use of cement and bentonite together in an engineered barrier system may have undesirable consequences for safety, it is unlikely that interactions between cement used in a repository and a natural mud rock host formation will be problematic. Favourable factors are:

- The volume of cement relative to the volume of the host formation will be very small hence the host formation will be able to buffer chemical conditions.
- In a mud-rock transport is likely to be dominated by diffusion, which will result in only a very small migration of alkaline pore fluid originating in the cement.
- The width of the disturbed zone in such a rock will be negligible.

The chemical instability of cement in fractures in contact with ambient groundwater was also discussed. This instability will cause the properties of the cement and wall-rocks to evolve.

- The chemical stability of cements may not be relevant for repository safety if the cement is used for grouting, the purpose of which is to control groundwater inflow over the relatively short interval of repository construction and operation.

- In circumstances where a barrier function is required, then alternative materials should be considered.
- Effects on the transport properties/sorption/retardation properties in fractures need to be evaluated.

The discussions highlighted that variations in transport properties of a bentonite barrier system as a function of interaction with cement pore fluids is somewhat uncertain. In particular, the effect of alteration processes on the transport mechanism is unclear.

- In experimental alteration of bentonite by alkaline pore fluids, the possibility that the mass transport mechanism may change from diffusion-dominated to advection-dominated, as a result of the alteration of bentonite, needs to be considered.
- There is a possibility that, if high-specific molar volume phases such as CSH phases form during alteration of bentonite, the permeability of the bentonite will remain low. As a result, even if there is significant alteration, the transport mechanism will remain diffusion dominated.
- Conversely, there could be mass transport driven by gas evolution, which might influence the pore fluid chemistry and hence the chemical reactions that occur and the performance of the barrier.

The degree to which chemical conditions would be buffered by chemical reactions in the bentonite was discussed and the consequences of this for safety were considered. It was highlighted that it is important to distinguish the pH-buffering capacity of bentonite interactions from the ‘buffering intensity’ of these reactions. Relevant issues are:

- Buffering capacity is a mass balance constraint, which represents the total amount of alkaline pore fluid that can be buffered by a particular mass of bentonite.
- Buffering intensity represents the rate of change of pH as a function of reaction progress and effectively controls the actual value of pH as a function of reaction.
- A high chemical buffering capacity does not necessarily ensure safety, since such buffering implies significant reaction and alteration. If this reaction and alteration compromises the physical integrity of the barrier, then there may be negative consequences for safety. Nevertheless, buffering is a key barrier role for EBS materials in many repository concepts.

The possible cementation of bentonite by silica was pointed out as a process that could have negative consequences for safety. It was suggested that such a process could be a negative effect of using sacrificial material (which will react preferentially with alkaline pore fluid originating in cement, thereby increasing pH) if silica dissolves and causes cementation. However, this risk could be eliminated by use of a Pre-fabricated EBS Module (PEM), which uses a steel container to enclose and protect a bentonite barrier.

5.2.5 Issues concerned with modelling

The discussions of research models focused on four main themes:

- the availability and limitations of thermodynamic data;
- the availability and limitations of kinetic data;
- simulations of transport processes;
- simulations of mechanical processes.

A major limitation with simulations of cement-bentonite interactions is the availability of thermodynamic data for relevant primary and secondary phases in both cement and bentonite. Potential approaches for addressing these limitations were discussed, highlighting that:

- Chemically and structurally similar phases could be grouped together and uncertainties in thermodynamic data estimated from the ranges of reported thermodynamic parameter values across the entire group.
- Many simulations of reactions involving cement and bentonite could be done using different combinations of phases selected from each group of structurally and chemically similar minerals. For example, if a particular reaction produced a certain zeolite, then several simulations could be done, each one using thermodynamic data for a different, but structurally and chemically similar zeolite.. Such calculations would establish whether poor thermodynamic data for a particular phase would be significant for the overall alteration.

The discussions emphasised that care needs to be taken when using data for one phase to carry out simulations of a related phase. For example, using thermodynamic data for muscovite to represent mixed-layer smectite-illite during the alteration of bentonite would be invalid. However, it was also pointed out that it is possible to test thermodynamic properties of minerals that are estimated from thermodynamic properties of the constituent oxides. Possibilities that were suggested are:

- Observed mineral assemblages in natural groundwater systems can be compared with mineral assemblages that are predicted using the estimation techniques.
- Predictions of the mineral parageneses actually occurring in natural analogues such as Maqarin can be made.

The validity of the range of kinetic laws employed received some consideration it was suggested that Transition State Theory (TST) rate laws should not normally be used under high pH conditions and that reaction affinities are uncertain under these conditions. It was pointed out that:

- There is no theoretical treatment that relates affinity to reaction rate at high pH.
- Empirical equations, such as that of Cama et al (2000) can be used.

It was mentioned that simulations of the coupling between the migration of an alkaline pore fluid plume and chemical reactions are very sensitive to the choice of rate law and the values of kinetic parameters. For example:

- Depending upon the reaction kinetics, quartz or montmorillonite are predicted to dissolve in simulations of quartz-bentonite alteration by alkaline pore fluids.
- Depending upon the reaction kinetics, montmorillonite dissolution could lead to increases in permeability of several orders of magnitude.

However, there was also some discussion as to the merits of assuming equilibrium conditions when carrying out simulations. It was suggested that under high-pH conditions where the reacting mineral phases have high surface areas, it might be appropriate for simulations to assume that reactions equilibrate rapidly.

- Experiments have tended to produce results that are not far from equilibrium.
- The assumption of equilibrium in simulations will often be conservative since they will then predict the maximum amount of mineralogical transformation.

The discussions pointed out that simulations of alkaline pore fluid migration from cement into bentonite or a mudrock formation have tended to concentrate on diffusion-controlled transport.

- Such an approach is valid for systems where low-permeability formations such as mudrock will host a repository, but under certain circumstances advection may occur (e.g. where cement grout-bearing fractures in certain crystalline rocks are juxtaposed against bentonite barriers) and then the approach may not be valid.
- If advection occurs, metastable phases could be important.

Other issues that were discussed in connection with research models are:

- When modelling the deformation of bentonite as a function of alteration and groundwater flow, the effect on bentonite strength of confining pressure due to overburden needs to be considered.
- When developing molecular dynamics (MD)/ homogenization analysis (HA), it would be valuable to consider that different solutes show different migration behaviour and different portions of the total porosity can be accessed by different solutes.
- Variations in the dielectric constant of water in bentonite should be taken into account by MD/HA.
- When simulating cement alteration it is desirable to consider the variability in the composition of interacting groundwaters (notably potentially adverse effects of dissolved Mg, Ca, SO₄ and Cl and ionic strength of waters).

Key issues that were considered in connection with the development of PA models are:

- When developing approaches to PA of cement-bentonite systems, it is important to

consider the range of secondary minerals that may form and the temporal sequences in which they form.

- Care should be taken when representing actual mineral phases by pure phases in PA calculations.
- The coupling between mechanical, transport and chemical processes must be considered by PA.
 - Is it possible to predict these couplings?
 - Swelling pressures can be calculated, but how can these be related to other processes adequately?

5.2.6 Issues for project management

A need for a more unified approach to identifying and implementing potential solutions to problems with using cement and bentonite in barrier systems was highlighted. In particular it would be desirable to improve communication between management, researchers investigating cement-bentonite interactions and engineers and workers in the construction industry who will design and implement the barrier systems.

It was pointed out that regulatory frameworks usually lag behind technological innovations and may constrain the use of materials other than cement, when account is taken of the timescales of repository projects.

The timescale available to develop alternatives to cement is an important issue.

- Alternatives to OPC need to be developed before the start of disposal, for example development of low pH cements ($\text{pH} < 11$).
- Alternatively, the acceptability of using cement needs to be confirmed before the start of disposal.
- These requirements need not necessarily interfere with the initial development of a repository since cement can possibly be used in parts of the excavations that are remote from the emplacement localities. For example, the underground rock characterisation facility ONKALO at Olkiluoto has been designed in such a manner that it can later function as access routes and auxiliary rooms of the repository. It is considered that OPC can be used in the upper parts of the ONKALO excavations even if it is later proved that other materials are more suitable close to the actual deposition galleries.

5.3 Responses to a questionnaire

Prior to the workshop, a list of key questions was distributed to the invited experts. The answers obtained from the invited experts, as well as from other workshop participants are summarised below. Answers by one expert are shown as an example in bold; additional answers and comments from other respondents are provided in italics.

1. Does mass transfer occur over an interface of highly compacted bentonite and concrete (both directions)?

Yes, both ions and neutral species can pass over the interface. The ion concentrations in the clay are likely to be governed by ion equilibrium. The equilibrium conditions are electric neutrality and the same ion activity product inside and outside the bentonite. The concentration of introduced ions will thereby be significantly lower than in the surrounding groundwater since highly compacted bentonite has a high concentration of exchangeable cations.

OH⁻, Na⁺, K⁺, Ca²⁺, and maybe SO₄²⁻ will diffuse from the concrete into the bentonite. Mg²⁺, CO₃²⁻, H₃SiO₄⁻, Cl⁻ and maybe SO₄²⁻, depending on the relative concentrations, will diffuse from the bentonite into the concrete. Mass transfer depends on the diffusion coefficients in the two media and on the evolution of these parameters (e.g. due to clogging of the porosity).

It was pointed out that mass transfer is the key process. Mass transfer rates as a function of time at the bentonite-cement interface as well as at different depths in both materials should be recorded in experiments and simulations, whenever possible.

2. What governs the effects of cement on bentonite? Are they governed by the rate at which OH⁻ ions enter the buffer Is the pH (i.e. concentration of OH⁻ ions in the entering solution) actually irrelevant and the effects on bentonite governed only by the flux of OH⁻ ions (moles per year) entering the buffer?

No, for several reasons. One is the ion equilibrium effect (see answer to Question 1). A high groundwater solute concentration will lead to a small difference between groundwater and pore water concentrations. Theoretically, a 1.0 M NaOH concentration in free water will decrease to a 0.3 M concentration in the pore water (decrease ~3 times; Figure 11). However, a low groundwater concentration will lead to a much larger difference. Theoretically, a 0.1 M NaOH solution will be reduced to 0.002 M in the pore water (decrease ~50 times).

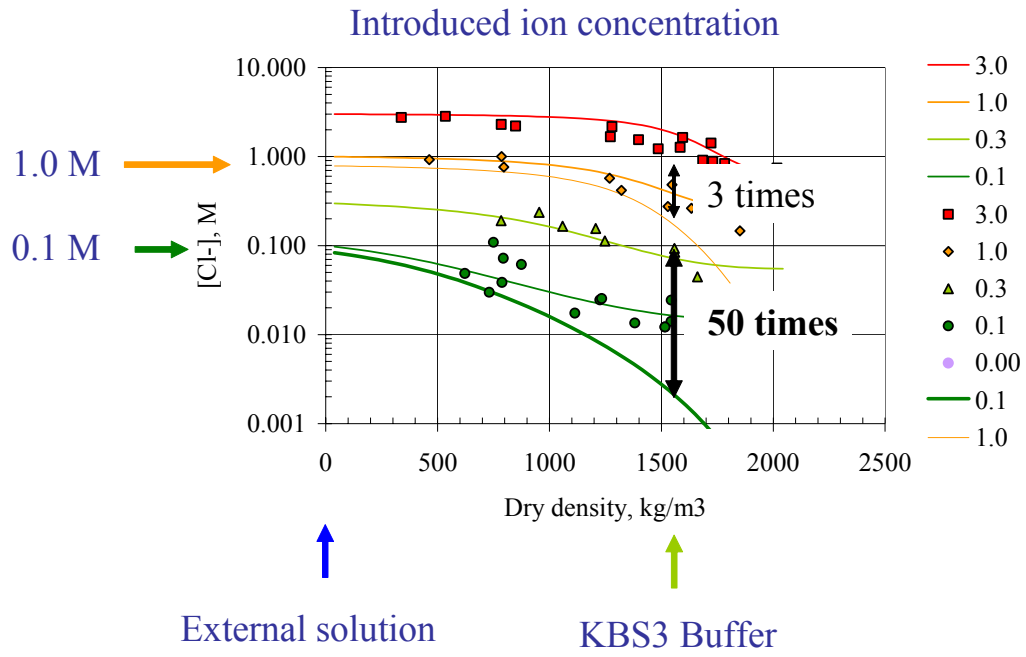


Figure 11: Theoretical anion activity (Cl⁻ or OH⁻) from NaCl or NaOH solutions in Na-montmorillonite as a function of montmorillonite dry density.

Furthermore, different initial pH will lead to different silica solubility and different equilibrium conditions, resulting in the formation of different secondary minerals.

Are the entering cations (e.g. Ca^{2+} , Na^+) important from the point of view of buffer performance?

Yes, they contribute to the chemical potential in the clay pore water, which at least partly governs the physical properties (item 1 in Question 4).

As long as thermodynamic equilibrium is not reached and kinetics are fast enough, inward migrating OH will react with bentonite. Resulting products depend on local composition, particularly on the pH, but also on the cocktail of cations. The stoichiometry of the actual transformation determines the buffer capacity.

It was noted that the pH scale depends on temperature. From the point of view of buffering the invading alkaline solution, the mass transfer rate of OH ions is the key factor, i.e. the buffering capacity of the bentonite in terms of moles of OH ions per kg of clay is not considered to be significantly dependent on the pH (see also answer to Question 6). However, the effects on the bentonite depend on the pH, i.e. different reactions dominate at different pH levels. The cations (e.g. Ca^{2+} , Na^+ , K^+) and the ionic strength (salinity) of the intruding groundwater (and cement pore water) are important from the point of view of mineralogical transformations in the bentonite. Also the local chemical conditions in the bentonite, in particular the pCO_2 , have a great impact on the buffering reactions. However, dissolution of cementitious materials will not affect the ionic strength significantly. Ca ions produced from cementitious materials will affect the type and fraction of inter-layer cations. In general, Ca-smectite shows higher permeability and lower swelling properties. The link between the pH of the bentonite pore water and the bentonite's dry density should be considered. This aspect has not been incorporated in geochemical codes.

3. If the dissolution rate of montmorillonite (smectite) were low enough, the effects of cement would not be so significant. From this point of view, the investigations of the dissolution rate under alkaline conditions should be a focus of experimental studies. How does the dissolution rate of montmorillonite (smectite) govern the kinetics of the cement/bentonite interaction processes?

The montmorillonite dissolution reaction seems to be very fast according to experiments on both un-compacted and highly compacted bentonite. The main question is therefore what the governing conditions are. Probably, the silica activity is the most important factor.

It was noted that if the dissolution rate of montmorillonite is low, the buffering capacity would also be low. The mineralogical perturbation of the bentonite would be low, but the extent of the high pH plume might be significant. The effects of the alkaline solution on the accessory minerals of the bentonite should also be taken into account. However, even if the rates of reaction are such that bentonite alteration does not affect the chemistry of the alkaline plume, the plume's chemistry will still evolve over time as a result of the cement being leached by flowing groundwater. If even a small amount of bentonite cementation occurs, the secondary minerals formed could coat the primary

minerals and decrease the dissolution rate of smectite, thereby causing the alkaline plume to extend over a wider volume of the bentonite.

4. What are the effects of a high pH plume on montmorillonite and accessory minerals in highly compacted bentonite? Which effects are the most important ones for the performance of the buffer?

At least two different effects are important:

- 1) **Osmotic ion equilibrium effects, i.e. the ion activity of the external solution in relation to the activity of ions in the interlamellar water solution (see answer to Question 2).**
- 2) **Mineralogical alteration of bentonite components.**

Dissolution of accessory minerals may lead to reduced buffer functions if the dissolution products are transported away and/or if the secondary products have higher densities than the original minerals. On the other hand, the porosity will decrease if neo-formed minerals have lower density than the original minerals. However, apart from general cementation by secondary phases the most important effect is doubtless dissolution of montmorillonite, which will lead to reduced buffer functions under almost any conditions. Several probable neo-formed minerals have indeed lower density than the original montmorillonite, which leads to a reduced porosity, but the governing condition for most of the physical buffer properties is the ratio between montmorillonite and water masses. This ratio will decrease if neo-formed minerals have a density higher than the mean montmorillonite - water density, which is set to 2000 kg/m³ in the KBS-3 concept. Of minerals that may possibly form, only some sulphates have lower densities. Further, the effect of montmorillonite dissolution will also be large for relatively small changes in montmorillonite content due to the fact that several of the physical properties are exponentially dependent on the montmorillonite - water ratio (Figure 12).

Dissolution and precipitation are the most important processes. Ion exchange (Na ↔ Ca) will take place and may change the properties of the buffer, but will be less important. Concerning the effects on the buffer performance, see also answer to Question 9. Dissolution of accessory minerals may act to decrease the rate at which smectite dissolves. For example dissolution of accessory quartz will increase the aqueous SiO₂ content and inhibit smectite dissolution.

5. How can experimental results obtained in non-compacted conditions be applied to highly compacted system?

These data may give reaction rates (for example), and can be used in modelling where transport is taken into account. An important application is that the results enable the effects of ion equilibrium to be determined.

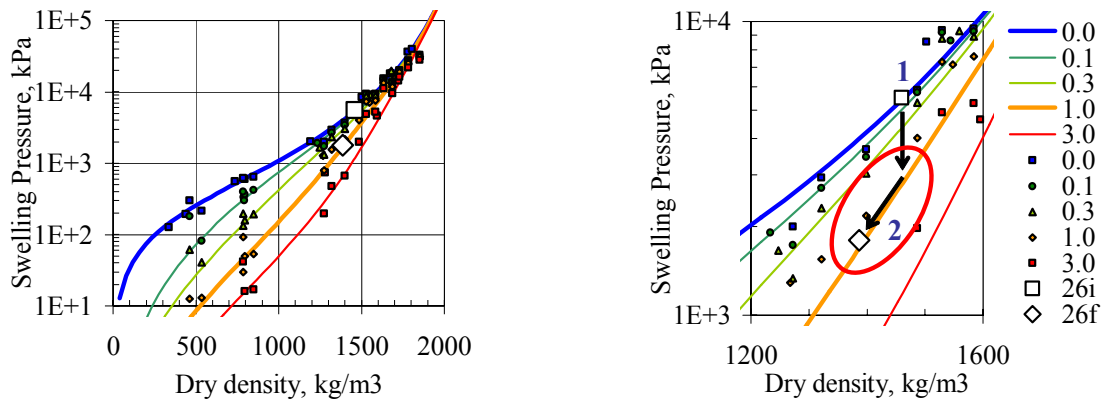


Figure 12: Montmorillonite swelling pressure as a function of dry density. No. 1 denotes the osmotic effect of 1.0 M NaOH solution, and No. 2 denotes the effect of mass loss due to dissolution of cristobalite, quartz and montmorillonite in a specific test. Note the logarithmic scale on the Y-axis.

It was noted that non-compacted bentonite and highly compacted bentonite are structurally quite different materials, and therefore experimental results are not directly transferable. There is no mechanistic model which adequately explains cement-bentonite interaction in compacted systems. Generally this problem is addressed by defining conservative analysis cases. In a highly compacted bentonite, the structure of the water molecule is influenced by the surface of the clay (owing to the electric double layer). This effect will decrease the activities of the ions in the pore water. Presently available geochemical modelling codes cannot really address this effect.

Highly compacted clay is also inhomogeneous. It is probable that some zones will be preserved (intact islets) and not affected by the diffusion of the alkaline plume. This effect will diminish the chemical buffering capacity of the barrier from a mass-balance point of view.

6. What is the buffering capacity of highly compacted bentonite, i.e. its ability to keep the pH, say below 11 or 10, in terms of moles of OH⁻ ions per kg of clay? Is this quantity a relevant measure of the buffering capacity of the buffer?

The following equilibrium conditions are valid according to PHREEQC modelling using the Minteq database. The pH decrease caused by reaction with cristobalite is around 19 mole of [OH⁻] per kg cristobalite. The reaction ceases at silica equilibrium, which means that 1.0 M NaOH solution drops in pH from 13.8 to 12.0, and a solution of pH 12.4 will show a decrease in pH to 10.8 if the high pH solution does not contain silica at the start of the reaction. Other reactions (i.e. precipitation or transport) have to take place for further pH reactions.

The pH reduction capacity is smaller for montmorillonite (around 5 moles [OH⁻] per kg montmorillonite). The capacity of quartz to reduce pH is intermediate between that of cristobalite and that of montmorillonite.

Buffering capacity is a key parameter. There is a fast (surface hydroxyl sites) and a slow (montmorillonite crystal lattice) component to the total buffering capacity. The maximum total buffering capacity of bentonite with a montmorillonite content of 75 wt% is approx. 9.5 moles of OH⁻ ions per kg of clay (see presentations by Lehikoinen and Takase). Precipitation of CSH phases (e.g. tobermorite) may also buffer the pH.

7. What are the relative propagation rates of diffusing OH⁻ ions and the reaction front characterised by the buffering and alteration processes in highly compacted bentonite? Is it possible that, due to the kinetics of reactions, the plume of high pH could reach a waste canister surface (and penetrate into a defective canister) before the buffering reactions neutralise the high pH?

This has to be thoroughly modelled in order to take into account the transport and reaction kinetics in each specific geometry. The diffusion rate was very fast in the ECOCLAY tests with compacted bentonite (regardless of accessory minerals), and a fast breakthrough was noticed at sufficiently high pH gradients. Also take into account the answer to Question 6.

According to experiments relatively fast propagation of a high pH plume in the buffer seems to be possible (see presentation by Karnland et al.). However, the low diffusion

coefficient and relatively high reactivity of the mineral system in the bentonite suggest that, the occurrence of such phenomena may be of low probability. The potential overall consequences depend, of course, on the disposal concept (thicknesses of the buffer and a possible concrete liner surrounding it; and on the different roles of bentonite and cement in the ILW/TRU and HLW/SF repository designs). Generally it is to be expected that if the dissolution rates of primary minerals are lower, then the pH at the surface of the canister will tend to be higher. However, the variation of pH with time at the surface of the canister will depend on many inter-related parameters. Notably, it will depend on the dissolution kinetics of primary minerals in the bentonite buffer, the kinds of secondary minerals produced, the precipitation kinetics of secondary minerals, and the diffusivities of both unaltered and altered bentonite buffer materials.

8. Concerning the effects of dissolution and (re)precipitation of siliceous and aluminous species and other accessory minerals of cement, ballast, rock and bentonite: Is there a risk of cementation of the bentonite buffer affected by a plume of high pH, when the pH eventually drops again?

Yes, the silica activity may reach molar values at pH 14, and the risk for cementation effects is obvious. I do, however, not know anything about the precipitation mechanisms. Laboratory experiments are planned for the near future.

The term “cementation” is often used in a broad sense to describe effects of chemical and mineralogical processes which can lead to various changes in the rheological properties of the buffer material, for example increased mechanical strength, brittleness or reduced swelling capacity. A number of completely different processes may cause similar effects, and the underlying reactions can occur directly in the montmorillonite mineral, in the interlaminar space between montmorillonite layers, or in accessory minerals. The resultant cementation does not necessarily have to appear in the same area as the underlying process, since released chemical species can be transported in the buffer by various prevailing gradients (thermal, concentration, etc.) and be precipitated in various locations and in various forms. (SR 97 Process Report, SKB TR-99-07).

It was noted that with some exceptions (i.e. calcite, gypsum) all the accessory minerals would form secondary minerals upon reaction with highly alkaline solutions. Since neo-formed precipitates often have larger molar volumes than the reactants, cementation may occur in the buffer.

9. What are the mechanical (e.g. swelling pressure, plasticity) and transport-related (e.g. diffusivity) properties of highly compacted bentonite altered by a high pH plume?

See answer to Question 4.

The properties of altered bentonite have not been investigated thoroughly. The likely and potential effects include, for example, loss of swelling capacity and plasticity, increase of permeability, loss of filtering capacity for colloids, and erosion at the bentonite–rock interface. Ion exchange resulting in conversion of Na-bentonite to Ca-bentonite reduces the swelling capacity and increases the permeability of the buffer.

10. In experiments, the transport of a high pH plume originating from a NaOH solution has been significantly faster than that of a high pH plume originating from a $\text{Ca}(\text{OH})_2$ solution. Is such a relationship between plume chemistry and migration rate likely to occur in an actual barrier?

No such fundamental conclusion can be drawn from the experiments we have performed. NaOH solutions with a concentration gradient of 1.0 and 0.3 M over 5 mm distance led to a high pH breakthrough, but a gradient of 0.1 M over 5 mm did not. Neither did 0.02 $\text{Ca}(\text{OH})_2$ (saturated) solution lead to a breakthrough during the test time.

Is this effect only due to the higher concentrations of OH^- ions in the NaOH solutions used, compared to those in the $\text{Ca}(\text{OH})_2$ solutions, where the OH^- concentration is limited by the solubility of $\text{Ca}(\text{OH})_2$?

Different secondary minerals may be formed in each case and thereby lead to different pH and transport conditions in the system.

The experiments by Karnland et al. seem to indicate that the faster penetration of the high-concentration, high-pH solution in the highly compacted bentonite cannot be explained only by the higher concentration gradient. Besides simple diffusion and mass-balance reactions, there seem to be other phenomena related, for example, to the Donnan effect and/or to the structure of the highly compacted bentonite affecting the penetration rates (see presentation by Karnland et al. and his answers above.). It was noted that longer experiment periods (or higher temperatures) should be used to see if the low-concentration solution also eventually penetrates through the highly compacted bentonite. However, it is noted that Na^+ and K^+ will control the concentration of OH^- only in the early stages of cement degradation. These concentrations are each about 0.1 mol/L. After leaching of Na^+ and K^+ from cement, concentration of OH^- is limited by the solubility of $\text{Ca}(\text{OH})_2$.

11. What are the issues specific to systems where massive cement or concrete surrounds or neighbours bentonite, such as where a thick tunnel liner occurs around the buffer?

The bentonite will be saturated by cement pore water, which initially will cause ion disequilibrium phenomena, leading to a faster chemical attack.

It was noted that this case, as long as mass transport is dominated by diffusion, is relatively easy to analyse. Potential consequences can be reduced by taking care of mass balances (thickness of the buffer vs. thickness of the concrete layer).

Appendix 1 - Workshop Programme

International Workshop on Bentonite – Cement Interaction in Repository Environments

**April 14-16, 2004
AIJ Hall (Kenchiku Kaikan), Tokyo, Japan**

Cement-based materials are normally used in rock construction for various purposes such as grouting, supports and tunnel floors. However, in the design of nuclear waste repositories the introduction of any foreign materials is considered with caution as they may effect adversary changes in the chemical conditions of the repository or the host rock. In this respect the use of normal Portland cements has been pointed out as a problem because of the high pH groundwater plume that it may give rise to. From the point of view of long-term safety it might be easiest and perhaps most prudent to avoid it completely and search for other materials to replace it. To this effect low pH substitutes are being developed and tested for some repository applications, but, especially for grouting purposes, it is still not clear whether such materials will be available at the time the need arises. Therefore, there continues to be interest to assess the implications of the use of cement-based materials on a broad basis.

For high-level waste repositories the main concerns as regards long-term safety, are related to the alteration of bentonite, the stability of the fuel matrix, and the validity of the performance assessment databases in a high pH (>11) environment. In the past years a large number of studies on bentonite alteration due to cement-bentonite interaction have been performed both in international projects (European Union 5th Framework Programme) and at national levels.

A number of questions have been identified, such as the buffering capacity and alteration of bentonite, alteration products, and the properties of the altered clay in highly compacted bentonite. Additional questions being discussed are e.g., the relative propagation rates of diffusing OH⁻ ions and the reaction front of the buffering and alteration processes in the highly compacted bentonite, and the fate and effects of dissolving siliceous and aluminous reaction products in the long-term.

In order to get a comprehensive overview on the present knowledge on the bentonite-cement interaction, and to identify key issues and how these should be approached by modelling and tests in Underground Research Laboratories and other laboratories, NUMO and POSIVA are launching this workshop. The expected outcome is a clearer definition of the key issues of bentonite-cement interaction to be considered in the design and performance assessment of HLW/SF repositories.

Wednesday, April, 14

13:30 Welcome address and working format

NUMO (Kazumi Kitayama and Hiroyoshi Ueda)
Posiva (Marjut Vähänen)

13:50 Session I: Introductory session: Repository concepts and use of cement

Chairs: Hiroyoshi Ueda and Marjut Vähänen

13:50-14:20 General overview on the use of cement in repositories for HLW and other radioactive wastes

Kazumi Kitayama¹, H. Ueda¹, N. Sasaki² and M. Hironaga³
¹ NUMO, ² JNFL, ³ CRIEPI

14:20-14:50 Planned use of cement in ONKALO, in a KBS-3V type and KBS-3H type repository in crystalline rock

Johanna Hansen Posiva

14:50-15:10 *Coffee*

15:10-15:40 Main issues in the use of cement in a spent fuel repository – what are we seeking answers for?

Timo Vieno VTT Processes

15:40-16:10 The bentonite/cement interaction problem; cutting the Gordian knot

Ian G. McKinley, R. Alexander, W. Kichmaier and
F. Neall Nagra

16:10 Session II: Mineralogy under B-C interaction

Chair: Seichi Sato Hokkaido Univ.

16:10-16:55 Evaluation methods for ion migration in concrete & prediction methods for concrete deterioration caused by chloride attack or calcium leaching

Nobuaki Otsuki
Tokyo Institute of Technology

16:55-17:40 Dissolution mechanism and kinetics of smectite under alkaline conditions

Tsutomu Sato¹, M. Kuroda¹, S.
Yokoyama¹, M. Tsutsui¹,
K. Fukushi², T. Tanaka³ and S.
Nakayama³

¹ Kanazawa Univ.,
² AIST, ³ JAERI

17:40 *End of Day 1*

Thursday, April 15

9:30 **Session III: Barrier Performance and functions under B-C interaction**

Chair: Patrik Sellin SKB

9:30-10:30 Experimental study on changes of bentonite mineralogy and physical properties as a result of exposure to high pH solutions

Ola Karnland¹, U. Nilsson¹, S. Olsson² and P. Sellin³
¹ Clay Technology, ² Geochimica, ³ SKB

10:30-11:00 Effects of saline alkaline attack on bentonite and crushed rock – experimental and modelling studies – ECOCLAY II

Ulla Vuorinen¹, Ari Luukkonen², Jarmo Lehtikainen¹ and Heini Ervanne³
¹ VTT Processes, ² VTT Building and Transport, ³ University of Helsinki

11:00-11:20 *Coffee*

11:20-11:50 Experimental study on dissolution of montmorillonite in compacted sand-bentonite mixture under Na-Cl-OH pore-water conditions

Tetsuji Yamaguchi¹, Y. Sakamoto¹, M. Akai¹, M. Takazawa¹,
 T. Tanaka¹, S. Nakayama¹ and T. Sato²
¹ JAERI, ² Kanazawa Univ.

11:50-12:20 Modelling of variation in permeability of compacted bentonite with alkaline fluid for long-term safety assessment of geological disposal system

Mayumi Takazawa, T. Yamaguchi, Y. Sakamoto,
 M. Akai and S. Nakayama JAERI

12:20-13:20 *Lunch (lunch box provided by NUMO)*

13:20 **Session III continues**

Chair: Patrik Sellin SKB

13:20-13:50 Cement-bentonite interaction issues, buffering capacity of bentonite

Jarmo Lehtikainen VTT

13:50-14:20 A long-term performance assessment for engineered barriers – study on barrier materials alteration –

Hiroyasu Kato¹, H. Asano¹ and N. Yamada²
¹ RWMC, ² Mitsubishi Materials

14:20-14:50 An analysis of cement-bentonite interaction and evolution of pore water chemistry

Chie Oda¹, A. Honda¹ and D. Savage²
¹ JNC, ² Quintessa

14:50-15:20 Development of MACBECE: Mechanical Analysis system considering Chemical transition of Bentonite-based and Cement-based materials

Hiroyuki Ito, M. Mihara and T. Ohi JNC

15:20-15:40 *Coffee*

15:40 **Session IV: Modelling; Detailed research models vs. PA models**

Chair: Masao Shiotsuki JNC

15:40-16:40 Modelling diffusion of an alkaline plume in two types of clayey systems

Eric Gaucher BRGM

16:40-17:10 Potential complications in the development of a thermodynamic database for hyperalkaline, argillaceous systems

Randy Arthur¹, Hiroshi Sasamoto² and
Mikazu Yui²
¹ Monitor Scientific, ² JNC

17:10-17:40 Nano/macro-based cation/water transport and adsorption in bentonite

Yasuaki Ichikawa¹, S. Prayongphan¹, S. Suzuki² and K. Kawamura³
¹ Nagoya Univ., ² IRI, ³ Tokyo
Tech.

17:40 *End of Day 2*

19:30 *Workshop Banquet hosted by NUMO*

Friday, April 16

9:30 **Session IV continues**

Chair: Margit Snellman SROY

9:30-10:30 Status of cement modelling – future investigations in the view of cement/bentonite interactions

Urs Berner PSI

10:30-11:00 Discussion on PA model development for bentonite barriers affected by chemical interaction with concrete: Do we have enough evidence to support bentonite stability?

Hiroyasu Takase Quintessa Japan

11:00-11:30 *Coffee*

11:30 **Session V: Concluding Discussions and Wrap-up (Conclusions from each session)**

Chair: Hiroyuki Umeki NUMO

12:30 *End of Workshop*

Deliverables

We are planning to compile a proceedings report of the workshop as POSIVA and NUMO Technical Reports, which will be open to the public and distributed to the workshop participants.

Language

The workshop language is English. Oral Japanese is allowable with simultaneous translation provided.

Discussion time

Discussion time is proposed as follows:

5 min. discussion for 30 min. presentation;

5 min. discussion for 45 min. presentation;

10 min discussion for 60 min. presentation;

These are flexibly changeable under the control of the chair person.

Practical information

Meeting time and place

The meeting starts on Wednesday, April 14th at 13:30 and ends on Friday, April 16th at 12:30. It takes place at AIJ Hall (<http://www.aij.or.jp/eng/about/map.html> or see the map attached. The hall is familiar to Japanese as “Kenchiku Kaikan”), 5-26-20, Shiba, Minato-ku, Tokyo

Hotel

Celestine Hotel, <http://www.celestinehotel.com/us/index.html>, is located close to AIJ Hall (7 minutes walk).

Information about Tokyo

Information in detail is available from WEB as:

<http://www.tourism.metro.tokyo.jp/english/index.html>

http://www.tcvb.or.jp/en/index_en.htm

<http://www.jnto.go.jp/eng/>

<http://www.jnto.go.jp/mapindex/E/Tokyo.html>

Appendix 2 – List of Participants

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Appendix 3 - Extended Abstracts

Kitayama K., Ueda H.¹, Sasaki N.², and Hironaga M.³ ‘General Overview on the Use of Cement in Repositories for HLW and Other Radioactive Wastes’. ¹Nuclear Waste Management Organization of Japan (NUMO), ²Japan Nuclear Fuel Limited (JNFL) and ³Central Research Institute of Electric Power Industry (CRIEPI), Japan.

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General overview on the use of cement in repositories for HLW and other radioactive wastes

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Introduction

The high-level radioactive waste, HLW, denotes in Japan the vitrified waste from the reprocessing plant, which includes fission products and minor actinides. All the other wastes from the reprocessing plant, the power plant and so on are categorized as LLW, low-level radioactive waste, which includes wastes from the operation and the decommissioning of the plants. LLW is categorized as L1, L2 and L3 wastes, TRU waste and Uranium waste according to their origins and radioactivity. L1, L2 and L3 wastes are generated from the operation and decommissioning of the power plants. The disposal of LLW is already started in Rokkasho site. TRU waste is generated from the reprocessing plant and includes relatively long-lived nuclides. Its disposal is still under discussion. LLW from the fuel fabrication plant is particularly called “Uranium waste”.

Each waste is disposed of according to its own disposal concept as shown in Fig. 1. L1, L2 and L3 wastes are disposed of near the surface or relatively shallow. The controlled disposal is applied to these wastes, i.e., there will be the period of monitoring and control for several hundred of years, after closure of the facility. On the other hand, HLW and TRU waste will be disposed of several hundred meters deep.

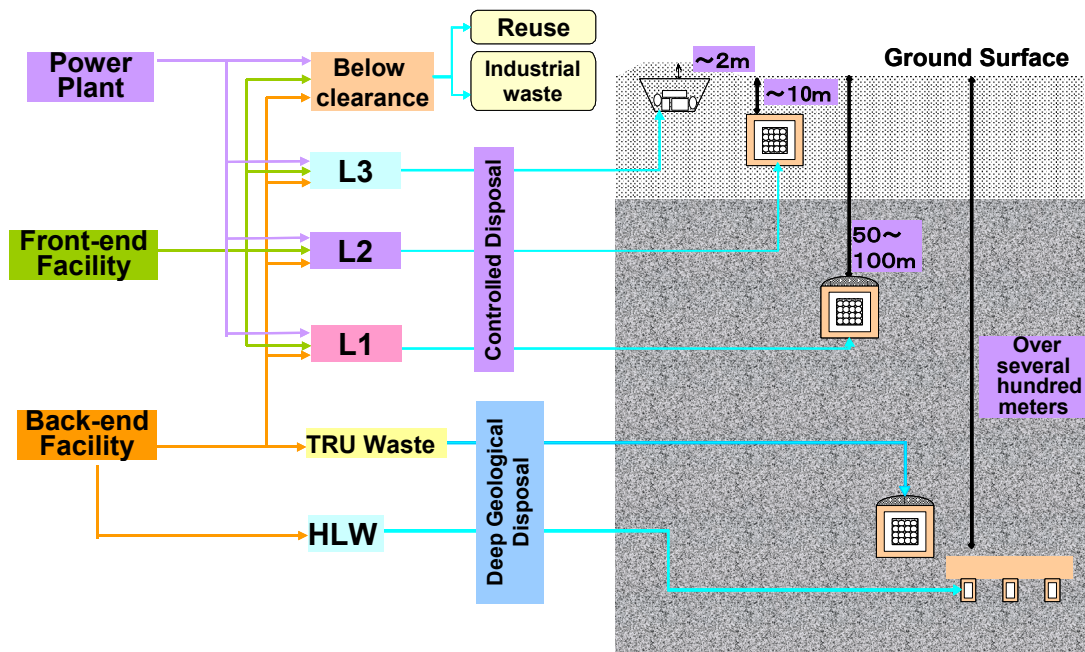


Fig. 1 Disposal concepts for radioactive wastes.

Use of cement

The disposal of L2 waste is already under operation at Rokkasho site. A view of its No.1 facility is shown in Fig. 2. This shows details of the engineered barrier system for L2 waste. Cement is used for the mortar backfill around the waste packages, the porous concrete and the structural concrete. Bentonite/sand mixture is used for the cover soil. Table 1 summarizes the functions and requirements of cement components in L2 disposal concepts. It should be mentioned that cement is considered as the barrier material particularly for relatively short-lived nuclides, expecting its low permeability and high sorption capacity.

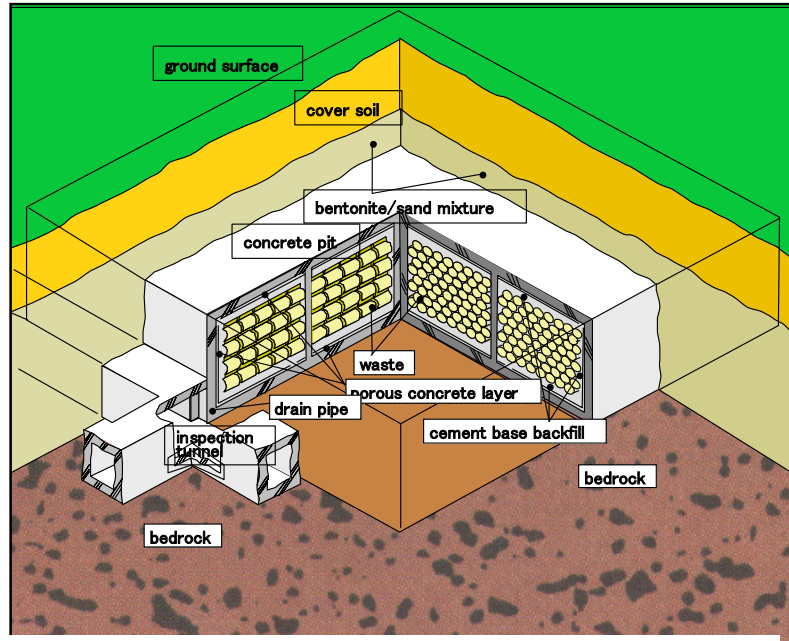


Fig. 2 View of No.1 disposal facility in Rokkasho.

Table 1 Functions and requirements of the cement components of L2 disposal.

	Operational period	Period of decay of short-lived nuclides (monitored and controlled)	Long-term period (uncontrolled)
Functions for EBS	Isolation of nuclides	Restriction of nuclide migration	—
Components	Requirements	Requirements	Requirements
Mortar backfill	Sealing High sorption capacity	Diffusive transport High sorption capacity	High sorption capacity
Structural concrete	Mechanical strength	—	—

Use of cement in HLW repository has been discussed so far. The liner, grout and mechanical plug are provisionally considered as shown in Fig. 3. The liner is needed for a soft rock formation to ensure mechanical stability of tunnels or shafts. Grouting with cement is considered as measures against water inflow during the pre-closure period. The mechanical plug confines and mechanically supports the backfill material for tunnels or shafts.

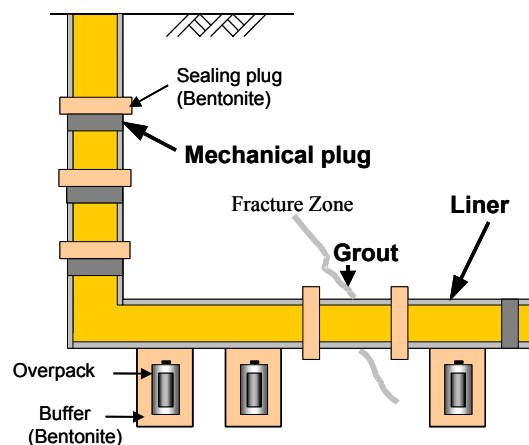


Fig. 3. Use of cement in HLW repository concept (examples).

Regarding HLW repository concept, cement is not considered as any barrier material, but as material for construction which functions during the pre-closure period as shown in Table 2. Relatively short-lived nuclides are isolated mainly with glass matrix and the overpack, not similarly as LLW disposal concept in which cement is used as the barrier material for short-lived nuclides. It may be mainly because cement is not suitable for the initial period of high heat generation of HLW due to the decay of short-lived nuclides.

Table 2 Functions and requirements of the cement components of HLW disposal (examples).

Components	Pre-closure		Post-closure	
	Functions	Requirements	Functions	Requirements
Mechanical plug	Confine and mechanically support backfill material	Mechanical strength	—	No detrimental effect on barriers
Liner	Ensure mechanical stability of tunnels and shafts	Mechanical strength	—	No detrimental effect on barriers
Grout	Suppress water inflow through fractures	Low permeability	—	No detrimental effect on barriers

Conclusion

It was illustrated how cement is employed or planned to be employed in the repositories with respect to each category of radioactive waste in Japan. The concept of the cement employment is fairly different between HLW and LLW disposal depending on the characteristics of the wastes. Cement is used only as “pre-closure” material for HLW while the barrier material to isolate short-lived nuclides for LLW. This is understandable in terms of the initial heat generation of HLW due to the decay of short-lived nuclides.

PLANNED USE OF CEMENT IN ONKALO, IN A KBS-3V TYPE AND KBS-3H TYPE REPOSITORY IN CRYSTALLINE ROCK

Johanna Hansen, Posiva

1. INTRODUCTION

The Posiva plans to construct a KBS-3 type repository for spent fuel in the crystalline bedrock on the Olkiluoto Island on the coast of the Baltic Sea. The Olkiluoto nuclear power plant, with two operating reactors and one under construction, and the VLJ Repository for low and intermediate level waste are also located on the island.

Underground rock characterisation facility (URCF) ONKALO will be constructed ahead of deep repository to confirm the suitability of site and bedrock masses. The excavation of ONKALO starts at summer 2004 and based on continued characterisation the investigation data needed for construction licence for repository should be available early 2010th decade. Construction of ONKALO will be done mainly with conventional excavation methods, but the requirements set to the repository should be fulfilled. The construction should not cause major disturbances in surrounding bedrock nor impair the long-term safety. Fulfilment of these requirements among other things set restrictions in use of stray materials and limits the seepage water in to the ONKALO and repository. This paper deals the planned use of cement in during the underground construction.

2. CONCEPT FOR FINAL DISPOSAL

The safety concept is based on multi barrier system, which guarantees the long-term isolation of spent fuel assemblies. Engineered barriers consist of durable copper-iron canisters, highly compacted bentonite buffer and the tunnels, which will be sealed by backfill materials and sealing structures. The crystalline bedrock offers a natural barrier for repository, which will be located at the depth of 400-700 metres. The repository design is of KBS-3V or KBS-3H type (Figure 2). In a KBS-3V type repository, a canister is emplaced in a vertical deposition hole bored in the floor of a tunnel. In the KBS-3H type repository, several canisters are emplaced in a horizontal deposition hole with a length up to 300 metres (Autio et al. 1996 & Birgersson et al. 2001). In both concepts, the space between the canister and rock is filled with highly compacted bentonite clay.

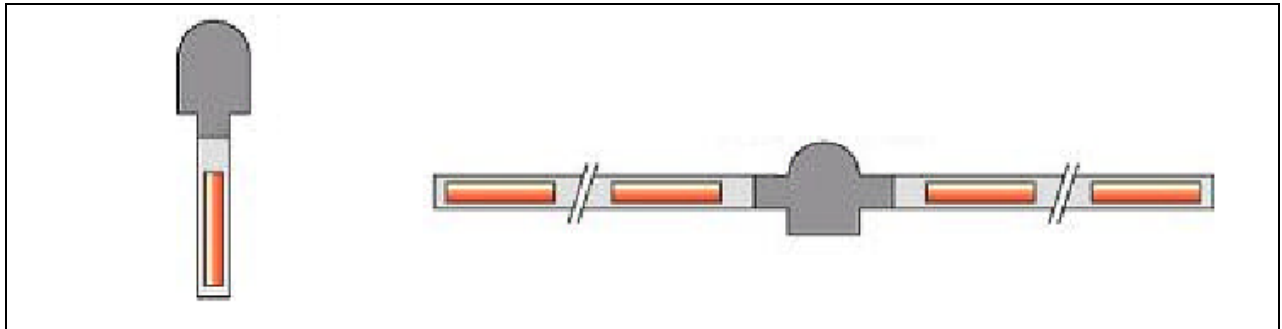


Fig. 2. KBS-3V and KBS-3H alternatives.

The design basis for repository may accommodate 5800 tU spent fuel from the Loviisa (2 x 488 MWe VVER-440 type PWR) and Olkiluoto (2 x 840 MWe BWR) nuclear power plants and also from the fifth reactor (OL3 1600 MWe PWR), which is under construction.

3. DESCRIPTION OF SITE CONDITIONS

Olkiluoto is an island (approx. 10 km²), close to the mainland, on the coast of the Baltic Sea. The topography is flat and thin layer of sandy tills covers the sparsely outcropped bedrock. The bedrock consists of Svecofennian metasediments and plutonic rocks of 1800-1900 million years in age. Migmatitic mica gneiss is the most abundant rock type, and is intruded by foliated grey gneisses and massive coarse-grained granites and pegmatites. At the depth of about 500 metres, the majority of the rock mass at Olkiluoto consists of intact rock between fracture zones and has been estimated as “normal” from the point of constructability (Anttila et al. 1999). This means that excavation and rock support can be carried out using conventional methods and materials generally used in underground constructions. Close to the depth of 700 metres, the rock has been estimated as “demanding” or “very demanding” in terms of its constructability, because of its relatively low uniaxial compressive strength ($\sigma_{ucs} = 80 - 140$ MPa) and the higher stress field ($\sigma_H = 35 - 40$ MPa at 700 metres). Severe spalling of the rock may occur, and special methods and materials (including for example shorter blasting rounds, temporal supporting with bolts and shotcrete, and pregrouting) may be needed when excavating and supporting the rock (Äikäs et al 2000).

In the upper parts of the bedrock the fracturing occur more intensively and hydraulic conductivity is somewhat larger. Fresh groundwater (content of Total Dissolved Solids (TDS) < 1 g/l) is found to the depth of about 150 metres, and brackish (TDS between 1 and 10 g/l), sulphate-rich groundwater between 100 and 400 metres. Deeper groundwaters are saline (TDS > 10 g/l). At the depth of 500 metres, TDS varies between 10 and 25 g/l. The most saline waters at depths greater than 800 metres have TDS values between 30 and 75 g/l. These deep saline waters seem to have been undisturbed during the most recent glaciation and even much longer in the past.

Table I. Main Water Types at Olkiluoto and Their Interpreted Origins and Formation Ages (Anttila et al. 1999 and Pitkänen et al. 1999). Table is taken from Vieno (2000).

Depth of occurrence (metres)	Water type	Origin of dominant end-members	Age estimate of dominant end-member type (years)
above 150	Fresh-brackish HCO ₃ -rich water	Meteoric water and present Baltic Sea water	0 – 2500
100 – 300	SO ₄ -rich brackish Na-Cl	Litorina Sea water	2 500 – 7 500
100 – 500	Brackish Na-Cl water	Pre-Litorina water containing fresh glacial meltwater	7 500 – 10 000
below 500	Saline Ca-Na-Cl water	Preglacial to Precambrian saline water	>> 10 000

During the construction and operation phases groundwater will be drawn into ONKALO and later into the repository from the surrounding bedrock. A design basis TDS value of 35 g/l has been recommended for a repository excavated at the depth of about 500 metres at Olkiluoto (Vieno 2000). All repository systems and engineered barriers should perform properly at least at groundwater salinities ranging from fresh water to 35 g/l (Autio et al. 2002).

4. DESCRIPTION OF URCF ONKALO

ONKALO consist of a system of exploratory tunnels accessed by a *shaft* and an *access tunnel*. The main objective of ONKALO work is to enhance the current geoscientific understanding of the site to allow the submission of the application for a construction licence for the deep repository. ONKALO efforts possibility also to test interactions between the rock and the engineered barrier system (Posiva 2003).

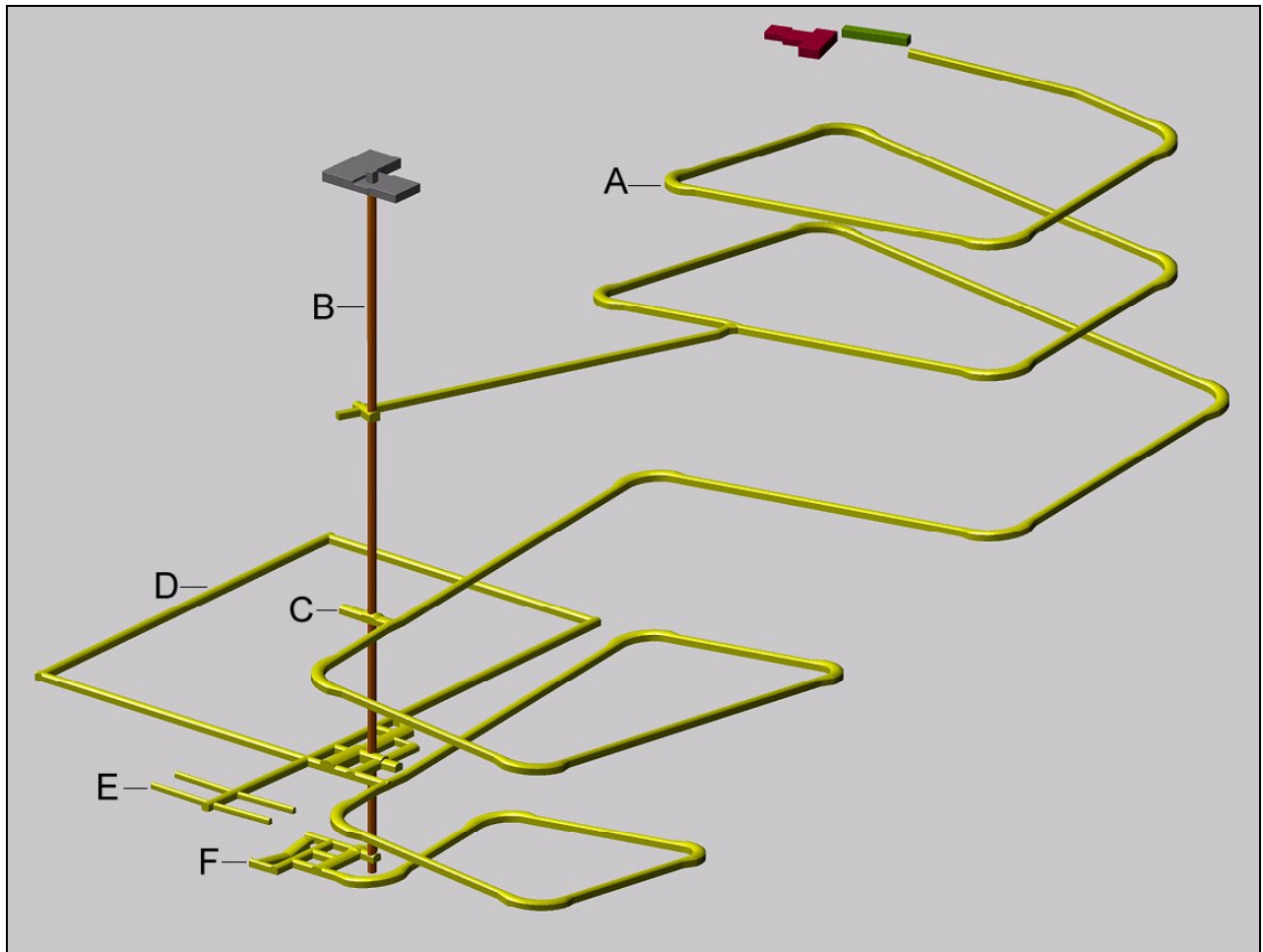


Fig. 3. Preliminary lay-out of ONKALO. A) ramp, B) shaft, C) upper characterisation level, D) main characterisation level, E) demonstration tunnels, F) lower characterisation level.

The ONKALO will be excavated by conventional drill and blast method. The total length of the spiral access ramp is 5 kilometres and the inclination of the ramp is 1:10. The preliminary dimensions of the ramp are 5.5 metres in width and 6.35 m in height with broadened bendings. The other access routes consist of few raise bored shafts, with height of 420-520 metres. The main characterisation level is located at the depth of 420 metres. Minor characterisation level at depth of 520 metres is connected to the main characterisation level by ramp. Combined length of the tunnels, characterisation loops, auxiliary rooms and shafts are 8 500 metres (Fig. 3). Total volume of the ONKALO underground facilities is approximately 330 000 m³. The influence of excavation will be monitored continuously during construction of the facility. The ONKALO construction should not cause any major disturbances for surrounding natural conditions (Posiva 2003).

5. USE OF CEMENT DURING CONSTRUCTION PHASES

The implementation of underground construction will be started in the middle of 2004. Support and sealing of crystalline bedrock will be performed by using of cementitious materials. The water conducting fractures will be grouted by micro cement. Usually pregrouting is used for sealing while post grouting may not be effective enough. The amount of injection grout should be limited because it is not removable from rock fractures. For ONKALO, the quantity of cement needed for injection has been estimated to be 3 000 000 kg, of which 2 500 000 kg is used in the access tunnels and ventilation shaft (Riekkola et al. 2003). For the other parts in the repository the current estimation is that about 2 000 000 kg of cement will be needed. (Hjerpe 2003) The bedrock surfaces will be covered by shotcrete for bedrock stabilisation purpose. Rock bolts and anchors will be grouted into the bedrock with cement. Several temporary and permanent construction installations will be made from cement based materials. Cast concrete is used for floors and walls. The elevators and the ventilation systems will be mounted in elements built inside the shafts. The final design is not yet determined. Here it is assumed that the elements will be made of 200 mm thick concrete (cement contents of 300 kg/m³), supported by steel meshes. In the access tunnels the cement amount in the concrete linings is estimated to be 1 400 000 kg. For the ventilation shaft a 300 mm thick lining will be used in the upper 100 m. (Hjerpe 2003)

6. REMAINING QUANTITIES OF CEMENT AFTER CLOSURE OF REPOSITORY

The removal efficiency for cement used for miscellaneous construction purposes is estimated to be 98%. Almost all concrete floors, walls etc are removable. Shotcreting is in theory removable but in the design it will most probably remain in the repository. There are several methods to remove the shotcrete, like excavation, mechanical pick dressing, hydraulic pick dressing and mechanical routing. The need of the removal of shotcrete will be evaluated later. (Hjerpe 2003)

Grout for sealing the fractures and rock bolts cannot be removed and it creates the largest quantities of cementitious materials, which will remain in the repository after closure. The estimated quantity is 5 300 000 kg. Each deposition tunnel is sealed with a plug of massive concrete that will remain after sealing in the repository. The plugs are 6 m long having a volume of 138 m³. The estimated quantity of cement needed for plugs is totally 4 700 000 kg. (Haaramo 1999, Hjerpe 2003)

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MAIN ISSUES IN THE USE OF CEMENT IN A SPENT FUEL REPOSITORY – WHAT ARE WE SEEKING ANSWERS FOR?

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Safety-related reasons to use cement

Besides engineering reasons and operational safety, there are reasons related to the long-term safety to use cement in a repository for spent nuclear fuel in crystalline bedrock. Inflow of groundwater into the excavations during the construction and operation phase may namely cause drawdown of groundwater table and significant movement and mixing of groundwater masses giving rise to

- desaturation and intrusion of air in the drawdown zone
- intrusion of superficial water – containing oxygen, carbon dioxide and organic substances – into the host rock
- at islands and coastal areas, intrusion of seawater – percolated through sediments and being rich in sulphate, bicarbonate and possibly in ammonia and organic substances
- upconing of deep saline groundwater towards the excavations
- consumption of the redox and pH buffering capacity of fracture fillings and rock matrix.

The disturbances can be reduced by applying methods commonly used in rock engineering, grouting of rock with cement and hydrostatic liners, to limit inflows (Riekkola et al. 2003).

Posiva has recently started the construction of an underground rock characterisation facility, called ONKALO, at the Olkiluoto island at the coast of the Baltic Sea (Posiva 2003a-c). The facility consists of a system of exploratory tunnels accessed by a tunnel and a shaft. The main characterisation level will be located at a depth of about 400 metres and the lower level at a depth of about 500 metres. The total underground volume of ONKALO will be approx. 330 000 m³ with the combined length of tunnels and shafts of approx. 8500 metres (Posiva 2003d). ONKALO is designed in such a manner that it can later function as access routes and auxiliary rooms of the repository for spent fuel.

If no sealing of rock were made, the inflow of groundwater into ONKALO could be as high as 600 000 m³/yr and drawdown of groundwater table and upconing of deep saline groundwater several hundred metres (Vieno et al. 2003a). The salinity of groundwater in the vicinity of the tunnels at the characterisation levels might locally rise up to 50 g/l, whereas it ranges in the present natural state from 10 to 25 g/l. A major part of the inflow comes from the subhorizontal fracture zones, which the access tunnel and shaft intersect at a depth between 70 and 330 metres. To minimise the disturbances, the leakages into the excavations will be limited to a level as low as practically achievable. The amount of cement remaining in the host rock after the closure of the repository has been estimated to be about 5400 tons for the ONKALO excavations and in total 10000 – 23000 tons for a repository containing about 5800 tons of spent fuel (Hjerpe 2003a-b).

Cement-related issues: general

A review of potential effects of cementitious leachate in the vicinity of a spent fuel repository highlighted the following issues (Vieno et al. 2003a–b)

- Alteration of the bentonite buffer may take place.
- The redox stability of spent fuel is questionable if it comes in contact with a high pH solution. It was noted that the spent fuel itself also contains alkaline and earth-alkaline metals, notably cesium, which, when released from the fuel, may increase the pH inside the canister.
- Solubility and sorption databases specific to the KBS-3 concept and crystalline rock at high pH conditions are scarce. Databases developed for cementitious LLW/ILW/TRU disposal concepts are, of course, available, but the databases used in past assessments of the KBS-3 concept cannot reliably be extrapolated to pH >11.
- The effects of superplasticizers and other (organic) admixtures of cement and concrete are not well known.
- In the long term degrading concrete structures – for example, injection boreholes, liners and floors – may become preferential flow and transport pathways.

Less significant concerns were associated with the effects of cement on fracture fillings and rock matrix (Baker et al. 2002) as well as with potential generation of colloids at sharp pH gradients. The reviews of corrosion of the copper canister (King 2002) and of the zircaloy cladding of the fuel pins (Johnson & McGinnes 2002) indicate no significant negative impacts due to alkaline conditions.

Mass transport analyses of cement

Assessment of release and transport of cement in the geosphere and its intrusion into the Engineering Barrier System (EBS) of the repository is an inverse problem to radionuclide release and transport. The same modelling concepts can be used, but in the cement case the source term is dispersed in heterogeneous conditions in the grouted rock around the excavations. The analyses of groundwater flow and transport of cement in the vicinity of ONKALO show (Vieno et al. 2003a) that

- The subhorizontal fracture zones, which the access tunnel and shaft intersect at depths of 70 – 130 metres and 290 – 330 metres divide the flow pattern into layered zones. It is unlikely that significant amount of cement from these zones or from the sparsely fractured rock between and above them would be transported into the sparsely fractured rock below the lower zone.
- The water leaving a grouted rock spot will not have the pH and other properties of cement porewater, but is diluted by the groundwater flowing around/through the grouted area. This source term dilution is enhanced by the fact that groutings are made at fracture zones and other locations where flow rates are highest.
- Further buffering and dilution take place during transport in the geosphere. In open fractures with a limited buffering capacity and a small WL/Q (half of the “flow wetted” surface divided by the flow rate), the leachate may, however, be transported over long distances.
- Transfer of OH⁻ ions from water-conducting fractures intersecting a deposition hole is limited by the boundary layer (film) resistance between the flowing groundwater and the stagnant porewater in the buffer. The fraction of OH⁻ ions entering the buffer decreases with an increasing flow rate of groundwater along the fractures.

- In the assessment of the effects of OH⁻ ions entering the buffer from rock fractures, one must take into account that the attack is localised. The shape and volume of the affected bentonite are governed by diffusion processes and reactions between the intruding solution and the clay.

In general, it was estimated as fairly unlikely to encounter a plume with a pH significantly higher than 11 at a distance of several tens of metres (which corresponds to the minimum distance between the ONKALO excavations and the deposition galleries) from the nearest grouted spot. In the case of ONKALO, the groundwater flow and mass transport analyses showed that it is very unlikely that cement transported from ONKALO, especially from the major subhorizontal fracture zones and from the sparsely fractured rock above and between them, could significantly impair the key functions of the bentonite buffer and other components of the EBS in the deposition holes of the repository.

Recommendations and areas deserving further studies: general

Cement-bentonite interaction is a key issue. In all modelling studies special attention should be paid on mass balances and mass transport rates.

Uncertainties in the transport analyses could be reduced by further experiments and modelling studies on transport and effects of cement in fractured rock. Posiva is considering participation in the proposed second phase, Long-term Cement Studies (LTC), of the Hyperalkaline Plume in Fractured Rock (HPF) project in the Grimsel rock laboratory in Switzerland.

Grouting experiences could be revisited to check whether any indications of a high pH plume can be found. Most convincing evidences could be obtained by systematic measurements of groundwater pH around past groutings in backfilled and saturated excavations in deep crystalline bedrock, if such can be found, or around cemented deep boreholes.

As concerns radionuclide release and behaviour, areas deserving further studies include stability of the spent fuel and performance assessment databases for the KBS-3 concept in a high pH environment.

Potentially harmful effects of cement could, of course, be minimised by minimising the amount of ordinary cement remaining in the host rock. Posiva is developing low-alkali cementitious and non-cementitious grouts in cooperation with NUMO and SKB. Effects of new materials introduced into the host rock need, of course, be studied carefully. The effects of superplasticizers and other admixtures of cements and grouts need to be studied, too.

Main issues of cement-bentonite interaction

In short, the main issues of cement-bentonite interaction are

- What happens to the bentonite buffer and cement/concrete, if they are in contact with each other, for example, within a sealing structure?
- What happens to the bentonite buffer affected by cementitious leachate?
- Can cementitious leachate penetrate through the bentonite without significant

buffering and attack the canister and spent fuel?

Ten questions (and some comments) on cement-bentonite interaction

1. Mass transfer over an interface of highly compacted bentonite and concrete (both directions). In the simulations, the mass transfer rates as a function of time should be recorded also at different depths in the materials.
2. Are the effects on bentonite governed by the entering rate of OH^- ions into the buffer? Is the pH (i.e. concentration of OH^- ions in the entering solution) actually less important and the effects on bentonite governed only by the flux of OH^- ions (moles per year) entering the buffer? Are the effects of 10 litres/yr of pH 11 solution similar to those of 1 litre/yr of pH 12 solution? Note also that the pH scale is temperature-dependent: at higher temperatures, ion product and solute concentrations of OH^- and H^+ increase, while pH decreases. What is the role of the cations (e.g. Ca^{2+} , Na^+ , K^+) and ionic strength (salinity) in the solution entering the buffer?
3. In experiments with highly compacted bentonite, the transport of a high pH plume originating from NaOH solution has been significantly faster than that of a high pH plume originating from $\text{Ca}(\text{OH})_2$ solution. Is this only due to the higher concentration of OH^- ions in the used NaOH solutions, and thus a higher diffusive mass transfer rate, than from the $\text{Ca}(\text{OH})_2$ solutions, where the OH^- concentration is limited by the solubility of $\text{Ca}(\text{OH})_2$?
4. Extension and shape of the altered bentonite layer as a function of time? Note that the attack from rock fractures or through the repository excavations may be localised. Is the growth of the altered zone governed by diffusion processes and reactions between the intruding solution and the clay?
5. Relative propagation rates of diffusing OH^- ions and the reaction front of the buffering and alteration processes in highly compacted bentonite. Is it possible that, due to the kinetics of reactions, the plume of high pH could reach the canister surface (and penetrate into a defective canister) before the buffering reactions neutralise the high pH? What are the effects of alkaline and earth-alkaline metals (e.g. cesium) released from the spent fuel on the solution chemistry inside the canister?
6. What are the effects of a high pH plume on montmorillonite and accessory minerals of highly compacted bentonite? Which effects are the most important ones for the point of view of buffer performance?
7. What is the buffering capacity of highly compacted bentonite, i.e. its ability to keep the pH, say below 11 or 10, in terms of moles of OH^- ions per kg of clay? Is this quantity a relevant measure of the buffering capacity of the buffer?
8. Mechanical (e.g. swelling pressure, plasticity) and transport-related (e.g. porosity, diffusivity, sorption) properties of highly compacted bentonite altered by a high pH plume.
9. Effects of dissolution and (re)precipitation of siliceous and aluminous species and other accessory minerals of cement, ballast, rock and bentonite: Is there a risk of cementation of the bentonite buffer affected by a plume of high pH, when the pH eventually drops again?
10. Effects of superplasticizers and other admixtures of cement on bentonite and radionuclide mobility.

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Extended Abstract

The bentonite/cement interaction problem: cutting the Gordian knot

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Introduction

A basic principle which contributes to our ability to make confident predictions of the safety of deep geological repositories for long-lived waste is avoiding high energy systems. The geological environment itself is (usually!) selected to be stable with low hydrologic, thermal and geochemical driving forces. The engineered barriers emplaced should, ideally, maintain this situation. It is, therefore, desirable to avoid use of materials which are mutually incompatible or are incompatible with the host rock.

A particular problem arises due to the extensive use of cement and concrete in the civil engineering and mining industries. Very extensive practical experience with well-characterised and relatively cheap cementitious materials makes them the natural choice for many applications involved in repository construction. Such use is, however, incompatible with the use of highly compacted bentonite as a key safety barrier; the interactions between these materials being the main focus of most papers presented at this workshop.

Despite the efforts being expended, we feel that there is no possibility of rigorously excluding significant long-term degradation of bentonite barriers which interact with cement leachates - at least within the foreseeable future. Even if understanding of the degradation processes increases, such a dynamic system with time-varying properties will be extremely difficult to characterise. In such a case, modifying designs to ensure that such interaction does not occur in the first place seems a more robust approach. Two cases are distinguished, "TRU" type long-lived ILW - where replacement of bentonite is suggested - and HLW / SF where we recommend protecting bentonite from any interaction with cement leachate.

TRU

The case for TRU is relatively clear; concrete is a major component of the packaged waste and hence there is no point in restricting use of cement and concrete for construction. The question is thus - what role does bentonite serve and can it be taken over by another material?

The geochemical environment within the monolithic, microporous near-field in most TRU designs ensures effective immobilisation of most radionuclides. Actinides, in particular, are likely to display low solubility and high sorption. The most problematic radionuclides are those which are highly mobile in such situations - e.g. anions (I-129), organics (organic C-14) and alkali metals (e.g. Cs-135). Even for these, releases may be greatly limited within a low permeability concrete.

One role attributed to bentonite is to further reduce these releases by ensuring that solute transport through the near-field is dominated by diffusion. For this particular case, there are certainly alternative approaches and materials which could provide the same net effect - the most robust of which is probably a high permeability hydraulic cage (assuming that a host rock cannot be found which provides such a situation naturally – e.g. Opalinus Clay).

The problems mainly arise when the evolution of the concrete monolith is considered. Over a relatively short period cracking is quite likely, for example due to:

- settling / earth movements (creep, fault movement, ...)
- gas production
- swelling of corrosion products (rebars, canisters, ...)
- biodegradation
- construction defects, monitoring equipment and other anthropogenic influences

In such a case, a number of problematic scenarios need to be considered:

1. advective water flow; driven by hydraulic gradients
2. advective water flow; driven by gas pressure
3. release of gaseous radionuclides (e.g. C-14 methane)
4. release of radionuclides as colloids, macromolecular complexes or associated with microbes

The presence of an intact, highly-compacted bentonite barrier would avoid (1) and (4) above, but do little for (2) and (3). A simple hydraulic cage would also avoid (1) in the case of minor cracking and might reduce the effects of (3) by providing a macroporous gas buffer which might minimise direct gas release to the geosphere.

The problem with the bentonite barrier is its uncertain long-term performance. Even if mineralogical alteration is slow, cementation due to carbonate or silicate precipitation may be relatively rapid. Coupled with gas production, this leads to cracking scenarios which would result in loss of both advective flow barrier and colloid filtration roles.

By comparison, the hydraulic cage is much more robust. Cementation / cracking causes little significant effect and massive precipitation with a major reduction in porosity would be needed to cause a decrease in hydraulic conductivity.

If an enhanced barrier is needed, an external hydraulic cage can be combined with an additional colloid filter with low permeability, but this should be immune to degradation by hyperalkaline conditions. Candidates would be special plastic (or self-healing) concretes or zeolites. As the latter are often identified as the end-products of bentonite alteration, their stability is well supported. Zeolites have wide ranges of properties, which include molecular filtration and highly-specific sorption, indicating that an optimised solution is possible. It should be noted that, in this regard, much can

also be done in terms of designing the waste emplacement system for improved long-term performance.

HLW

A particular problem occurs with the use of cement and concrete in repositories for HLW (or SF) in which bentonite plays a key barrier role (Table 1). The option of replacing bentonite is not considered here; instead we focus on avoiding any processes which could affect its longevity. The best option is to avoid all use of cementitious materials in the vicinity of waste emplacement zones. For hard host rocks, a lot can be achieved by careful design and construction, aligning tunnels for maximum mechanical stability, using construction techniques which cause minimum mechanical damage and support systems which do not involve use of concrete. An example of this approach is described in the recent Entsorgungsnachweis project. Even when massive structures are required (tunnel seals); use of concrete can be avoided by a bit of lateral thinking (e.g. use of natural stone plugs).

The challenge is to replace all the planned use of cementitious materials in sensitive areas. Such uses include:

- ⇒ tunnel / borehole liners
- ⇒ tunnel / borehole plugs & seals
- ⇒ grouts for hydraulic sealing
- ⇒ floors, walls and other structural elements

In the case of liners, it is worth distinguishing between the cases where such liners are required for mechanical support and those where they are needed only to reduce water inflow during the operational period. In the former, alternative materials which can be considered include steel, ceramics and natural stone. Although there may be some cost consequences, these must be seen in terms of total project costs and opportunities for global cost optimisation. In the latter, there may additionally be options for sealing of “wet areas” using resins and / or simply amending the EBS design to allow practical operation with higher water inflow rates (e.g. use of pre-fabricated EBS modules – PEMs).

As noted above, in many cases concrete can be avoided in plugs by use of natural stone. There certainly are a number of options for use of other designs using metal plugs or packers – especially where the plug is required only during the operational period. Costs are unlikely to be critical here and alternative designs may even have significant advantages (especially if remote handled emplacement is considered).

Replacing conventional cement-based hydraulic grouts for sealing major water inflow zones is probably the biggest challenge at present. Many alternative materials are possible – for example clay-based, alternative carbonate- or silicate-cementation systems or resins. The main problem is the lack of a development programme for such materials which includes accumulation of experience under relevant conditions (many systems which work well in the laboratory fail when tested in-situ). Nevertheless, with the rapid advances in materials technology, this should not be regarded as a hopeless option – especially when combined with efforts to better characterise

problematic features at a potential site and minimise sealing requirements by optimisation of layout.

The structural use of concrete are, in contrast, generally easiest to work around; avoid entirely by design changes (e.g. replace floors by rails directly on the rock / liner) or use of alternative materials (e.g. concrete floors replaced with gravel plus natural stone paving).

It is quite probable, if avoiding use of concrete is taken to be a design prerequisite, alternative options can be found for most host rocks presently considered.

Although maybe a second-best choice for most disposal concepts, if the use of concrete liners or cement grouts cannot be avoided, there are options to protect bentonite from degradation – particularly during the initial high temperature / high alkalinity phase where risks are greatest.

Two examples are illustrated (although others are certainly possible). The first is a variant of the PEM theme, where the bentonite is protected for a period of time due to the external steel handling shell. To maximise protection, pozzolanic or glassy material (e.g. crushed tuff) is used to backfill the annulus around the PEM. This material reacts rapidly at high pH and hence acts as a pH buffer. As it has no particular barrier role apart from space-filling, this reaction will have no effect on long-term performance.

An alternative is the CARE option considered by NUMO. In this design massive, casks containing around 20 HLW packages are emplaced in caverns which are kept open for a planned period of 300 years before sealing and closure of the repository. Even if concrete liners and floors are used in this design, the problems are greatly reduced by very extensive carbonation of all such structures during the long period of high temperatures and active ventilation.

Conclusions

It will be very difficult to make a safety case which depends on the longevity of bentonite which can be degraded by interaction with cementitious materials. Rather than expend effort to better understand this degradation process, it may be better to avoid it by design.

For TRU, the best approach is to replace bentonite with an alternative material. A good option seems to be a hydraulic cage with an inner zeolite layer. In any case, for such waste there is great optimisation potential by considering the EBS design as a whole.

In the case of HLW, it is best to avoid all use of concrete in critical areas. A number of alternatives have been suggested. If concrete must be used, design changes to reduce the risk of interaction with bentonite can be examined.

Bentonite role	Degradation by cement	Key problem
Diffusion barrier	Major	Cementation / cracking
Colloid filter	Major	Cementation / cracking
Radionuclide sorption	Some	Ion exchange
Plasticity (gas flow)	Major	Cementation
Thermal conductivity	None	
Mechanical buffer	Some	Cementation
Microbe barrier	Some	Cementation / cracking

Table 1 Key roles of bentonite and their sensitivity to degradation by cement.

**Evaluation Methods for Ion Migration in Concrete
&
Prediction Methods for Concrete Deterioration
Caused by Chloride Attack or Calcium Leaching**

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Background

In recent years, several kinds of deterioration in concrete structures are reported, and it is clarified that the performance of concrete becomes lower.

According to the previous studies...



The one of the reasons about these concrete deteriorations is due to ion migration in concrete.



It is important to study Ion migration in concrete and to establish the evaluation and prediction methods for these deteriorations.

Purposes

- (i) To construct the evaluation and prediction methods for the concrete deterioration due to ion migration
- (ii) To validate these methods

The deteriorations considered in this study are **Chloride Attack** and **Calcium Leaching**, though there are several kinds of concrete deteriorations.

Chloride Attack

The one of the main deteriorations in Japan.

Calcium Leaching

This deterioration must be remarkable one when constructing the underground facility for keeping the high-level radioactive waste material.

Chloride Attack & Calcium Leaching

Chloride Attack is the one of the well-known degradation phenomenon of concrete. The steel bar in concrete corrodes by Cl^- permeating from the external environment, and this corrosion generates the crack by the swelling pressure of the rust.

Calcium Leaching is the phenomenon of Ca dissolving out from concrete into the external water. Therefore, Ca Leaching occurs the decrease of the strength of concrete as well as the increase of the void ratio. This deterioration can occur when concrete is in contact with water for the long time (100years or more).

- Today, I would like to talk mainly about calcium leaching.

Part1 Establishment of Numerical Analysis Method for the Prediction of Leaching of Calcium From Concrete Considering Migration of Multiple Ions.

Part2 Fundamental Study on Prediction of Concrete Deterioration Caused by Calcium Leaching over 100 Years.

Part1 Establishment of Numerical Analysis Method for the Prediction of Leaching of Calcium From Concrete Considering Migration of Multiple Ions.

The propose of this study is to establish and propose a numerical analysis method for predicting the long-term leaching of calcium from concrete.

Basic theory of ion migration and calcium leaching model

Assumptions

- 1. Concrete is a macroscopically homogeneous material.**
- 2. Ion migration in concrete follows the Nernst-Planck equation for electrochemical mass transfer. Namely, the driving force for ion motion in concrete is developed by the concentration gradient and electrostatic potential gradient.**

Basic theory of ion migration and calcium leaching model

Assumptions

- 3. The influence of ionic strength on diffusion can be considered using the Debye-Hückel equation.**
- 4. The migration of multiple ions depends on the electro-neutrality condition.**
- 5. All pores in concrete can be thought of as continuous capillaries filled with pore solution.**

Basic theory of ion migration and calcium leaching model

Assumptions

6. The ions that dissolve from cement paste are Ca^{2+} and OH^- only.

7. The leaching of calcium from cement paste to concrete can be represented by Buil's model, a solid-liquid equilibrium model.

8. While 1 mole of Ca^{2+} dissolves from cement paste to the pore solution, 2 moles of OH^- dissolve.

Basic theory of ion migration and calcium leaching model

Assumptions

9. The porosity created by leaching a given quantity of calcium hydroxide is equal to the volume of the same quantity of crystalline $\text{Ca}(\text{OH})_2$.

10. The apparent absolute mobility, which is an index for ion migration in concrete, can be determined from the pore ratio and tortuosity factor.

11. It is assumed that six types of ion are contained in pore solution. That is, only Ca^{2+} , Na^+ , K^+ , OH^- , Cl^- , SO_4^{2-} .

Introduction of the Ion Migration equation

Nernst-Planck equation, Debye-Hückel theory, electro-neutrality condition

Nernst-Planck equation

$$J_i = -k \cdot T \cdot B_i \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot \frac{\partial C_i}{\partial x} - e \cdot Z_i \cdot B_i \cdot C_i \cdot \frac{\partial \phi}{\partial x}$$

where, i is the ionic species, J is flux (mol/cm²/sec), k is the Boltzman number ($=1.38 \times 10^{-23}$ J/K), T is temperature (K), B is absolute mobility (cm/sec/dyne), γ is the activity coefficient, C is the concentration of ions (mol/cm³), x is the distance from the exposure surface (cm), e is the elementary electric charge ($=1.60 \times 10^{-19}$ C), Z is the ionic charge number, and ϕ is electrostatic potential (V). The first term describes diffusion, in which the driving force is the concentration gradient, and it is referred to as the 'diffusion term'. The second term describes the electro-migration, which is driven by the electrostatic potential gradient. This member is referred to as the 'electro-migration term'. Note that equation (1) shows that the ion migration index of diffusion and electro-migration is the absolute mobility B_i only.

Introduction of the Ion Migration equation

Nernst-Planck equation, Debye-Hückel theory, electro-neutrality condition

Debye-Huckel theory

$$\log \gamma_i = - \frac{u \cdot Z_i^2 \cdot \sqrt{I}}{1 + v \cdot a_i \cdot \sqrt{I}}$$

where, a is an ion size parameter (cm), I is ionic strength (mol/l), u is a constant ($=0.5115$ dm^{3/2}/ mol^{1/2}), and v is a constant ($=0.3921 \times 10^8$ dm^{3/2} /mol^{1/2}).

Ionic strength is defined by the following equation:

the ion size parameters a_i of many ions are about 3 Å .

$$I = \frac{1}{2} \sum_i (Z_i^2 \cdot C_i)$$

Introduction of the Ion Migration equation

Nernst-Plank equation, Debye-Hückel theory, electro-neutrality condition

The electro-neutrality condition

$$\sum_i (Z_i \cdot J_i) = 0 \quad \text{Eq.(6)}$$

The electro-neutrality condition means that cations and anions maintain electrical neutrality in passing through an arbitrary section. This condition, described by ionic charge number and flux in equation (6), shows that the multiple ions in concrete migrate while maintaining a charge balance.

Introduction of the Ion Migration equation

Nernst-Plank equation, Debye-Hückel theory, Electric quantity equation

Ion Migration Equation

$$J_{ion} = -k \cdot T \cdot B_{ion} \cdot \left(1 + \ln 10 \times C_{ion} \times \frac{-0.51 \cdot Z_{ion}^4}{4 \cdot \sqrt{I} \cdot (1 + \sqrt{I})^2} \right) \cdot \frac{\partial C_{ion}}{\partial x} - \frac{1}{F} \cdot k \cdot T \cdot \sum_n \left(Z_n \cdot \left(1 + \ln 10 \times C_n \times \frac{-0.51 \cdot Z_n^4}{4 \cdot \sqrt{I} \cdot (1 + \sqrt{I})^2} \right) \cdot B_n \cdot \frac{\partial C_n}{\partial x} \right) - Z_{ion} \cdot B_{ion} \cdot C_{ion} \cdot \frac{-i}{\sum_n (Z_n^2 \cdot B_n \cdot C_n)}$$

Advantages of using this equation

- To calculate the electro-migration flux as well as the diffusion flux.
- To evaluate the influence of coexistence ions on the migration of an ion species.
- To consider that the total sum of the electric charge of the ions passing through an arbitrary section is equal to the electric charge quantity given from outside.
- To calculate the distributions of multiple ions.

The migration of an arbitrary ion species is influenced with the electric current & the concentration of the coexistence ions.

Calculation of Mobility

Engineering mobility

$$B_i = \frac{\epsilon}{\tau^2} \cdot B_{0,i}$$

where, ϵ is pore ratio (cm³/cm³),
 τ is tortuosity factor,
 B_0 is absolute mobility in dilute solution (cm²/sec/dyne),
 ϵ , τ are unknown.

Ionic species	Absolute mobility [cm ² /sec/dyne]
Ca ²⁺	1.66 × 10 ¹⁵
Na ⁺	2.75 × 10 ¹⁵
K ⁺	4.13 × 10 ¹⁵
OH ⁻	1.11 × 10 ¹⁶
Cl ⁻	3.94 × 10 ¹⁵
SO ₄ ²⁻	1.84 × 10 ¹⁵

Calculation of Void Ratio after Ca Leaching

Void ratio

$$\epsilon = \epsilon_0 + \frac{M_{CH}}{d_{CH}} \cdot (C_{c0} - C_c)$$

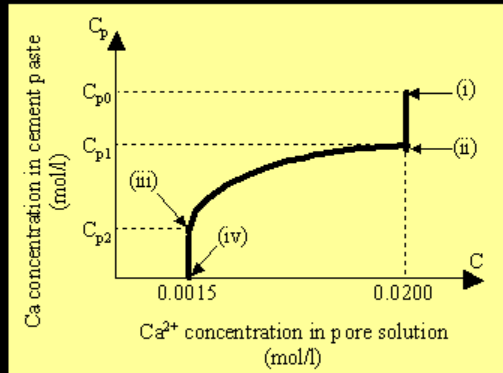
where, e is pore ratio (cm³/cm³), e_0 is initial pore ratio (cm³/cm³), M_{CH} is the molecular weight of Ca(OH)₂ (=74 g/mol), d_{CH} is the density of Ca(OH)₂ (=2.23 g/cm³), V_c is the volume ratio of cement ($V_c = 1 / (d_c \times W/C + 1)$, d_c : density of cement), C_{p0} is the initial Ca quantity in the solid phase per unit volume of concrete (mol/l), and C_p is the quantity in the Ca concentration of solid phase per unit volume of concrete (mol/l).

Chemical Equilibrium Model for calculating ion concentration

- **Ca Leaching from $\text{Ca}(\text{OH})_2$**

- $C_{\text{Ca}^{2+}} \cdot C_{\text{OH}^-}^2 = K_{sp}$ ● $C_{\text{H}^+} \cdot C_{\text{OH}^-} = K_w$ ● $\sum_i Z_i \cdot C_i = 0$

- **Ca Leaching from C-S-H**

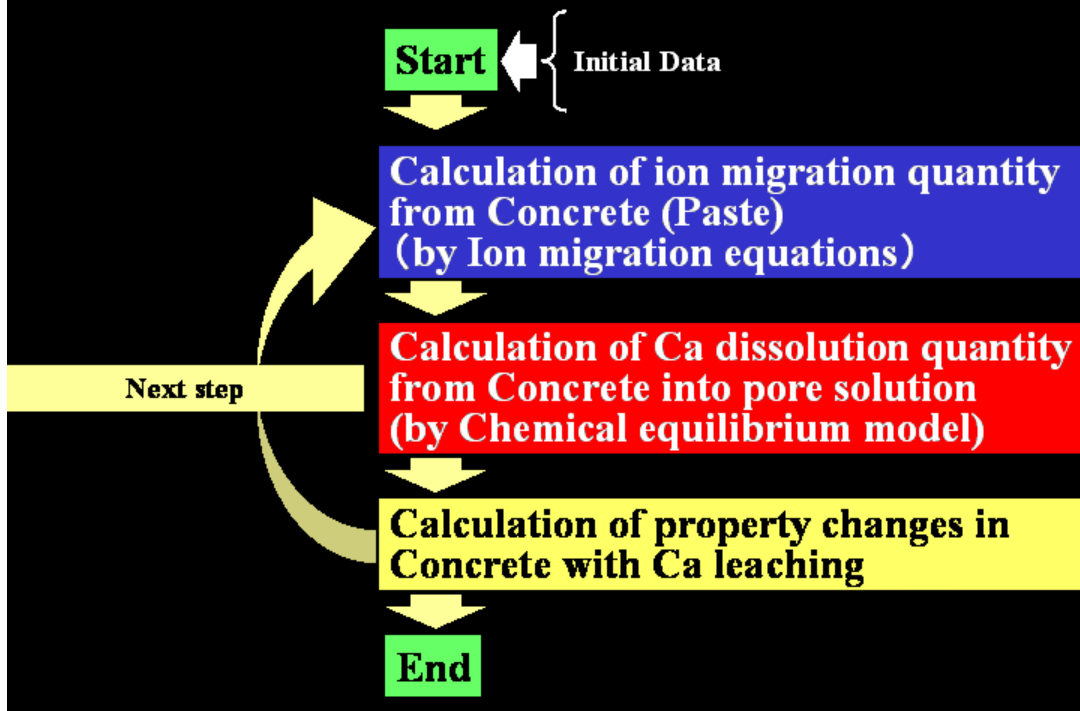


- $C_{\text{H}^+} \cdot C_{\text{OH}^-} = K_w$

- $\sum_i Z_i \cdot C_i = 0$

- **The line is decided by the data obtained from some previous studies.**

Formulation of Numerical Analysis Method



Boundary conditions

The boundaries of this method are interface- m , which is the exposure surface, and interface- 0 , which is the deepest part of the concrete.

The ion concentration at interface- m is assumed to be equal to the external solution. Also, the engineering absolute mobility at interface- m is assumed to be equal to that of absolute mobility in the dilute solution. In other words, at interface- m , the pore ratio e and the tortuosity factor t are assumed to equal 1. Incidentally, the ion concentration gradient, required when calculating the flux at interface- m , is defined as shown in Figure 3 (in page 9). Also, ion migration does not occur at the interface- 0 .

Validity of the Numerical Analysis Method

Mix Proportions of Surveyed Members (From the data of the surveyed structure)

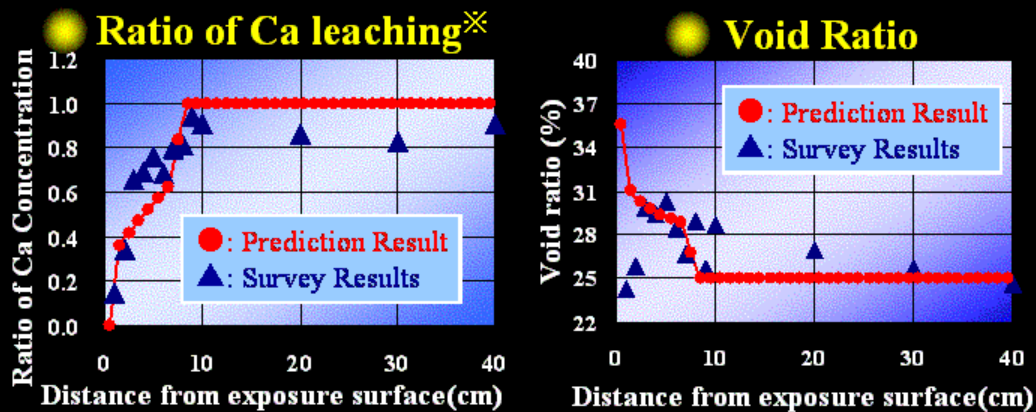
	W/C	Unit content (kg/m ³)			
	(%)	Water	Cement	Fine aggregate	Coarse aggregate
Concrete member	72	109	152	688	1427
Mortar member	72	253	352	1595	-

Estimated Initial Values and Ion Concentration in Pore Solution of Surveyed members

Estimated Initial Values and Ion Concentration in Pore Solution	Concrete member	Mortar member
Pore ratio (cm ³ /cm ³)	0.11	0.25
Water-cement ratio (%)	71.7	71.7
Paste volume in unit volume of concrete (m ³ /m ³)	0.049	0.115
Density of cement (g/cm ³)	3.15	3.15
Initial Ca concentration in cement paste (mol/l)	10.6	10.6
Ca concentration in cement paste at the time of calcium hydrate disappearance (mol/l)	8.48	8.48
Initial Ca ²⁺ concentration in pore solution (mol/l)	0.0200	0.0200
Initial Na ⁺ concentration in pore solution (mol/l)	0.0342	0.0342
Initial K ⁺ concentration in pore solution (mol/l)	0.0381	0.0381
Initial Cl ⁻ concentration in pore solution (mol/l)	0.0004	0.0004
Initial OH ⁻ concentration in pore solution (mol/l)	0.1060	0.1060
Initial SO ₄ ²⁻ concentration in pore solution (mol/l)	0.0030	0.0030

Validity of the Numerical Analysis Method

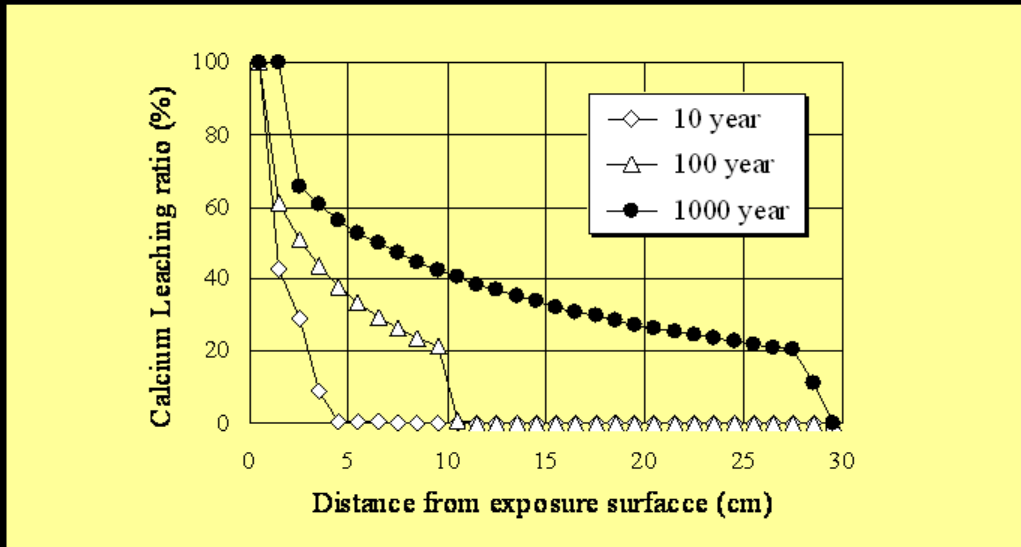
- Comparing the prediction results with the survey results obtained from the existing concrete member in contact with water 100 years



$$\text{Ratio of Ca leaching} = \frac{\text{Ca concentration in concrete}}{\text{Initial Ca concentration in concrete}}$$

Estimation of Ca Leaching after 1000 years

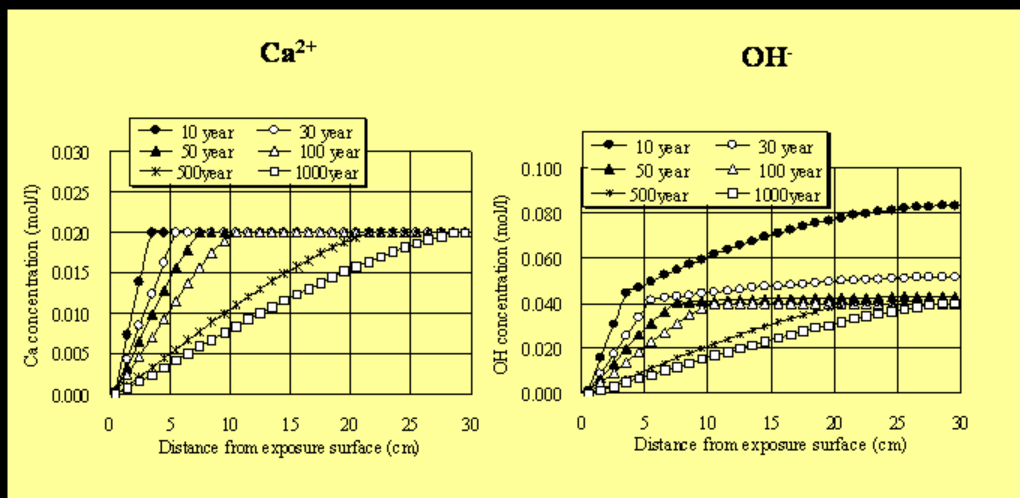
Distribution of Ratio of Ca Leaching



$$\text{Ratio of Ca leaching} = \frac{\text{Ca concentration in concrete}}{\text{Initial Ca concentration in concrete}}$$

Estimation of Ca Leaching after 1000 years

Distribution of Ion Concentration



Conclusions

1. A numerical analysis method for the prediction of calcium leaching from concrete was established using one-dimensional differential calculus.

2. The leaching of calcium from concrete and mortar members over 100 years was predicted using the new method. The prediction results were then compared with the actual results of surveys carried out on old members that had been in contact with water for 100 years. From this comparison, it is clear that the predictions correspond with the surveys; hence, the validity of this method is confirmed.

Conclusions

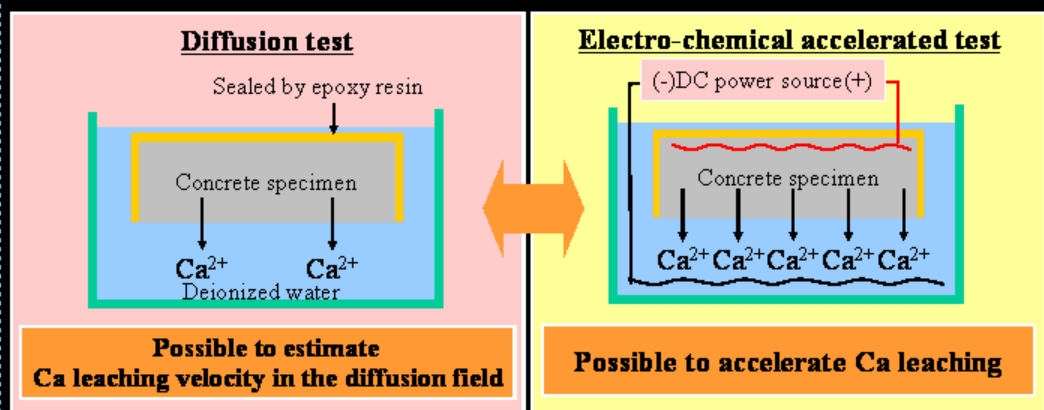
3. Using the new method, the leaching of calcium from concrete over 1000 years was predicted. Leaching of calcium was found to reach the region 30 cm below the exposure surface. Also, if the region where Ca(OH)_2 dissolves completely is defined as the physical deterioration region, physical deterioration of the 1,000-year-old concrete can be expected to reach within 27 cm below the exposure surface.

Part2 Fundamental Study on Prediction of Concrete Deterioration Caused by Calcium Leaching over 100 Years.

The propose of this study is to propose an experimental method for predicting the long-term leaching of calcium from concrete and the resultant concrete. Using this method, we can predict the strength distribution of concrete after leaching of calcium.

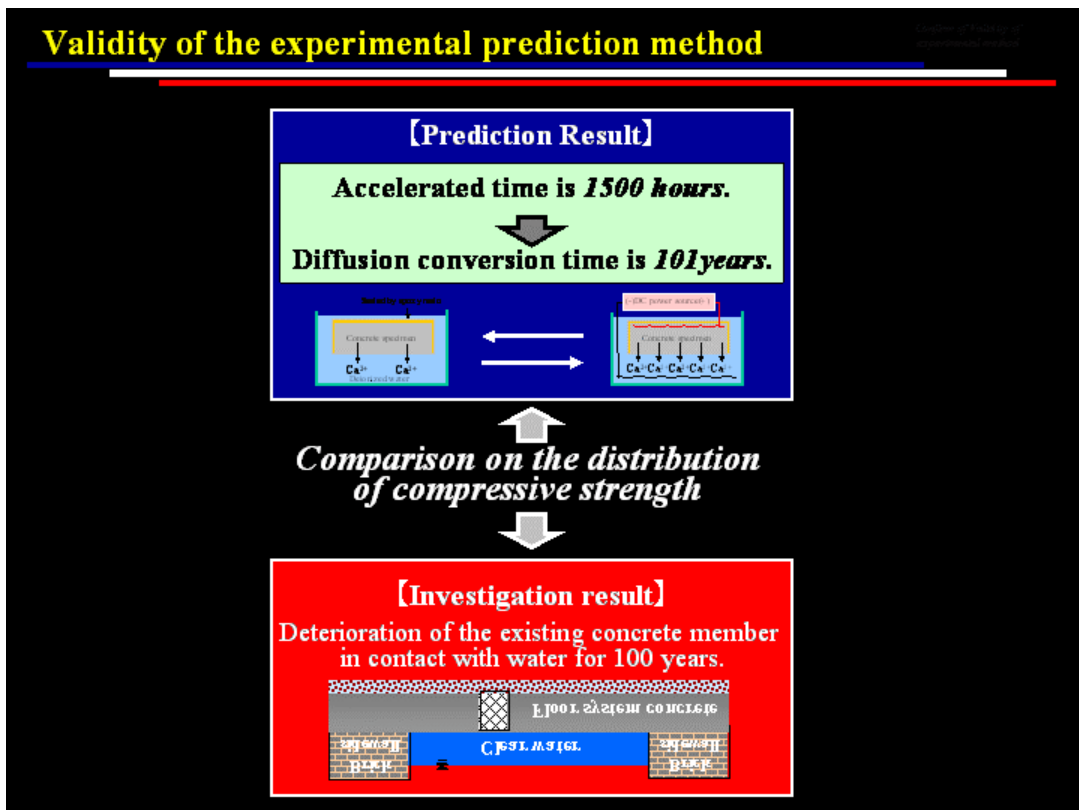
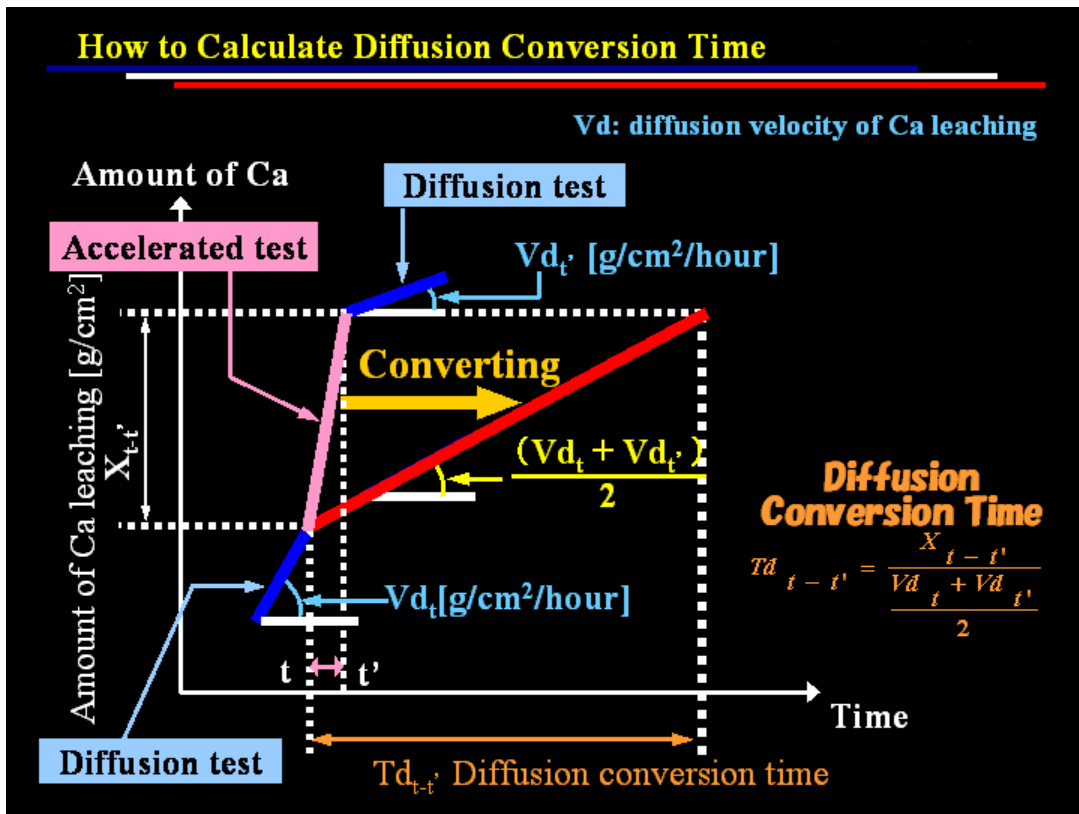
Concept & Advantage of Experimental Prediction Method

Concept : To Combine the good points of each method

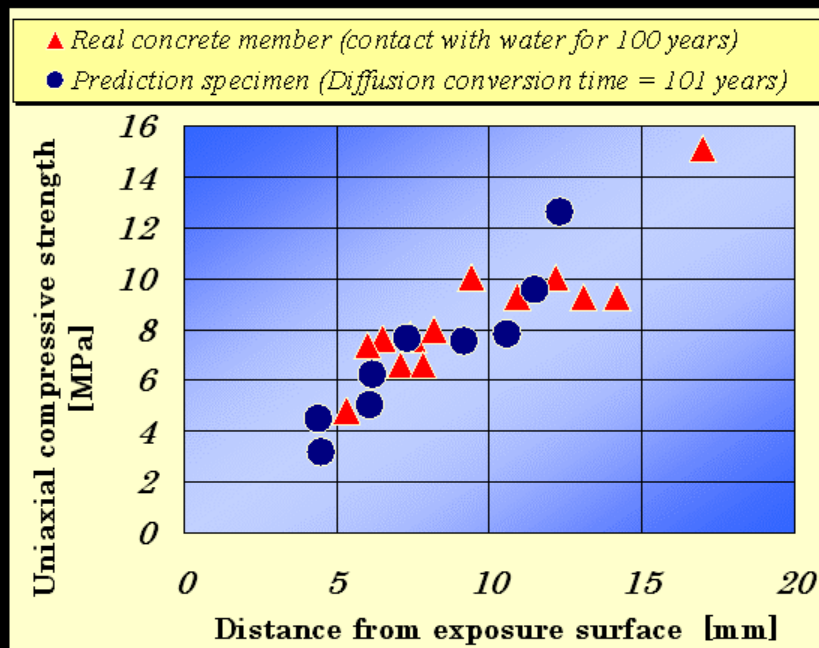


--Advantage--

Using the results of these tests, accelerated time by Electro-chemical accelerated test is converted into the real diffusion time (called "**the diffusion conversion time**"). Therefore it is possible to obtain the specimen in which the promotion magnification of the deterioration is known.



Validity of experimental Prediction Method



Conclusions

1. An experimental prediction method was established to predict calcium leaching from concrete and the resulting deterioration over 100 years. The predictions were compared with a survey of a real concrete structure that had been in contact with water for about 100 years using the needle penetration test. From this comparison, the validity of the method was confirmed. It is concluded that this experimental method can reliably predict the deterioration of concrete caused by calcium leaching.
2. It was clarified that the Vickers hardness and Ca/Si molar ratio of bulk concrete at a particular DCT are high in the case of (1) high unit cement content, (2) cement containing mainly belite, and (3) low water-cement ratio. Also, chemical analysis demonstrated that the fall in Vickers hardness occurs as a result of calcium leaching.

DISSOLUTION MECHANISM AND KINETICS OF SMECTITE UNDER ALKALINE CONDITIONS

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INTRODUCTION

Extensive use of cement for encapsulation, backfilling, and grouting purposes is envisaged in geological repositories of radioactive waste. Degradation of cement materials in the repositories can produce a high pH pore fluid initially ranging from pH 13.0 to 13.5. The pH of fluid progressively decreases to moderately alkaline range with the formation and evolution of subsequent materials (Atkinson, 1985). The high pH pore fluids can migrate from the repository and react chemically with the host rock and bentonites which were employed to enhance repository's integrity. These chemical reactions can affect the capacity of the rocks and bentonites in retarding the migration of radionuclides. Smectite, main component of bentonite, can lose some of their desirable properties at the early stages of bentonite-cement fluid interaction. This has been a key research issue in performance assessment of radioactive waste disposal. The effect of high pH fluid on the chemical and physical behavior of smectite, especially dissolution behavior and rates is of utmost importance.

A mineralogical conversion during the interaction with high pH fluids and its effect on swelling and sorption capacities have been roughly understood (for example; Johnston & Miller, 1984, Duerden, 1992, Savage et al., 1992, Eberl et al., 1993, Bauer & Berger, 1998, Amaya et al., 1999 and Sato, 2001). However, most of the previous studies have focused mainly on the mineral conversion under high pH and high temperature conditions. Only a few studies on smectite dissolution rate under different pH conditions and relatively low temperature expected in the repository have been systematically carried out. In the above studies, reliable data was probably obtained because the experiments were carefully performed under the given conditions. However, as following two reasons, the experimental results are difficult to compare a priori for discussing the pH effects on the dissolution rate of smectite. Firstly, most of the authors used not an almost pure smectite but a bentonite containing other minerals such as cristobalite, quartz, calcite, feldspar, and so on. The sample studied by Cama et al. (2000) was mainly composed of an illite/smectite interstratified mineral with about 85-90% smectite. Secondly, the dissolution rates have been obtained from the different systems, i.e., flow-through (open) or batch (close) systems. In the batch system performed by many authors, the degree of saturation (i.e., deviation from equilibrium) should be changed as function of time, and then the smectite dissolution does not attain a constant rate (Oelkers et al., 2001). In this context, stirred-flow-through dissolution experiments were carried out to determine reliable dissolution rates of smectite from neutral to highly alkaline condition and to formulate the effect of pH and temperature on smectite dissolution rate. Atomic force microscopy (AFM) using fluid cell also performed to determine the reactive

surfaces and reliable dissolution rate in smectite dissolution and to understand mechanism of the dissolution under alkaline condition.

EXPERIMENTS

Flow-through system was employed in this study because the flow-through experiments allow us to measure the dissolution rate under steady state condition. Experiments were carried out using stirred-flow Teflon® reactors with long cylindrical shape. To avoid pH change due to the solution-CO₂ interaction, the preparation, stock and collection of the solution were performed in glove box filled with N₂ gas atmosphere.

The experiments were performed for mixed NaOH-NaCl or KOH-KCl aqueous solutions with ionic strength of 0.3 M. Purified smectite (Kunipia-P® provided from Kunimine Industry Co Ltd) was reacted at the pHs from 8-13 and constant temperature of 30, 50 and 70°C. For each experiment, 120 mg of the sample was added to the 120 ml of the solution in the reactor. The concentrations of Al in the contacted aqueous solutions were determined by using inductively-coupled plasma mass spectroscopy (ICP-MS), and Si was determined as SiO₂ through molybdenum-blue spectrometry. The dissolution rates were calculated from the steady-state Si and Al concentrations.

Adsorption of protons and hydroxyl ions with the sample was investigated by acid/base titration. The titration was performed under N₂ gas bubbling to exclude CO₂, constant ionic strength (0.3 M NaCl) and at temperatures used in the experiments (T = 30, 50 and 70°C). Acidimetric titrations were performed until pH 4, while alkalimetric titration were conducted until pH 10.

The following three setups for the dissolution experiments by AFM observations were prepared (referred here as Run X); Run I: short-term *in situ* batch dissolution experiment at room temperature (22°C); Run II: long-term *in situ* flow-through dissolution experiment at room temperature (22°C); and Run III: long-term dissolution experiments at 50°C. The dissolution experiments were conducted under highly alkaline conditions (pH 13.3 ± 0.1) using 0.3 M NaOH solutions. For Run III, the samples mounted on mica plates were immersed and heated in 50 mL 0.3M NaOH solutions inside Teflon containers. The samples are allowed to react for a period ranging from 6 to 33 days at 50°C and then placed inside the fluid cell of the AFM to prevent further dissolution with entrained alkaline reacting solution. The samples mounted on the mica plate were observed under AFM at 22°C to detect changes in particle volume after the dissolution reactions. A hundred particles were observed to be statistically viable.

RESULTS AND DISCUSSION

In the present study, possibilities of other variables were except for pH and temperature eliminated by conducting all experiments at constant of the factors. Therefore, the observed difference in the dissolution rates should be attributed to the difference in the pH and temperature of the solution. From the rates obtained in the dissolution experiment, it is unambiguously shown that the pH strongly affects the dissolution rate under alkaline condition, and the rates increase with an increase in the pH. Fig. 1 is plot of the logarithm of the rate versus the pH of the solution. Good linear relationships are observed between pH and log rate. The rate laws were calculated by fitting the dissolution log rate to the pH value, and yielded the following equations:

$$Rate(mol^{-2}s^{-1}) = 10^{-13.58} a_{H^+}^{-0.15} \quad (\text{in } 30^\circ\text{C NaOH solution})$$

$$Rate(mol^{-2}s^{-1}) = 10^{-13.84} a_{H^+}^{-0.24} \quad (\text{in } 50^\circ\text{C NaOH solution})$$

$$Rate(mol^{-2}s^{-1}) = 10^{-13.52} a_{H^+}^{-0.27} \quad (\text{in } 70^\circ\text{C NaOH solution})$$

The dissolution rates calculated cover a range of alkaline pH. The rates become more pH-dependent with increasing temperature.

The changes in ln rate at constant pH as a function of 1/T are shown in Fig. 2. The calculated values of E_{exp} for smectite dissolution range from 37.89 to 63.88 kJ mol⁻¹. The lowest values are at near neutral pH but the rates increase with increasing pH. The changes in E_{exp} as a function of pH are shown in Fig. 3. The variation in activation energy with pH causes rates to become increasingly sensitive to pH at elevated temperature. Above pH 8, the obtained relation between pH and activation energy is shown following equation:

$$E_{exp} = 6.80pH - 18.07$$

In order to formulate the effect of pH and temperature on the dissolution rate, model of two parallel reaction paths are proposed according to Cama et al. (2002), gives

$$\frac{Rate_i}{\rho_r} = k_1 \cdot F_1 \frac{b_1 \cdot a_{H^+}}{1 + b_1 \cdot a_{H^+}} + k_2 \cdot F_2 \frac{b_2 \cdot a_{H^+}}{1 + b_2 \cdot a_{H^+}}$$

where F_i is the maximum surface coverage of protons on site i , b_i is a constant related to the energy of adsorption on site i and a_{H^+} is the activity of protons in solution.

A pH-independent apparent activation energy for each of the reaction paths is calculated by plotting an Arrhenius plot of the rate coefficients (k'_1 and k'_2) at 30°C, 50°C and 70°C, which were obtained from the fitting of the experimental data to the proposed model. The apparent activation energies were determined from a best-fit of rate coefficients that were obtained by fitting the experimental results at each temperature. The following equation was obtained by fitting the whole data set into a single equation

$$Rate = 4.74 \cdot 10^{-6} \cdot e^{-396/RT} \cdot \frac{177 \cdot e^{204/RT} \cdot a_{OH^-}}{1 + 177 \cdot e^{204/RT} \cdot a_{OH^-}} + 1.70 \cdot e^{-697/RT} \cdot \frac{0.0297 \cdot e^{235/RT} \cdot a_{OH^-}}{1 + 0.0297 \cdot e^{235/RT} \cdot a_{OH^-}}$$

The proposed model shows that smectite dissolution rate may be described by a rate law using activation energies being pH-independent. The dissolution mechanism can be interpreted in terms of surface complexation theory. In this study, the surface properties of smectite at different temperature, reactive surface parameters and distribution of reactive sites as a function of pH were systematically investigated. As the result of investigations, the first and second reaction sites in the above equation are Si site and Al site, respectively. Combining the above equation (the terms of effect of temperature and pH) and $f(\Delta G_r)$ obtained from Cama et al. (2000) into the general rate law (Lasaga 1995, 1998) gives

$$Rate = (4.74 \cdot 10^{-6} \cdot e^{-396/RT} \cdot \frac{177 \cdot e^{204/RT} \cdot a_{OH^-}}{1 + 177 \cdot e^{204/RT} \cdot a_{OH^-}} + 1.70 \cdot e^{-697/RT} \cdot \frac{0.0297 \cdot e^{235/RT} \cdot a_{OH^-}}{1 + 0.0297 \cdot e^{235/RT} \cdot a_{OH^-}}) \cdot (1 - e^{(-6 \cdot 10^{-10}) \cdot (\Delta G_r / RT)^6})$$

In Run I, the observed reduction in smectite particle volume can be attributed solely to edge surface dissolution. Dissolution rate calculated based on the surface area defined by the ESA (observed edge surface area) is 1.30×10^{-9} mol/m²·sec. On the other hand, there were no detectable changes in particle volume in Run II which is already achieved a steady state for dissolution. The relatively faster dissolution in Run I was also observed at the initial stage in the flow-through dissolution experiments. The dissolution rates were therefore different between at initial and steady state conditions. In Run III, the dissolution rate was calculated based on the median values of the basal surface areas of particles. The reduction in particle volume is mainly attributed to dissolution along edge surface areas despite the formation of a

few etch pits on the basal surface. Based on the surface areas defined by the ESA, the dissolution rate was $1.11 \times 10^{-11} \text{ mol/m}^2 \cdot \text{sec}$. The rate is fairly close to that obtained from the flow-through dissolution experiment at 50°C and pH 13.3 ($1.20 \times 10^{-11} \text{ mol/m}^2 \cdot \text{sec}$). From AFM observation, the dissolution rates derived at longer observation periods were directly comparable with the results from the flow-through dissolution experiments. Furthermore, the actual reactive sites (e.g. ESA) in the dissolution reactions were determined and used in the calculations of dissolution rate, which reflect the real dissolution rate of smectite. On the contrary, the rates obtained from flow through dissolution experiments were sufficiently reliable because of the above correspondence in the obtained dissolution rates

ACKNOWLEDGEMENT

This is a part of study funded by Radioactive Waste Management Funding and Research Center, Japan.

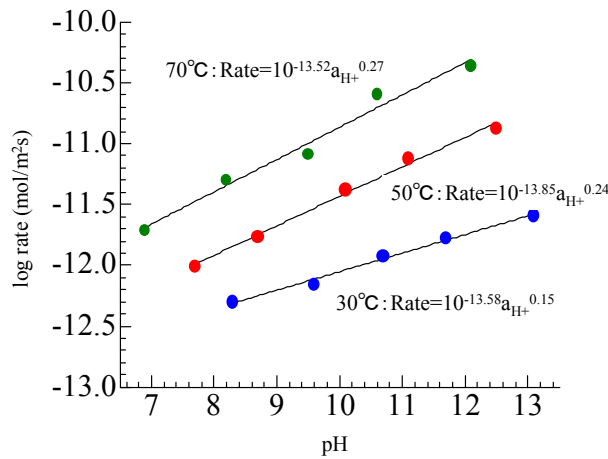


Fig. 1 Relationship between logarithm of the dissolution rates and the pH of NaOH solution each temperature (30, 50, 70°C).

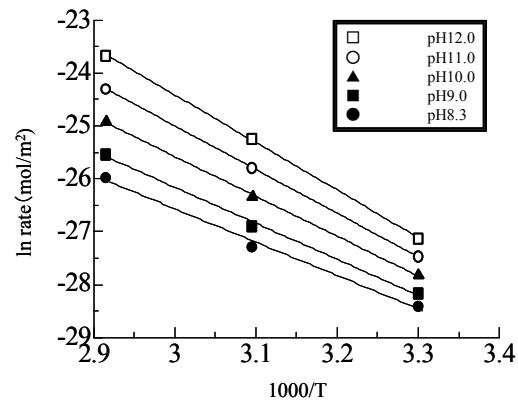


Fig. 2 Arrhenius plots of smectite dissolution rate at different pH of the solution.

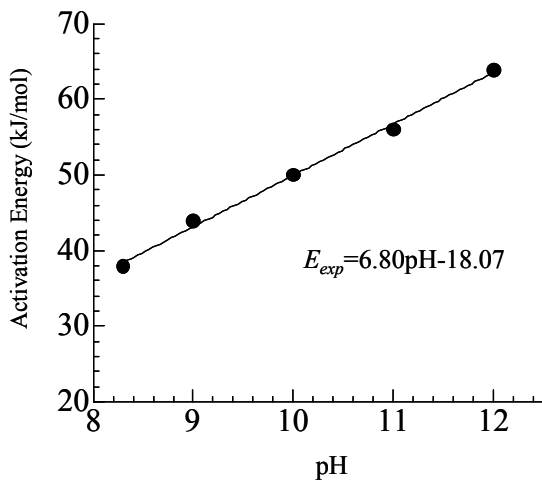


Fig. 3 Experimental activation energy (E_{exp}) for dissolution of smectite as a function of pH.

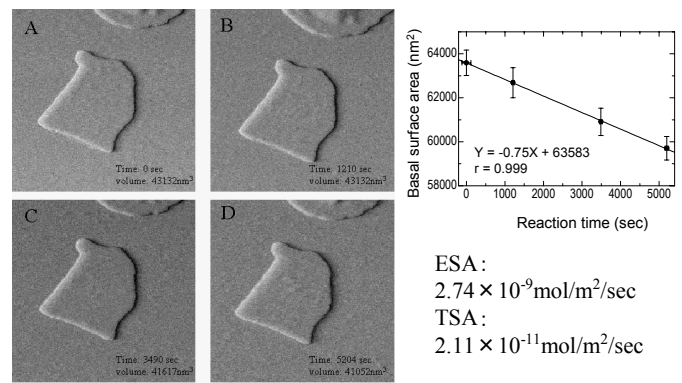


Fig. 4 Changes in AFM images and basal surface area of the sample particle in the dissolution process (22°C, pH=13.3). Calculated dissolution rates based on edge surface area and total surface area also shown in this figure.

Experimental study on changes of bentonite mineralogy and physical properties as a result of exposure to high pH solutions

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INTRODUCTION AND OBJECTIVS

In a repository for spent nuclear waste, it will be most practical to use concrete in many constructions, and cement for sealing rock fractures. In the Finnish ONKALO underground facility, the estimated quantity of injected cement is 3E6 kg, and in the Swedish planned KBS3 repository the corresponding figure is around 9E5 kg. The high pH in cement pore water may affect the stability of repository components, and is therefore of concern for the performance and safety assessment analyses. In a KBS3-type repository, the high pH may influence fracture minerals, the bentonite buffer, canister components, and the spent fuel in case of a canister failure. The pH evolution in the bentonite is of special interest, since it completely surrounds the fuel canisters and therefore may protect the canister and fuel. Such pH buffering capacity may be due to accessory mineral reactions, montmorillonite surface reactions and montmorillonite crystal lattice reactions. Fresh cement may raise pH to values between 13 and 14, and in matured cement materials pH is governed by portlandite (Ca(OH)₂), which gives a pH of around 12.4. Compared to ground water conditions this leads to an increase of the cation/proton activity ratio and into the stability field of Feldspars, and up to four orders of magnitude higher silica activity.

Several studies have been made concerning the interaction between bentonite and cement pore-water, of which most have been batch experiments with high water/solid ratio. The present study focuses on highly compacted bentonite since e.g. ion-equilibrium and transport restrictions significantly may affect possible reactions and reaction rates. The overarching objectives were to gather information concerning pH evolution in compacted bentonite, pH buffering capacity, changes in mineralogy, changes in swelling pressure, and possible specific effects of accessory minerals on the above items,.

EXPERIMENTAL

Commercial Wyoming bentonite from American Colloid Co. (MX-80) was used as starting material for all tests. The original material was used to produce almost pure homo-ionic montmorillonite with Na⁺, K⁺, and Ca²⁺ as exchangeable cations, respectively. Tests were made with the purified and the original material. The test solutions were chosen to be 0.1, 0.3 and 1.0 M NaOH, and saturated Ca(OH)₂ solution. The corresponding pH values as calculated by PHREEQC are 12.9, 13.3, 13.7 for the NaOH solutions, 12.4 for the Ca(OH)₂ solution. The samples had a 35 mm diameter, and a 55 mm height. The proposed KBS3 buffer density of 2000 kg/m³ at full water saturation was aimed at in all tests.

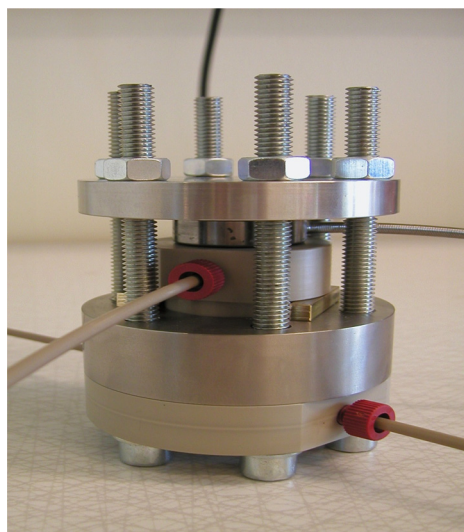
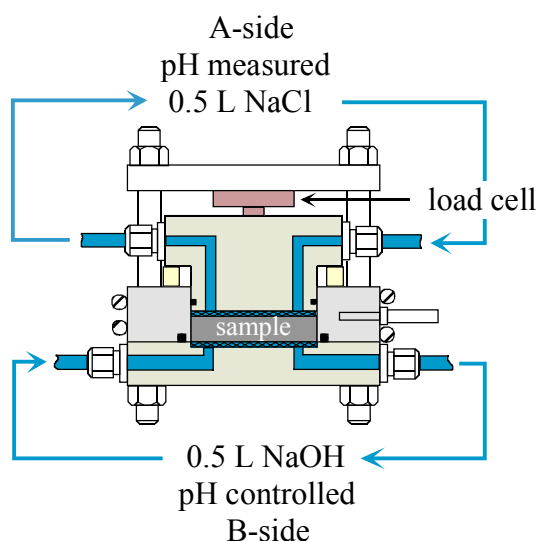


Figure 1 Schematic drawing and photo of a sample holder.

Air dry test material (water ratio ~10%) was slightly over-compacted compared to the intended density and placed in the cylindrical sample holders made of titanium and PEEK (Figure 1). The samples were water saturated by slowly circulating 0.5 L de-ionized water behind the filter by means of a peristaltic pump. After reaching pressure equilibrium, the water was changed to the predefined chloride solutions, and after reaching new pressure equilibrium, the chloride solutions at the bottom side (B) were changed to 0.5 L hydroxide solutions (high pH), and the 0.5 L isotonic chloride solution were left on the upper side (A). In a few tests the same solution was used on both sides and successively changed on both sides. At test termination the solutions were disconnected and the samples were quickly removed, split, and characterized with respect to physical and mineralogical properties.

MEASUREMENTS AND ANALYSES

The temperature and swelling pressure were automatically measured every half hour, and pH was measured virtually daily in the low pH solutions, and weekly in the high pH solutions. The type of exchangeable cations was determined by exchange with ammonium ions, and the cation exchange capacity was determined by exchange with copper(II) triethylenetetramine. XRD scans were made both of random powders and as oriented samples. Mineralogical quantification was made by use of the Siroquant software based on Rietveld technique. Element analyses were made by use of ICP/AES for both the clay and the test solutions. Anions were analysed by use of ion chromatography (IC). Scanning electron microscopy and microanalyses (EDX) were used to study microstructure and mineral distribution.

RESULTS

The measurements and analyses were fully carried out for the 12 separate tests. Significant reductions in swelling pressure were found for the samples contacted to high concentrations of sodium chloride and hydroxide solutions. A major difference was, though, that the chloride solutions gave a fast drop to a new stable pressure value, while contact to the hydroxide solution led to a continuous lowering of the swelling pressure. Figure 2 (left) shows the pressure response from one sample successively exposed to pure water, 1.0 M NaCl, 1.0 M NaOH, 1.0 M NaCl, and finally pure water. A significant continuous swelling pressure reduction was also observed for all samples exposed to 0.3 M NaOH solutions. However, no swelling pressure change was noticed in the samples exposed to 0.1 M NaOH or to saturated Ca(OH)₂ solution.

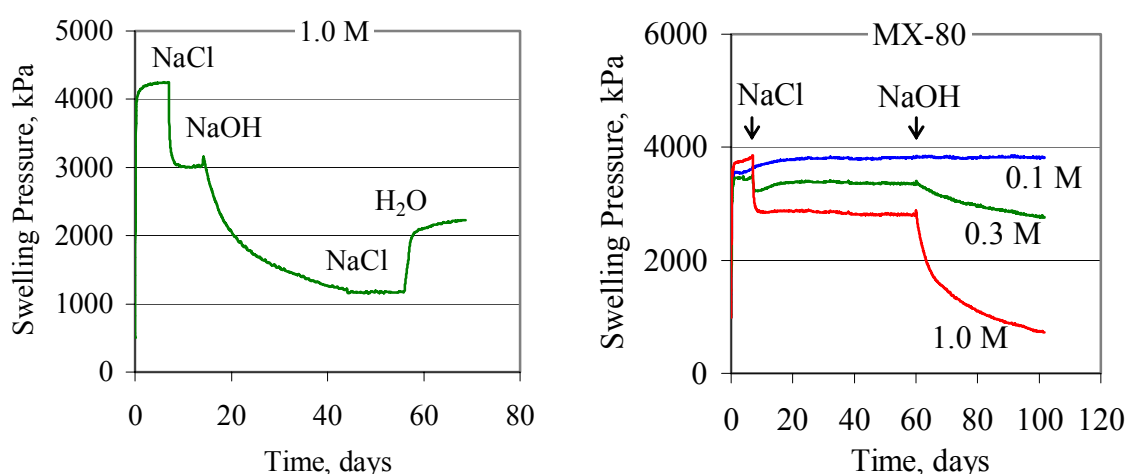


Figure 2. Left: Pressure response from a MX-80 sample successively exposed to pure water, 1.0 M NaCl, 1.0 M NaOH, 1.0 M NaCl, and finally pure water. Right: Swelling pressure evolution in three MX-80 samples. All samples were initially saturated with pure water, subsequently exposed to the chloride solutions (5 days), and finally to the hydroxide solutions on one side (60 days).

A pH increase in the NaCl solutions was measured in the four tests exposed to 1.0 M and 0.3 M solutions. Logically, the increase came earlier and was more pronounced in the tests with the highest concentration. A systematic release of silica was found in these tests (Table 1). No pH increase was measured after 45 days in tests with 0.1 M solutions, and neither after an exposure time of 110 days in the four tests with saturated Ca(OH)₂ solutions..

Table 1. ICP/AES analyses of solutions from tests with MX-80 exposed to NaOH solutions. Concentrations are expressed in mM.

	Sample	pH	Al	Ca	Mg	K	Si	Ti
NaCl side	21	n	0.001	0.185	0.084	0.394	0.119	0.000
	22	11.8	0.000	0.416	0.132	0.421	0.620	0.000
	23	12.3	0.000	0.170	0.000	0.605	1.336	0.000

NaOH side	21	12.9	0.004	0.013	0.000	0.231	0.419	0.000
	22	13.3	0.005	0.000	0.000	0.305	1.890	0.003
	23	13.7	0.013	0.000	0.000	0.463	4.167	0.041

A significant increase in CEC was noticed for all samples exposed to the NaOH solutions. The increase was significant on both sides of the samples except for the NaCl side of the MX-Na sample exposed to the 0.1 M solutions. No significant change in CEC was measured in the samples exposed only to NaCl solutions (sample 31 and 32), or to the four samples exposed to the 0.015 M Ca(OH)₂ solutions. No neoformation of minerals was indicated in any of the MX-Na samples. A small amount of soft gel material was found outside of the filter on the low pH side in one test. The ICP/AES element analyses show that the silica/aluminium ratio decreased significantly in samples exposed to the NaOH solutions, and an Si/Al gradient from the NaOH to NaCl solutions side.

DISCUSSION AND CONCLUSIONS

It is obvious from the present results that a pH plume may pass through highly compacted bentonite at a sufficiently high pH gradient. It is also obvious that it is strongly affected by reactions between the hydroxide and bentonite minerals, and the effective transport is not well described by diffusion parameters only.

In the present experiments the bentonite swelling pressure was strongly reduced by exposure to 0.3 (pH 13.3) and 1.0 M (pH 13.7) NaOH solutions. The reduction seems to be due to an instant osmotic effect, and to a continuous dissolution of silica minerals leading to mass loss. The decrease rate due to dissolution was reduced after a relatively short time, and a subsequent almost constant decrease rate was observed. The initial decrease rate is likely governed by dissolution of cristobalite, and the latter due to dissolution of montmorillonite and quartz when cristobalite is depleted.

A significant increase in CEC was observed in samples exposed to the NaOH solutions. The structural formulas of the exposed montmorillonite were calculated based on the ICP/AES and CEC data, and show a significant release of silicon from the montmorillonite structure. This incongruent dissolution leads to a charge increase in the tetrahedral layers and a first step towards beidellite. This observed moderate charge increase can be seen as a minor problem with respect to the buffer functions. However, the physical properties of the clay will change dramatically if this reaction continues until a high charge mineral is formed, or a general breakdown of the structure takes place. The silicon release rate from montmorillonite in this specific geometry was determined to be $1.6\text{E-}9 \text{ g}\cdot\text{g}^{-1}\text{clay}\cdot\text{s}^{-1}$ for the 1.0 M NaOH solutions conditions and $5\text{E-}10 \text{ g}\cdot\text{g}^{-1}\text{clay}\cdot\text{s}^{-1}$ for the 0.3 M conditions. No effect on swelling pressure was found in the samples exposed to 0.1 M NaOH (pH 12.9) and saturated Ca(OH)₂ solutions (pH 12.4). No mineralogical/chemical effect except ion exchange from sodium to calcium was found in the samples exposed to the Ca(OH)₂ solution.

The similar pressure response of bentonite exposed to NaCl and NaOH solutions indicate that ion-equilibrium is established between the external hydroxide solutions and the clay pore-water, which then leads to reduced pH inside the clay. This effect increases theoretically with bentonite density and with decreasing pH in the external solution (groundwater). The chemical reactions between the introduced hydroxide and the clay will therefore be less intense, more localized, and lead to lower final pH. At moderately high pH, the combined effect leads to a large calculated difference between batch experiments and experiments with highly compacted bentonite with respect to mineralogical alteration rate. Ion equilibrium conditions may consequently explain the minimal physico-chemical changes in the samples exposed to 0.1 M NaOH and saturated Ca(OH)₂ solutions.

Acknowledgments

The authors wish to acknowledge that this paper is a result of work funded by the Swedish Nuclear Fuel and Waste Management Company (SKB) and the European Commission.

EFFECTS OF SALINE ALKALINE ATTACK ON BENTONITE AND CRUSHED ROCK – EXPERIMENTAL AND MODELLING STUDIES – ECOCLAY II

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INTRODUCTION

The use of concrete and shot crete in constructing a deep disposal vault for spent fuel has raised questions about the effects of an alkaline perturbation on the buffer materials used and the possible consequences to the safety of the final disposal system. In order to facilitate an assessment of the propagation of an alkaline plume in the bentonite buffer and to detect alterations brought about by such a plume laboratory studies were initiated within the European 5th frame work project ECOCLAY II.

EXPERIMENTAL

Six flow-through cylinders, each containing site specific crushed rock (<1.5 mm) from Olkiluoto, Finland in one half, and compacted bentonite (2 000kg/m³) (commercial Wyoming bentonite MX-80) in the other half. The cylinders were subjected to an attack of a slow flow of solution. The solution rate used was 2.5mL/day, comparable to groundwater flow rate in deep disposal conditions. Three different solutions were used, saline alkaline (pH=12.5), saline (pH=8.3) and fresh (pH=8.8) solutions, one solution for each cylinder in the two sets of cylinders. Both cylinder sets were started at the same time and ran simultaneously. The experiments were performed at ambient temperature inside a glove-box with nitrogen atmosphere in order to avoid disturbances of atmospheric CO₂ on the alkaline system. Solution samples were collected at the out-flow end for analyses and measurement of pH. The first set of three cylinders were dismantled after about a year and the other set of three after about 1.5 years. The solids, crushed rock and compacted bentonite, were sectioned and analysed for mineral alterations. Bentonite pore water was analysed in several bentonite specimen sampled along the cylinder length, as well as the amount of exchangeable cations (Na, Ca, K, Mg).

Batch experiments were also conducted using the same solid materials as in the flow-through cylinder experiments. The solids were treated separately with three alkaline solutions (fresh alkaline pH 12.5, saline alkaline pH 12.5 and saline hyper alkaline pH 13.5). The solid/solution ratio used was 1/10 and the equilibration periods 1 week, 1 month, 6 months, 1.5 years. The batch experiments were also conducted in nitrogen atmosphere at ambient temperature. After completion of each period the phases were separated by centrifugation and filtration. Both the solutions and solids were analysed. The mineral alterations were more prominent in the batch experiments than in the flow-through experiments. The solution analysis results were the basis in the modelling (inverse) of the mineral reactions occurring.

RESULTS AND DISCUSSION

Flow-through experiments

The saline alkaline solution affected bentonite throughout the entire column to some extent as all the determined exchangeable cation capacities (CEC) either increased or decreased when compared

to the initial MX-80 bentonite values (Figure 1). There was a clear decreasing trend in the column with more prominent changes at the in-flow end. However, the pH values in the bentonite pore water samples (Figure 2) supported alkaline changes only near the interface with a clear decreasing trend towards the cylinder end. The out-flow solution had reached a pH value around 9.5 by the end of the experiment and showed an increasing trend (Figure 3). If the alkaline pH was to keep its trend the estimated time needed for the out-flow solution pH value to reach a value around 11 would be about 6 years and to reach the initial value of 12.5 would take about 10 years. In the saline and fresh experiments the out-flow solution pH values levelled off at around 9.5 and about 8, respectively.

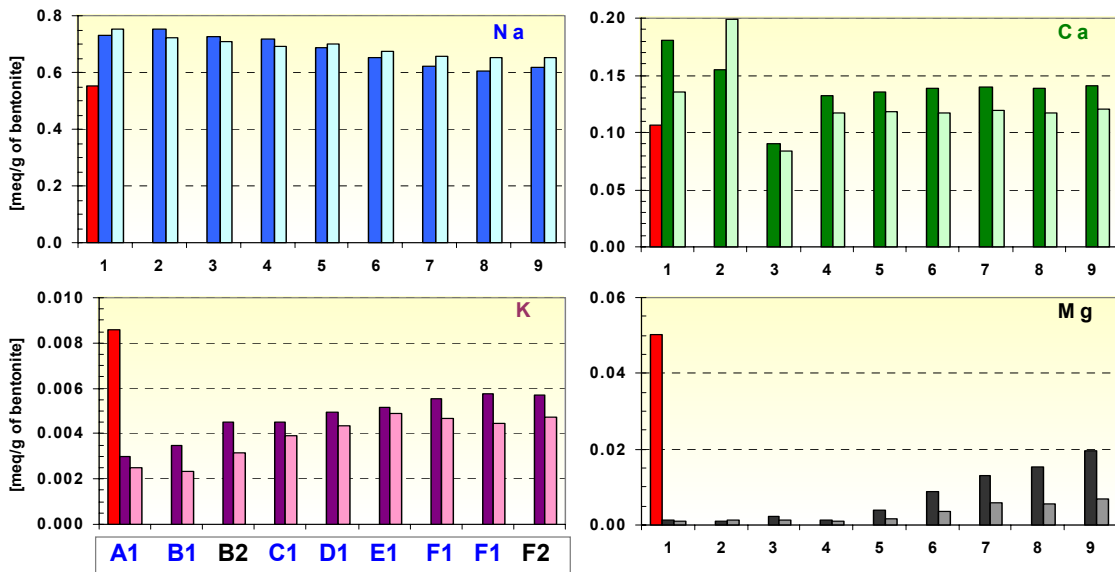


Figure 1. Measured CEC (cation exchange capacity) values (meq/g of bentonite) for the four elements in the saline alkaline case. The red bar on the left shows the initial CEC of MX-80. The text box in the figure indicates the bentonite samples along the flow-through column (A=in-flow end, F=outflow end, 1=interfac specimen, 2=below interface specimen) in each category.

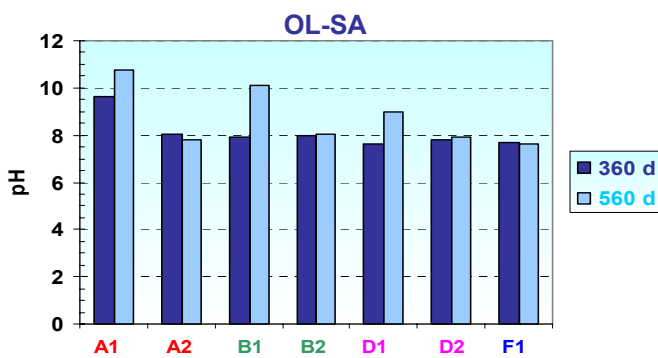


Figure 2. Bentonite pore water pH in the saline alkaline experiment for both the 360 d and 560 d cylinder.

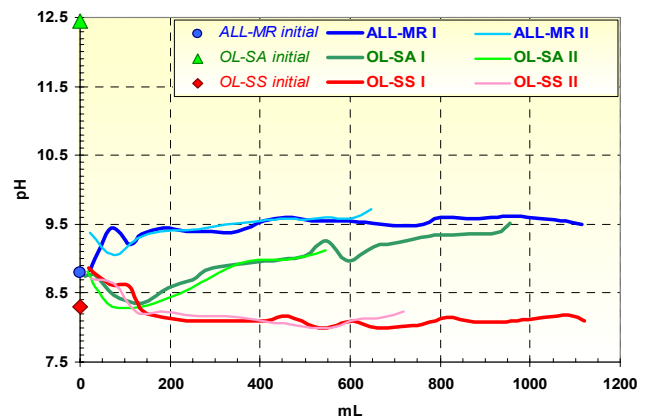


Figure 3. pH values of the out-flow solutions during the experiment versus the amount of solution (mL) passed through the cylinders. In green the saline alkaline values (I=360d, II=560d).

The initial saline solutions did not contain K^+ , Mg^{2+} , SO_4^{2-} , or $Si(aq)$. The levels of K^+ were quite similar in both saline cylinder experiments, both in the determined exchangeable cations and in the out-flow solutions indicating that interactions with bentonite were well reflected in the out-flow solution composition. This was also true for SO_4^{2-} and $Si(aq)$, based on pore water and out-flow solution results. In the case of exchangeable Mg^{2+} the amount left in the bentonite samples of the saline alkaline case was less than in the saline case, but this was not reflected in the Mg^{2+} contents of the out-flow solutions even if the pore water analysis showed depletion of Mg^{2+} . This indicates that Mg^{2+} remained to some extent inside the alkaline column undergoing possible reactions.

The depletion of Ca^{2+} in the pore water and the decreasing trend in the out-flow solutions in the saline alkaline case, which was contrary to the increasing trends in the other two experiments, supports the retention of Ca^{2+} in the column and possible undergoing reactions as well.

An increase in the CEC of bentonite in all alkaline experiments and also in the saline flow-through experiment was observed. The increase was more significant in the batch experiments. The cause of the increase is not quite clear at this point, especially in the saline experiment, but in the alkaline cases partial alteration of montmorillonite to beidellite can be an explanation as indicated by the mineral analyses.

Batch experiments

As expected greater changes to the initial solution pH values occurred in the bentonite batches (Table 1), nevertheless, the pH decreased somewhat in all cases.

Table 1. The measure pH values of the contacting solutions after phase separation.

duration days	Rock			MX-80		
	fresh alkaline	saline alkaline	saline hyper alkaline	fresh alkaline	saline alkaline	saline hyper alkaline
6	12.3	12.4	13.5	11.6	10.8	13.5
30	12.4	12.5	12.6	11.5	10.6	13.4
180	12.6	12.2	12.9	11.4	10.3	12.8
540	12.4	12.1	13.1	11.2	10.2	12.9

The most prominent changes in the solution chemistries were met in the saline hyper alkaline experiments (Table 2), but the trends were rather similar in the other solutions as well;

- Ca content decreases, Si content increases, except in the fresh alkaline MX-80 solution which gave the highest concentration after 6d and thereafter decreased (gel-formation).
- More Al appears in the rock solutions than MX-80 solutions

Table 2. The analysis results of the contacting solutions. The initial solution composition is given in the yellow row.

	duration in days	Na	Ca	K	Mg	Al	Si	Fe	Cl	SO ₄	EC
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(mS/m)
		17710	12.8	<2	< 0.1	0.21	6.97	< 0.03	13700	< 1	9800
Bentonite	6	18480	0.25	38.4	< 0.1	0.19	981	< 0.03	13900	304	9200
	30	18740	0.52	26.5	0.16	0.22	1215	< 0.03	13300	321	5000
	180	17563	0.73	45.5	< 0.1	0.28	1965	< 0.03	15750	300	4750
	540	16640	<0.1	21.0	< 0.1	0.22	2346	0.08	13800	310	3900
Rock	6	18860	3.58	36.4	< 0.1	19.0	38.7	0.58	13700	< 1	11000
	30	18160	1.41	39.1	< 0.1	41.2	65.3	0.99	14100	< 1	11000
	180	17800	0.55	45.1	< 0.1	95.9	141	0.5	11000	7.02	9900
	540	17570	0.43	67.8	< 0.1	91.8	155	0.49	11500	< 1	6100

Mineralogical summary

Crushed rock alterations

The crushed rock was prepared from Olkiluoto mica gneiss (75 wt%), granite pegmatite (20 wt%) and tonalite (5 wt%). The rock material was crushed to grain sizes <1.5 mm. All materials, including the fine fractions were mixed together. The mineralogy of the mixture is given in Table 3.

Table 3. Estimated initial mineral composition (in wt%) for crushed rock used in the experiments.

Mineral	wt%	Mineral	wt%	Mineral	wt%
Quartz	23.2	Sillimanite	5.4	Zircon	0.2
Oligoclase	19.2	Muscovite/Sericite	2.9	Carbonate	0.1
Microcline	17.1	Hornblende	1.6	Apatite	0.1
Biotite	20.1	Chlorite	1.2	Sulphides	0.3
Cordierite	8.3	Epidote/Saussurite	0.3		

In the batch experiments (Table 4) microcline was found to react. A corresponding increase in sericite was interpreted from the hyperalkaline case. The dissolution of oligoclase was probable in all experiments. In the hyperalkaline experiment the low Ca²⁺ solute concentration promoted dissolution of the anorthite part of oligoclase, and possibly minor production of saussurite. In the fresh alkaline experiment the albite part of oligoclase was believed to dissolve more readily. It seems that the high Na⁺ solute concentrations in the saline experiments inhibited dissolution of albite. The saline experiments also indicated dissolution of hornblende and cordierite. It is suggested that a significant part of hornblende was altered to chlorite, and Mg²⁺ needed for this conversion was partially produced from the decomposition of cordierite. The final water results of the batch experiments indicated a sink for Na⁺. In the saline experiments small precipitation of halite was a partial sink. It is believed that the newly-formed surface edge sites of the recently crushed rock were a distinct Na⁺-sink as well. The overall mass transfer in the crushed rock batch experiments was low. However, as a response to the small drops in pH, the batches produced minute amounts of CSH-gel. This gel gave a sink for Ca²⁺.

In the flow-through experiments (Table 4) minimal detectable changes in the crushed rock occurred. The reactivity of bentonite is much higher than that of crushed rock. In the saline alkaline flow-

through experiment similar changes to those in the saline alkaline batch experiment were assumed. Interpretations were, however, subject to ambiguities because of the compositional variations in the crushed mixture. In the near-neutral-pH experiments the crushed silicates were expected to be non-reactive. Small amounts of precipitated halite were observed in the saline flow-through experiments. It was also assumed that the fresh surfaces of crushed minerals were potential for Na^+ adsorption.

Table 4. Summary of the crushed rock mineralogical observations interpreted from the batch and flow-through cell experiments.

+ increase in final bentonite, – decrease in final bentonite, () inferred but not observed.

	Batch Experiments			Flow-through Experiments		
	Fresh Alkaline	Saline Alkaline	Saline . Hyperalk	Fresh	Saline	Saline Alkaline
Hornblende	(–)	–	–			–
Chlorite	(+)	(+)	(+)			(+)
Cordierite		–	–			–
Microcline	–	–	–			–
Sericite	+	+	+			+
Oligoclase	–	–	–			–
Na-part (albite)	–					
Ca-part (anorthite)		–	–			–
Saussurite		(+)	+			(+)
Halite		+	+		+	+
CSH-gel (Tobermorite?)	+	+	+			+
NaX	+	+	+	+	+	+

MX-80 alterations

In the batch experiments (Table 5) the initial Na_x -montmorillonite was found to alter partially to Na_x -beidellite. The degree of conversion was related to the Na/Ca ratio of the initial solution and pH. The long-term (e.g. 540 days) hyperalkaline attack produced smectite that indicated good resemblance to crystallography of Na_x -beidellite. The main sink for Na^+ was apparently the cation exchange sites of the altered smectite. However, according to Hong and Glasser (1999, 2002) also CSH gel is a Na^+ -sink especially in high Na^+ solute conditions. The CEC studies with altered solids indicated an increase in the exchange sites as a result of the alterations. The other main cations were released from bentonite. K^+ remained in the final solution, while Mg^{2+} assumably adsorbed or precipitated into CSH gel (cf. Taubald et al. 2000). The main sink for Ca^{2+} was CSH gel and to a minor extent calcite. Especially in the hyperalkaline case quartz dissolved partially and albite almost completely. Significant amounts of halite precipitated in the saline batch experiments.

In the flow-through cylinder experiments (Table 5) the changes in smectite were found to be diverse. The dilute near-neutral-pH fresh water injection resulted in complexly fluctuating cation distributions in bentonite. The constant release of Na^+ and silica from bentonite seems to have caused interlayer deficiencies in montmorillonite. Due to the relatively low Na/Ca ratio, the near-neutral-pH saline water caused smectite to transform towards Ca_x -montmorillonite. The saline alkaline water interaction indicated comparable smectite alteration to the equivalent batch experiment. The near-neutral-pH experiments released Na^+ while the alkaline experiment adsorbed Na^+ into the cation exchange sites. In the near-neutral-pH saline experiment, the released Mg^{2+} was left to final solution while in the saline alkaline experiment Mg^{2+} was apparently caught by CSH gel. In all experiments, the sink for Ca^{2+} was either Ca_x -montmorillonite or CSH gel. Small amounts of calcite were precipitated in all cylinders. In the near-neutral-pH experiments no formation of CSH

gel occurred, and apparently no significant increases in the CEC. In the saline experiments a small amount of halite precipitated in bentonite.

Table 5. Summary of the bentonite mineralogical observations interpreted from the batch and flow-through cell experiments.

+ increase in final bentonite, – decrease in final bentonite, () inferred but not observed.

	Batch Experiments			Flow-through Experiments		
	Fresh Alkaline	Saline Alkaline	Saline. Hyperalk	Fresh	Saline	Saline Alkaline
Na _x -Montmorillonite	–	–	–	–	–	–
Ca _x -Montmorillonite					+	
Na _x -Beidellite	+	+	++			+
Deficient Montmorillonite				+		
Gypsum	–	–	–	–	–	–
Albite	(–)	–	–			–
Quartz	(–)	(–)	–			(–)
Halite		++	++		+	+
Calcite	+	+	+	+	+	+
CSH-gel (Tobermorite?)	++	+	+			+
NaX	+	+	++	--	--	+
KX		–	–		–	–
CaX ₂		–	--		++	–
MgX ₂	–	--	--		–	--
CEC increase	+	+	++			+

Modelling

A simple thermodynamic forward model developed for montmorillonite was applied to describe the uptake of sodium and calcium on MX-80 bentonite reacted with saline hyper-alkaline solution. The experimental findings were adequately explained by the model, provided that sorption of calcium takes place predominantly by way of precipitation of calcium-bearing mineral phases.

Forward modelling considered quartz, calcite, microcline and albite as primary accessory minerals of MX-80. In the hyper-alkaline modelling, the minor solid assemblage of bentonite was completely destroyed upon reacting with the solution, which resulted in the formation of zeolite and silicate phases. At the point of modelling, the mineralogical interpretation of the secondary solid phases was fraught with uncertainties, however.

The inverse modelling results for MX-80 and crushed rock replicated most mineralogical alteration processes identified in the mineralogical studies. In MX-80 the important processes were the partial conversion of smectite (from Na_x-montmorillonite to Na_x-beidellite), complete dissolution of albite and partial dissolution of quartz. Laboratory observations indicated significant production of CSH-gel and that was interpreted analogous to structurally defect 14Å-tobermorite. In the crushed rock experiments the main alteration processes were partial dissolution of microcline and hornblende. Since the geological conditions otherwise are similar to the bentonite experiments, CSH-gel was assumed to form accordingly. Evidently, however, the reaction rates in the crushed rock experiments are lower due to the overall smaller reactive surface area than in the bentonite batches.

In the inverse modelling of the hyperalkaline experiments significant difficulties were met with charge balancing the analytical results. Uncertainties in the concentrations of Na⁺, Cl[–] and OH[–] were

reflected as difficulties to adjust the cation exchange to the correct level in both MX-80 and crushed rock batch experiments.

Acknowledgements

The authors wish to acknowledge the European Commission and Posiva Oy for funding the work presented here, which was carried out under a cost-sharing contract with the European Atomic Energy Community (EURATOM) within specific programme on "Nuclear Energy" (1998-2002), Key Action on Nuclear Fission, Area: "Safety of the Fuel Cycle – Waste and Spent Fuel Management and Disposal".

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Experimental study on dissolution of montmorillonite in compacted sand-bentonite mixture under Na-Cl-OH pore-water conditions

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INTRODUCTION

Highly alkaline environments induced by cementitious materials in radioactive waste repositories are likely to alter montmorillonite, the main constituent of bentonite buffer materials, and are likely to cause the physical and/or chemical properties of the buffer materials to deteriorate. We focus our experimental efforts on predicting long-term variations in permeability of compacted sand-bentonite mixture because the variations induce major uncertainties in the radionuclide migration analysis and have not been quantitatively understood. The dissolution rate of montmorillonite and the diffusivity of hydroxide ions in the compacted sand-bentonite mixtures are essential parameters, which quantify the effects of alteration caused by the alkaline environments on the permeability of a bentonite buffer.

There are not a few studies on the dissolution rates of clays in near neutral to alkaline solutions (Bauer *et al.*, 1998; Bauer and Berger, 1998; Cama *et al.*, 2000; Huertas *et al.*, 2001; Sato *et al.* 2002). In these studies, the rates were obtained for far from equilibrium conditions, where the solid/solution ratio employed in their experiments is much lower than the disposal conditions. It is of concern if the rates are straightforward applicable to predict alteration of compacted bentonite under disposal conditions. For this reason, we have performed experiments to acquire quantitative data on the rate of dissolution of montmorillonite and diffusivity of the alkaline source in compacted, cylindrical bentonite samples under highly alkaline, saline groundwater conditions. This experimental configuration was employed because it reflects repository conditions such as the use of compacted bentonite and saline groundwater that is nearly saturated with respect to silicon and aluminum.

EXPERIMENTS

The dissolution rate of montmorillonite was obtained through a time-dependent variation in the quantity of montmorillonite in sand-bentonite mixtures. The mixtures of granules of Na-type bentonite (Kunigel V1, [Ito *et al.*, 1993]) and silica sand of two different granule sizes (0.1 – 0.85 mm: SiO₂ 94.6%, 0.85 – 2 mm: SiO₂ 99.78% [Suzuki & Fujita, 1999]) were compacted to cylindrical specimens of 20 mm in diameter and 10 mm in thickness. The mixture ratio of the bentonite and silica sands was 70:15:15 in dry weight. The density of the specimens was 1.6 Mg m⁻³. Alteration experiments using compacted specimens require much longer time periods than

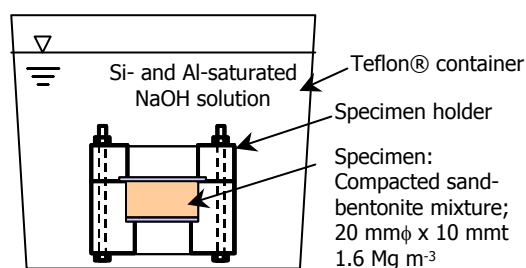


Fig .1 Schematic drawing of the experimental configuration for the alteration experiment.

those using granules. Temperatures were selected to be 50°C to 170°C, and pH values were 13.0 to 14.0 to observe montmorillonite dissolution over a reasonable time period. The results will be extrapolated to repository conditions. A specimen set in the holder in a Teflon[®] container, schematically shown in Fig. 1, was contacted with 0.08 dm³ of pH-adjusted, simulated alkaline, saline groundwater. The simulated groundwater was prepared by equilibrating NaCl-NaOH mixed solutions of the Na concentration of 1 M with bentonite granules under the same temperature (50 to 170°C) as those employed in the alteration runs for the equilibration period of 4 to 8 weeks. The container assembly (Fig. 1) was placed in a sealed stainless steel container and kept at desired temperatures in ovens. Each of the assembly was taken from the oven at the fixed sampling time and the compacted mixture specimen was removed from the holder, freeze-dried at -110°C, and the amount of montmorillonite that remained was determined by the methylene-blue adsorption titration method. The reacted solid was analyzed by X-ray powder diffraction (XRD). The concentrations of Al and Ca in the contacted aqueous solutions were determined by using inductively-coupled plasma mass spectroscopy (ICP-MS), and Si was determined as SiO₂ through molybdenum-yellow spectrometry.

The diffusivity is the rate of spreading of the alkaline plume in the sand-bentonite mixtures, and it also gives some indication as to whether the dissolution of montmorillonite or the transport of hydroxide ions limits the alteration of bentonite. For this reason, the two phenomena, alteration of bentonite and diffusion of hydroxide ions in bentonite, have to be quantified separately. The diffusivity of hydroxide ions in compacted sand-bentonite mixtures was obtained by the through-diffusion method using an polysulphon diffusion cell as shown in Figure. 2. The specimens of compacted sand-bentonite mixtures, which are the same in size and in mineral composition as those used in the alteration experiment, were employed in the hydroxide ion diffusion experiment. The water in one of the reservoirs (referred to as “high-pH reservoir”) was replaced with simulated cementitious water, and the other (referred to as “low-pH reservoir”) with simulated fresh-type groundwater. The experimental runs were conducted in the temperature range 10 to 90°C. The through-diffusion runs were conducted under the ambient atmospheric condition. At 7-day intervals, the pH of the aqueous solutions in the two reservoirs was measured.

RESULTS AND DISCUSSION

The amount of montmorillonite in the compacted sand-bentonite mixtures decreased in a few days to several months under the employed conditions of pH and temperature, as seen in Fig. 3. X-ray diffraction patterns of sand-bentonite mixtures indicated the decrease of montmorillonite. Crystalline silica also dissolved, and a secondary mineral, analcime

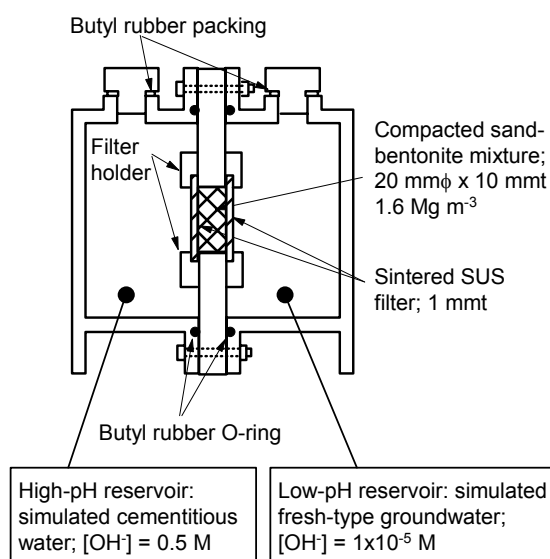


Fig. 2 Schematic drawing of the through diffusion cell used in the hydroxide ion diffusion experiment.

($\text{NaAlSi}_2\text{O}_6$), was formed. The linear decrease in the amount of montmorillonite with time clearly differs from the widely-accepted exponential decrease in dissolution of minerals (e.g., Stumm & Morgan, 1996). The linear decrease can be expressed as $W(t) = W(0) - R_A t$, where $W(t)$ denotes the density of montmorillonite (Mg of montmorillonite/ m^3 of sand-bentonite mixture), $W(0)$ the initial density ($1.758 \text{ Mg}/3.14 \text{ m}^3 = 0.56 \text{ Mg m}^{-3}$), R_A ($\text{Mg m}^{-3} \text{ s}^{-1}$) the rate of density decrease and t (s) the time after the contact with the simulated groundwater. The R_A is a function of pH and temperature as shown in Fig. 4, and can be expressed as

$$R_A = 0.8 [\text{OH}]^{1.4} e^{-48000/RT} \quad (1)$$

where R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The activation energy of $48 \pm 10 \text{ kJ mol}^{-1}$ is close to that of formation of analcime, $52 - 60 \text{ kJ mol}^{-1}$ (Kim, 2001), and higher than that of dissolution of montmorillonite, 30 kJ mol^{-1} (Huertas *et al.*, 2001). The alteration rates estimated by Eq (1) were compared with previous data from batch dissolution experiments for smectite obtained in hyperalkaline solutions at 35°C and 80°C (Bauer and Berger, 1998) in Fig. 5. The dissolution rates of montmorillonite obtained for compacted sand-bentonite mixtures in [Mg -montmorillonite / m^3 -bentonite / s] were converted to [$\text{mol-Si} / \text{m}^2 / \text{s}$] using the SiO_2 content in the montmorillonite of 61.3 % (Ito *et al.*, 1993) and the specific surface area of $2.7 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ (Shibutani *et al.*, 1999). The dissolution rates of montmorillonite obtained for compacted sand-bentonite mixture are lower than those in the batch dissolution experiments by one order of magnitude or more. The dependence on concentration of OH^- is higher for compacted sand-bentonite mixture than that in the batch dissolution experiments. The dissolution of montmorillonite in compacted sand-bentonite mixture is likely to result from some different mechanisms from that occurring in the far-from-equilibrium batch dissolution experiments.

In the hydroxide ion diffusion experiments, it took a few tens of days for the ions to diffuse through the 10 mm-thick compacted sand-bentonite mixture disks. Hydroxide ions were mainly consumed by dissolution of soluble silicate minerals during the delay. After the delay, the activity in the low-pH reservoirs began increasing. The increasing rate becomes

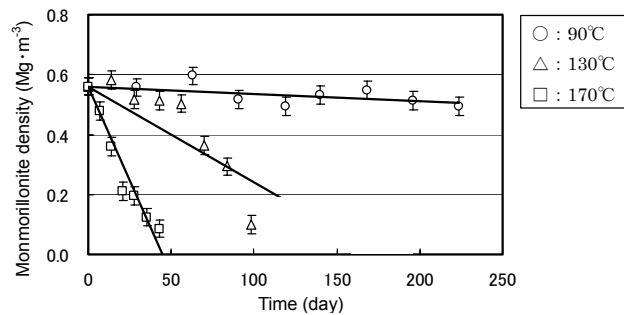


Fig. 3 Dissolution curves of montmorillonite in compacted sand-bentonite mixture as a function of time at $[\text{NaOH}] \sim 0.3 \text{ M}$.

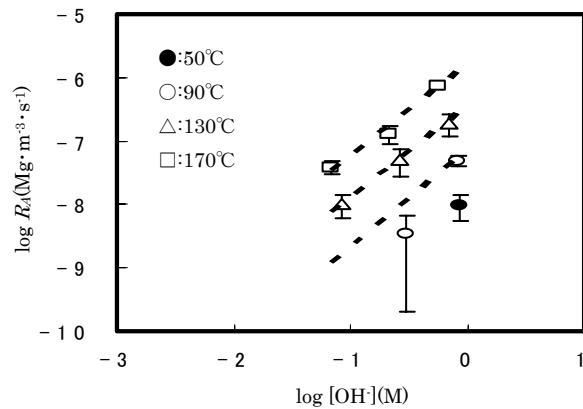


Fig. 4 Dependence of the montmorillonite dissolution rate, R_A ($\text{Mg m}^{-3} \text{ s}^{-1}$) on temperature and on $[\text{OH}^-]$.

close to the decreasing rate of the activity in the high-pH reservoirs, and when the two values of the rate were identical, the steady state flux of hydroxide ions was established in the specimens. The diffusivity was calculated by using the identical values of the rate. The obtained D_e values were $(3.9 \pm 0.6) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 10°C , $(4.6 \pm 2.3) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 20°C , $(1.1 \pm 0.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 30°C , $(8.9 \pm 2.2) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 40°C , $(1.1 - 2.3) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 50°C , $(1.8 \pm 0.7) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 70°C and $(0.9 - 5.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 90°C , which are summarized in Fig. 6. The dependence of D_e on temperature follows the Arrhenius equation of $D_e = \exp(-15.1 - 21000/RT)$. The diffusivity of ions in compacted bentonite materials is known to depend strongly on their bulk density, ρ (Mg m^{-3}), and to be proportional to $e^{-5.4\rho}$ for I^- (Mihara *et al.*, 1999) which is analogous monovalent anion to OH^- . The effective diffusivity of hydroxide ion in compacted bentonite materials can be expressed as a function of the temperature and the bulk density as

$$D_e = \exp(-7.8 - 21000/RT - 5.4\rho) \quad (2)$$

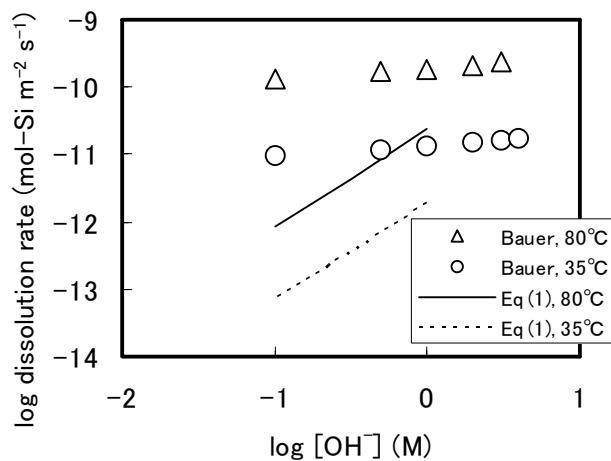


Fig. 5 Comparison between dissolution rates of montmorillonite obtained in this study and those obtained by Bauer and Berger (1998).

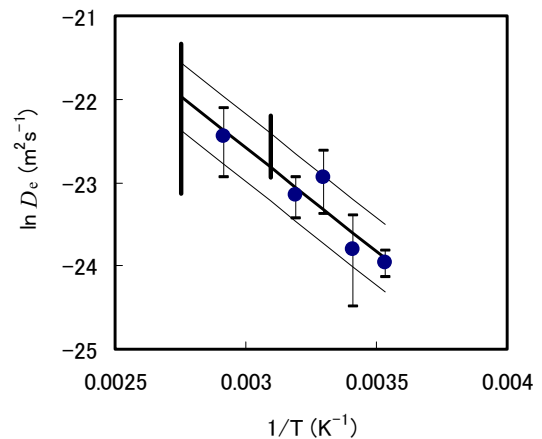


Fig. 6 Effective diffusivity, D_e ($\text{m}^2 \text{ s}^{-1}$), of hydroxide ion in compacted sand-bentonite mixture at the temperature of $10 - 90^\circ\text{C}$.

CONCLUSIONS

Dissolution of montmorillonite and diffusion of hydroxide ions in compacted sand-bentonite mixtures were measured under the simulated alkaline groundwater environments. Dissolution of montmorillonite followed the linear dependence on time under the employed experimental conditions of pH 13 to 14 and temperatures of 50 to 170°C . The slope gives the dissolution rate, R_A . The dissolution rate is a function of pH and temperature (K), and expressed as $R_A = 0.8[\text{OH}^-]^{1.4} \exp(-48000/RT)$, where R is the gas constant. The effective diffusivity was found to be in the order of 10^{-10} to $10^{-11} \text{ m}^2/\text{s}$ at 10 to 90°C and expressed as $D_e = \exp(-7.8 - 21000/RT - 5.4\rho)$. These equations will be provided for the long-term prediction on the permeability of a bentonite buffer. The dissolution rates we obtained in this study are smaller than previous data which were obtained by far-from-equilibrium batch dissolution experiments. Dissolution mechanisms under high solid/solution ratio and near-equilibrium,

which is representative of the waste repository, is required to be understood to provide reliable data for the long-term prediction of the bentonite buffer performance.

ACKNOWLEDGEMENT

This is a part of study funded by the Japanese Ministry of Economy, Trade and Industry.

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Modeling of variation in permeability of compacted bentonite with alkaline fluid for long-term safety assessment of geological disposal system.

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INTRODUCTION

Uncertainties should be quantitatively assessed in a long-term assessment of radioactive waste disposal. We focus our experimental efforts on parameters that induce major uncertainties in the radionuclide migration analysis and that have not been quantitatively understood. Alteration of the bentonite buffer material by highly alkaline environments induced by cementitious materials used in geological disposal facilities is a prioritized study. The highly alkaline environments may alter montmorillonite, the main constituent of bentonite buffer materials, and are likely to cause the physical and/or chemical properties of the buffer materials to deteriorate. Mathematical models have been developed to predict long-term alteration of bentonite such as permeability⁽¹⁾. However, the relationship between changes in the mineralogical composition of bentonite and variations in its permeability has not been understood for reliable long-term prediction.

APPROACH

The purpose of our investigation is to quantify the effect of alteration caused by the alkaline environment on permeability of bentonite buffer. Our goal is to predict the time- & space-dependent permeability of compacted sand-bentonite mixtures in radioactive waste repositories. The structure of the approach is shown in Figure 1. The amount of remained montmorillonite, $M(x, t)$, is predicted by *Coupled Mass-transport/Chemical-reaction Analysis* as a function of time and space. The analysis needs a number of input parameter values including thermodynamics on minerals, chemistry of groundwater, configuration of waste package and structural materials, and boundary conditions on the alkaline source and natural barriers. The predicted $M(x, t)$ is combined with M - & ionic-strength-dependent permeability values, $k(M, I)$, to finally yield the time- & space-dependent permeability, $k(x, t)$, of compacted sand-bentonite mixtures. Data of M -dependent permeability values, $k(M, I)$, are obtained through measurements and literature survey (*Permeability Measurement & Literature Survey*). A series of year-long permeability measurements (*Long-term Permeability Experiment*) will be carried out for the purpose of validation of this approach.

COUPLED MASS-TRANSPORT/CHEMICAL-REACTION CODE

A conceptual model of one-dimensional coupled mass-transport/chemical-reaction for geological disposal system is illustrated in Fig. 2. This model allows us to predict long-term alteration of bentonite buffer accompanied with space- and time-dependent changes in porosity, permeability and diffusivity. The flow of the model calculation is shown in Fig. 3. A widely-used and verified geochemical code, PhreeqC ver. 2.8⁽²⁾, is in charge of the chemical reaction calculations.

A trial calculation was performed to reproduce hydroxide ion diffusion at 70 °C (preceding report⁽³⁾). The one-dimensional model for the calculation is shown in Fig. 4. In this calculation, the dissolution rate of montmorillonite in a sand-bentonite mixture was given as R_A ($\text{Mg m}^{-3} \text{ s}^{-1}$) = $0.8 C_{\text{OH}}^{1.4} \exp(-48000/RT)$ where C_{OH} (mol L^{-3}) is the concentration of OH^- in pore water, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) the gas constant and T (K) the absolute temperature. The results of the calculation are compared with the experimental data in Figs. 5 and 6. The calculation reproduced the time-dependent variations in OH^- concentration in through-diffusion experiments (Fig. 5), and concentrations of Na and Ca (Fig. 6). This comparison illustrates that the coupled-mass transport/chemical reaction code we are developing expresses quantitatively the mass transfer in a sand-bentonite mixture under highly alkaline conditions. The concentration of Si was slightly overestimated in the calculation probably because kinetics of the dissolution of SiO_2 was not considered. The overestimation of the concentration of Si probably led to the underestimation of the concentration of Al because they are related by the solubility products of analcime, $\text{NaAlSi}_2\text{O}_6$.

According to the structure of the approach shown in Figure 1, our next step is to verify the computer code by using long-term variations in permeability that will be obtained through *Long-term Permeability Experiment*.

ACKNOWLEDGEMENT

This is a part of study funded by the Japanese Ministry of Economy, Trade and Industry.

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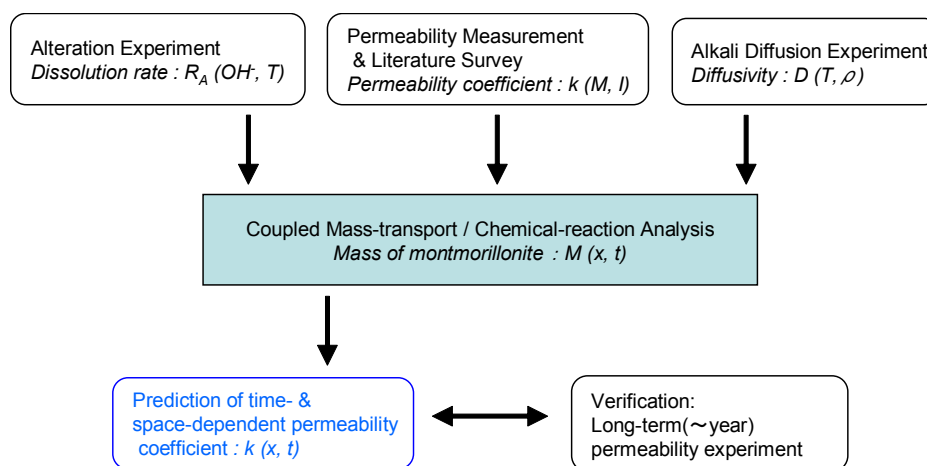


Fig.1 Structure of the approach to predict effects of bentonite alteration on permeability of altered compacted sand-bentonite mixture.

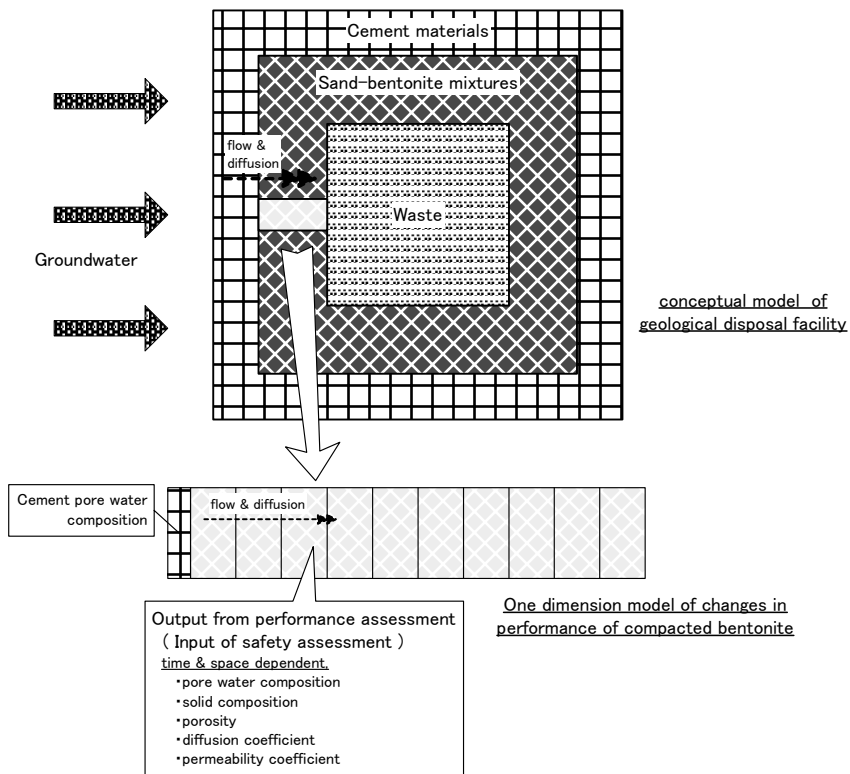


Fig. 2 Conceptual model for a geological disposal facility and one-dimensional calculation cell of the coupled mass-transport/chemical-reaction code.

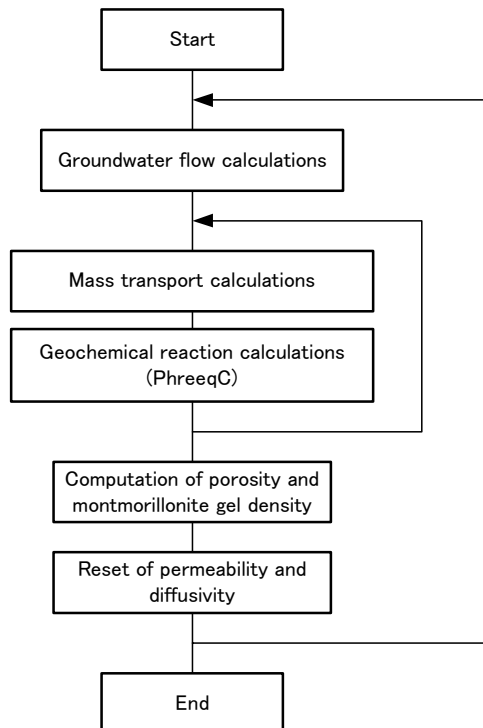


Fig. 3 Flow of the calculation in the coupled mass-transport/chemical-reaction analysis code

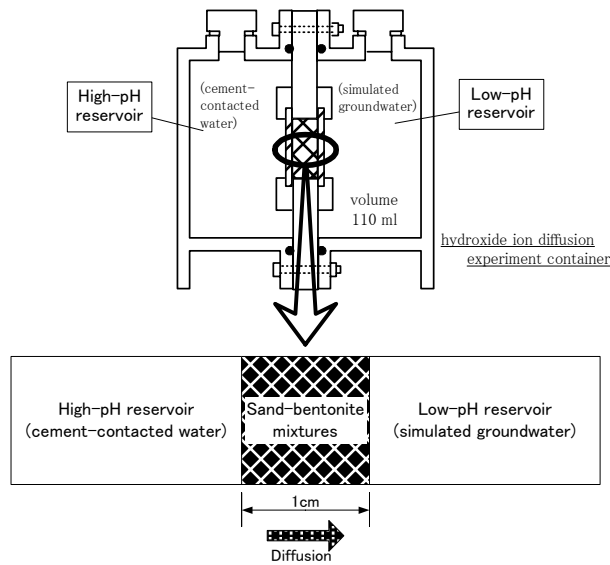


Fig.4 Schematic drawing of the through-diffusion cell used in the hydroxide ion diffusion experiment for compacted sand-bentonite mixtures.

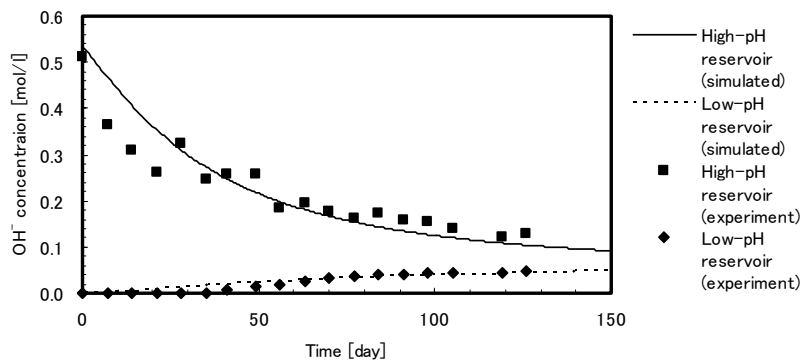


Fig.5 Concentrations of OH⁻ in high- and low-pH reservoirs in a through-diffusion experiment. The plots are experimental results from Yamaguchi et al.⁽³⁾.

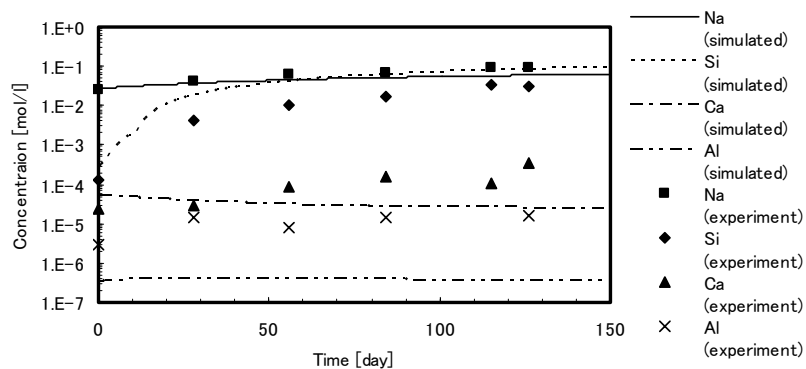


Fig.6 Concentration of Na, Si, Ca and Al in the low-pH reservoir in a through-diffusion experiment. The plots are experimental results from Yamaguchi et al.⁽³⁾.

CEMENT-BENTONITE INTERACTION ISSUES, BUFFERING CAPACITY OF BENTONITE

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Introduction

The main concern when clay minerals are exposed to a high-pH environment created by leaching cementitious materials relates to their stability on prolonged contact. The mineralogical alterations of the smectite clay could lead to disadvantageous changes in its hydraulic and mechanical characteristics, such as plasticity and swelling capacity, which could impair its performance as a buffer.

The cement-bentonite interaction is one between two thermodynamically incompatible materials, which contradict rather than complement (Glasser, 2002). To mitigate this incompatibility, the development of low-pH cementitious materials has been initiated and is now underway.

Buffering capacity

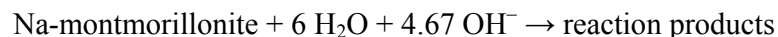
In the present context, the buffering capacity is understood as a measure of bentonite's ability to exert control on the solution pH. The buffering capacity of montmorillonite, the main component of bentonite, is the 'sum' of two contributions,

1. The surface hydroxyl sites ($\equiv\text{SOH}$) situated along the edges of the clay platelets.
2. The montmorillonite crystal lattice itself.

The buffering of the $\equiv\text{SOH}$ sites is based upon their amphoteric nature, that is, they can protonate ($\equiv\text{SOH}_2^+$) or deprotonate ($\equiv\text{SO}^-$), depending on the solution pH. The capacity of these sites, which has usually been determined in short-term titration experiments¹, is about 10% of the cation exchange capacity of the clay (i.e., <0.1 moles per kg of clay).

The rate of pH buffering by the $\equiv\text{SOH}$ sites is fast, while that of the montmorillonite matrix is governed by reaction kinetics. Once the capacity of the $\equiv\text{SOH}$ sites is used up, the second component begins to operate.

The interaction between the montmorillonite crystal and hydroxide ions takes place according to



Hence, the dissolution of 1 mole of Na-montmorillonite consumes 4.67 moles of OH^- . This means that the theoretical buffering capacity of montmorillonite is 12.7 moles of OH^- per kg of clay. The capacity of the $\equiv\text{SOH}$ sites is therefore very limited in comparison to the second component (less than 1%). A bentonite with a montmorillonite content of 75 wt% (such as MX-80) has a buffering capacity of $0.75 \times 12.7 = 9.5$ moles of OH^- per kg of clay.

In what follows, with reference to the buffering capacity of bentonite, no differentiation between montmorillonite crystal lattice conservative or destructive processes will be made *per se*.

In laboratory scale batch experiments, interactions of clays with highly alkaline fluids have been reported to yield as reaction products (Vieno et al., 2003),

- Ca/Mg (aluminium) silicate hydrates
- Framework silicates or zeolites

¹ Therefore, it tacitly assumes chemical inertness of the montmorillonite crystal lattice.

- Hydroxides
- Carbonates
- Sheet silicates, such as illite or mixed-layer clays

The rise of temperature and the increase of time, solution pH and the solution-to-solid ratio tend to favour the reaction progress. In addition, the nature of reaction products is strongly affected by the cation content of the reactant fluid.

The potential of bentonite to consume OH^- released from concrete was examined by Oscarson et al. (1997), who carried out alkalimetric titrations on pre-equilibrated smectitic clays by adding solid $\text{Ca}(\text{OH})_2$ in amounts ranging from ~5 to 80 mg to the suspensions and allowed them to react for two weeks. The results from the titrations for Avonlea bentonite (~80 wt% smectite) are depicted in Figure 1a. In comparison to the theoretical pH as a function of added $\text{Ca}(\text{OH})_2$ without a clay in Figure 1b, Avonlea bentonite is seen to exhibit a substantial buffering capacity. Also, Jefferies et al. (1988) stated that for the three smectite-containing clays they investigated, at least one mole of OH^- per kg of clay was required to reach a high pH (>11). Based on these results, it was considered in Vieno et al. (2003) that bentonite can retain the pH below 11 by neutralizing at least 0.5 moles of OH^- ions per kg of clay before the buffering capacity is used up.

Supporting evidence that the buffering capacity of bentonite could be ≥ 0.5 moles per kg of clay was gained from the results of the recent ECOCLAY II project. In one of the experiments, 3.8 g of MX-80 bentonite was let to react for 540 d at room temperature with 38 ml of a fresh alkaline, saline alkaline and saline hyper-alkaline aqueous solution (Vuorinen et al., 2004). The starting pH for these solutions was 12.5, 12.5 and 13.5, respectively. At the end of the reaction period, the 'equilibrium'² pH attained was 11.2, 10.2 and 12.9. It can be estimated that approximately 0.36, 0.43 and 3.07 moles of OH^- per kilogram of MX-80 was neutralized in these experiments. According to the X-ray diffractograms of the reacted solid phases, a significant montmorillonite component was present in the first two solutions (thus, MX-80 would still possess buffering capacity against further alkaline attack). For the saline hyper-alkaline solution, a fraction of the montmorillonite appears to have transformed to beidellite (a smectite).

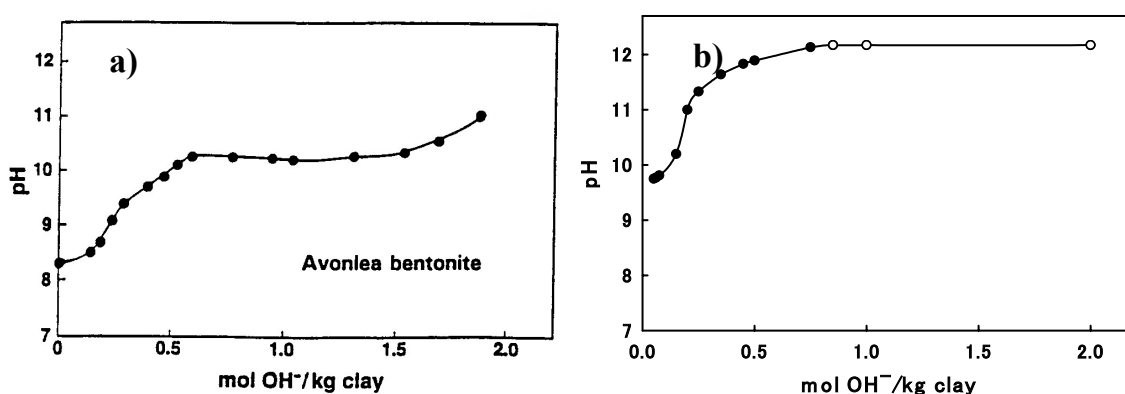


Figure 1. a) Experimental titration curve for Avonlea bentonite (Oscarson et al., 1997); b) Theoretical pH for $\text{Ca}(\text{OH})_2$ – synthetic granitic ground water of Oscarson et al. (1997) with no clay added. Open symbols denote saturation with respect to $\text{Ca}(\text{OH})_2$.

² True equilibrium was likely not established, and the dissolution of montmorillonite was still in progress. Upon approaching equilibrium, the rate of dissolution will decrease, however.

Mass balance considerations

Assume that the total amount of cement remaining in ONKALO at the time of the backfilling of the repository is at most 5 400 tonnes (Vieno et al., 2003). Hydrated ordinary Portland cement (OPC) contains about 20% of portlandite ($\text{Ca}(\text{OH})_2$), i.e. 5.4 moles of OH^- per kg of cement, which constitutes the main chemical threat to bentonite in the long term. The 5 400 tonnes of cement could thus release $\sim 3 \cdot 10^7$ moles of OH^- . A repository of the KBS-3V type contains about 60 000 tonnes of bentonite clay in the buffer in the deposition holes. Therefore, this amount of bentonite can theoretically buffer about $64 \cdot 10^7$ moles of OH^- , which is 20 times the maximum imaginable release of OH^- from OPC.

However, in Vieno et al. (2003), a value of 0.5 moles of OH^- per kg of clay ($\sim 5\%$ of the theoretical value) was (quite conservatively as it seems) selected for the buffering capacity of bentonite, which is, in theory, just the limit to alter all the bentonite in the deposition holes. Although it is highly unlikely that the OH^- from cement could be transported without any buffering and dilution into the deposition holes, the question of the extent of OH^- attack bentonite can, in practice, tolerate remains.

Model calculations

A potential means of gaining a deeper insight into the extent of alteration of compacted bentonite subjected to a long-term high-pH attack could be by way of model calculations and optimisation of the parameters in long-term laboratory experiments, carried out in parallel.

So far, predictive model calculations on the long-term evolution of the bentonite buffer in contact with high-pH solutions have been highly speculative, the model results ranging from a small amount of montmorillonite dissolution in one million years to total removal of primary bentonite minerals up to 60 cm from the contact with cement in about 1 000 years (Vieno et al., 2003). Unfortunately, integrated mass flow rates of OH^- ions and other solutes entering the bentonite from concrete were not recorded in any of these simulations. A common problem with all the model calculations with complex mineral assemblages is poor knowledge of possible reaction products and of mineral dissolution and growth kinetics, which are thus subject to considerable uncertainty.

Simple model calculations

The dissolution kinetics of montmorillonite in Huertas et al. (2001) has been incorporated into a simple one-dimensional non-linear diffusion-reaction equation. The underlying assumptions of the model are

- only one solute, OH^- , is involved
- at the solid-solution interface, $\text{pH} = 12.5$ (25°C)
- the fate of OH^- is determined by diffusion and consumption by montmorillonite dissolution
- the diffusivity is given by the Bruggeman equation, $D = \phi^{3/2} D_0$, where ϕ is the volume fraction of pores and $D_0 = 5 \cdot 10^{-10} \text{ m}^2/\text{s}$ has been selected arbitrarily
- the volume is made up of the montmorillonite, porosity and reaction products, $\phi_m + \phi + \phi_r = 1$
- initially, the pore fluid pH is 8.5, $\phi \approx 0.43$ and $\phi_r = 0$
- the changes in the volume fractions ϕ_m and ϕ_r are related by, $d\phi_r = -\kappa d\phi_m$, where κ is 0.5, 1.0 and 1.5.

The results of the calculation at $t = 1 \text{ ka}$ are shown in Figure 2. Depending on the value of κ , 1 to 8 cm of montmorillonite will convert to secondary phases. The extent of this conversion is seen to be a strong function of the evolution of porosity. Albeit highly simplified, the model results readily allow the calculation of the consumption of OH^- .

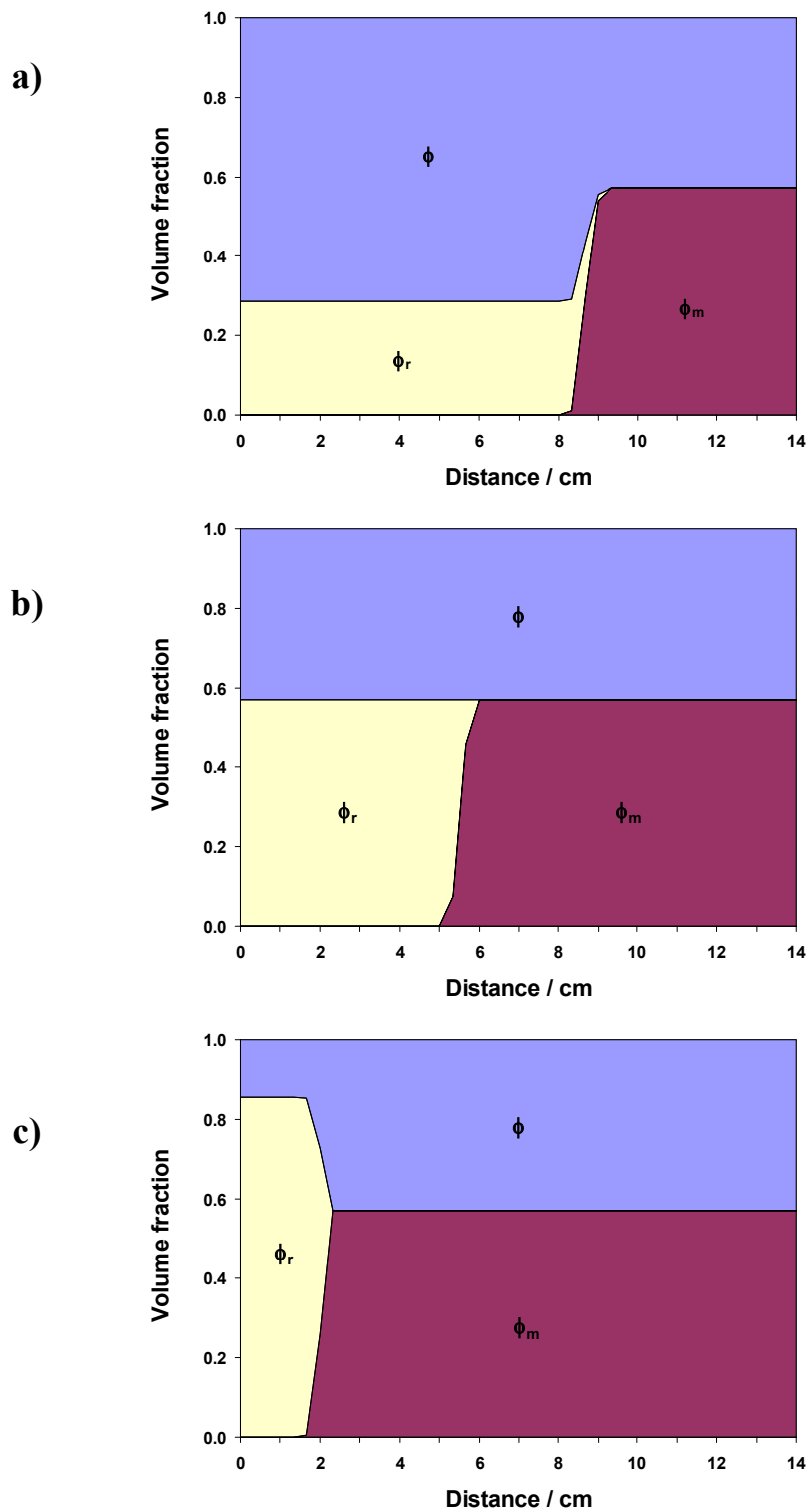


Figure 2. Volume fractions of montmorillonite, pores and reaction products after 1 ka as a function of distance from the solid-solution interface for a) $\kappa = 0.5$, b) $\kappa = 1.0$ and c) $\kappa = 1.5$.

Discussion and questions

The functional form for the pH dependence of the dissolution rate, k (mol/m²/s), is typically of the form, $\log k = \alpha + \beta \text{pH}$, where $\beta = 0.34$ for montmorillonite (Huertas et al., 2001). Upon lowering the solution pH from 11 to, say, 10, will the difference in $\log k$ be significant enough to improve the long-term stability of bentonite, and, if so, would there be a need to one reconsider the pH limit of 11, which seems to have been selected more or less arbitrarily (Bradbury and Baeyens, 1997)?

In addition to montmorillonite, bentonite may have as accessory minerals other powerful pH buffers, such as quartz (15 wt% in MX-80), which have a faster dissolution kinetics than montmorillonite. Uncertainty about the role the accessory minerals in bentonite play in the chemical buffering of the solution pH in these experiments remains, however. It would be of interest to know how much of the buffering capacity of bentonite can be assigned to these minor solids in practice.

The solid-to-solution ratio (s/s) is an important parameter when assessing the interaction between the clay and highly alkaline solution. In Vuorinen et al. (2004), this ratio was relatively low, 1:10 (3.8 g:38 ml). It is likely, however, that the solution pH will be buffered to lower values by bentonite when the solid-to-solution ratio is increased. This anticipated trend would then also pertain to repository conditions, where compacted bentonite (s/s \approx 1:0.26 for the bentonite dry density of 1.6 g/cm³) is in contact with its own pore fluid and diffusion-control prevails.

Interesting in this context is the extent to which bentonite is able to buffer the ingress of an aggressive alkaline plume close to the solid-solution interface, where far-from-equilibrium conditions result in the highest montmorillonite dissolution rate, and if the solid reaction products possess enough molar volume to reduce or even clog the pore space of the altered bentonite.

When investigating mineral transformations in batch systems, the whole surface area of the clay is typically exposed to the high-pH solution. However, in systems where compacted clay is put in direct contact with a leachate from a cementitious material, the alteration of the clay will be diffusion-controlled. Mineral transformation in compacted bentonite under diffusion control is expected to be a powerful chemical buffer against a high-pH solution, which is supported by the scarcity of hard evidence for the propagation of such a plume (Vieno et al., 2003). However, a potential exception is the study by Ichige et al. (2001), who discovered a non-negligible zone of zeolitization in only 20 days for compacted Kunipia-F bentonite (smectite content \sim 99%) in contact with a solution pH of 14 at elevated temperatures (130 °C and 200 °C). The extent of zeolite formation was a function of temperature. On the other hand, the same experiments performed with a solution saturated with portlandite (pH 12.5) gave only small zeolite peaks in 6 months. Also, the relatively fast diffusion of hydroxide ions through bentonite with apparently little chemical buffering (Karnland et al., 2003) clearly warrants a closer look into the topic. In particular, the propagation of OH⁻ in relation to the buffering rate of compacted bentonite and the potential of slowly-dissolving siliceous species to precipitate and cause cementation of the highly compacted bentonite should be investigated in more detail.

The effect of a high-pH fluid on the mineralogical stability of clays and the concomitant buffering capacity has also been studied with percolation tests. Usually no or minor mineralogical alterations and insignificant buffering of the injection fluid pH were observed within the duration of the tests, which can be explained by the relatively high flow rates used to percolate the fluid. Under these conditions the potential of the clay to buffer the chemistry is bound to be limited in short-term experiments. By adjusting the flow rate and/or composition of the percolating fluid to better conform to sluggish mineral dissolution and growth rates, it was possible to observe a buffering effect of the clay on the effluent pH (Vieno et al., 2003; Vuorinen et al., 2004).

Future research

It is suggested that continued effort be put on

- Performing long-term alkalimetric titrations to find out the buffering capacity of untreated and purified bentonite for a number of solid-to-solution ratios.
- Clarifying the extent to which compacted bentonite is able to buffer the ingress of an aggressive alkaline plume at the solid-solution interface, where far-from-equilibrium conditions prevail and the montmorillonite dissolution rate is the highest (i.e. the propagation of OH^- in relation to the buffering rate of compacted bentonite). On-line monitoring of the evolution of pH inside the bentonite (see Figure 3).
- Performing experiments on systems, where the degrees of freedom are constrained to a minimum (for example, pure homoionic montmorillonite in contact with NaOH or $\text{Ca}(\text{OH})_2$). This way, uncertainty of the neoformed secondary phases is also minimized. If possible, keep a record of mass balances to ensure back calculation.
- Investigating in more detail the potential of slowly-dissolving siliceous species to precipitate and cause cementation of the highly compacted bentonite.
- Conducting a careful analysis of the reaction products.
- Carrying out supporting numerical calculations. Acknowledging the uncertainties associated with chemical kinetics, sensitivity analyses might be needed. A successful blind prediction of a simplified system would lend credence to the capability of geochemical models to reproduce the observed phenomena.

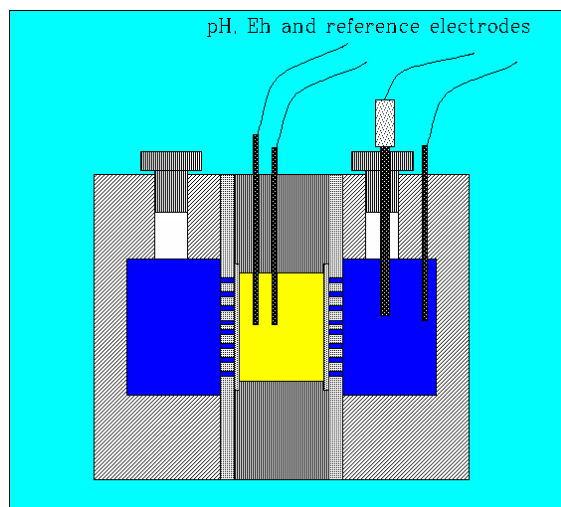


Figure 3. Schematic view of the diffusion cell for on-line monitoring of the evolution of pH in compacted bentonite (courtesy of Dr. A. Muurinen, VTT, Finland).

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A long-term performance assessment for engineered barriers - Study on barrier materials alteration -

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Introduction

In TRU waste repository, large amount of cementitious materials will be used as waste form, fillings, structure and lining. Bentonite material also will be used as buffer material in order to restrict groundwater movement into the repository. Quantitative ratio of cementitious materials to bentonite materials at the TRU waste repository is larger than that of HLW repository. Therefore bentonite-cement interaction is one of the important phenomena to evaluate long-term performance of engineered barriers.

In the first progress report on TRU waste disposal in Japan ¹⁾, the performance of engineered barriers had been pessimistically evaluated because of uncertainty of their long-term behavior. However, at present, more realistic evaluation might be possible by accumulation of recent experimental knowledge for alterations of cementitious materials and bentonite materials in the repository environment, development of modeling and numerical analysis method for their alteration process.

In this study, based on a recent knowledge, numerical analysis for a long-term alteration of engineered barrier system (EBS) was performed as a preliminary calculation. From this result, key technical issues on engineered barriers alteration process were identified in order to improve the reliability of a long-term performance assessment for EBS in TRU waste repository

Alteration analysis of EBS

A long-term evolution of EBS of TRU waste repository was evaluated based on the most recent knowledge about chemical, mineralogical, hydrological and mechanical processes in the system. Then, according to the influence on the performance of the repository system, important processes were selected.

Coupled geochemistry and mass transport calculation code (PhreeqC-Trans) was used in these analysis.(Figure 1) This code treats geochemical reactions and mass transport (diffusion and advection). In this code, hydraulic conductivities, diffusion constants and porosities were renewed in accordance with the change of mineralogy and concentration in EBS, and mass transport conditions were recalculated at regular time intervals.

Because of the uncertainty which lies in the parameters and models, several sensitivity analysis were performed under different parameters or models listed below.

- Cement minerals to be considered in the geochemical analysis
- Bentonite minerals to be considered in the geochemical analysis
- Source of thermodynamic database
- Effect of the change in hydraulic conductivity of cementitious materials/bentonite materials
- Effect of the change in diffusion constants of cementitious materials/bentonite materials.
- Dissolution model of bentonite minerals.
- Types of the groundwater
- Groundwater flow rate in host rock

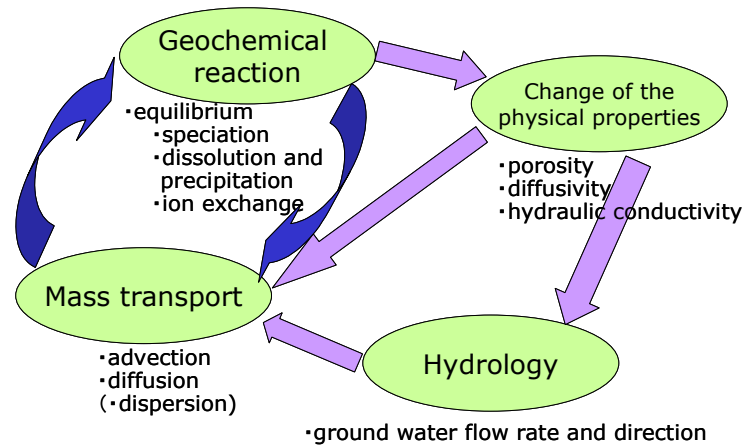
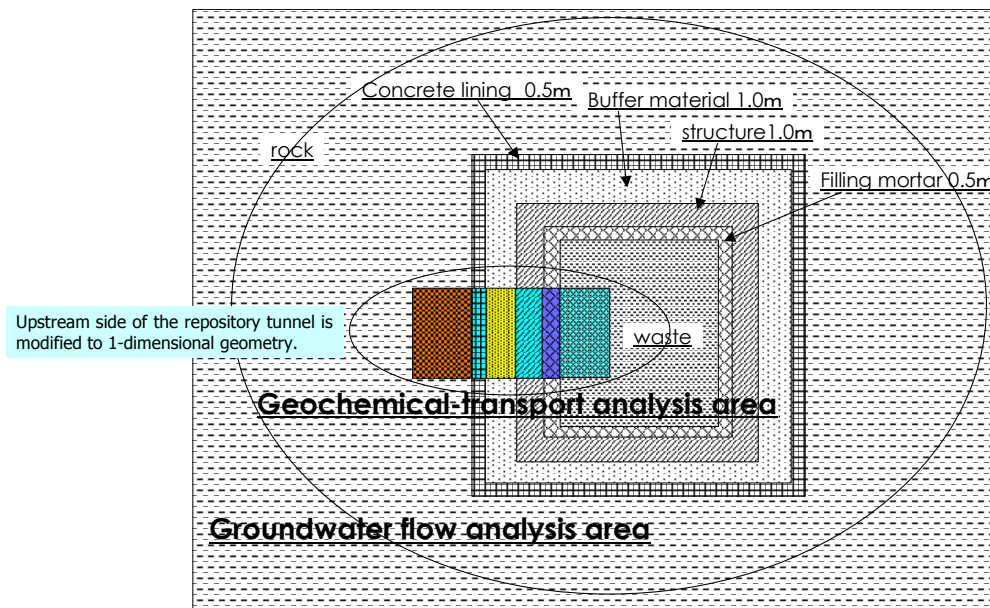


Figure 1 Phenomena and their coupling on the alteration analysis of EBS

System configuration for numerical analysis

Geometry of the analysis is shown in Figure 2. TRU waste repository system consist of waste package, filling mortar, concrete structure, buffer material (bentonite/sand mixture), concrete lining and rock. Representative section of this system was selected and modeled as 1 dimensional mesh. In the alteration analysis, ordinary portland cement and kunigel V1[®] are considered as cementitious and bentonite materials respectively.



Results

Figure 3 shows a typical result of the analysis. Dissolution of chalcedony was confirmed in the bentonite/sand mixture layer. Most of montmorillonite was altered to analcime at the interface of bentonite/sand mixture layer and concrete structure. Portlandite in cementitious material dissolved to form low Ca/Si ratio CSH with silica ions from chalcedony. As the result of these reactions, porosity increased in the bentonite/sand mixture layer. On the contrary, porosity at the interface of concrete structure and bentonite/sand mixture layer significantly decreases by the precipitation of low Ca/Si ratio CSH.

Figure 4 shows the change of hydraulic conductivity and diffusivity in accordance with alteration of the properties of EBS. The numbers of the layers shows the calculative mesh positions in each barrier material, and the 1st layer is the most outer layer. Hydraulic conductivities of the bentonite material increased, at first, by the ion exchange of inter layer Na to Ca, and alteration of montmorillonite to analcime. The long-term change is caused by the dissolution of chalcedony. The diffusivities in the structure decreased by the precipitation of CSH, and the diffusivities in the filling mortar slightly increase by the dissolution of portlandite.

As a result of sensitivity analysis, following important parameters, which affect the resulting total performance of EBS, were confirmed.

- Different thermodynamic data shows quantitatively and qualitatively different time dependent mineralogical change.
- Different dissolution rate of montmorillonite shows qualitatively different time dependent of montmorillonite alteration.
- High concentration of CO_3^{2-} and NaCl can change the mineralogy of cementitious materials and montmorillonite respectively.

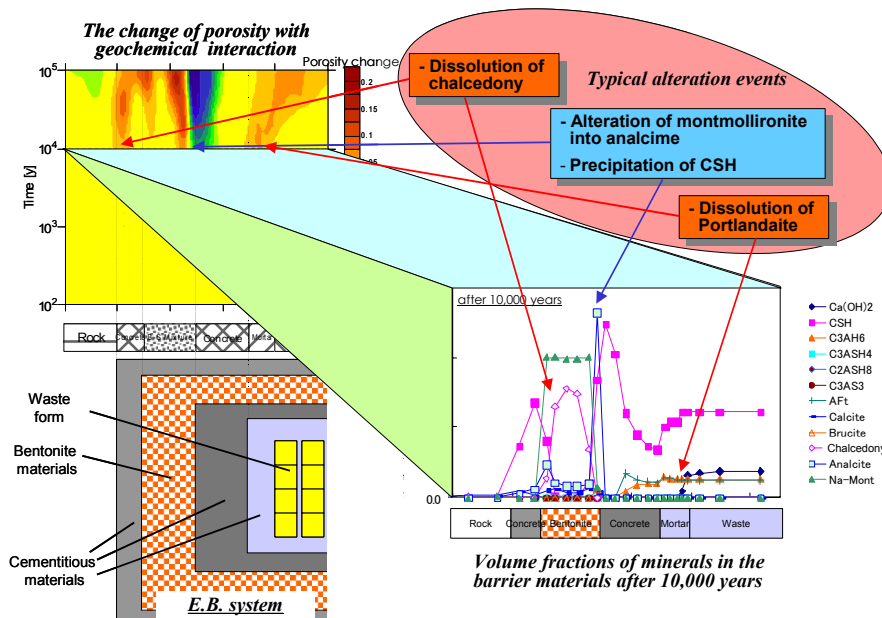
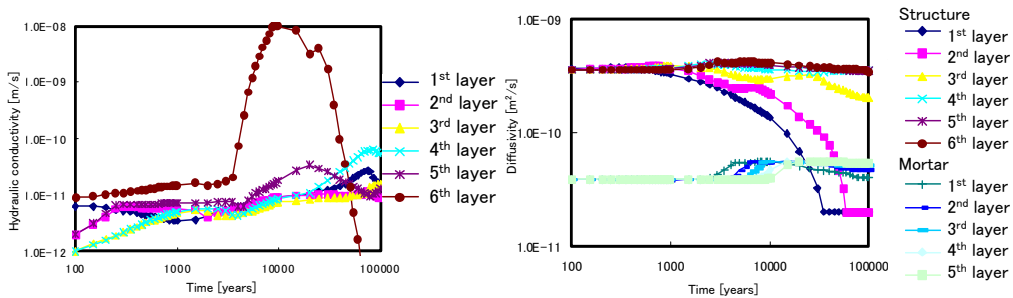


Figure 3 Typical alteration events and porosity change occurred in engineered barriers. (GW type: FRHP)



(a) Change of the hydraulic conductivity of bentonite materials (b) change of the diffusivity of cementitious materials

Figure 4 Evaluated barriers performance as a function of the time

Discussion

Through the above preliminary alteration analysis, following key technical issues on evaluation of a long-term alteration of EBS are identified from a view point of improvement of reliability on a long-term performance assessment for EBS in TRU waste repository

1. Considering of ignored components in engineered barrier on modeling
 - Necessity of consideration of aggregates in mortar or concrete and mixed sand in bentonite materials on the analysis.
 - Treatment and modeling of crack in cementitious materials
2. Experimental acquisition of parameters and its review
 - Geochemical model
 - Initial minerals composition of hydrated cement in the model
 - Thermodynamic data of montmorillonite and analcime about bentonite alteration
 - Geochemical reaction
 - Thermodynamic model of C-A-S-H, and change of more stable minerals by thermal effect in cementitious materials
 - Experimental identification of secondary minerals and dissolution rate under alkaline condition in bentonite materials
 - Mass transport
 - Effect of pore structure, hydraulic conductivity and diffusivity in extremely low porosity.
3. Experimental validation of typical alteration events to be predict from the analysis
 - Remarkable decrease of the porosity ant the vicinity of cement/bentonite boundary caused by precipitation of secondary minerals such as calcite, C-S-H and ettringite
 - Selective dissolution of chalcedony, reverse alteration reaction of analcime into montmorillonite, montmorillonite dissolution rate close to its saturated concentration and significant alteration of montmorillonite into analcime in saline water in bentonite materials.

*This study was commissioned by METI, Japan.

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An Analysis of Cement-Bentonite Interaction and Evolution of Pore Water Chemistry

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INTRODUCTION

Performance assessments for TRU waste repositories have shown that soluble and poorly sorbing nuclides such as I-129 and Cl-36 dominate the dose [1]. These nuclides are expected to migrate with groundwater flow, hence hydraulic conditions and their evolution with time in the repository are key issues for repository safety. Cementitious material will be used for waste packaging, backfilling and structural material in a TRU waste repository. Bentonite is also expected to be used for some TRU wastes to provide the function of a hydraulic barrier in the disposal system. It is known that the logarithm for the dissolution rate of smectite is proportional to the logarithm for the activity of hydroxide ion [2]. Therefore there is concern that the coexistence of cementitious material and bentonite cause the alteration of smectite due to interaction with hyperalkaline leachates and consequent deleterious perturbation of the function of bentonite as a hydraulic barrier. Many research studies have been performed to identify possible mechanisms of cement-bentonite interaction. However, uncertainties still exist in our understanding of the precise chemical scheme of bentonite alteration in highly alkaline conditions, especially the spatio-chronological variation of secondary mineral occurrences.

In this work, the possible multiple scenarios of chemical-mineralogical evolution were considered on the basis of the information of both experimental results and observations of natural systems. The range of variable chemical conditions according to each scenario was examined in terms of the potential for locally-attained chemical equilibrium. These analyses have been intended to provide reasonable assumptions on simulations using the chemistry-transport-hydrology coupling models that aimed at estimating possible evolution of hydraulic conditions of bentonite in a TRU waste repository.

Understanding alteration processes of bentonite

There have been several experimental studies on smectite alteration under hyperalkaline conditions at low temperature and these are summarized below. From the experimental results, it is likely that different parageneses of secondary minerals are possible.

- Mineral stability with respect to the composition of the solution phase

The types and abundances of secondary solid phase will reflect the composition of the solution phase (e.g. pH, the concentration of alkali/alkali earth elements, and the Si/Al ratio). Under hyperalkaline conditions produced by the presence of KOH, illite and phillipsite have been observed in the experiments [3][4][5][6]. In Na-rich conditions, analcime, a zeolite mineral mainly formed in experiments at temperatures in excess of 373 [K], is formed, even at low temperature [7]. In highly alkaline conditions due to the presence of Ca(OH)₂ or the combination of Ca(OH)₂, NaOH and KOH, CSH, CAH, CASH minerals, mixed-layer minerals, analcime and phillipsite have been observed in experiments [8]. Zeolites have been

observed as products of many laboratory experiments and natural analogues of hyperalkaline water-rock interaction.

Mariner et al. [9] showed that the Si/Al ratio of zeolites decreased with increasing pH. Accordingly, analcime and phillipsite (low Si/Al ratio zeolite) preferentially form at high pH, whereas mordenite and clinoptilolite (high Si/Al ratio zeolite) preferentially form in an environment of lower pH. Savage [10] hypothesized that the Si/Al ratio of zeolites potentially forming in the hyperalkaline disturbed zone of a waste repository should increase with distance away from the source of hyperalkaline fluid, mirroring the decrease in pH with distance away from the repository.

- Transformation of solid phases from a metastable to a thermodynamically stable state

On the other hand, the sequential variation of secondary minerals from metastable phases to stable phases was also observed in laboratory experiments using high pH solutions at low temperature as follows:

- Opalinus Clay → CASH and mordenite → illite and calcite [11]
- smectite → illite → phillipsite → K-feldspar [3]

These reactions seem to be controlled by kinetic factors rather than by attainment of thermodynamic equilibrium. The formation of the metastable phases occurring occasionally in sedimentary rocks is explained by the empirical Ostwald step rule, where the surface free energy and degrees of supersaturation are important factors. Consequently, rapidly-growing metastable phases which lower the overall free energy of the system may be observed, rather than phases which are thermodynamically more stable [18].

Transformation from metastable to stable phases appears in natural environment, for example:

- mordenite, phillipsite → clinoptilolite, analcime, K-feldspar [12]
- phillipsite → clinoptilolite, analcime [13]
- smectite → illite [14]

These findings from natural environments of lower pH show similar trends to those experiments at high pH and low temperature conditions, indicating that the high-pH conditions greatly increase reaction rates [11][15].

The relationship between natural zeolite formation during burial diagenesis of sedimentary rocks and thermal history has been reported extensively in the literature. From these studies, it is concluded that at low temperatures zeolites with a high Si/Al ratio (e.g. clinoptilolite, and mordenite), form whereas at greater burial depths (higher temperature), zeolites with a lower Si/Al ratio (e.g. heulandite and analcime), formed, and where even higher temperature existed, laumontite was produced [16]. This observation seems also to follow an Ostwald step rule postulating that the precipitate with the highest solubility (i.e. the least stable solid phase) will form first in a sequential precipitation reaction [17].

It could be regarded that the formation of zeolites with a higher Si/Al ratio is faster than that of zeolites with a lower Si/Al ratio, so that pH may control the reaction rates in analogy with the effect of temperature. Furthermore, it is considered that a wide range of secondary minerals, CSH, CAH, CASH, clay minerals (illite, mixed-layer mineral, low Si/Al zeolite, high Si/Al zeolite) and K-feldspar could appear due to the variation of pH with time and space under repository conditions. The formation of K-feldspar may, however, take more than 1 million years at low temperature [18].

Analysis using Geochemical Modeling Code

The chemical conditions in the engineered barriers will change sequentially during the alteration of cement and bentonite over the long term. It is hard to determine precisely to what degree the alteration may progress over PA timescales. To estimate the range of possible chemical evolution, an analysis of spatio-chronological variation of mineralogy and pore water chemistry in the cement-bentonite system was conducted with consideration of the local equilibrium and sequential transfer of solutes between modeled regions.

- Bentonite Alteration Scenarios

Bentonite alteration scenarios for this analysis were determined on the basis of the information mentioned above.

At first, the guidelines for making scenarios for smectite alteration were considered as follows:

Guideline 1 : The precipitate with the highest solubility (i.e. the phase of least positive saturation index) forms first in a sequence of precipitation reactions.

Guideline 2 : The Si/Al ratio of zeolite increases with decreasing pH.

Guideline 3: The alteration of mineral assemblages progresses rapidly at high pH and more slowly at lower pH.

The temperature in repositories is assumed to be less than 353[K], and the maximum pH in the engineered barrier systems lies between that of ambient groundwater and that of the hyperalkaline pore fluid typical of cement. Some minerals were selected as being representative of mineral types likely to form in such systems as follows:

- CSH, CASH: metastable in all the range of environmental conditions
- illite, mixed-layer minerals: metastable in hyperalkaline condition, but more stable than smectite
- analcime: alkalic zeolite stable over the wide range of environmental conditions
- laumontite: calcic zeolite stable in hyperalkaline conditions, but difficult to form at low temperature
- (K, Na)-phillipsite : alkalic zeolite stable in weakly alkaline conditions
- (Ca, Na)-clinoptilolite: calcic and alkalic zeolite stable in weakly alkaline conditions
- (Na, Ca)-mordenite: alkalic and calcic zeolite stable in neutral – weakly alkaline conditions
- K-feldspar: Stable over the wide range of environmental conditions, however difficult to form at low temperature

A set of scenarios was prepared in accordance with the above classification and the guidelines. A schematic of the scenarios is shown in Fig.1. The bentonite region is adjacent to the cementitious region. A model groundwater is equilibrated with the hydrated cement and the consequent cement pore water is transferred into the bentonite region. The cement pore water changes with time according to regions I, II and III [19]. The bentonite pore water builds up through the interactions of cement leachate and

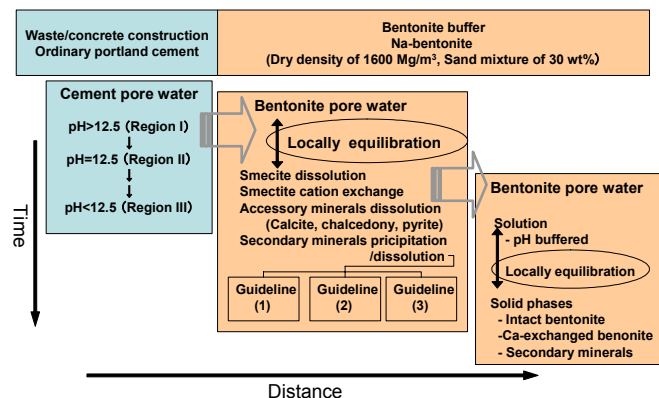


Fig.1 Schematic of scenarios for the analysis of pore water evolution during cement-bentonite alteration

bentonite involving each sequence of reactions in accordance with the guidelines.

- Calculation using Geochemical Modeling Code

The scoping calculations using the geochemical modeling code, PHREEQC [20] were performed according to the scenarios outlined above.

Chemical Modeling of Cement Pore water

Following Berner’s method [21], the mineralogical composition of hydrated cement paste (W/C=70) was determined based on the chemical composition of Ordinary Portland Cement. The CSH-gel was modeled as a series of calcium silicate hydrate minerals in which the equilibrium constant is varied by Ca/Si ratio, following Atkinson’s model [22]. The compositions of cement pore water of region I, II and III were calculated with the mixing tank model in which the equilibration between the fresh-type model groundwater [23] and the minerals of hydrated cement paste was repeated many times with the remaining solid phases. The thermodynamic data set for minerals of hydrated cement paste [24] was used.

Chemical Modeling of Bentonite Pore water

The dissolution and precipitation reactions of minerals and cation exchange reactions on smectite were taken into account in the scoping analysis. The bentonite buffer (dry density =1600 [Mg m⁻³]) contains 30% of silica sand. The mineralogy of the bentonite buffer and the cation exchange constants on smectite were assumed to be the same as in the previous PA report [1]. Equilibrium constants were taken from Hatches, ver.14 [25] for all species and mineral hydrolysis reactions other than for the minerals CASH,CAH, clinoptilolite [26], mordenite [27] and phillipsite [28]. Unfortunately, few reliable thermodynamic data for CASH and CAH currently exist. In our calculations, gehlenite and katoite [24] were used as proxies for CASH minerals and phillipsite was excluded because of the large uncertainties in published data. Muscovite was used as a proxy for mixed-layer silicate.

The results of analysis

The results of scoping calculations are summarized in Fig.2. The layout of data in Fig.2 represents the concept of this analysis in accordance with the scenarios. The precipitation of

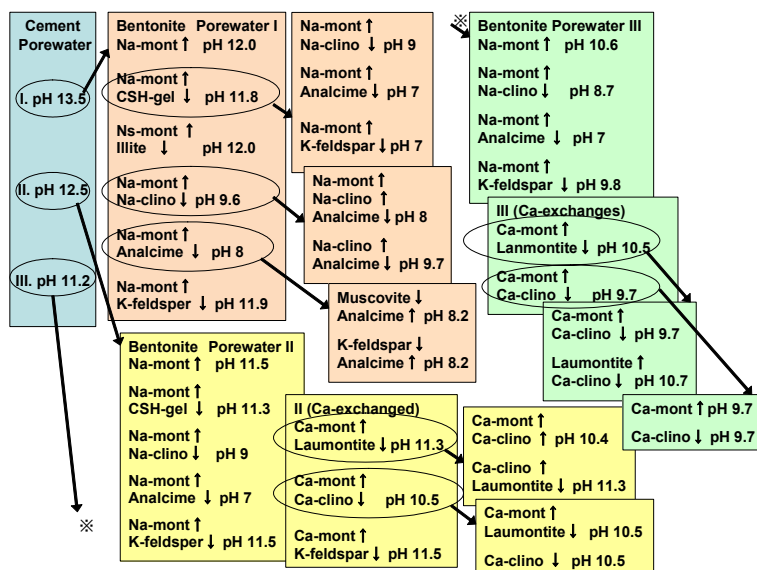


Fig.2 Summary of the results of scoping calculations

zeolites, especially analcime, readily neutralized the pH of bentonite pore water for all cement leachates of region I, II and III. The neutralization may inhibit the dissolution of smectite. Once stable zeolite precipitated, the resultant changes in pore water composition became minor. The pH neutralizing trends with the precipitation of CSH, CASH minerals, mica group and K-feldspar were weak, so that the inhibition effect of these reactions on the dissolution of smectite, therefore, is considered to be

weak. The pH variation of bentonite pore water through the Na-type smectite alteration process is larger than that in the presence of Ca-exchanged smectite.

Summary and Conclusions

An analysis of the mineralogical-chemical evolution in the engineered barrier was performed. To estimate the range of probable chemical evolution, scoping calculations of spatio-chronological variation of mineralogy and pore water chemistry were examined by considering local equilibrium with the bentonite alteration scenarios. The guidelines were considered to identify the probable scenarios on the basis of the information of experimental results and observations of natural systems. The results of this analysis showed that the estimated bentonite pore water evolution depends on sequences of secondary mineral occurrence. It is suggested that the pore water may allow for a greater degree of local pH buffering when the alteration from smectite to zeolites only partially occurs, thus providing preferable conditions for smectite retention in the whole bentonite buffer region.

This work suggests that the results are helpful for the simulation of the evolution of probable hydraulic conditions due to cement-bentonite interaction.

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Development of MACBECE: Mechanical Analysis system considering Chemical transition of Bentonite-based and Cement-based materials

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1. Introduction

TRU wastes in Japan are being considered for emplacement in large underground cavities utilizing cementitious materials as fillers and structural materials, surrounded by a bentonite buffer according to the current disposal concept [1]. The performance assessment for this concept pointed out that I-129 and Cl-36, contained in some of these wastes, are regarded as the predominant nuclides in dose evaluation. Since these nuclides are soluble and poorly sorbed, groundwater flow in the near-field has a significant effect on the transport of these nuclides.

It is expected that the groundwater flow in the repository will be restricted by a multi-engineered barrier system (EBS). However, the porosity of cement-based material increases due to leaching of hydrates. Subsequently, bentonite properties tend to change as a result of the influence of high pH leachate from the cementitious material. In addition, changes in the mechanical properties affect the deformation behavior of the repository. Groundwater flow is related to volumetric change, which subsequently has an effect on chemical evolution (see Fig. 1). Therefore, a deterioration of material properties and the resultant effects on EBS deformation need to be understood to evaluate hydraulic conditions. An analytical system has been developed to calculate near-field groundwater flow with chronological variation in alteration and deformation over a long period.

The principal aim of this work is the development of a mechanical analysis system, which can calculate the deformation of cement-based and bentonite-based material in the repository environment. In this study, flow-through tests of cement paste were conducted in order to investigate the changes in mechanical/hydraulic properties reflected by chemical alterations. Various laboratory tests of bentonite were performed to examine the effect of cation exchange on these properties. The test results were also applied to the modeling of mechanical behavior. Finally, a mechanical analysis system, Mechanical Analysis system considering Chemical transition of Bentonite-based and Cement-based materials (MACBECE), was developed together with these relationship and modeling. The long-term deformation and the change of permeability distribution in the near-field were preliminary evaluated based on the assumed chemical evolution.

2. Mechanical properties of hydrated cement during deterioration

(1) Laboratory tests with cement paste

Coupled processes during degradation of the chemical, mechanical and hydraulic (C-M-H) properties of concrete have been studied [e.g. 2,3]. A flow-through test is used to directly measure a series of C-M-H data for samples with higher porosities. Using a batch test makes it easier to handle samples with a wide range of porosities and to estimate their mechanical properties from hardness measured in a small, degraded area.

In this study, flow-through tests and batch tests were systematically conducted to obtain C-M-H processes for the wide range of porosities possible in the repository environment. Hardened paste specimens of Ordinary Portland Cement (OPC) were mixed in the same batch and subjected to the tests. The porosity and elements distribution in both solid and aqueous

phases were measured simultaneously. A comparison of the tests and their relative advantages/disadvantages is shown in Table 1.

(2) Test results and modeling

Hydraulic conductivity, K , and compressive strength, σ_c , of the specimens, which had been degraded by distilled water (DW) and a 1M- NaNO_3 solution percolation, are shown with porosities, p , in Fig. 2 and Fig. 3, respectively. It is clear that both properties are strongly dependent on the porosities. Relationships between porosity and each property were empirically fitted by suggested equations. The fitted lines indicate good agreement to the values of unaltered specimens through a wide range of porosities. These results suggest that mechanical and hydraulic properties of cement paste could be evaluated by the degree of degradation.

To analyze deformation of cementitious material, a stress-strain relationship is required. A bi-linear relationship composed of a compressive strength and an elastic modulus was taken into account. Furthermore, in the long-term, the cement-based material in the repository will shrink due to both the deterioration of mechanical properties as well as the swelling pressure of the bentonite buffer thereby resulting in strain-softening material behavior (see Fig. 4). An analytical iterative procedure [4] was applied to the representation of the stress-strain curve indicating both peak strength and residual strength.

3. Mechanical properties of Ca-bentonite

(1) Laboratory tests with consideration of calciumization

Various laboratory tests were conducted to investigate the effect of both (a) cation exchange of Na-bentonite for calcium ions (termed “calciumization” in this paper) and (b) the swelling behavior of bentonite on its mechanical and hydraulic properties. The test results were applied to the extension of an elasto-plastic constitutive model of bentonite. A constitutive model is required to determine the volumetric change. Several constitutive models, such as proposed by Sekiguchi and Ohta [5], have been developed to evaluate the mechanical behavior of natural sedimentary clay. However, the models cannot sufficiently illustrate the volumetric change of bentonite due to swelling.

Several laboratory tests, which were divided into consolidation and shear behaviors, were conducted with the intent of investigating the effect of modifying parameters that corresponded to the Sekiguchi-Ohta model for clayey materials. A matrix of the tests is summarized in Table 2.

Bentonite specimens with calciumization ratios (CR) of 0% (equivalent to natural Na-bentonite, KUNIGEL V1[®]), 50% and 100% were prepared for the tests. In the cases of CR=50 and 100%, half and all, respectively, of the intercalated cations of the KUNIGEL V1[®] were artificially exchanged by calcium ions using a calcium chloride solution. The dried, powdered bentonite was compacted with various initial void ratios. The void ratios employed in the tests corresponded to a swelling of 0-40%, where the 0% swelling corresponded to a bentonite dry density of 1.6 Mg/m³. After compaction and prior to the laboratory tests, the bentonite specimens were saturated without volumetric change.

(2) Experimental results and modeling

- Consolidation behavior

The typical relationships between void ratio, e , and the logarithm of consolidation stress, p' , (e - $\log p'$) measured in the consolidation tests are shown in Fig. 6 and Fig. 7. The normal consolidation (NC) line of the bentonite is independent of the calciumization ratio. The gradient of the NC line (compression index, C_c) is approximately 0.3-0.4. The non-linearity of the swelling behavior of the bentonite becomes more pronounced with decreasing CR. The

gradient (swelling index, C_s) becomes larger with increasing over-consolidation ratio (OCR), where $OCR = p_o'/p'$, p_o' is the mean effective stress at the pre-consolidation state and p' is the mean effective stress at the current state.

Maximum swelling deformation and equilibrium swelling pressure were measured in swelling deformation/pressure test. The results plotted in the $e-\log p'$ plane are close to the $e-\log p'$ relationships obtained from the consolidation tests. They could be estimated from the $e-\log p'$ relationship, when the initial void ratio and pressure are measured.

The swelling behavior of bentonite, which is different from that of natural sedimentary clay, was modeled [6]. It was initially assumed that the variation in void ratio due to swelling could be separated into mechanical effects due to unloading, \dot{e}_m , and ionic effects due to seepage, \dot{e}_s , where the symbol ‘ $\dot{}$ ’ indicates the material time derivative. The $e_s - \ln p'$ relation normalized by p_o' , in other words the $e_s - \ln(OCR)$ relationship, could be empirically represented with an exponential equation of a material constant, ξ (see Fig. 5). The equation has the advantage that only a single additional parameter is involved and the derivation of the model is simplified. The model of the swelling behavior can therefore be written as

$$\tilde{K} = \frac{\kappa}{\xi(OCR) \exp\{\xi(OCR-1)\} + \kappa} K, \quad \tilde{G} = \frac{3}{2} \frac{1-2\nu'}{1+\nu'} \tilde{K}, \quad (1)$$

where \tilde{K} is bulk modulus considering the volumetric change of bentonite due to seepage, K is the bulk modulus, $\kappa (= 0.434C_s)$ is the swelling index defined in the $e-\ln p'$ relationship, \tilde{G} is the shear modulus and ν' is the effective Poisson's ratio. By substituting Eq. (1) into generalized Hooke's law, the non-linear elastic component, expanded to express the swelling behavior of bentonite, was obtained. The expanded model describes the non-linear swelling behavior of bentonite by varying the material parameter ξ .

- Shear behavior

The effective stress paths and the relationship between deviatoric stress and axial strain were obtained from the tri-axial \overline{CU} tests as shown in Fig. 8 and Fig. 9. The critical state parameter, M , which determines the shape of the yield surface, is important for investigating the elasto-plastic behavior of bentonite. Its value is independent of calciumization and the confining pressure related to initial void ratio. In addition, the values agree to previous studies [7,8]. It could be treated as a material property (approximately 0.4-0.5).

Fig. 9 shows that the bentonite with CR=100 indicates a peak strength similar to an over-consolidated clay even when confining pressure was 5MPa. On the other hand, the stress-strain profile with CR=0 is analogous to a normally consolidated clay at the same confining pressure of 5MPa. However, the stress path of each bentonite is comparable in shape. There is a possibility that the effect of calciumization can be described as being similar to increasing the pre-consolidation pressure. At the beginning of shearing, in the cases of CR=0 and 50%, the bentonite behaves as an elastic material even when the confining pressure is 5MPa (below the O-A lines in Fig. 8). The elastic behavior can be interpreted theoretically if the O-A line is equivalent to the K_0 -line.

- Permeability

For modeling the effects of volumetric change on the permeability, the relationship between permeability and void ratio are shown in Fig. 10. The permeability obtained from consolidation tests and previous studies [7,9] is also plotted in the figure. The permeability becomes larger in accordance with increasing CR.

4. System development to evaluate long-term deformation in the repository

The finite element analytical code MACBECE is being developed to evaluate long-term deformation in the repository. The system includes the effects of chemical alteration. An

analytical flow chart of the system is shown in Fig. 11. The initial conditions of the chemistry and the corresponding mechanical properties are set. An incremental deformation of the EBS is then calculated using the non-linear elastic model for the strain-softening of the cementitious material and the extended constitutive model for the bentonite. Permeability is modeled based on volumetric strain and calciumization. The current chemical module can simulate only calciumization of the bentonite-based materials and calcium leaching of the cement-based materials, which are assumed to occur in the repository. After a revision of the chemical profiles, the calculation cycle loops and the above-mentioned C-M-H procedures are re-calculated.

Using MACBECE, a preliminary analysis of the long-term deformation and the change in permeability distribution in the TRU repository was performed based on the assumed change in chemical profiles. The analytical results obtained from the present prototype system indicate that both the deformation of the EBS as well as the influence of the deformation on permeability are limited.

In the future, the chemical module will be replaced by an analytical code. The mechanical properties of the concrete and the buffer will also be refined based on current studies of the influence of the aggregates used in the concrete and of the sand used in the buffer material. The completed system will calculate deformation and its effect on permeability under various cases of chemical alteration, which will enhance the robustness in determining the hydraulic condition in nuclide transport analysis.

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Table 1 Comparison between flow-through and batch tests

	Flow-through test	Batch test
W/C of samples	Preferable with high W/C (-)	Applicable to wide range of W/C (+)
Dissolution behavior	Accelerated Easier to prepare larger degraded sample (+)	Similar to repository environment (+) A large gradient of degrading degree within a sample (-)
Items measured		
Permeability during degradation	Directly measurable (+)	Estimated from porosity (-)
Compressive strength and elastic modulus after degradation	Directly measurable (+)	Estimated from Vickers hardness measurable in a small area (-)
Experimental condition in this study	- Size : $\phi 40\text{mm} - h40\text{mm}$ - W/C: 85%, 105% - Percolated by DW* or 1M-NaNO ₃ - Surrounded by Ar gas, 20°C	- Size : $\phi 30\text{mm} - h10\text{mm}$ - W/C : 40%, 55%, 70%, 85%, 105% - Preserved in regularly renewed DW* - Surrounded by Ar gas, 20°C

DW*: deionized and de-gassed water (+): advantages (-): disadvantages

Table 2 Laboratory test matrix for modeling

Characteristics	Tests	Parameters	Modeling	
Soil skeleton	Consolidation test	mean effective stress p' void ratio e compression index Cc	Elasto-plastic behavior Effects of calciumization on $e - \ln p'$ relations	
		mean effective stress p' void ratio e swelling index Cs	Elastic behavior Non-linearity of swelling behavior	
	Swelling pressure/ deformation test	mean effective stress p' void ratio e compression index Cc swelling index Cs	Elasto-plastic behavior Equilibrium swelling pressure and maximum swelling deformation in $e - \ln p'$ relations	
	Shearing	Tri-axial \overline{CU} test	critical state parameter M mean effective stress p' deviatoric stress q	Elasto-plastic behavior Effects of calciumization on critical state parameter
Pore water	Migration	Permeability test	permeability coefficient k void ratio e	Effects of calciumization on $e - k$ relations

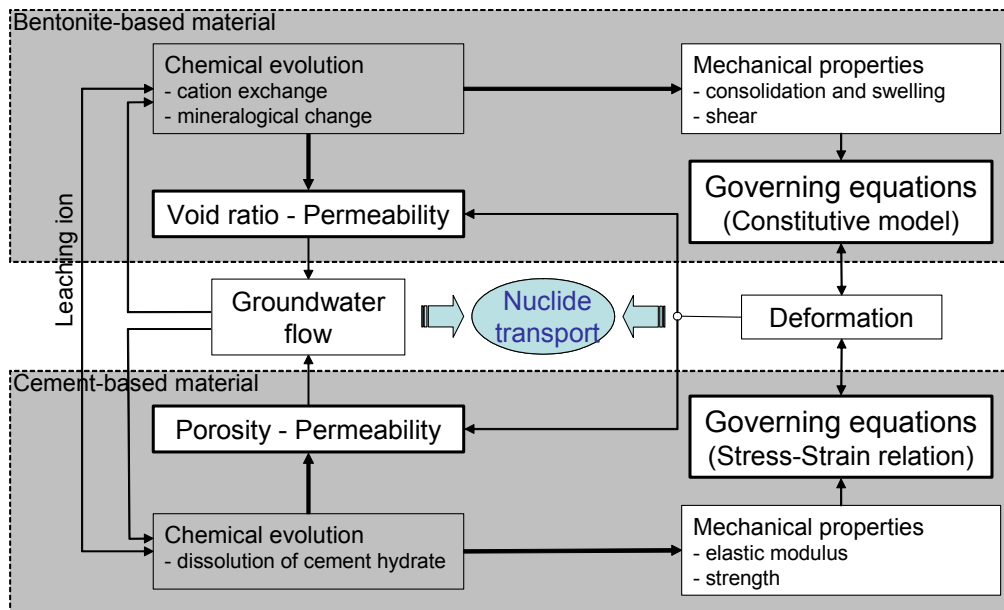
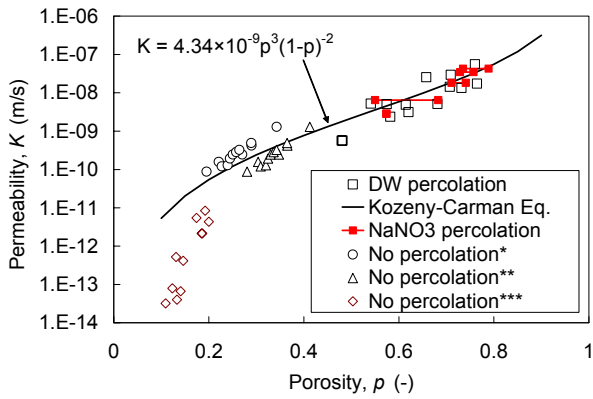


Fig. 1 Interactions of Chemical, Mechanical and Hydraulic processes in cement and bentonite system



* back-calculated on F=1.0 from Powers, T.C. (1958)
 ** back-calculated on F=0.8 from Powers, T.C. (1958)
 *** Day and Konecny (1989)

Fig. 2 Relationship between permeability and porosity

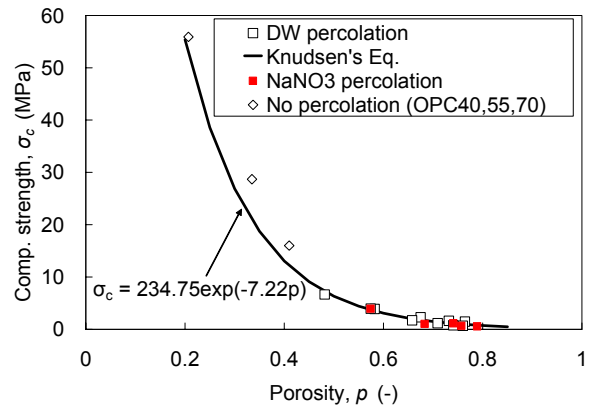
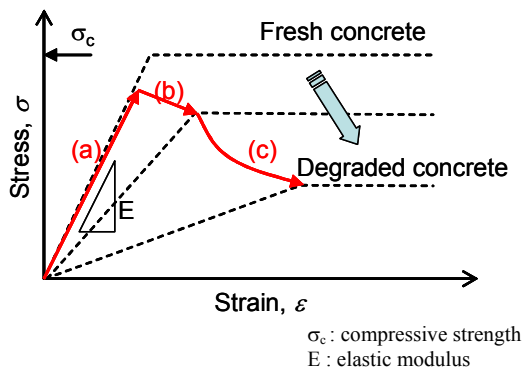


Fig. 3 Relationship between strength and porosity



- (a) compression due to self-weight and swelling pressure
- (b) compression due to deterioration of E
- (c) compression due to deterioration of σ_c and E

Fig. 4 Conceptual model of concrete deformation

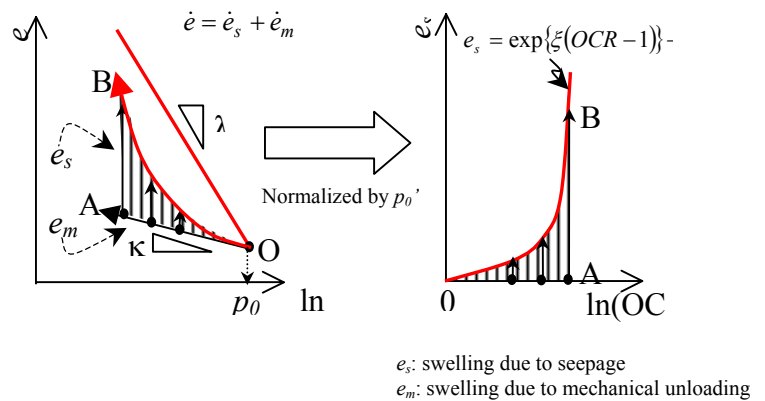


Fig. 5 NC line and swelling behavior in the $e-\ln p'$ relation
 Bentonite swells along O-B, while other popular clay swells along O-A.

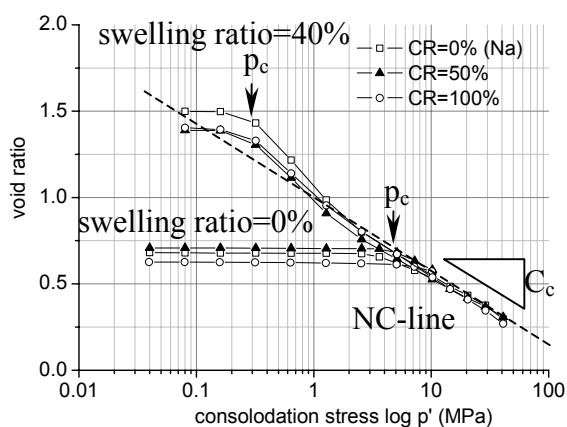


Fig. 6 Normal consolidation line of bentonite with various CR (swelling ratio = 0, 40%)

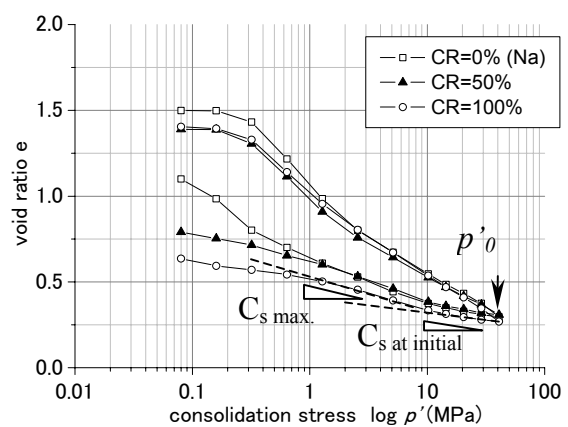


Fig. 7 Swelling behavior of bentonite with various CR (swelling ratio=40%)

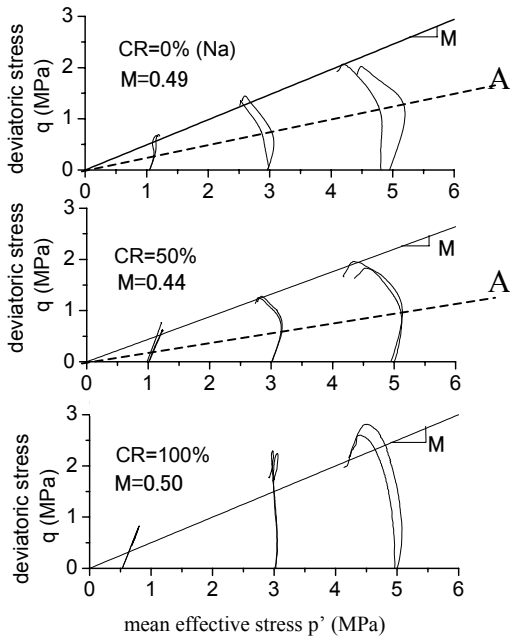


Fig. 8 Effective stress paths with CR (swelling ratio = 0%)

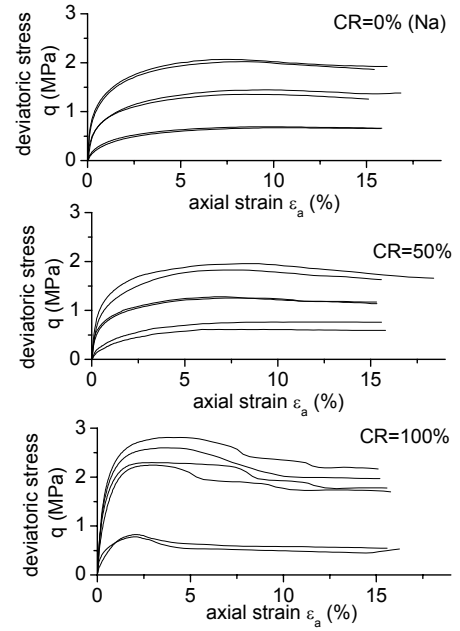


Fig. 9 Relationship between deviatoric stress and axial strain (swelling ratio = 0%)

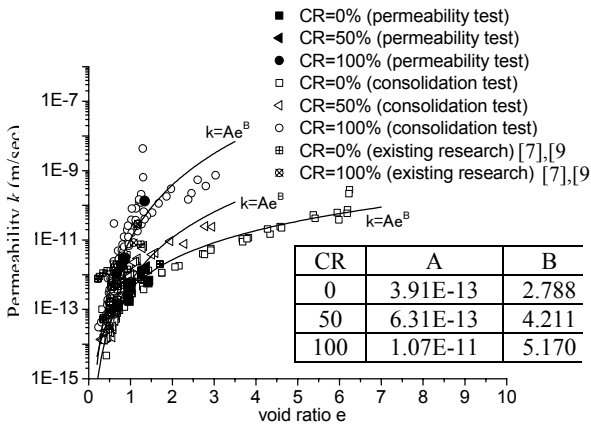


Fig. 10 Relationship between permeability and void ratio

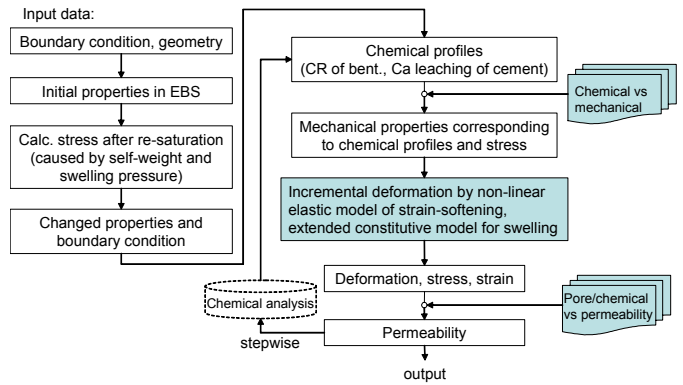


Fig. 11 Analytical flow of the system

Modelling diffusion of an alkaline plume in two types of clayey systems

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1. Introduction

Concrete will be used extensively in the ANDRA design to construct the disposal chambers in the host formation (Callovian-Oxfordian argillite COX), and also as waste containment material. The large excavated chambers that will hold the containers of radioactive waste are constructed with concrete and will be separated from the repository access galleries by bentonite plugs, several metres thick. The volume of concrete is likely to be much higher than that of the bentonite plugs. After being sealed, the repository will become saturated with interstitial waters from the Callovian-Oxfordian argillite, which will produce high pH solutions through interaction with the concrete. The aggressiveness of these alkaline solutions, when in contact with the bentonite, may weaken the clay's confinement properties (bentonite and argillite) with respect to long-lived radionuclides by change of the mineralogy. The dominant transport mechanism in these impermeable formations is assumed to be diffusion. The aim of this study is to determine, firstly, the critical processes affecting the two clayey media (bentonite and argillite) during the diffusion of an alkaline plume and secondly, the extension of the perturbation in space and time. We test also our numerical capacities to model such phenomena in a complex geochemical system.

The calculations were carried out in two steps: first, definition of the more complete mineralogy as possible for the initial systems in equilibrium with the interstitial pore water of the Callovian-Oxfordian argillite, then diffusion of the alkaline plume from the concrete through the clayey media. Calculations were carried out over a simulated period of 100,000 years using PHREEQC.

The experimental work made in the European Ecoclay II project allows a selection of reaction paths and of new phases for the thermodynamic database used in the calculations.

2. Construction of the model

Clayey systems

The two clayey systems were defined by their mineralogy (% of phases). Taken into account a porosity of 10% for the bentonite (MX80) and 4.6% for the COX, input data were converted to molar scale. The molar concentrations of exchange sites were 6.47 eq/kg_w for the MX80 and 4.38 eq/kg_w for the COX. The partial pressure of CO₂ was not imposed in the simulations of reference, it was considered that a complex mineralogy with carbonaceous minerals is able to fix this parameter.

Database and Calculation

Aqueous species and mineral solubility products were taken from the LLNL Phreeqc Database. We had added the thermodynamical properties of 15 “cement” phases. 50 phases were presented or susceptible of precipitation in the model. The exchange constants (Gaines-Thomas convention) were from Fletcher and Sposito [*Clay Minerals*, 1989] for the MX80 and were determined especially for the COX in our laboratory. Considering the very long time of interaction between minerals and solution due to the low diffusion coefficient, all calculations were made at the thermodynamical equilibrium. No kinetics was taken into account.

Cement porewater

A cement porewater was calculated by Andra to simulate an evolved (OPC) cement porewater (table 1).

Table 1 Chemical composition (mol/kg_w) for the concrete pore water.

pH	12.50
pe	-8.6
Na (mol/kg _w)	$8.02 \cdot 10^{-3}$
K (mol/kg _w)	$2.21 \cdot 10^{-2}$
Ca (mol/kg _w)	$2.19 \cdot 10^{-2}$
Si (mol/kg _w)	$3.01 \cdot 10^{-5}$
S (mol/kg _w)	$1.20 \cdot 10^{-4}$

The mineralogical and chemical evolution of the concrete was not taken into consideration in this study for several reasons. First, this evolution is not documented over a long period of time and, second, the huge volume of concrete relative to the volume of bentonite expected in the repository, allowed us to assume the concrete medium was infinite. Nevertheless, it is clear that the chemistry of the concrete will evolve with time. The selection of a solution of pH 12.5, can represent a “moderately evolved” concrete pore water.

Transport and Mesh

In simulating the alkaline plume, the transport of solutes into the clay barrier was considered to be a pure diffusion process in a saturated medium with interconnected porosity. The boundary conditions were those of a semi-infinite medium for the clay barrier, and constant, fixed fluid concentrations, in the concrete. The mesh of the barrier was not linear with 10 small cells of 2.5cm near the interface with the concrete, followed by 10 cells of 5cm and 75 cells of 10cm. The high number of small cells near the concrete allows a fine description of the interface. The simulation covered a period of 100,000 years in 10,000-year steps. Based on the diffusion coefficient obtained by the CEA in this project, 3 orders of magnitude were tested: $10^{-9} \text{ m}^2/\text{s}$, $10^{-10} \text{ m}^2/\text{s}$, $10^{-11} \text{ m}^2/\text{s}$.

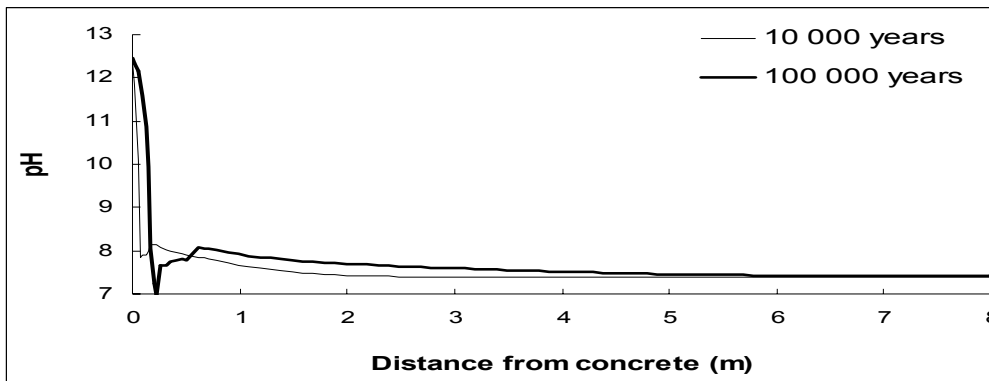


Figure 1 MX80 Change in the pH of the barrier pore water. Diffusion coefficient $10^{-11} \text{ m}^2/\text{s}$.

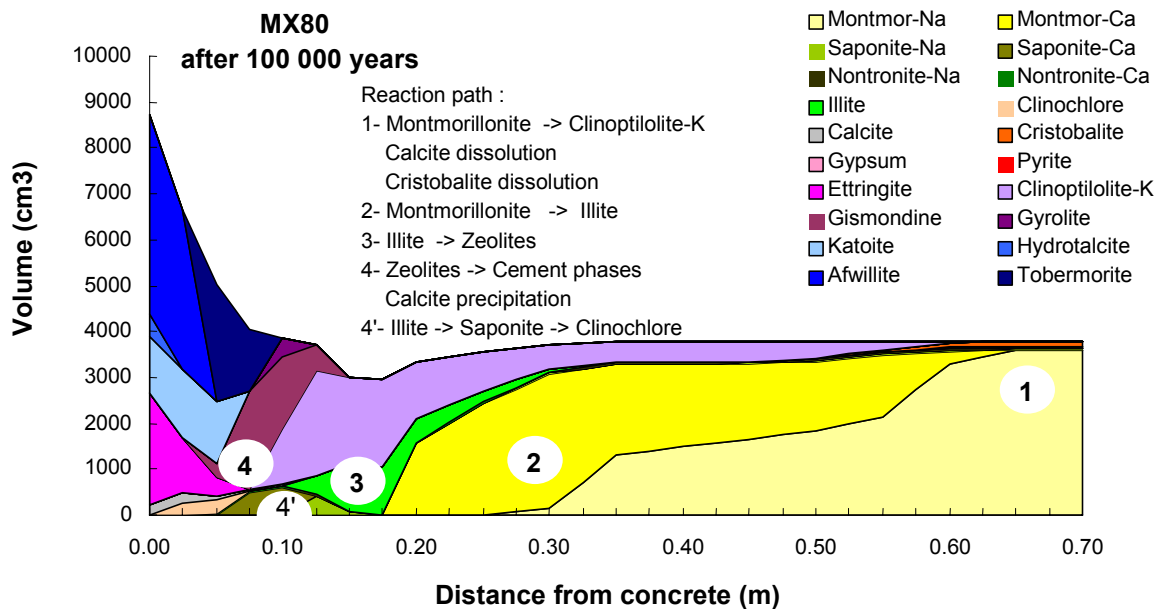


Figure 2 MX80, Mineralogical composition of the barrier after 100,000 years, diffusion coefficient $10^{-11} \text{ m}^2/\text{s}$.

3. Results

MX80. One of the most expectable chemical changes in the barrier would be the increase of the pore water pH (Figure 1). However, at 100,000 years, a very strong buffering of the pH is observed and the pH front does not evolve much from 10,000 to 100,000 years. The pCO_2 is not externally imposed in all our calculations. Carbon dioxide is thus produced by the mineral assemblage itself. This indicates that the mineralogical assemblage is rich enough to fix internally the pCO_2 , which act as an important acid buffer. Another major buffer effect is the consequence of the dissolution of the minerals, which consumes the hydroxide ions.

Important change involved the dissolution/precipitation of mineral phases (Figure 2) after a diffusion period of time of 100,000 years:

Between 0.40 and 0.70 m from the interface, the dissolved potassium concentration increases because the concrete porewater is more potassic than the host water and the precipitation of K-clinoptilolite is favoured at the expense of Na-montmorillonite and cristobalite. Partial dissolution of montmorillonite provides magnesium that is incorporated in Na-saponite. Within this zone, Na-montmorillonite is progressively replaced by Ca montmorillonite since concrete porewater is slightly richer in calcium. Between 0.10 and 0.40 m, both Ca and Na-montmorillonite are illitized. Zeolites become the predominant phases and replace illite, which is entirely dissolved at 0.10 m from the concrete. Mg released by illite dissolution is included in Na and Ca-saponite. Between 0.00 and 0.10 m, cement phases (Afwillite, Tobermorite, Katoite and Hydrotalcite) precipitate in replacement of zeolite phases. The increase in pH favours the precipitation of calcite. The strong increase of the total molar volume (9000cm^3) near the interface can be considered as a closure of the porosity. This phenomenon will diminish the extent of the perturbation.

COX. As the COX is a more complex rock than the MX80, the buffer effect on the pH is stronger and no instability in pH is observed near the interface. Some differences are observed in the mineralogical evolution of the barrier, however the major reaction paths are conserved.

An empirical relation has been calculated given the extension of mineralogical transformation in function of both diffusion coefficient (D , m^2/s) and time (t , year). The best-fitting expression for the empirical relation has the following form:

$$P = A \cdot \sqrt{t \cdot D} \quad \text{with } A = 498 \text{ for COX and } 555 \text{ for MX80.}$$

4. Conclusion

The simulation of the effects of an alkaline perturbation on some complex mineralogical systems including surface reactions is possible with the actual numerical means.

The simulation of the diffusion of an alkaline plume from concrete through two types of clayey barriers shows:

- a strong pH buffering effect close to the clayey/concrete interface ($< 2\text{m}$ for $D=10^{-9}\text{m}^2/\text{s}$ and 100,000 years)
- an important mineralogical transformation of the barrier close to the concrete interface

These modelling meet several limits: (i) the use of one single diffusion coefficient, (ii) the diffusion coefficient do not change when the total molar volume of the minerals changes. Our modelling do not take into account (iii) the effect of inhomogeneous diffusion in the matrix as observed at Mol URL and (iv) a pre-oxidised zone resulting from the introduction of O_2 in the galleries of the disposal. However, compare to natural analogues, the results seems realistic. They can be exploited for safety analyses and for the scenarios of evolution of the disposal.

Potential complications in the development of a thermodynamic database for hyperalkaline, argillaceous systems

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Background

Geological disposal concepts for radioactive wastes generally call for a bentonite buffer and/or bentonite-containing backfill to be emplaced between the host rock and other components of the engineered-barrier system (EBS; including the waste form, metallic containers and cementitious materials used for encapsulation, structural support and backfilling purposes). When fully water-saturated at high compaction densities, bentonite is an ideal barrier material due to its favorable physical and rheological properties under such conditions. These properties include:

- an extremely low *hydraulic conductivity*, which ensures that a diffusional transport barrier will exist between the host rock and EBS;
- a *permeability* to gas flow that is high enough to allow any gases generated by corrosion of metallic components of the EBS to pass through the barrier without forming permanent permeable channels or cavities;
- a *swelling pressure* that is sufficiently high to establish and sustain good contact with the host rock and EBS, but not so high as to deform individual components of the EBS, or fracture the rock;
- a *deformability* that is high enough to absorb rock movements, but not so high as to cause the position of EBS components to shift in their deposition holes or drifts;
- a *filtration* capacity that effectively stops the migration of colloidal-sized particles; and
- a *thermal conductivity* that is sufficiently high to ensure rapid dissipation of radiogenic heat.

These properties arise from the unique mineralogical characteristics of bentonite. Bentonites contain dioctahedral smectite clays (montmorillonites, and possibly also nontronites and/or beidellites) along with lesser amounts of quartz, feldspars, zeolites, carbonates and sulfides. The clay minerals have a characteristic 2:1 lattice structure consisting of one octahedrally coordinated layer between two tetrahedrally coordinated sheets. Isomorphous substitutions in the octahedral and tetrahedral layers result in a low interlayer charge, which allows the crystalline lattice to expand rapidly and reversibly as hydrated cations are exchanged for less hydrated cations in interlayer positions. The expandable nature of the smectite clays controls the swelling pressure of bentonite as a function of water content, water chemistry and compaction density. The swelling pressure in turn directly affects the hydraulic conductivity, gas permeability, deformability and filtration properties of this barrier material.

Given the importance of mineralogy in controlling the physical and rheological properties of bentonite, the question arises whether plausible conditions in a repository environment could adversely affect the long-term stability of bentonite minerals. The potential for such alteration by hyperalkaline fluids, which are likely to be produced by the interaction of cementitious materials in the repository with groundwater (*e.g.*, Berner, 1992), is a matter of some concern because the expandable clay minerals may not be stable in the presence of high-pH solutions (*e.g.*, Savage *et al.*, 2002). Resultant reactions could lead to irreversible changes in mineralogy, and thus to undesirable changes in the physical, chemical and rheological properties of bentonite barriers.

Literature review

Experimental, natural-system and modeling studies dealing with the alteration of clay-bearing materials by high-pH solutions were reviewed in the present study. The objective of this work is to identify minerals, aqueous species and reactions that should be included in a thermodynamic database that can be used with appropriate geochemical models to assess the long-term stability of bentonite barriers in geologic repositories for nuclear wastes. Our review covers the period from 1999 to the present. The older literature is summarized by Savage *et al.* (2002).

Batch experiments at relatively high temperatures ($\approx 50^\circ - 200^\circ\text{C}$), along with a limited number of open-system experiments, modeling studies and field studies of natural high-pH systems, all demonstrate that clay-bearing materials can be strongly altered by contact with hyperalkaline fluids containing high concentrations of Na or K. Details concerning the extent of alteration and associated changes in mineralogy are not completely consistent among these studies. In general, however, alteration appears to involve the following sequence of reactions:

- partial rearrangement of the stacking sequence of smectite layers, and possible amorphization of clay particles;
- dissolution of discrete smectite, or selective dissolution of smectite in mixed-layer clays, with possible neoformation of different smectite types (*e.g.*, beidellites, saponites) by direct precipitation from aqueous solution or by isomorphous substitution on octahedral or tetrahedral sites;
- formation of illite from smectite via a layer-by-layer replacement process or by a dissolution-recrystallization process;
- precipitation of zeolites (often including Na-, K-phillipsites and analcime); and
- precipitation of K-feldspar and quartz.

Carbonates, CSH and/or CASH solids/gels, and Ca-Mg hydroxides may also precipitate, and may later dissolve, at all stages of the above reaction sequence.

These results suggest that a thermodynamic database supporting models of bentonite-cement interactions should include properties (*e.g.*, equilibrium constants or derived standard molal

thermodynamic quantities) for both the dioctahedral and trioctahedral smectite clays. Similar properties should also be included for minerals that directly or indirectly affect the stabilities of these clay minerals (*i.e.*, illites, zeolites, CSH/CASH phases, carbonates, Ca- and Mg-hydroxides, K-feldspar and quartz). There has been little experimental investigation of the aqueous-speciation behavior of key mineral-forming elements (*e.g.*, Si and Al) under hyperalkaline conditions.

Conceptual uncertainties related to the thermodynamic properties of bentonite minerals

The studies considered in our literature review reveal several sources of conceptual uncertainty that could complicate efforts to develop a reliable thermodynamic database for clay-bearing, hyperalkaline systems:

- the mineralogy, structural formulae and crystallinity of secondary solids produced by the interaction of clay-based materials with high-pH fluids have not generally been well characterized;
- the basic thermodynamic properties of representative clay minerals, zeolites and CSH/CASH solids/gels are poorly known in many cases;
- early mineral assemblages tend to be metastable, and may slowly transform to a series of progressively more stable assemblages over time scales as long as thousands to millions of years;
- precipitates may be amorphous or poorly crystalline, and may persist metastably with respect to their crystalline counterparts over long periods of time; and
- crystalline solids are often complex solid solutions that exhibit a considerable compositional range depending on the chemistry of the coexisting aqueous phase (especially pH, $\text{SiO}_2(aq)$ activity and cation content).

Minerals that should be represented in a thermodynamic database for such systems thus tend to be complex, possibly metastable solids having highly variable compositions that have not, in general, been well characterized experimentally or thermodynamically. Given the high costs and technical difficulties in conducting experimental investigations of the basic thermodynamic properties of minerals and aqueous species, it seems unlikely that such studies would be able to provide all the needed data in a timely manner.

A pragmatic approach that could be used to help deal with these problems involves the use of a consistent set of empirical methods to estimate missing thermodynamic parameters, combined with uncertainty analyses to assess the importance of the resultant, possibly large uncertainties on models of the alteration of clay barriers by high-pH fluids (*e.g.*, Savage *et al.*, 2002; Gaucher *et al.* 2001). An estimation technique that is particularly useful for silicate minerals, for example, uses a set of elemental building blocks composed of unique polyhedra to represent a mineral's crystalline structure, composition and coordination environment (Hazen, 1988). By summing the contributions from each polyhedron, thermodynamic properties can be estimated for the complete mineral. This representation is useful because it permits routine calculation of the thermodynamic properties of minerals for which experimentally determined properties are unavailable, and calculation of ranges in property

values that are consistent with minerals having variable compositions. The reliability of the estimated data can be checked by comparison of predicted and observed stability relations in laboratory and natural systems, and by comparison of estimated values with their available experimental counterparts.

Conclusions

Minerals that should be represented in a thermodynamic database supporting models of bentonite-cement interactions include the smectite clays, as well as other minerals that directly or indirectly affect the stabilities of these clay minerals (*i.e.*, illites, zeolites, CSH/CASH phases, carbonates, Ca- and Mg-hydroxides, K-feldspar and quartz). Calorimetric, solubility and/or phase-equilibrium studies on the thermodynamic properties of the clay minerals, zeolites and CSH/CASH phases are generally lacking. Interpretation of such properties based on the limited experimental data that are available is further complicated by solid-solution behavior and associated ranges in mineral chemistry, by a common tendency to form metastable mineral assemblages that may persist over long periods of time, and by variations in crystallinity. An approach that could be used to help deal with these problems would utilize existing empirical techniques to estimate missing thermodynamic properties (*i.e.*, Gibbs free energies and enthalpies of formation, and standard entropies, heat capacities and volumes) and uncertainty analyses to evaluate the importance of associated uncertainties on models of bentonite-cement interactions. Additional experimental work may be needed to refine the estimates for key minerals identified in the uncertainty analyses, and to better characterize the aqueous-speciation behavior of mineral-forming elements in concentrated high-pH solutions.

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Nano/macro-based cation/water transport and adsorption in bentonite

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Abstract Microscale sorption characteristics of bentonite are treated together with the diffusion mechanism under a coupled molecular dynamics (MD) simulation and homogenization analysis (HA). The diffusion coefficient is evaluated by MD. The sorption caused at the edge part of clay minerals is modeled as a source term in the microscale equation of HA (*micro-sorption*). A through-diffusion experiment is simulated numerically. The calculated concentration and macroscale break-through curve are agreeable.

Key words: bentonite, clay hydrate, micro-sorption, diffusion, homogenization

INTRODUCTION

Bentonite is a candidate buffer material for high-level radioactive waste (HLW) disposal [1]. Bentonite mainly consists of micrometer scale quartz particles and nanometer scale smectite clay minerals such as montmorillonite and beidellite. Chemical properties of the bentonite are characterized by the clay minerals. One clay mineral is a platelet (Fig. 1), which is called a layer, with the thickness ca.1 nm and the width ca.100×100 nm. The mineral surface is negatively charged. Several layers cohere to form a stack, and a group of stacks constitutes an aggregate or a ped. Microscope images of Kunigel V1 of Kunimine Co. are shown in Fig. 2.

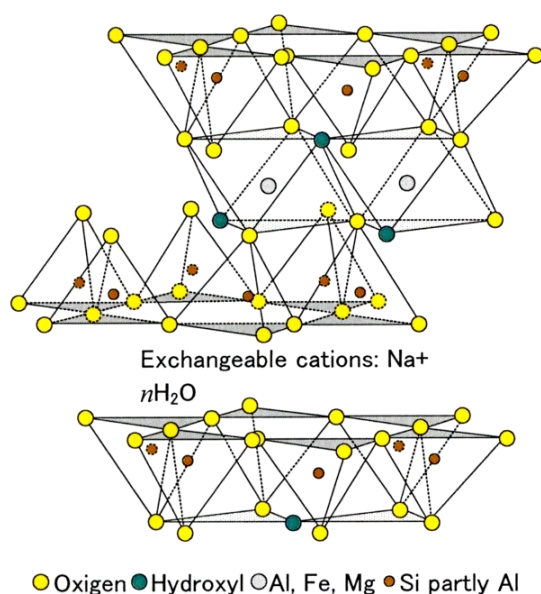


Fig. 1 Atomic structure of montmorillonite

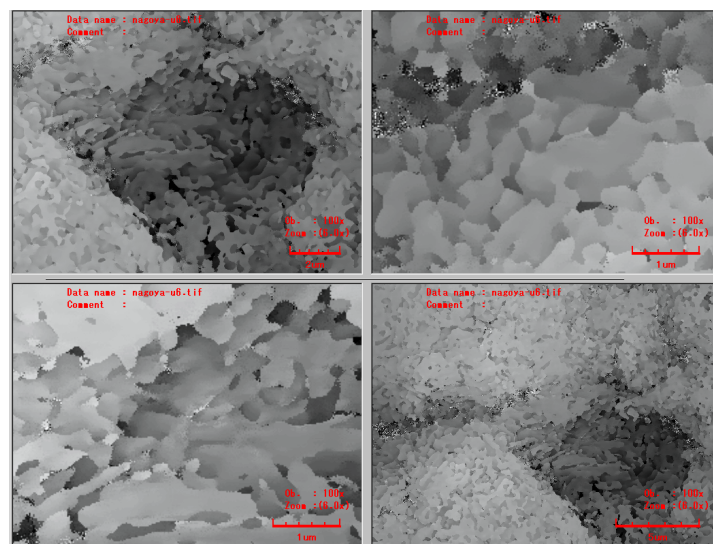


Fig. 2 High-resolution images of a bentonite sample by confocal laser scanning microscopy

The sorption behavior is commonly treated by evaluating the distribution factor K_d [1]. The K_d value is determined by the batch method or by a combination of the non-steady state method (i.e., the in-diffusion method giving an apparent diffusivity D_a) and the steady state method (i.e., the through-diffusion method giving an effective diffusivity D_e). Both are related as

$$D_a = \frac{D_e}{n + (1-n)\rho_s K_d}$$

where n is the porosity, and ρ_s is the true density of solid-part of clay minerals (ca. 2.7 Mg/m³). A lot of discussions have been given on these experimental methods, since the distribution factor K_d for each chemical species determined by these experiments is severely scattered. In addition let us observe the following conventional diffusion equation including retardation coefficient R_d

$$R_d \frac{\partial c}{\partial t} - \frac{\partial}{\partial x_i} \left(D_e \frac{\partial c}{\partial x_i} \right) = 0, \quad R_d = 1 + \frac{(1-n)\rho_s K_d}{\rho_w}.$$

Here ρ_w is the water density, and R_d represents the sorption characteristics. We understand that only the ratio of R_d to D_e can be determined in this equation. This may be physically unacceptable. The conventional theory must involve difficulties to simulate the true diffusion procedure including sorption.

We here show that the diffusion/sorption behavior in compacted bentonite can be treated by considering adsorption at edges of clay mineral and diffusion in the interlayer spaces of clay minerals. The sorption behavior is given as a microscale source term, and we call this a micro-sorption mechanism. For this purpose we develop a new homogenization analysis (HA) method to explain the micro-/macro-diffusion behavior including micro-source term due to edge-sorption. The diffusion characteristics are specified by the molecular dynamics (MD) simulation.

MD SIMULATION

Crystalline structures of layered silicates, [alkaline metal]-Mg-Al-Si-H-O, such as

Muscovite	$KAl_2(OH)_2[Si_3AlO_{10}]$	Phlogopite	$KMg_2(OH)_2[Si_3AlO_{10}]$
Paragonite	$NaAl_2(OH)_2[Si_3AlO_{10}]$	Pyrophyllite	$Al_2(OH)_2[Si_4O_{10}]$
Talc	$Mg_3(OH)_2[Si_4O_{10}]$	Kaolinite	$Al_2(OH)_4[Si_2O_5]$

are well-known. The 2-body and 3-body interatomic potential functions for MD are determined so that material properties of the above silicates (e.g., the lattice constants) and water (e.g., density and dielectric constant depending on temperature) are represented well. Details are found in [2].

The material property which we need in the subsequent HA is diffusivity in the interlayer space of clay minerals for each chemical species. In our analysis we treat cesium ion Cs^+ , and by a MD simulation we have the diffusion coefficient $2.0 \times 10^{-9} \text{ m}^2/\text{s}$ in external pore water and $2.62 \times 10^{-10} \text{ m}^2/\text{s}$ in inter-layer space.

HA WITH MICRO-SORPTION

The governing equation of mass transport is given by

$$\frac{\partial c^\varepsilon}{\partial t} + v_j^\varepsilon \frac{\partial c^\varepsilon}{\partial x_j} - \frac{\partial}{\partial x_i} \left(D_{ij}^\varepsilon \frac{\partial c^\varepsilon}{\partial x_j} \right) + f^\varepsilon = 0 \text{ in } \Omega_f. \quad (1)$$

where c^ε is the mass concentration (the upper script ε implies a locally rapid-changing value), \mathbf{v}^ε the velocity vector, D_{ij}^ε the diffusion coefficient, f^ε the source term and Ω_f the flow region. We consider the adsorption at the edges of clay minerals, so f^ε consists of the true source term $\dot{\gamma}$ such as chemical reaction and the adsorption term $\dot{\gamma}^{\text{ad}}$ at the microscal edge domain Ω_{ad} (Fig. 3):

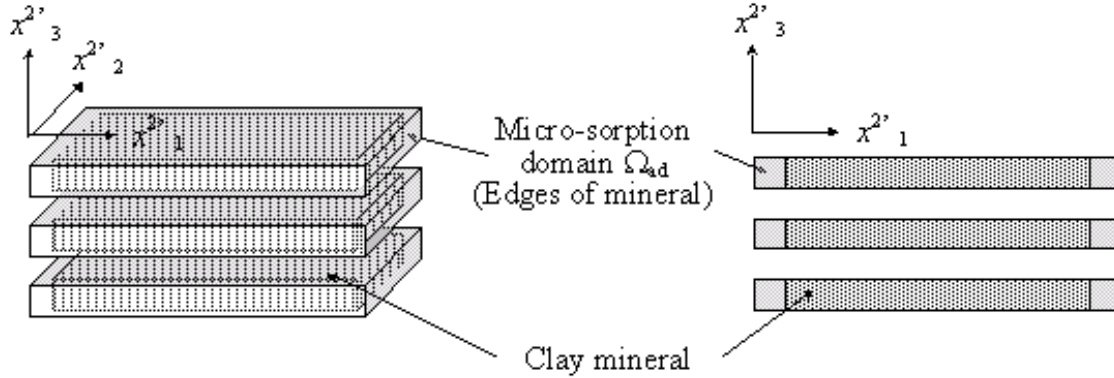


Fig. 3 Micro-sorption domain at the clay edge

$$\dot{\gamma}^{\text{ad}} = \begin{cases} s(c^l - c) & \text{if } c < c^l \\ 0, & \text{if } c = c^l \end{cases} \quad (2)$$

Here s is the adsorption coefficient determined by the data of the site number, pH etc. [3], and c^l is the limit value of concentration adsorbed at the edge domain Ω_{ad} . Note that the domain Ω_{ad} is determined by the ion radius and the number of adsorbed layers [3].

1. Two-scale HA We introduce a two-scale system such as \mathbf{x}^0 , the global coordinates in the macro-domain Ω_1 , and \mathbf{x}^1 , the local coordinates in the micro-domain Ω_2 . Then the differentiation of (1) changes to

$$\frac{\partial}{\partial x_i} = \frac{\partial}{\partial x_i^0} + \frac{1}{\varepsilon} \frac{\partial}{\partial x_i^1}. \quad (3)$$

The perturbation is introduced for the concentration $c^\varepsilon(\mathbf{x};t)$ by

$$c^\varepsilon(\mathbf{x};t) = c^0(\mathbf{x}^0, \mathbf{x}^1; t) + \varepsilon c^1(\mathbf{x}^0, \mathbf{x}^1; t) + \dots \quad (4)$$

where c^α s ($\alpha=0,1,2,\dots$) are periodic functions. The micro-sorption term (2) is set into the source term as

$$f^\varepsilon = \varepsilon^{-1} \Gamma_i(\mathbf{x}^1) \frac{\partial c^0}{\partial x_i^0}; \quad \dot{\gamma}^{\text{ad}}(\mathbf{x}^1; t) = \Gamma_i(\mathbf{x}^1) \frac{\partial c^0}{\partial x_i^0} \quad (5)$$

The reason why we introduce this term will be clarified later. Substituting (3), (4) and (5) into (1) and taking $\varepsilon \rightarrow 0$, we get the following partial differential equations corresponding to each ε -term.

$$\varepsilon^{-2}\text{-term: } \frac{\partial}{\partial x_i^1} \left(D_{ij}^\varepsilon \frac{\partial c^0}{\partial x_j^1} \right) = 0 \Rightarrow c^0(\mathbf{x}^0, \mathbf{x}^1; t) = c^0(\mathbf{x}^0; t) \quad (6)$$

$$\varepsilon^{-1}\text{-term: } -\frac{\partial}{\partial x_i^1} \left[D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} \right) \right] + \Gamma_k \frac{\partial c^0}{\partial x_k^0} = 0 \quad (7)$$

Let us introduce the characteristic function $N_1^k(\mathbf{x}^1)$ such that

$$c^1(\mathbf{x}^0, \mathbf{x}^1; t) = -N_1^k(\mathbf{x}^1) \frac{\partial c^0(\mathbf{x}^0; t)}{\partial x_k^0} \quad (8)$$

Then (7) is reduced into the following *microscale PDE*:

$$\frac{\partial}{\partial x_i^1} \left[D_{ij}^\varepsilon \left(\delta_{jk} - \frac{\partial N_1^k}{\partial x_j^1} \right) \right] - \Gamma_k = 0 \quad (9)$$

This can be solved under a microscale periodic boundary condition. Now the reason why the micro-sorption term (5) is introduced is obvious if we observe (7), (8) and (9).

$$\varepsilon^0\text{-term: } \frac{\partial c^0}{\partial t} + v_j^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} \right) - \frac{\partial}{\partial x_i^0} \left[D_{ij}^\varepsilon \left(\frac{\partial c^0}{\partial x_j^0} + \frac{\partial c^1}{\partial x_j^1} \right) \right] - \frac{\partial}{\partial x_i^1} \left[D_{ij}^\varepsilon \left(\frac{\partial c^1}{\partial x_j^0} + \frac{\partial c^2}{\partial x_j^1} \right) \right] = 0 \quad (10)$$

We introduce the volume average for (10) in the micro-domain Ω_1 , then all the terms concerning $\partial(\cdot)/\partial x_i^1$ are vanished due to the periodic condition. So we have the following *macroscale PDE*:

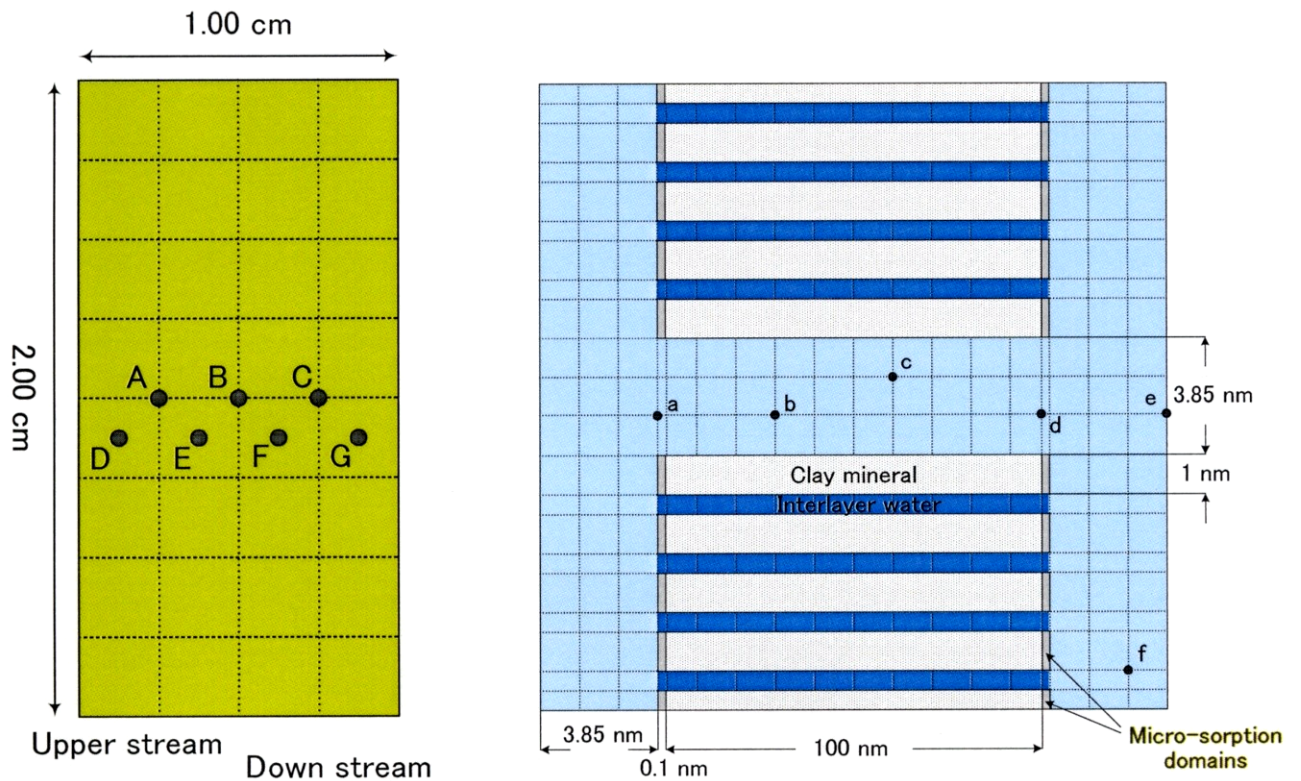
$$\frac{\partial c^0}{\partial t} + v_j^H \frac{\partial c^0}{\partial x_j^0} - \frac{\partial}{\partial x_i^0} \left(D_{ij}^H \frac{\partial c^0}{\partial x_j^0} \right) = 0 \quad (11)$$

$$D_{ij}^H = \frac{1}{|\Omega_1|} \int_{\Omega_1} D_{ik}^\varepsilon \left(\delta_{kj} - \frac{\partial N_1^k}{\partial x_j^1} \right) d\mathbf{x}^1, \quad v_j^H = \frac{1}{|\Omega_1|} \int_{\Omega_1} v_j^\varepsilon d\mathbf{x}^1$$

The first order approximation of the mass concentration can be given as

$$c^\varepsilon(\mathbf{x}; t) = c^0(\mathbf{x}^0; t) + \varepsilon c^1(\mathbf{x}^0, \mathbf{x}^1; t) = c^0(\mathbf{x}^0; t) - \varepsilon N_1^k(\mathbf{x}^1) \frac{\partial c^0}{\partial x_k^0} \quad (12)$$

2. Numerical example We simulate a through-diffusion experiment of a pure smectite clay specimen with thickness 1 cm as shown in Fig. 4(a). In the micro-domain given in Fig. 4(b) we introduce 8 stacked clay minerals with thickness 1 nm and width 100x100 nm, which are randomly distributed in the macro- domain. As shown in the MD analysis the diffusion coefficient in the external pore water is calculated as $2.0 \times 10^{-9} \text{ m}^2/\text{s}$, and one in the inter-layer space is as $2.62 \times 10^{-10} \text{ m}^2/\text{s}$. The upper stream boundary concentration c^{Up} is given as 1.0×10^{-2} , 1.0×10^{-3} , and $1.0 \times 10^{-4} \text{ mol/l}$. The microscale model involves adsorption edge parts whose volume is determined as follows: the total edge surface is estimated as $35 \text{ m}^2/\text{g}$ by the BET method [4] and its half is effective, so the total amount of Cs which can be adsorbed on edge surface is $m_{lim} = 6.51 \times 10^{-5} \text{ mol/g}$. Here the ion radius r of Cs is assumed as 0.334 nm, and the shape of one clay mineral as $100 \times 100 \times 1 \text{ nm}$. The adsorption volume is set at each edge site in the microscale model with the thickness 0.1 nm where the above amount of adsorption occurs. That is, in the edge volume we have the condition $c \leq c^l$ where the limit value c^l is calculated by using m_{lim} . The calculated time- dependent change of concentrations at the points D and G of Fig. 4(a) are given in Fig. 5 in which the cases without adsorption are shown for comparison. Note that the unit of the vertical axis of Fig. 5 is a percentage to the upstream concentration.



(a) Macro-domain model

(b) Micro-domain model

Fig. 4 Through-diffusion model

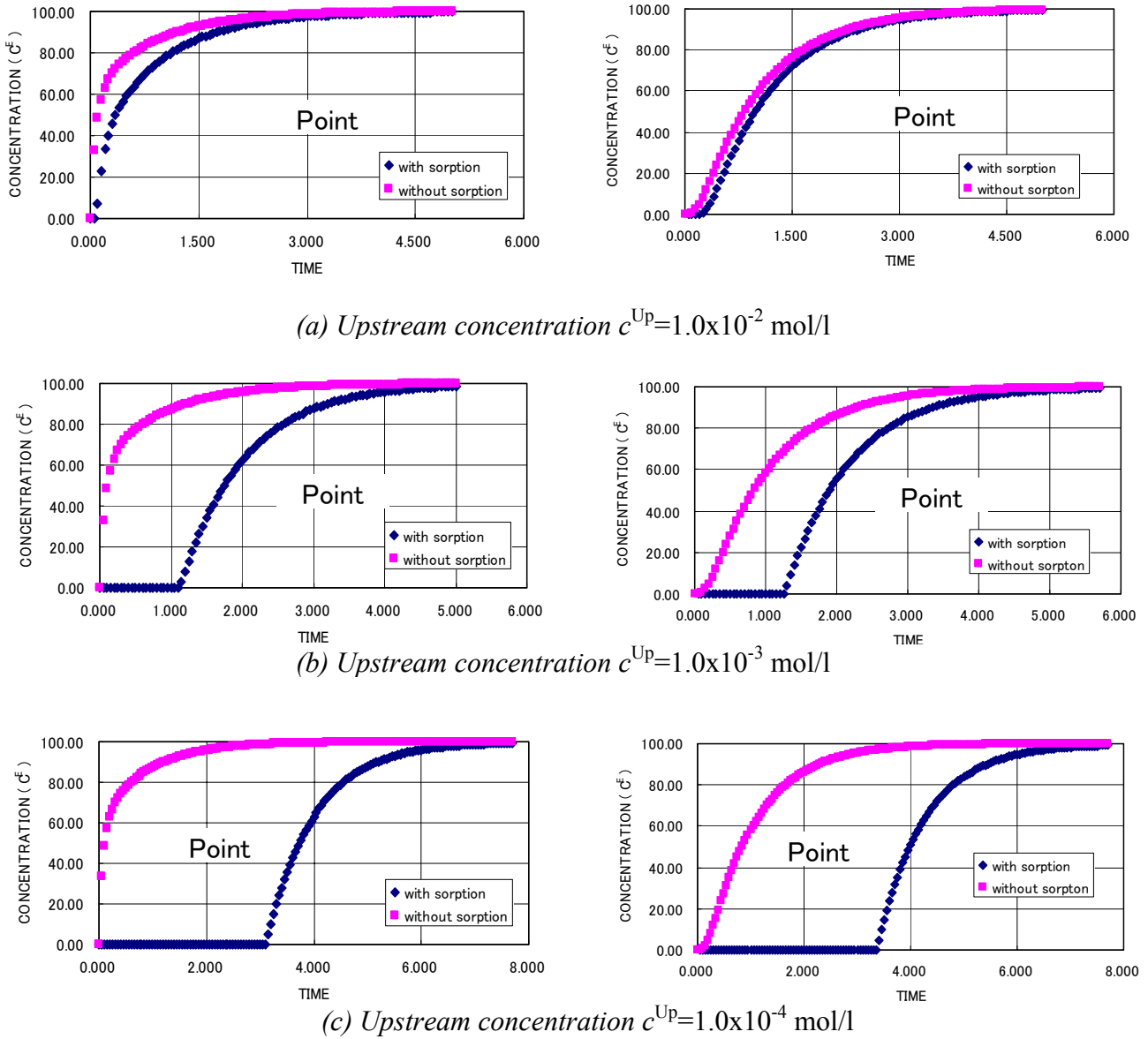


Fig. 5 Break-through curves

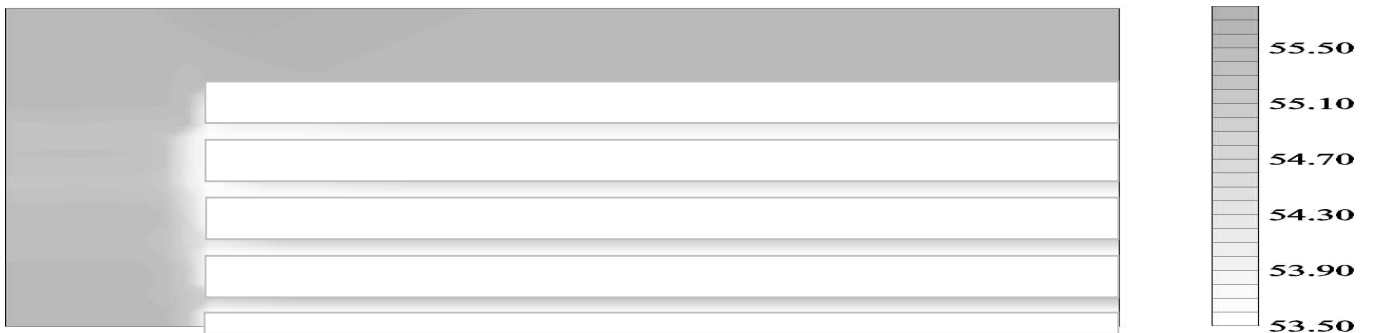


Fig. 6 Distribution of mass-concentration in the micro-domain for the above case (b). (Representing the 1/4 domain and the scale indicates the percentage to the upstream boundary concentration $c^{Up}=1.0 \times 10^{-3}$ mol/l.)

CONCLUSIONS

In existing theories the adsorption is usually treated as the the distribution factor K_d , which gives the ratio of the mass of solid part to the mass of liquid part. Theoretically this does not completely give the correct chemical procedure of adsorption for the bentonite clay. We here showed a new method to represent the microscale adsorption behavior.

Bentnite consists of nanometer scale of smectite clay minerals. The adsorption of smectite is mainly induced at the edge part of minerals, and the adsorption is treated as a microscale source term at the edge domain under a homogenization analysis (HA) method. We call this as the micro-sorption term. Note that the microscale diffusion property is specified by the molecylar dynamics (MD) simulation.

The calculated break-through curve (Fig. 5) is acceptable. In further development we will extend this to a multiscale problem.

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Status of Cement Modelling

Future investigations in the view of cement/bentonite interactions

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Contribution to an International Workshop on Bentonite – Cement Interaction in Repository Environments, Tokyo, Japan, April 14-16, 2004

Interactions of cement with bentonite, or more generally, the interplay between high-pH systems and clayish solids are topics that are discussed since the beginning of waste solidification with cementitious materials. Although substantial progress was achieved in many associated scientific areas, till this day a crucial overall break-through did not take place in the “pH-plume” topic.

This may be because a deeper understanding of this topic requires that many different chemical and physical processes, which themselves may proceed in parallel with different time constants, must be linked with one another. The substantial progress as mentioned above was made in e.g., diffusion in compacted systems, in large-scale hydrological systems, in rock mechanics or in the chemistry and thermodynamics of solid phases. However, combining all these new scientific realisations to a comprehensive picture in order to achieve the mentioned break-through requires the definition of a waste disposal system as realistic as possible. Unfortunately it is not sufficient to achieve progress in discrete and independent investigation areas.

The presentation specifically considers the issue of cement modelling. From a chemical point of view, cement represents some kind of a singularity when located in a quasi-natural environment like a bentonite barrier. Large chemical gradients will establish between the cement and its neighbourhood, thus generally inducing a material flow from the cement to the bentonite. Exceptions to this may include carbonate and magnesium, maybe also sulfate and chloride. In such environments the cement and its pore solution behave as source term. Hence, investigations dealing with the mentioned interactions call for elementary knowledge on the thermodynamic characteristics of cement phases and wherever possible on their kinetic behaviour.

Since about 20 years the geochemical behaviour of cement phases is described using more and more realistic models having continuously increasing complexities [1-9]. Three distinct stages may be differentiated when hydrated cement is degraded under ambient and natural conditions:

- (i) the release of well soluble alkali hydroxides. This stage is short. It depends on the alkali content of the cement and on corresponding transport parameters. The release of hydroxide is of crucial importance when reactions with the surrounding bentonite/clay are considered. The hydroxide accelerates the dissolution of clays and accompanying Na^+ and K^+ promote the formation of secondary phases like illites or zeolites,
- (ii) the release of portlandite $(\text{CaOH})_2$ from the cement. This stage lasts for a long time. Reactions with the clay materials produce secondary CSH-phases with smaller Ca/Si ratios in the contact zone. Changes of the porosity need to be considered. However, the surrounding clay buffers such reactions (as it buffers reactions under (i)). In the Swiss case where plans foresee emplacement of cemented ILW wastes in Opalinus clay, about 1 m^3 of host rock is required to chemically buffer 4 m^3 of cemented waste matrix. This translates to only 0.5 m of transformed Opalinus clay around an 8.5 m in diameter emplacement tunnel when 100 % of the buffer capacity is utilized,

(iii) the release of silicates and aluminates. This phase lasts for a very long time. The chemical gradients have almost disappeared, but the former cement and the former clay still differ in structure. Compared to stage (i), a completely altered pore space needs to be considered due to phase transformations.

The results of a PSI long-term cement degradation experiment are used as a thread (Fig. 1), guiding through the formerly mentioned stages. The state of ongoing (PSI) research associated with the different stages is pointed out and summarised.

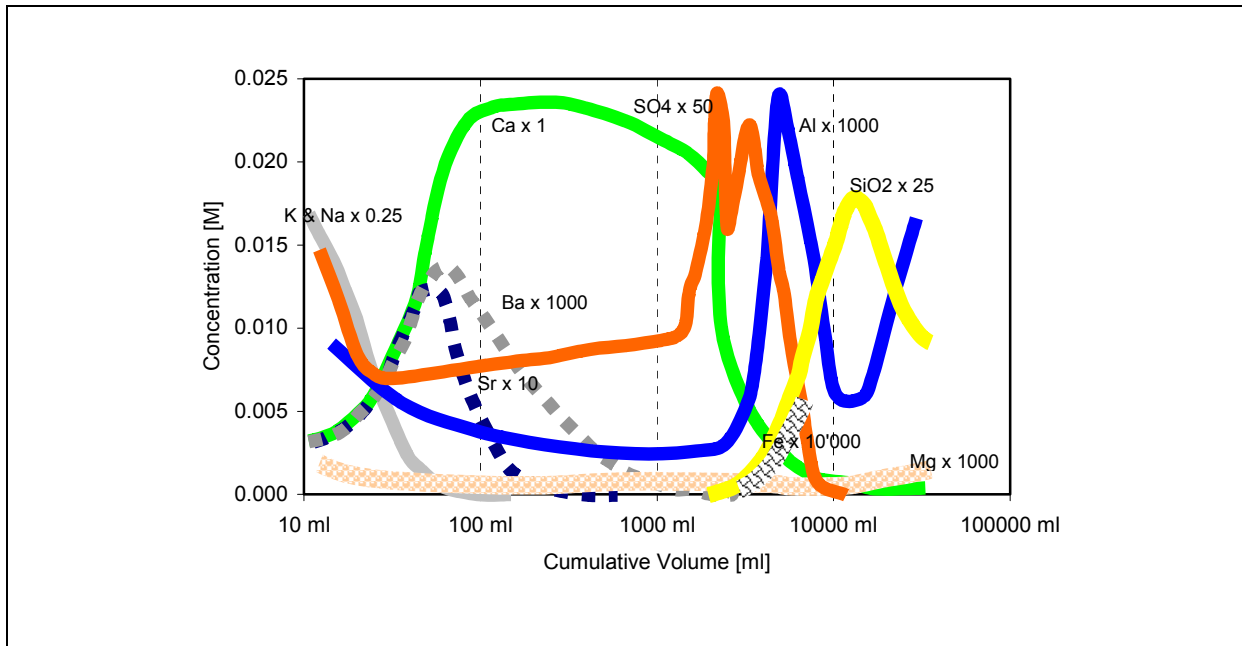


Fig. 1: A cement disc (volume 13 ml) was leached with pure CO₂-free water for more than 3 years (about 3000 pore volumes). The strongly schematised analyses are conveniently normalised to the size of the diagram.

An initial stage is governed by the dissolution of portlandite in strongly alkaline solution. Here, a still open problem is the distinction between the true solubility of portlandite and the formation of the complex $\text{Ca}(\text{OH})^+$. The question becomes particularly important when quantitative modelling at high pH and/or the composition of thermodynamic databases becomes an issue. In this pH-range the properties of both species belong to the essential thermodynamic data. A sensible and consistent evaluation of thermodynamic parameters for calcium silicates and -aluminates is hardly possible without them. However, the stabilities of both species just fall into that critical concentration range where activity corrections become an important issue. As long as an independent determination of the $\text{Ca}(\text{OH})^+$ -stability is missing, the understanding of this simple system is crucially influenced by the choice of the activity correction model (e.g., Davies, Extended Debye-Hückel, SIT, Pitzer). Unfortunately, this choice will affect the entire high-pH database and has to be done very carefully.

Important progress was made in the thermodynamic description of hydrated calcium silicates (CSH). Former model concepts on the basis of phase pure CSH solids initially provided good insights into this class of compounds, but it seems that these former models become now outdated. Today, solid solution concepts become state-of-the-art. These alternative concepts describe available solubility data as did former models, but they do it in a more fundamental way and with a substantially increased flexibility in quantitative applications. It turned out that structural aspects of the solid phases may and will become very important model

parameters. Therefore, future investigations must give special attention to sophisticated and differentiated analysis of the solids structural aspects, be it by classical (e.g., microscopic, XRD) or by all the different modern spectroscopic techniques. From my point of view two things are important when considering B/C interactions: (i) studying the retention of alkali hydroxides by neo-formation of CSH phases with alkalis. A retarded release of (“less high”) hydroxide concentrations may alter the vector of secondary precipitates, (ii) studying the formation of secondary CSH phases in the contact zone cement/clay, which has direct impact on the hydraulic system parameters.

Hydrated calcium aluminates do not contribute very much to the cement’s mass balance. However, for performance assessment this class of compounds (laminated calcium aluminates, ettringites, hydrotalcites) is important because it has a large potential for retaining anions within its structure. The present literature describes mainly solubilities and thermodynamic data for ettringite, which unfortunately exhibit a very large scattering among different authors. Data of this quality are of limited use only in quantitative applications. For the present PSI undertakes literature reviews to investigate the hydrated calcium aluminates. As a first result in this area, over 60 years old literature data on the solubility of hydrogarnet could smoothly be explained with the help of a simple ideal solid solution approach.

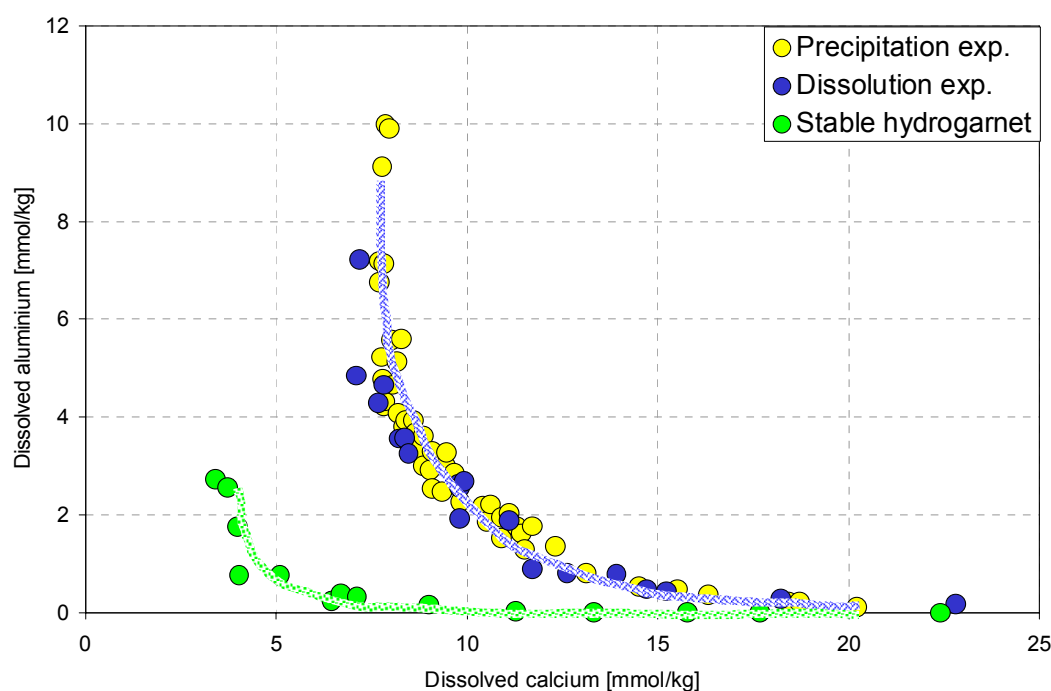


Fig. 2: Literature data on the solubility of stable (green dots) and metastable (yellow and blue dots) hydrogarnet in water [10]. A simple ideal solid solution approach produces very satisfying results (blue curve).

The convincing results will serve as basis for further investigations including more complex systems with additional anions such as sulfate or carbonate. Just as in the case of CSH phases, it was recognised that constricted thermodynamic stability fields, metastability (kinetic constraints) as well as structural aspects form important model parameters. Studies on the (solubility) behaviour of calcium aluminates in the presence of common anions are sparse and only few data are available. Instead, much more is known about the formation of solids

including these anions. Calcium aluminates do not have direct impact on B/C interactions, but are very important compounds when sorption and/or retention characteristics of secondary minerals need to be addressed. Relevant future fields of work on this topic were called.

Since the formation of secondary phases like illites, chlorites, zeolites, CASH phases, hydrotalcites, Mg-silicates etc. is not really the topic of this presentation, it's referred to the relevant literature, e.g., [11]. However, secondary mineral formation changes porosity and thus the hydraulic characteristics of the contact zone and its adjacent environments. From the point of view of cement the reaction of portlandite with the carbonate from the bentonite/clay pore water is essentially of interest. The thermodynamics of this reaction are undisputed and the precipitation of calcite is not kinetically hindered. This simple chemical system is well suited to demonstrate the expected fundamental effects. Figure 3 shows results of a two-dimensional model exercise of calcite formation after 500 and 2000 years of pure diffusion. A cement structure simulated by $\text{Ca}(\text{OH})_2$ (inside of the ring-shaped region) reacts with carbonate from the surrounding Marl pore water. Calcium from the cement diffuses into the host rock and carbonate from the host rock into the cement. Precipitated calcite reduces porosity to almost zero and decreases the hydraulic conductivity by orders of magnitude. A largely non-studied, "open field" in this context is the impact of changing geometries (porosity) on the hydraulic parameters.

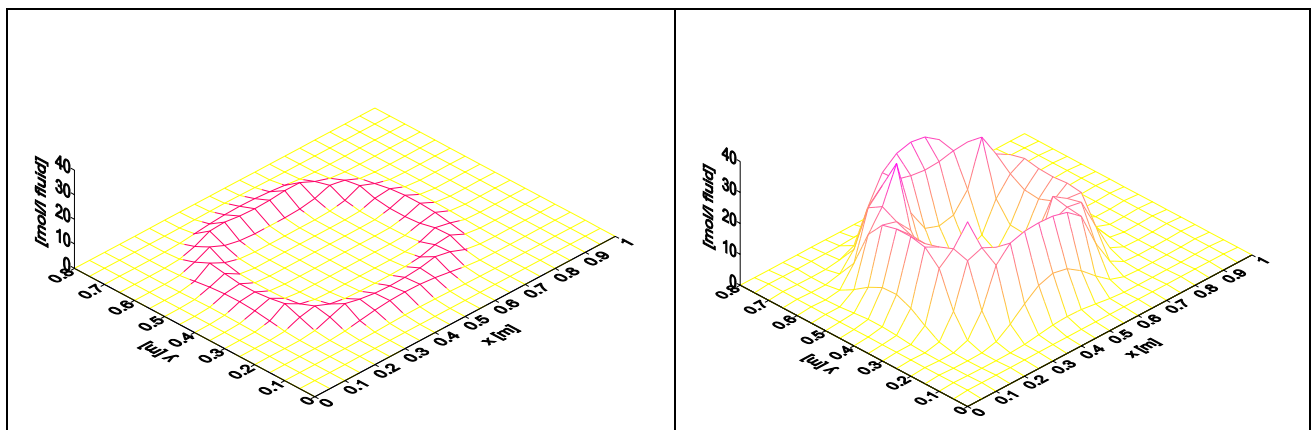


Fig. 3: Simulation of cement pore water reacting with carbonate groundwater, calculated for 500 (left) and 2000 (right) years. A peripheral rim characterized by substantial calcite precipitation forms in the contact zone around the cement. Pure diffusion system, hydraulic conductivity assumed to be $K=10^{-12}$ m/s [12].

Similar effects are to be expected for all ongoing mineral conversions, but of course do not all reactions decrease porosity. For example, Adler [11] predicts a complete clogging of the Opalinus clay (the Swiss host rock) after few years, based on corresponding experiments. The conclusions from these findings are self-evident: Porosity changes induced by mineral transformations as well as the respective changes of transport parameters should get high priorities in further investigations.

One has to note that such investigations should not be performed without simultaneously looking at real or very close to real systems. Laboratory studies are essential and will be able to point out general trends and maybe fundamental effects related to single, independent systems. However, repository systems, of which B/C-interactions are just a part, are highly integrated systems. Transport processes and chemical processes tend to affect each other

mutually strongly, and thus investigations with real materials under close to real conditions are indispensable as well.

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Discussion on PA model development for bentonite barriers affected by chemical interaction with concrete: Do we have enough evidence to support bentonite stability?

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1. Introduction

In many cases designs for geological disposal facilities for radioactive wastes adopt cement together with bentonite clay as engineered barriers. However, there are concerns that the mineralogical composition of the bentonite will not be stable under the hyperalkaline pore fluid conditions typical of cement and its properties will change over long time periods. Use of the low pH cement may solve this potential problem but, taking into account that vast amount of experience of using the Ordinary Portland Cement (OPC) in the similar environment exists, it is desirable to keep OPC as an option so that flexibility in designing and constructing the facility can be guaranteed. Thence alteration of bentonite clay under the hyperalkaline conditions remains as an issue in performance assessment.

In order to assess potential impact of the chemical alteration of the bentonite on its barrier performance, the following key questions have to be answered:

- How will the bentonite clay be altered by reactions with the hyperalkaline pore fluid?
- How much bentonite will be altered in the PA relevant time scale?
- Will the chemical alteration of bentonite lead to any significant adverse effect on its barrier performance?

In this presentation existing evidence relating to these questions is reviewed so that level of the current understanding can be assessed. In addition issues for further R&D are identified.

2. Processes relating to bentonite alteration

Reactions of bentonite clays with hyperalkaline fluids have been investigated in many studies (e.g. Steefel and Lichtner, 1994; Bauer and Berger, 1998; Savage et.al, 2002; Fujiwara et.al., 2003). Many of these studies note that short-term interactions are dominated by ion exchange processes, whereas in the longer-term and/or at high temperatures, mineral dissolution-precipitation reactions become more important. These two groups of processes have to be coupled together when we assess their significance since:

- Ca ion in solution will be removed when secondary minerals precipitate, resulting in retardation of ion exchange processes;
- Decrease in effective bentonite density due to dissolution will enhance partial loss of swelling capability caused by ion exchange.

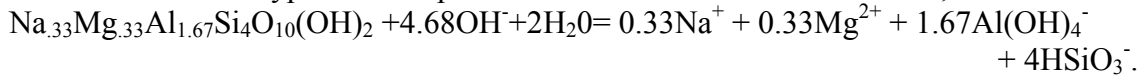
3. Three approaches to model bentonite dissolution

Since ion exchange is likely to take place in the entire buffer region fast enough within the PA time scale (Fujiwara et.al., 2003), we focus on the amount of montmorillonite that will dissolve in the time scale of interest. There are three distinct controls on total amount of bentonite to be dissolved in the hyperalkaline pore fluid. These are namely;

- constraint by mass balance,
- constraint by mass transport,
- constraint by reaction kinetics.

3.1 Constraint by mass balance

Assuming that HSiO_3^- is the dominant silica species in solution, dissolution of montmorillonite in the hyperalkaline pore fluid can be formulated as follows;



This implies that dissolution of unit mole of montmorillonite consumes 4.68 moles of OH^- . Assuming further;

- 8,000 moles of OH^- will be produced by reaction of 1 m^3 of concrete,
 - around 1,500 moles of montmorillonite is involved in 1 m^3 of buffer material,
 - montmorillonite is dissolved preferentially among the constituents of the buffer material,
- 10 cm thick OPC liner around a disposal tunnel of 2.2 m diameter filled with compacted bentonite (dry density 1.6 g/cm^3 ; mixture of 70% Kunigel V1 and 30% sand) can dissolve up to 20% of the initial amount of montmorillonite. This poses a constraint on amount of montmorillonite that can be dissolved by reacting with concrete. In case of thicker tunnel support and/or existence of concrete wall as in L/ILW repository, total amount of montmorillonite dissolution constrained by mass balance increases in proportion to the amount of concrete existing in the EBS. The constraint derived from this simple calculation, however, is uncertain for a number of reasons. Firstly precipitation of secondary minerals will contribute to consumption or generation of OH^- . For example, precipitation of tobermorite ($\text{Ca}_5\text{Si}_6\text{H}_{21}\text{O}_{27.5} = 5\text{Ca}^{2+} + 6\text{HSiO}_3^- + 4\text{OH}^- + 5.5\text{H}_2\text{O}$) will enhance pH buffering capacity and decrease the amount of montmorillonite to be dissolved, whereas precipitation of analcite ($\text{Na}_{.96}\text{Al}_{.96}\text{Si}_{2.04}\text{O}_6 \cdot \text{H}_2\text{O} + 2.04 \text{OH}^- + 0.92\text{H}_2\text{O} = 0.96\text{Na}^+ + 0.96 \text{Al}(\text{OH})_4^- + 2.04 \text{HSiO}_3^-$) and laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O} + 4 \text{OH}^- = \text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 4 \text{HSiO}_3^-$) will generate OH^- and increase amount of montmorillonite dissolution. If we assume that all the silica generated by montmorillonite dissolution precipitates as analcite or laumontite, 10 cm thick OPC liner is sufficient to supply OH^- ion required to dissolve all the montmorillonite existing in the 2.2m diameter disposal tunnel. Secondly a significant fraction of OH^- generated by concrete reaction can migrate out of the EBS and react with the near field host rock, resulting in decrease of montmorillonite dissolution. Thirdly minerals in the buffer material other than montmorillonite, e.g., quartz and chalcedony, can dissolve and consume OH^- , leading to decrease of montmorillonite dissolution. In summary it is difficult to specify a useful constraint on the amount of montmorillonite dissolution based on consideration of mass balance unless sequence of secondary mineral precipitation, transport of OH^- out of the EBS and relative time scale of dissolution of various pH buffering minerals in the buffer material are taken into account.

3.2 Constraint by mass transport

All the OH^- ion to be generated by concrete reaction may not react with bentonite since slow diffusive transport of OH^- into the buffer material, in comparison with advective transport around the tunnel, could limit cumulative amount of OH^- reacting with the bentonite. This leads us to consider a constraint on the amount of montmorillonite dissolution by mass transport. OH^- initially existing in concrete will dissolve into solution and react with montmorillonite and other pH buffering minerals. At this stage OH^- will be in the form of HSiO_3^- that can be transported in and around the buffer material. Following this step, precipitation of secondary minerals will take place. As we described above, candidates of the secondary minerals that will precipitate under hyperalkaline conditions,

e.g., tobermorite, tend to consume OH^- , whereas candidates for secondary minerals under milder pH conditions such as analcite and laumontite will generate OH^- . This implies that OH^- will be stored in the high pH product initially and gradually return into the solution as those minerals dissolve again at lower pH. This, together with formation of OH^- generating secondary minerals, will retard the pH decrease and result in prolonged tail of hyperalkaline plume. Dissolution of montmorillonite constrained by transport of OH^- ion in and around the buffer material together with its storage in and release from the sequence of secondary minerals can be simulated by combining mass transport equations with a number of mineral reactions including montmorillonite assuming local instantaneous equilibria. Figure 1 illustrates an example of such simulations, which provides a less pessimistic constraint than the one derived by considering mass balance (see 3.1). We need to be careful, however, since this is constrained by mass transport through the altered bentonite region where information that can be used to specify type of secondary minerals to form in the PA time scale is very much limited. Our estimate on the mass transport characteristics of this layer of unidentified secondary minerals thence inevitably includes significant uncertainty. This might be acceptable in case of the interface between the concrete structure of L/ILW repository and the bentonite clay surrounding it since unaltered bentonite around the altered region will provide barrier against advective transport and a reasonable upper bound for effective diffusion coefficient in the altered bentonite region may be assumed. On the other hand bentonite alteration at its interface with the surrounding concrete liner may initiate advective transport if altered bentonite exhibits greater hydraulic transmissivity, leading potentially to “fingering” of the alteration front.

Existing experimental studies (e.g.; Jefferies et al., 1988; Fujiwara et al., 2003) suggest that dissolution of montmorillonite coupled with precipitation of the secondary minerals can result in net decrease in porosity, effective diffusion coefficient and hydraulic conductivity. However it is likely that the secondary minerals observed in the experiments will be slowly transformed into more stable minerals and it is difficult to justify assuming barrier function of the altered bentonite region over PA time scale.

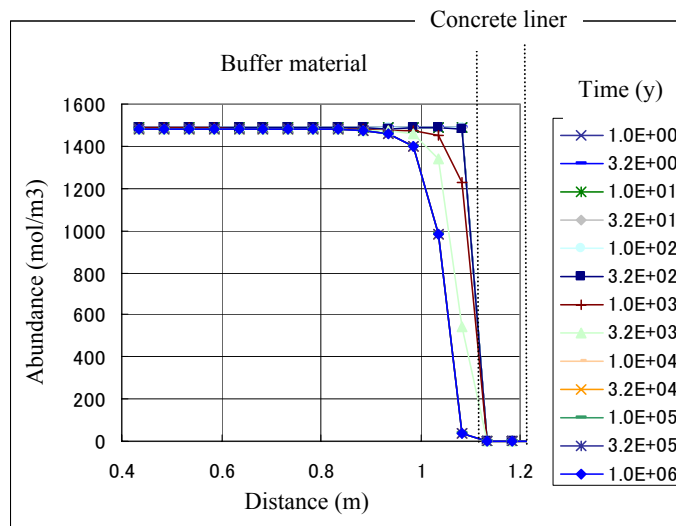


Figure 1 Amount of montmorillonite dissolution constrained by mass transport (HLW)

3.3 Constraint by reaction kinetics

Kinetics of montmorillonite dissolution can be regarded as a direct constraint on the amount of dissolution. A number of studies have been carried out on reaction kinetics of the montmorillonite dissolution. In many of them enhanced dissolution rate under higher pH is observed (e.g.; Huertas et al., 2001; Fujiwara et al., 2003; Sato et al., 2002). Dependence of dissolution rate on degree of saturation is also reported (Cama et al., 2000). Combining these existing information, the following options for the rate expressions were proposed (Fujiwara et al., 2003);

Model 1: $k.A.(a_{H^+})^n \cdot \{1 - \exp[-a(\log Q/K)^6]\}$, $a=6e-10$,

Model 2: $k.A.(a_{H^+})^n \cdot (1 - Q/K)$,

where $\text{Log } k = -17.1$, $n=-0.34$. Dependence on the degree of saturation in Model 1 is based on the empirical expression suggested in (Cama et al., 2000) whereas that in Model 2 is derived from the transition state theory but not necessarily consistent with the experimental results. As depicted in Figure 2, dissolution rates derived from these two model options are vastly different. Results of reaction transport calculations taking into account kinetic control on montmorillonite dissolution are sensitive to selection of these model options. Figure 3 shows the result of a calculation corresponding to Model 1 where loss of montmorillonite due to dissolution is negligibly small whereas the result corresponding to Model 2 is almost identical to the instantaneous equilibrium model (Figure 1).

A parametric survey using Model 1 revealed that the result shown in Figure 3 is insensitive to choice of secondary minerals (including a case without any secondary mineral), boundary conditions and variation in effective diffusion coefficient in the altered bentonite region.

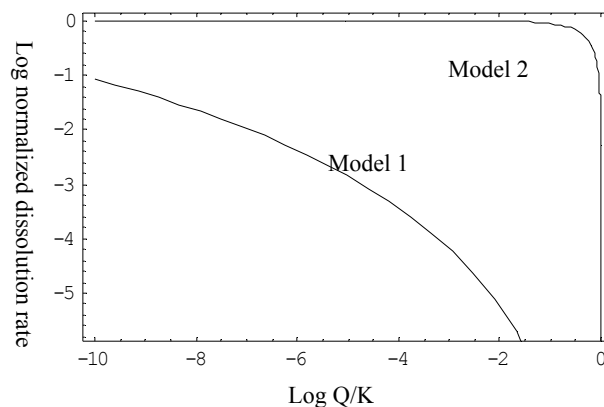


Figure 2 Model options for montmorillonite dissolution kinetics

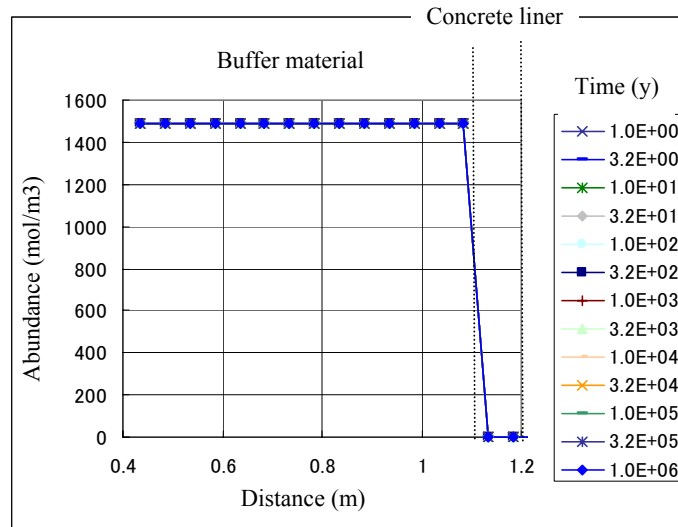


Figure 3 Amount of montmorillonite dissolution constrained by reaction kinetics (HLW)

4. Effects of bentonite alteration on barrier performance

Once amount of montmorillonite to be dissolved by reaction with hyperalkaline pore fluid is estimated, its potential impact on the barrier performance need to be assessed. Although there remains a possibility that altered bentonite region may provide good enough barrier function against flow, diffusion resistance and colloid filtration, it is difficult to guarantee over long time periods. Hence we need to focus on barrier function of remaining montmorillonite that is likely to have been transformed to Ca-montmorillonite by ion exchange. Flow test on Na-bentonite and Ca-bentonite over a range of effective bentonite density indicates that hydraulic conductivity of Ca-bentonite is similar to that of Na-bentonite if the effective bentonite density is greater than 1.5 g/cm^3 and that hydraulic conductivity of Ca-bentonite increases drastically for the lower effective density (Mihara et al., 2000). Hence, by calculating effective density of remaining bentonite, potential impact of chemical alteration on the barrier performance against flow can be assessed. In this calculation, loss of montmorillonite and other initial minerals in the buffer, volume of degraded concrete and secondary minerals need to be taken into account. In addition expansion of corroded overpack and structural stability of concrete facility need to be considered in case of HLW and L/ILW repository respectively.

It needs to be noted that the flow tests in (Mihara et al., 2000) were conducted under hydraulic gradient that is several orders of magnitude greater than that is expected in the repository. In other study it was observed that hydraulic conductivity of Ca-bentonite with effective density lower than 1.5 g/cm^3 decreases as the hydraulic gradient becomes small (Fujiwara et al., 2003). In addition there was evidence suggesting that increased hydraulic conductivity of low density Ca-bentonite was due to gap between bentonite sample and the flow column possibly caused by combination of decreased swelling capacity and greater water pressure gradient. As for the diffusion coefficient and colloid filtration, experiments on Ca-montmorillonite with wide range of effective density are yet to be carried out.

5. Issues for further R&D

Based on the discussions in the previous sections, issues for further R&D will be identified and presented at the workshop.