

Cementitious Materials in Safety Cases for Geological Repositories for Radioactive Waste: Role, Evolution and Interactions

A Workshop organised by the
OECD/NEA Integration Group
for the Safety Case

and hosted by ONDRAF/NIRAS



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NUCLEAR ENERGY AGENCY

Radioactive Waste Management Committee

CEMENTITIOUS MATERIALS IN SAFETY CASES FOR RADIOACTIVE WASTE: ROLE, EVOLUTION AND INTERACTIONS

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Executive Summary

This report presents the proceedings of a workshop on the roles, evolution and interactions of cementitious materials in geological disposal facilities for radioactive waste. The workshop was organised by the OECD Nuclear Energy Agency (NEA) and hosted by the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (Ondraf/Niras). The workshop was held in Brussels, Belgium on 17-19 November 2009.

Cementitious materials are ubiquitous in geological disposal. They have been proposed for use as roadways and floors, tunnel linings, waste conditioning matrices, waste packages, overpacks, buffers, backfills, tunnel plugs and seals, and fracture grouts. Although some of these cementitious materials may be removed before repository closure, large quantities (e.g. several million kilograms) may remain in high-level waste and spent fuel repositories after closure. Even larger quantities of cementitious materials will remain in repositories for low- and intermediate-level radioactive wastes.

Although few geotechnical problems (e.g., issues of settlement, early structural failure of barriers, seepage) are expected in installing cements and concretes in geological disposal facilities, this may need to be confirmed by further underground testing and demonstration. There will also be a need to consider the variability and quality of concrete materials as supplied, and to develop procedures to verify the quality of concrete structures emplaced in geological disposal facilities.

Physical degradation effects (e.g. desiccation, shrinkage, cracking) tend to lead to changes in porosity and permeability, and this may cause the materials to develop spatially heterogeneous properties that can affect patterns of water and gas flow. In detail, the relationships between permeability and porosity in these systems can be complex and uncertain. Physical degradation of cementitious materials is often not represented explicitly in safety assessments but is instead addressed through the selection of parameter values (e.g. for permeability) averaged over appropriate spatial scales. In some cases such parameter values are chosen for a series of degradation states or points in the degradation history.

There is good consensus regarding the chemical processes that occur within cementitious materials. Our understanding of Ordinary Portland Cement (OPC) systems has increased significantly over the last few decades and detailed thermodynamic databases and models of the chemistry of these cements are available. Our understanding and ability to model the chemistry of low-pH cement systems has also increased in the last few years, but is less well advanced.

There are strong couplings between the chemistry of cementitious materials and the solubilities and sorption behaviour of some radionuclides, and these couplings need to be considered in performance assessment. This is usually approached through the selection of relevant solubility and sorption data, and various approaches have been taken in performance assessments to account for the effects of the chemical evolution of cementitious materials on radionuclide behaviour.

Although detailed chemical models of cementitious materials are available, it is difficult to develop detailed coupled models that also include physical/mechanical processes (e.g. cracking) and take account of the associated hydrological changes. The occurrence of cracking and the potential for spatially heterogeneous flow and patchy, localised chemical

conditioning, leads to uncertainty in models of radionuclide transport behaviour. There may, therefore, be a need for work on upscaling the detailed knowledge of physical and chemical processes that can occur in cementitious systems. Although approaches have been proposed and applied for upscaling certain hydrological problems, these techniques have not yet been applied for considering radionuclide transport in cementitious systems at repository scales. However, it is emphasised that a complete understanding of the behaviour of cementitious materials and their interactions is not necessarily required for a robust safety case for waste disposal to be developed. The remaining uncertainties may not be significant and/or may be managed through appropriate disposal system design.

In geological disposal facilities for low- and intermediate-level wastes, waste degradation and metal corrosion may cause significant quantities of gas to be produced. Some recent studies suggest the possibility of using cementitious materials to form an engineered release pathway for the gas. In some host rocks (e.g. clays), gas generation may mean that the near-field of the repository is only partially hydrologically saturated for long periods of time (thousands of years). Models of partially-saturated cementitious systems are in their infancy, and there may be important couplings between processes in such systems, including between hydraulic saturation and gas generation. Partially-saturated cementitious systems also occur in near-surface radioactive waste disposal facilities, and there may be scope for transfer of information between performance assessment programmes being conducted in these two areas.

Interactions between cementitious materials and other disposal system components tend to be localised in their effects. These effects can have positive or negative impacts. For example cementitious materials may:

- Enhance rates of vitrified high-level waste dissolution.
- Slow the corrosion of steel and copper by causing passivation.
- Cause localised alteration of bentonite (e.g. cementation, embrittlement).
- Lead to local alteration of the host rock (e.g. mineral dissolution and precipitation, porosity changes, clogging of fractures).

Because the interactions are local effects, they can be managed using a combination of research and design studies. The research studies are aimed at understanding the materials and quantifying the processes of interest, while the design studies are aimed at selecting suitable barrier materials and using these in appropriate combinations and masses or thicknesses so that any negative interactions are insignificant to the performance of the entire disposal system.

Selecting a suitable design will involve various modelling studies aimed at considering effects over longer timescales than can be accessed by experiment. At a research level, models of such interactions have improved considerably over recent years but, in contrast, safety assessments tend to represent interactions between cementitious materials and other repository components using rather simple, conservative approaches. These simple performance assessment representations may be easier to defend, but still tend to give a pessimistic view of disposal system performance. In particular, some potentially positive effects of such interactions (e.g. clogging of fractures in the host rock as a result of precipitation of cement-related minerals) have been identified but are not included in safety assessment models.

There are always uncertainties when using models to consider long periods of time, but some evidence or corroboration can be sought from studies of relevant natural and anthropogenic systems. For example, studies of natural systems, such as the cement-like rocks at Maqarin in Jordan, can provide useful information on the processes that occur in such systems. This type of information may help to build confidence that performance assessment models include the relevant effects and processes, and may also provide other qualitative safety arguments.

Uncertainty and sensitivity analyses can also be used to help build confidence that a facility will provide an acceptably safe disposal solution. Uncertainty analysis should be a central part of safety assessment. Recent advances in computing power mean that it is now reasonable to expect safety cases to include and be supported by extensive structured uncertainty and sensitivity analyses.

Overall, cementitious materials clearly fulfil important and beneficial roles in the disposal of long-lived radioactive wastes, but there are some potentially negative effects that have to be assessed and managed by using the safety case to inform disposal system design.

Acknowledgement

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Abbreviations

BFS	Blast Furnace Slag
CSH	Calcium Silicate Hydrate
CASH	Calcium Aluminium Silicate Hydrate
EBS	Engineered Barrier System
EC	European Commission
ESDRED	EC Project on Engineering Studies and Demonstrations of Repository Designs
ESC	Environmental Safety Case
FEPs	Features, Events and Processes
FORGE	EC Project on Fate of Repository Gases
HLW	High-Level Waste
IGSC	Integration Group for the Safety Case
ILW	Intermediate-Level Waste
LLW	Low-Level Waste
MIC	Microbially-Induced Corrosion
NEA	Nuclear Energy Agency
OECD	Organisation for Economic Co-operation and Development
OPC	Ordinary Portland Cement
PFA	Pulverized Fly Ash
SAFIR-2	Belgian 'Safety Assessment and Feasibility Interim Report 2'
SF	Silica Fume
SPL	Superplasticisers
URL	Underground Research Laboratory

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Introduction

Disposal of high-level, long-lived radioactive waste in engineered facilities, or repositories, located deep underground in suitable geological formations, is being investigated world-wide as a long-term management solution. Cementitious materials will be used in almost every programme developing such a geological repository for radioactive waste. For example, many waste disposal concepts use cementitious materials in fracture grouts, tunnel plugs and backfills.

Cementitious materials are in routine use as industrial materials, but have mainly been studied with respect to their evolution over periods on the order of several decades. The disposal of long-lived radioactive wastes, however, requires understanding and assessing the evolution and interactions of cementitious materials with other repository materials, host rocks and ground waters over thousands of years.

The OECD Nuclear Energy Agency (NEA) Integration Group for the Safety Case (IGSC) organised a workshop to assess current understanding on the use of cementitious materials in radioactive waste disposal. The workshop was hosted by the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (Ondraf/Niras), in Brussels, Belgium on 17-19 November 2009.

The workshop brought together a wide range of people involved in supporting safety case development and having an interest in cementitious materials: namely, cement and concrete experts, repository designers, scientists, safety assessors, disposal programme managers and regulators.

The workshop was designed primarily to consider issues relevant to the post-closure safety of radioactive waste disposal, but also addressed some related operational issues, such as cementitious barrier emplacement. Where relevant, information on cementitious materials from analogous natural and anthropogenic systems was also considered. The workshop agenda is included as Appendix A.

The workshop focused on:

- The uses of different cementitious materials in various repository designs.
- The evolution of cementitious materials over long time scales (1 000s to 100 000s of years).
- The interaction of cementitious materials with surrounding components of the repository (e.g. waste, container, buffer, backfill, host rock).
- The workshop comprised:
 - Plenary sessions in which the state-of-the-art on repository design and understanding the phenomenology of cementitious materials and their interactions were presented and discussed.
 - Dedicated working group sessions, which were used to discuss key safety assessment and safety case questions in more detail. For example:

How strong is the scientific basis for incorporating the various aspects of the behaviour and interactions of cementitious materials in safety assessments and safety cases?

How can the behaviour and interactions of cementitious materials best be incorporated within the safety case, and how can the safety case be used to help inform repository design choices?

Which are the main open questions and uncertainties?

In preparation for the workshop, a review was undertaken to identify and describe relevant examples of the use and functions of cementitious materials in geological disposal concepts from a range of settings. In accordance with the intent of the workshop, the review covered geological disposal concepts for high-level wastes (HLW) and spent fuel, as well as for intermediate-level wastes (ILW) and their equivalents.

Abstracts and supporting papers for oral presentations and posters presented at the workshop are included as Appendices C and D.

This report provides a synthesis of the workshop, and summarises its main results and findings. The structure of this report follows the workshop agenda:

- Section 2 summarises plenary and working group discussions on the uses, functions and evolution of cementitious materials in geological disposal, and highlights key aspects and discussions points.
- Section 3 summarises plenary and working group discussions on interactions of cementitious materials with other disposal system components, and highlights key aspects and discussions points.
- Section 4 summarises the workshop session on the integration of issues related to cementitious materials using the safety case.
- Section 5 presents the main conclusions from the workshop.
- Section 6 contains a list of references.
- Appendix A presents the workshop agenda.
- Appendix B contains the abstracts and, where provided, technical papers supporting oral presentations at the workshop.
- Appendix C contains the abstracts and, where provided, technical papers supporting posters presented at the workshop.
- Appendix D records the workshop participants and the composition of the working groups.

Uses & Evolution of Cementitious Materials in Geological Disposal

Plenary Session 1

The presentations and discussions during the first day of the workshop were focussed on the use and evolution of the cementitious materials. This section provides a summary of the papers presented in Session 1 and related discussion points.

Uses and Functions of Cementitious Materials in Geological Repositories for Radioactive Wastes

The workshop began with an introductory presentation by David Bennett of TerraSalus Limited on the intended uses and functions of cementitious materials in a range of ILW, HLW and spent fuel disposal concepts.

The focus of the presentation was on identifying the main functions and requirements of the cementitious materials, and noting similarities and differences in approaches between disposal programmes.

Key points were:

- Cementitious materials are ubiquitous in geological disposal; all disposal concepts reviewed (Appendix B) include cementitious materials in their designs. For example, cementitious materials have been proposed for use as roadways and floors, tunnel linings, waste conditioning matrices, waste packages, overpacks, buffers, backfills, tunnel plugs and seals and fracture grouts. These uses range from those related to operational safety through to those related to post-closure safety.
- There are complex relationships between components of the Engineered Barrier System (EBS) and safety functions. Individual EBS components often have several functions. The EBS needs to be considered as a system and the interactions between its components understood and assessed. For example, some EBS components provide conditions that allow neighbouring components to fulfil safety functions.
- Cementitious materials play an important and positive role in many disposal concepts, but the associated effects of the materials on the disposal system environment must be taken into account.
- The process of determining or defining which safety functions individual repository components should fulfil needs to be as transparent as possible and should be consistent with the safety strategy, relevant safety case arguments, and results from safety and performance assessment (NEA and EC 2010).
- Many factors can affect the choice of materials for use within EBS, including cementitious materials. These factors range widely and may include technical implementation issues (feasibility), operational and post-closure safety issues, costs, the availability of materials, quality assurance and quality control, and conventional environmental impacts.

- There is no simple correlation between host rock type and the type of cementitious materials used. For example, OPC and low-pH cements have both been proposed for use in clay and for use in fractured crystalline host rocks. What is appropriate depends on the particular disposal programme and disposal system.

Engineering Feasibility of the Fabrication and Emplacement of Cementitious Repository Materials

María Cruz Alonso of the Spanish National Research Council gave a presentation that summarised relevant findings on cementitious materials from the EC ESDRED (Engineering Studies and Demonstration of Repository Designs) Project (Seidler, 2009). Concrete will be used for different purposes during the construction of geologic repositories for radioactive waste. These purposes include grouting, tunnel and drift lining, and tunnel plugging and sealing. Although some of the concrete may be removed before repository closure, a significant amount of concrete will remain in the repository.

An important concern regarding the use of cementitious materials in geologic repositories for HLW and spent fuel is their interaction with the bentonite buffer, backfill material, and the host rock close to the repository near-field. For this reason, the ESDRED project has developed a low-pH concrete formulation as an alternative to standard ordinary Portland cement (OPC) concrete formulations with the aim of reducing the interaction of the cementitious materials with the near-field components.

The main functional requirement required in the development of the low-pH material was a pore fluid pH < 11, which is considered acceptable for preventing or reducing the alteration of the bentonite EBS. Other functional requirements considered in the development of the low-pH concrete were:

- Hydraulic conductivity.
- Mechanical properties.
- Durability.
- Workability and pumpability.
- Slumping.
- Peak hydration temperature.
- Thermal conductivity.
- Use of organic components.
- Use of other products.

The development of the low-pH concrete involved laboratory work, as well as field testing at the Äspö underground research laboratory (URL) in Sweden, and in the Grimsel URL and at the Hagerbach site in Switzerland.

The ESDRED project demonstrated that low-pH cements can be formulated and used for production of concrete plugs and rock support (Figure 1).

Figure 1: Trials of the use of low pH cements for rock support (top) and tunnel plugs (bottom)



OPC can be used as the cement included in low-pH blends, but at least 55% of SiO_2 must be in the binder, or pozzolan additions above 40% have to be employed. However, uncertainties still remain with respect to the use of low-pH concrete, including its long-term performance and durability in contact with groundwaters, and associated with the risk of corrosion of carbon steel, which may be present in the form of reinforcement or fibres.

Compositions and Uses of Cementitious Materials: Experience from the ONKALO facility in Finland

Johanna Hansen of Posiva in Finland summarised experiences of working with cementitious materials in the Finnish disposal programme. Posiva is responsible for geological disposal of spent nuclear fuel from the Finnish nuclear power plants at Loviisa and Olkiluoto. Posiva plans to submit a construction license application in 2012 and, if

approved, repository construction will begin in 2014-2015. The geologic disposal facility will be a KBS-3 type repository (see Appendix B) at a depth of 400 to 500 m in crystalline bedrock.

Construction of the repository will require using a large quantity of cementitious materials. A 2007 estimate indicated that approximately 20 million kilograms of cementitious material will be introduced into the repository, although much of this material will be removed, with only approximately 6 million kilograms remaining in the repository after closure, mostly in the form of tunnel plugs.

To minimise the potential negative effects of cementitious materials, low-pH cement and colloidal silica both were studied as alternative materials. Based on experience gained in constructing the ONKALO underground characterisation facility, Posiva decided that from the spring 2008 onwards, mainly low-pH cement will be used as grouting material because the grout cannot be removed for repository closure.

The low-pH grout is composed of Portland cement, silica fume, and superplasticizer. Various recipes were tested in the laboratory, and field mixing and grouting tests were conducted at ONKALO. The effects of organics on radionuclide retention and the leaching of organics from the cement also were evaluated.

The studies indicated no impediments to the use of low-pH grout at ONKALO and showed that low-pH cementitious grout has better penetration ability and stiffness than regular grout. It was also concluded that the amount of cementitious materials in the repository can be reduced with careful design; for this, cooperation is needed between repository designers and long-term safety assessors.

Physical Degradation of Cementitious Materials during the Pre-closure Phase

Jian-Fu Shao of Lille University in France described a study into the physical degradation of cementitious materials. Desiccation can contribute to the degradation of structures made of cement-based materials. This study was conducted to:

- Characterise the damage and fractures that result from drying processes.
- Examine the effects of different aggregates.
- Develop relevant constitutive and numerical models
- Demonstrate the use of multiscale approaches. The nucleation and propagation of microcracks due to drying was studied using x-ray micro-tomography.

Microcracks were shown to initiate at the interface of the aggregate and the hardened cement paste. Experiments used aggregates in the size range 1 to 6 mm. Smaller aggregates resulted in higher desiccation strength and smaller damage densities. Smaller aggregates also resulted in higher mechanical strength of the hardened cement-based material.

Numerical modelling of fracture propagation was performed using the XFEM code, which uses a damage force criterion and is a code applied largely in mechanical engineering.

The approach developed in the study can be used to evaluate the effects of desiccation on the degradation of cement-based materials in a ventilated repository for radioactive waste.

Chemical Evolution of Cementitious Materials

Barbara Lothenback of EMPA, Switzerland gave an overview of the status of thermodynamic modelling for cementitious systems.

Thermodynamic modelling of cementitious systems has been greatly facilitated in recent years by the development of more sophisticated geochemical software, of solid solution models for various cement phases, and by the collection of thermodynamic data for minerals relevant to cementitious systems over a wide range of temperature (0 to 100°C).

Based on these developments, thermodynamic modelling, coupled with kinetic equations that describe the dissolution of clinker as a function of time, can be used to:

- Quantify the liquid and solid phase compositions of ordinary Portland cement and blended cements during the hydration process (e.g. Figure 2).
- Evaluate compositional changes that occur in cementitious materials due to the use of various aggregates and other mineral additives (e.g. silica fume and blast furnace slag).
- Predict degradation of cement in contact with the repository environment.

Discussion of the paper included:

What is our understanding of where aluminium resides in low-pH cements and what is our ability to model the behaviour of aluminium in these systems? The location of aluminium in low-pH cements depends on the overall Ca/Si ratio of the system and on the pH, but some aluminium enters the CSH gel as a CASH gel phase. The Swiss disposal programme is currently conducting some experiments to investigate this topic.

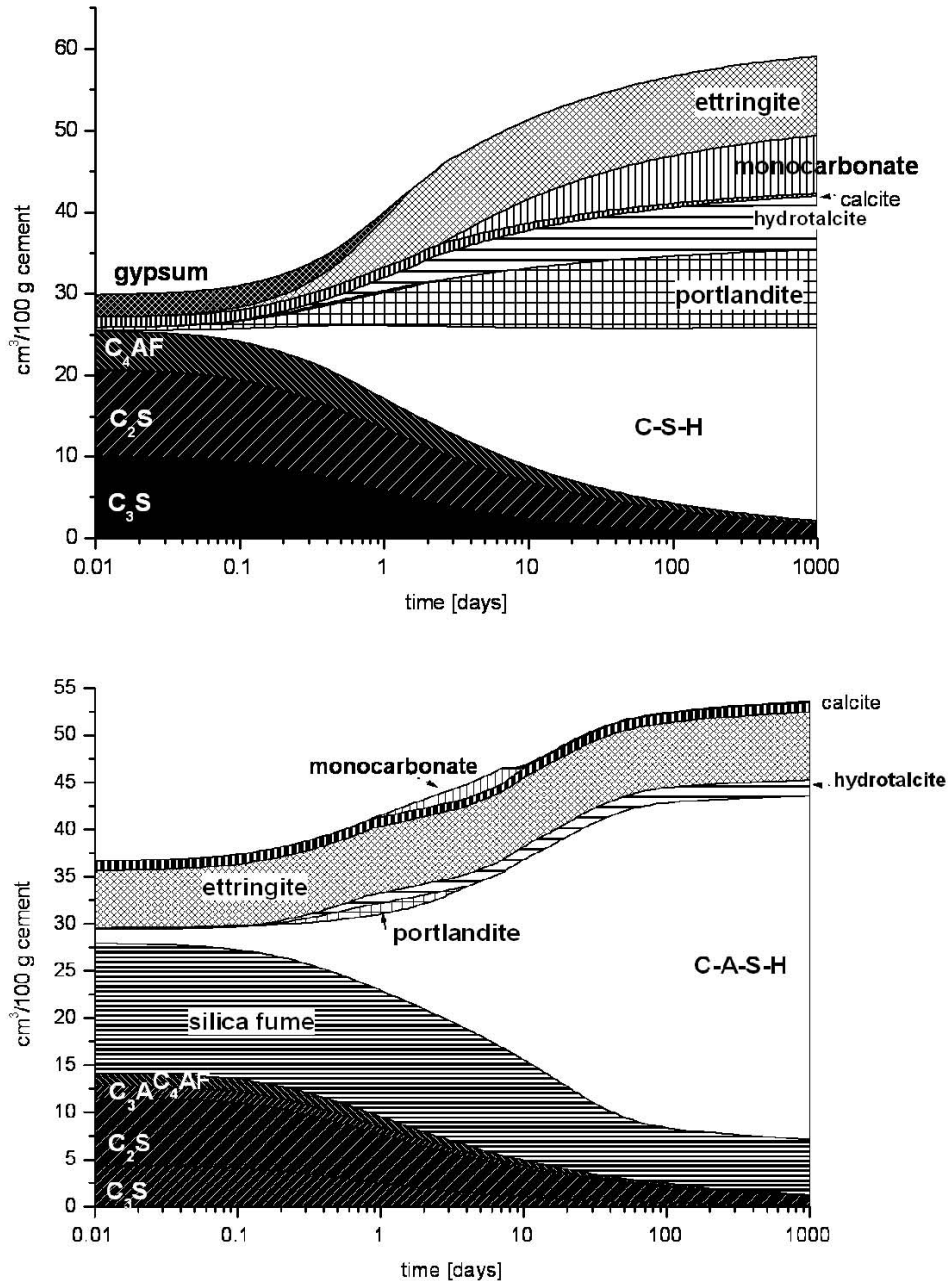
Effects of Cementitious Materials on Radionuclide Solubility and Retention

Simon Norris of the NDA described the current status of understanding of radionuclide solubility and retention in cementitious materials based on experience in the United Kingdom. Cementitious materials play a number of roles in the long-term management and disposal of radioactive wastes. One of these roles is to contribute to the post-closure containment and retention of radionuclides within a disposal facility by imposing conditions that minimise radionuclide solubility and provide sites for radionuclide sorption.

The chemical containment provided by the highly-alkaline, chemically reducing environment imposed by cementitious materials plays an important role in the long-term retention of many radionuclides. However, the mineralogy and other properties of cementitious materials that contribute to their physical and chemical barrier performance within the engineered barrier system will evolve due to several processes, including:

- Leaching.
- Reaction with groundwater solutes.
- Hydration and crystallisation.
- Reaction with wastes, their degradation products, and with non-cementitious waste forms.
- Cracking.

Figure 2: Solid phase development during hydration of OPC (top) and of a 40% SiO₂: 60% OPC low-pH cement (bottom).



Some of these processes are better understood than others. For example, the evolution of pH within a homogeneous repository near field can be modelled based on knowledge of cement dissolution combined with expected groundwater compositions and flow rates. The calculated changes in pH can then be coupled to radionuclide solubility and sorption in safety assessment models.

Other processes are not as well constrained. Reaction of cementitious materials with groundwater will lead to changes in the mineralogical composition of the cements, accompanied by changes in porosity and permeability, and cracking can lead to localised

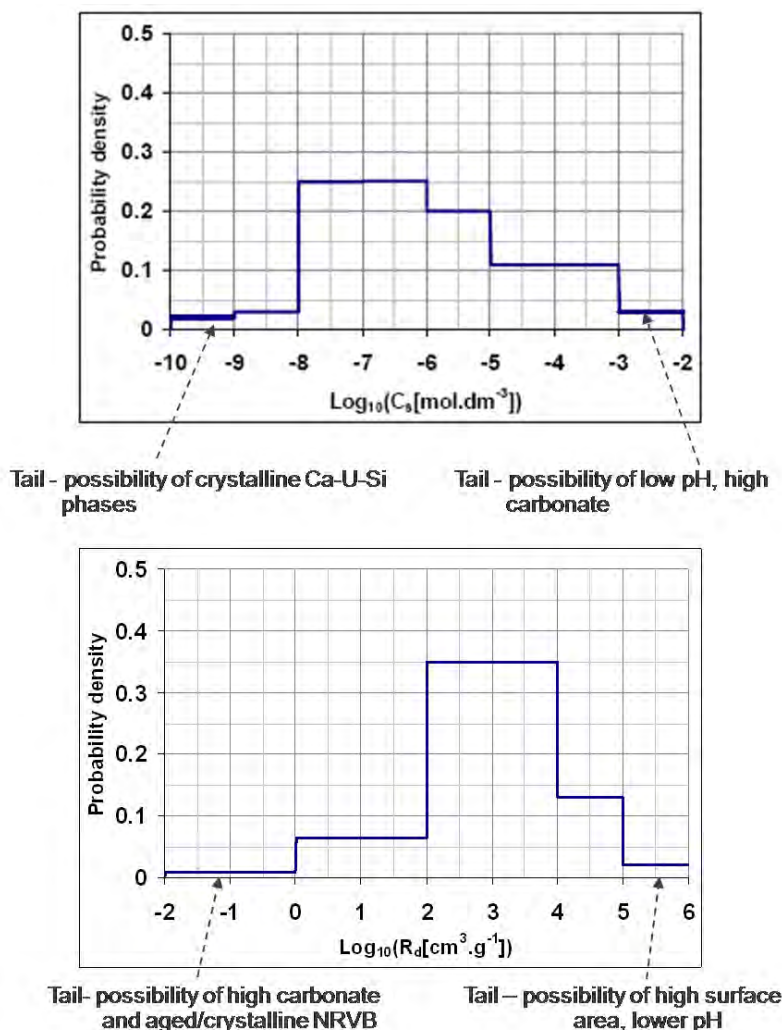
water flow along the cracks and preferential leaching or deposition of reaction products. These processes can also alter the sorption properties of the cementitious materials. Additional complexities result from the heterogeneous distribution of cementitious backfill and waste in the repository.

Uncertainties in the processes affecting cement evolution contribute to uncertainty in the long-term solubility and sorption of radionuclides that need to be taken into account in performance assessment calculations. One approach is to use expert groups to review available data in the context of the expected evolution of the system and define appropriate probability distribution functions (e.g. Figure 3).

Discussion of the paper included:

Is there a requirement that the cementitious backfill should not include superplasticisers? The backfill does not include superplasticisers, but the effects of organics need to be considered because some wastes contain or degrade to release organic complexants.

Figure 3: Probability distribution functions for the solubility (top) and sorption (bottom) of uranium (VI) in cementitious backfill in the absence of organics over the pH range 9 to 12.3



Key messages from Plenary Session 1

The following points summarise the main themes and outcomes of the presentations:

- Cementitious materials are ubiquitous in geological disposal.
- Cementitious materials have been proposed for use as roadways and floors, tunnel linings, waste conditioning matrices, waste packages, overpacks, buffers, backfills, tunnel plugs and seals and fracture grouts.
- Although some of the cementitious materials may be removed before repository closure, large quantities (e.g. several million kilograms) may remain in HLW/spent fuel repositories after closure. Even larger quantities of cementitious materials will remain in repositories for low- and intermediate-level radioactive wastes.
- Although cementitious materials play an important and positive role in many disposal concepts, the associated effects of the materials on the disposal system environment must be taken into account.
- To minimise the potential effects of cementitious materials, low-pH cements and colloidal silica have been studied as alternative materials. Low-pH grouts are typically composed of Portland cement, silica fume, and superplasticizer.
- The properties and behaviour of OPC concretes are well known and there has been considerable progress over recent years in our understanding and ability to model the chemistry and evolution of blended cements and low-pH cements.
- However, uncertainties still remain with respect to the use of low-pH concrete, including its long-term performance and durability in contact with groundwaters, and associated with the risk of corrosion of carbon steel, which may be present in the form of reinforcement or fibres.
- Some processes that occur in cementitious systems are better understood than others. For example, pH evolution can be modelled fairly easily based on cement dissolution models and knowledge of expected groundwater compositions and flow rates. The calculated changes in pH can then be coupled to changes in radionuclide solubility and sorption in safety assessment models. Other processes are less well constrained. For example, reactions of cementitious materials with groundwater will lead to mineralogical changes, changes in porosity and permeability, and cracking. These processes can alter the hydrological and retardation properties of the cementitious materials.
- Uncertainties in processes affecting cement evolution contribute to uncertainty in near-field hydrological properties and in the long-term solubility and sorption of radionuclides. There are various approaches for taking account of these uncertainties in performance assessment calculations, including the use of expert judgement and expert elicitation techniques to define relevant input data for the assessments (e.g. in terms of hydraulic conductivities, solubilities and distribution coefficients).

Working Group Session 1

The first plenary session was followed by working group sessions in which the topics of the plenary were discussed in more detail. The working groups included participants from a range of national radioactive waste disposal programmes and had a variety of expertise in the phenomenology of cementitious materials and in engineering and safety assessment activities. The following subsections summarise the working group discussions.

Working Group 1: Construction

To what extent is technology available and proven to construct or use different cementitious components in a repository? What are the possible engineering and constructional constraints that might have an impact on safety?

The group considered that there are no real problems associated with the use of cement for conditioning low- and intermediate-level radioactive waste. Both OPC and low-pH concretes have successfully been used for LLW and ILW packages. However, construction and use of cementitious materials at depth may be more difficult. Relevant technologies are available, but more testing of the in situ behaviour of the material is needed.

Several members of the group pointed out that that experience in the production of low-pH cementitious materials is limited to laboratory work, although a few tests at pilot scales have been conducted. Therefore, further testing is needed at industrial scale and also in situ with environmental conditions similar to repository conditions.

The importance of quality assurance and quality control for these rather new products was emphasised. Performance confirmation measures need to be developed and adopted, consistent with the functional requirements of the cementitious materials in the disposal system. Consideration should also be given to the time frames in which the materials are required to function (e.g. during construction, repository operation and in the long-term evolution of the repository).

It was pointed out that structural elements of the repository will have to be adapted to existing construction standards or new, repository-specific standards will have to be developed. It was mentioned as an example, that existing construction/engineering standards require reinforcement of tunnel plugs, but the design work and 3D-models shows that reinforcement is not needed to achieve the required strengths and functions of the plugs. Reinforcement may instead create future problems as the steel rods will corrode and may cause cracking of the concrete.

In safety case studies it is necessary and important to have correct and detailed information about the composition of the material used in the different cementitious material. The group noted that the compositions of the materials used in the repository are likely to be different from those in use today as new products are likely to be developed. The composition and behaviour of the new products will have to be subjected to investigation and testing in the same way as the products now used.

Working Group 2: Physical Degradation

To what extent is the physical degradation of cementitious repository components considered in a safety case and is enough scientific and technical knowledge available to support the approaches taken in safety cases?

All of the countries represented in the working group study the physico-chemical evolution of concrete barriers to some level of detail. The demonstration of an appropriate level of system understanding regarding the evolution of the repository is considered an essential element of a safety case.

The working group considered that in broad terms, the physical evolution of concrete barriers under repository conditions is adequately known. However, none of the disposal programmes has so far represented explicitly the time-dependent physical degradation of cementitious barriers in performance assessment calculations for HLW or spent fuel disposal. Instead, the evolution of the properties of the cementitious materials is sometimes taken into account indirectly.

Uncertainties are usually treated by taking bounding values. The few performance assessments that have represented time-dependent changes (e.g. in barrier permeability) have done so by considering a series of step changes rather than by representing

continuous gradual changes. Examples of performance assessments that have attempted to represent the physical degradation of cementitious components relate mainly to near-surface disposal facilities for LLW and geological disposal facilities for ILW.

While many uncertainties clearly remain, especially for the long timescales considered in a safety case, these uncertainties are not considered critical. In other words, the working group members felt that the potential uncertainties in the physical evolution of concrete structures would not undermine safety and would not preclude a decision to start building a repository.

However, the group also considered that process-level knowledge should be further developed, particularly with respect to the long-term behaviour of the materials and processes that may lead to spatial heterogeneity. In particular, the working group suggested that advances could be made by looking at processes at the pore-scale (e.g. using imaging techniques and multi-scale modelling). The mechanisms of crack formation and healing were also identified as processes where further study would be beneficial.

The working group also considered that it will be important for the waste disposal organisations to maintain an appropriate awareness of, and skills in, the state-of-the-art. This could be achieved in part by following progress in the cement industry, and by exploring the use of new materials and additives, such as superplasticisers. In this way, concrete compositions may be further optimised.

Working Group 3: Chemical Modelling

How well advanced is chemical modelling of concrete degradation?

- Solid solution versus more classical chemical modelling?
- Incorporation of the role of aggregates?
- Evolution of redox condition?

Is there enough foundation to use the results of such chemical modelling in a safety case?

The OPC system is quite well defined and there is a good understanding of how the OPC system evolves with time. For other systems such as the low-pH cement system and also for leached systems there are a number of open questions.

There remains a lack of experimental information and data on some components in cementitious systems (data on phase stability, thermodynamic values, rate constants and molar quantities), especially those found in low-pH cements. The work of extracting data to support better modelling of low-pH and degraded cement systems was considered to require considerably more effort.

The varying chemical composition of fly ash and silica fume introduce large uncertainties. In addition, the uptake of Al, Na, and K in degraded or low Ca/Si calcium silicate hydrate (C-S-H) gels is not sufficiently well known, and the possible formation of some phases (siliceous hydrogarnets, thaumasite) is uncertain. Modelling also becomes more difficult when considering the influence of groundwaters.

One field of research that has improved significantly, is the modelling of solid solutions such as those found in the C-S-H system, where previously models were based on a number of discrete solid phases instead of a solid solution. A remaining issue is how to model the molar volumes of solid solutions as their composition varies. However, a larger question is whether it is necessary to include solid solutions in the models or whether this introduces larger uncertainties rather than improving modelling results.

Most modelling studies presently treat the aggregate component of concrete as being unreactive. The exceptions are when the aggregates consist of materials such as silica or

limestone. Interactions between the pore solution and the aggregates might in some cases lead to cracking of the concrete, typically by the well known alkali-silica reaction. However, coupling chemical and mechanical processes in models is very difficult, and is often not done.

Kinetic effects are also often not included in cement models. One opinion was that this is actually not necessary for the very long periods of time considered, and that we do not know enough about the kinetics involved in the reactions within these systems to currently include kinetics in the models. An alternative view was that kinetics have to be introduced when modelling the chemical evolution over time periods on the order of 100 years or more.

Reactions involving reduction and oxidation (redox processes) are also difficult to handle within geochemical models. Here, the kinetics of reactions involving sulphur are important. OPC is poorly poised with respect to redox, and although blast furnace slag (BFS) has a greater redox poisoning capacity, its content of chemically-reducing sulphur may be undesirable in barrier systems containing copper and/or carbon steel due to potential impacts upon corrosion.

In summary, there was a consensus within the group that the chemical models have developed greatly over the past 10 years and that there are means of simulating chemical processes occurring both within the concrete itself, and also between the concrete and other surrounding materials, such as bentonite. The working group was positive regarding the possibilities of introducing results from detailed modelling into the safety case, but some questions are still quite uncertain and require further study.

The working group also noted that there is a lack of understanding of cement-rock interactions, of upscaling models of cementitious materials to larger temporal and spatial scales, and of porosity-permeability changes as a result of precipitation/dissolution processes. Another major challenge for the coming years is how to couple the results from the modelling of the chemical evolution with models of the mechanical evolution of cementitious repository materials.

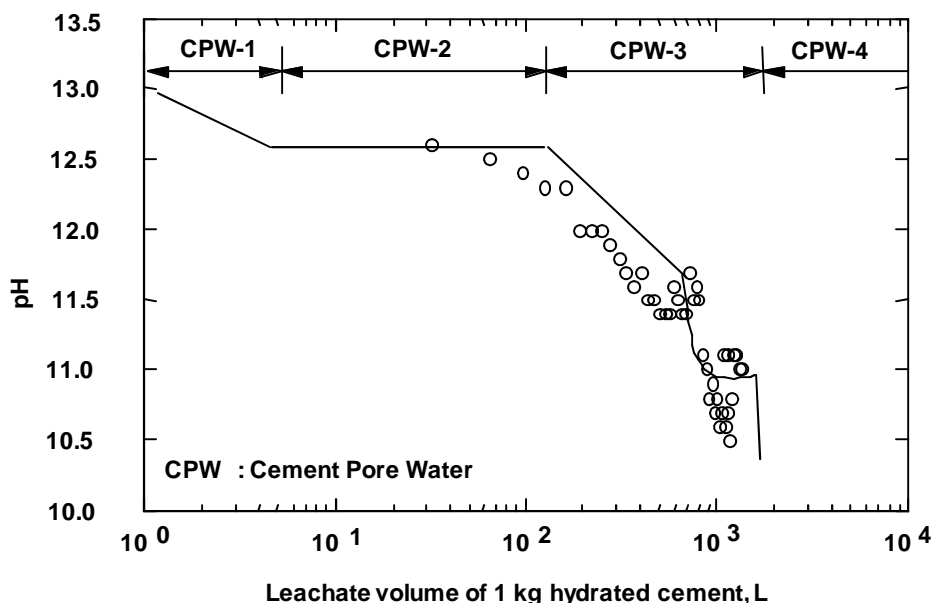
Working Group 4: Radionuclide Behaviour

How is the behaviour (sorption, solubility, etc.) of radionuclides treated considering the degradation of cementitious materials and is the available scientific basis sufficient to incorporate this in a safety case?

The working group identified several areas where data and scientific understanding are required to address these questions. These include:

- Detailed knowledge of the evolution of cementitious materials and the chemical characteristics of the contacting pore waters. Figure 4 provides an example of how the evolution of pH of a cement pore water might be evaluated and represented in performance assessment. The working group considered, however, that it is important to obtain specific information on the properties of individual cements, including both backfill and encapsulation cements, as well as on their behaviour in specific disposal environments.

Figure 3: The pH evolution of pore water in a cement based material (JAEA and The Federation of Electric Power Companies of Japan 2007).



- Knowledge of radionuclide speciation in the aqueous phase and role of any colloids and other potential complexants, including superplasticisers. Plasticiser degradation may lead to reaction products that have a complexing and mobilising effect. Plasticisers are therefore apparently not permitted in some disposal programmes. A reasonable objective may be to select a super-plasticiser having a minimal effect on radionuclide behaviour. Formulations of plasticisers are evolving and would be likely to change during the period of repository planning (i.e. a new plasticiser could be in use in 2020). In this area it appears that further experimental studies are needed.
- Knowledge of radionuclide solubility in the aqueous phase. This requires knowledge of how radionuclides are associated with specific phases in the cementitious waste forms and other cementitious materials, and an understanding of which solid phases will control radionuclide solubility.
- Knowledge of the interactions between cement leachates and surrounding barriers, in particular bentonite-type backfill and buffer materials.
- Knowledge of the adsorption behaviour of radionuclides on relevant materials under expected chemical conditions.

The working group discussed the various ways in which radionuclide solubility and sorption may be represented in a safety assessment. The implications of conservative assumptions were extensively discussed.

The group noted that it is not always easy to be certain that apparently conservative assumptions are actually conservative. For example, adopting an apparently conservative high K_d , may not actually be conservative for a fractured system in which colloids are important. The working group also noted that the selection of 'uniformly' conservative assumptions can lead to inconsistencies in models of system evolution and potentially lead to an unrealistic description of the system. Another possible drawback with conservative assumptions is a perception that they imply inadequate system understanding.

In summary, the main conclusions from the working group were:

- Although the key processes appear to have been identified, there are remaining data needs relating to modelling radionuclide sorption in cementitious materials.
- The properties of, and differences between, various cementitious materials, additives and repository environments need to be accounted using specific conceptual models.
- The role of conservatism in the safety case needs to be carefully considered.

Working Group 5: Key Processes

Is there consensus on which particular phenomena have low or only limited impact on the use and evolution of cementitious materials themselves? Is there consensus on which phenomena have potentially higher impacts?

The working group addressed these questions from the perspective of cementitious materials alone and did not consider phenomena associated with interactions between cementitious materials and other materials (e.g. bentonite, host rocks).

The group mainly discussed phenomena associated with heat, radiation, mechanical changes, corrosion, and hydraulic changes. Table 1 summarises the group's assessment of the relative impact of the various phenomena.

Table 1: Perceived significance of key processes affecting cementitious materials

Phenomena	Effects of limited impact	Effects of higher impact
Radiation		Pore water composition, saturation
Mechanics (cracks)	Geotechnics	Mechanical and transfer properties Chemical evolution
Waste chemical composition		Solid phase composition
Corrosion products	Radionuclide sorption on cements	Mechanical and transfer properties (gas production)
EBS composition	Bentonite pore water	Chemical composition/cement formulation
Hydraulic conditions		Pore and ground water composition

Heat is known to have a major impact on various processes in a repository. With regard to cementitious materials, the working group considered that the strongest effects would be on chemical evolution and mechanical properties. The effects of temperature changes on cement chemistry are known in general terms, but these are not fully described or quantified. Temperature may also have a strong influence on mechanical behaviour, especially with regards to processes such as creep, shrinkage, and cracking. It is difficult to describe and to model these processes at any particular temperature and more difficult under thermal gradients. The evolution of diffuse microcracks and their consequences on radionuclide transfer properties remain an uncertainty that the group considered need to be taken into account. On the other hand, it is possible to take account of, and model, the effects of temperature on diffusion coefficients. The group considered that temperature will have a limited impact on radionuclide sorption on cement phases. At a larger scale, temperature will probably have only a limited influence on the passivation of carbon steel in contact with concrete, and will not affect fluid flows through tunnel plugs.

The main effect of radiation on cementitious materials is on the pore water. Irradiation of concrete leads to radiolysis of the pore water, which affects the chemistry of the pore water, and particularly the redox conditions. The processes involved and their consequences are not yet fully understood. The significance of these processes in a safety

case depends on the wastes and the intensity of the radiation field, and on various other competing factors that may control or influence the chemistry of the porewaters.

The mechanical evolution of cementitious materials is strongly dependant on the boundary conditions and the types of concrete and structures considered. It is relatively easy to achieve the desired geotechnical properties through design and selection of appropriate materials, but the physical and chemical evolution of the materials can have a strong influence on radionuclide transfer properties (e.g. diffusion and permeability), and these influences are very difficult to model accurately.

The chemical evolution of cementitious materials in a repository will be influenced by the composition of the waste, as well as the formulation of the concrete used. In particular, the composition of the waste will have a strong effect on the solid phases present and that control radionuclide release.

The consequences of the expansion of corrosion products are known; potentially significant mechanical damage. Quantification of these effects remains a problem, but studies currently in progress may provide more information on the physical behaviour of the corrosion products, including the transfer of oxidised iron in concrete, and the kinetic growth of corrosion layers, etc. In contrast, the working group considered that the sorption of radionuclides on corrosion products was an effect of lower significance.

Hydraulic conditions are strongly site and concept dependant. The working group found it impossible to assess the consequences of hydrological changes without site-specific information. However, the hydraulic conditions will affect fluid flows and pore-water compositions, chemical evolution and radionuclide transport.

Finally, the group noted a lack of knowledge regarding the influence of microbial processes on cementitious materials.

Interactions of Cementitious Materials with other Repository Components

Plenary Session 2

The second plenary session was devoted to the interactions of cementitious materials with surrounding repository components, including the waste, the host rock and groundwaters as well as with non-cementitious waste containers, buffers and backfills.

Interactions with high-level waste and spent fuel

Karel Lemmens from SCK•CEN, Belgium, presented an overview of the possible interactions between cementitious porewaters and vitrified HLW and spent fuel in the Belgian disposal concept.

The Belgian disposal concept is based on the use of steel supercontainers containing considerable quantities of OPC concrete, which will be emplaced in the Boom Clay, a plastic clay formation. In this concept vitrified HLW and spent fuel will be enclosed by a carbon steel overpack and surrounded by a massive OPC cylindrical concrete buffer held in a steel liner (see Appendix B).

OPC concrete is used to provide a high pH (~13.5) and to minimise the rate of corrosion of the metallic overpack. Overpack failure is, however, a possibility several thousands of years after repository closure. The interactions of cement porewaters with HLW glass and with spent fuel therefore need to be considered.

Dissolution of vitrified HLW is expected to be more rapid at high pH leading to the formation of altered glass and secondary silicate phases, some of which may retain radionuclides. This conceptual model is supported by results from experimental studies on the dissolution rate of HLW. Although several processes will affect the chemical evolution of the concrete and will cause a decrease in porewater pH from an initial value of ~13 to a level of ~9 to 10, the rate of this pH evolution is difficult to quantify.

For spent fuel, corrosion of the overpack could in the long-term lead to interaction between alkaline concrete porewaters and the waste. Overpack failure is not expected to occur until after the thermal phase, when practically all short-lived beta- and gamma-emitting isotopes will have decayed. Radionuclide release from the spent fuel may then take place due to:

- The rapid release of radionuclides not held firmly within the spent fuel matrix (e.g. those at grain boundaries); this is often known as the instant release fraction.
- Dissolution of the spent fuel matrix. Matrix dissolution may occur through a relatively faster oxidative process leading to the release of uranium as U(VI), or through a slower non-oxidative process that releases uranium as U(IV).

Oxidative matrix dissolution could be induced by water radiolysis due to alpha-radiation. This effect, however, will decrease with time as the radiation field declines. The production of molecular hydrogen (H₂) from steel and iron corrosion is also expected to prevent oxidative dissolution.

Preliminary experimental results performed at INE-FzK in Germany indicate that the dissolution rate of spent fuel at pH 12.5 may be slightly lower than at neutral pH. However, colloids were observed in some of the experiments at high pH and, if confirmed, these might result in accelerated radionuclide release. On the other hand, the cementitious materials in the supercontainer may sorb radionuclides migrating away from the spent fuel. This latter effect has yet to be studied. In conclusion, high-pH porewaters are expected to have only limited effects on the long term stability of spent fuel, but there are still some processes that need further quantification.

Discussion of the paper included:

Are conceptual models of waste container deformation and waste dissolution realistic? It was noted that the molar volumes of glass and overpack corrosion products will be larger than of the un-corroded materials, and that such volume changes and their mechanical effects need to be considered when assessing waste container deformation and waste dissolution.

Will oxidative dissolution of spent fuel be faster at high pH? It was suggested that under high pH conditions, dissolved iron(II) concentrations in the system may be lower (partly as a result of passivation of the iron overpack), and that this may cause the spent fuel to provide fewer electrons to its surface. In this situation, the supply of electrons could be less than would be required to fully negate the oxidative effect of radiolysis and the net result could be oxidative dissolution and release of U(VI).

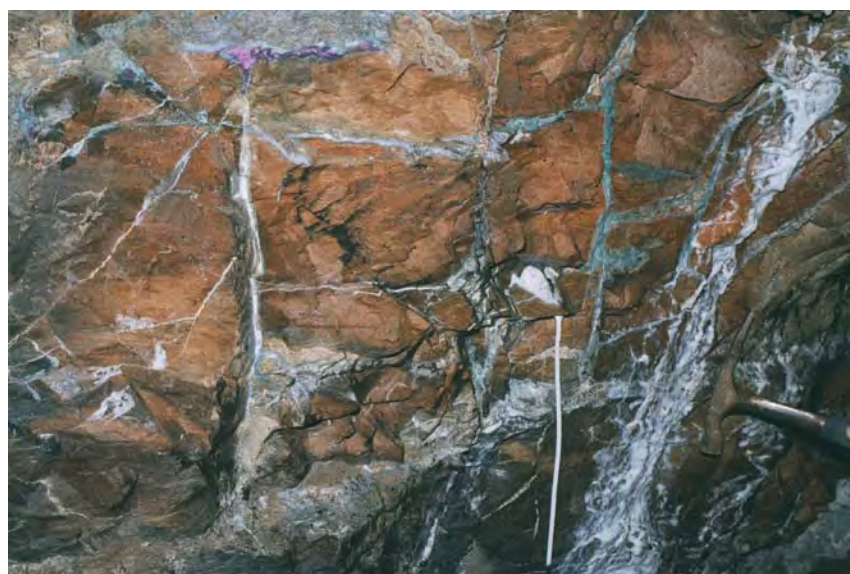
Interactions with fractured crystalline rocks

Russell Alexander from Bedrock Geosciences, Switzerland, gave a presentation on the possible effects of cement porewaters on a crystalline host rock. Field, laboratory and natural analogue studies as well as geochemical modelling indicate that cement leachates tend to induce the sealing of fractures in the rock (Figure 5).

These studies also indicate that strongly alkaline waters might:

- Accelerate the dissolution of vitrified waste, but probably not affect the dissolution rate of spent fuel.
- Degrade bentonite to some degree.

Figure 4: Photograph of fractures sealed by calcite due to the passage of high pH fluids at the Maquarin natural analogue site



To avoid some of the effects associated with the use of concrete, several approaches may be used:

- Minimisation and tracking/monitoring of the concrete masses.
- Development and use of low-pH cements and alternative grouting materials.
- The selection of less fractured rock volumes for a repository location.

The sealing of fractures evidenced in the Maquarin natural analogue study might contribute to limiting the extent of perturbations caused by an alkaline plume and is likely to create a hydraulic barrier that affects groundwater flow. The effects of these processes should be analysed in a safety case since they may support the idea of a self-sealing repository.

Uncertainties in the treatment of an alkaline plume in fractured rock include:

- The possible formation of colloids.
- Thermodynamic data for cement components and secondary mineral stability.
- Cement carbonation.
- The effects of superplasticisers.

Given these uncertainties, current assessments of perturbations around a HLW or spent fuel repository caused by cementitious materials are often conservative and provide a pessimistic view of disposal system performance.

Discussion of the paper included:

Will groundwater flows in deep systems be fast enough to cause pervasive sealing of fractures? The process of how a network of fractures may be sealed over time is uncertain. The flow field will be altered as fractures are sealed and this may cause flow rates in other parts of the fracture system to increase temporarily prior to sealing. The flow will then move to yet other parts of the network.

Will the supply of alkalinity from the concrete to the fracture network be maintained, and will the porosity of the concretes themselves become sealed (clogged) as a result of carbonation and calcite precipitation? Carbonation (cause by dissolved carbonate in groundwater) might well cause the concretes to become sealed. The tendency of the system to seal seems clear, but it is hard to predict with certainty where sealing might occur. This would need better integration amongst geologists, hydrogeological modellers and geochemical modellers to develop more consistent coupled models.

Will fracture seals formed by mineral precipitates persist or at least re-establish themselves after tectonic disturbance? There is ample evidence of multiple fluid flow and fracture sealing events in fractures, but there is a clear tendency towards calcite precipitation in systems involving carbonate bearing groundwaters and cementitious pore fluids. However, there was agreement that it would be difficult to rely on a safety argument that pervasive sealing of a fracture network would occur and persist. This is part of the reason why most disposal programmes aim to minimise pH perturbations (e.g. by minimising use of cements or using low-pH cements), rather than promoting fracture sealing by using large amounts of OPC cements.

Interactions with clay rocks

François Marsal from IRSN, France, gave an overview of the interactions between concrete and clays. His presentation focussed on safety issues related to the concrete tunnel seals designed in France for the disposal of intermediate-level long-lived waste and related to the tunnel plugs for HLW disposal. In the study described, three main effects were identified that need to be addressed:

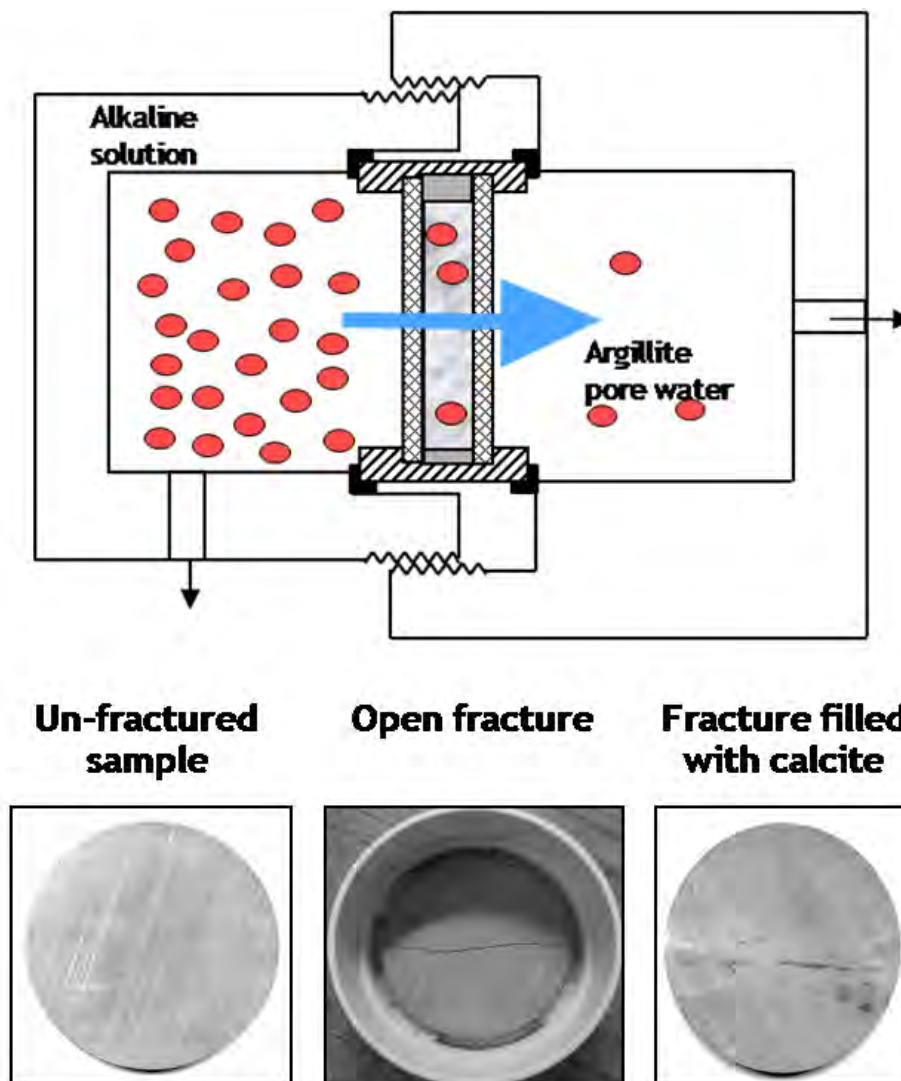
- Changes in mineralogy and porewater chemistry.

- The intensity and extent of the perturbations.
- The consequences in terms of changes in the chemical and hydraulic containment capacities of the repository system.

Addressing these questions requires a combination of laboratory experiments, engineered and natural analogue studies, and modelling of the long-term evolution of these systems.

Several laboratory results were presented (e.g. Figure 6). Among the engineered analogues, results from Tournemire were described. Numerical modelling is the only available tool that can tackle the spatial and temporal perturbations at a repository scale. There are still quite a number of uncertainties concerning the modelling of the mineralogical evolution of the clay in contact with cement porewaters. Furthermore, the hydraulic properties are still difficult to assess, for example the extent of clogging and the influence of heterogeneities.

Figure 5: Set up for experiments looking at the diffusion of alkaline waters through samples of clay (top) and photographs showing the sealing of a fracture as a result of calcite precipitation (bottom)



Interactions with salt rocks

Jürgen Wollrath from BfS, Germany, presented work on cementitious materials developed and used in salt repositories. The presentation focussed on the ERAM low-level waste repository, which has been developed in a former salt mine (see Appendix B).

The closure concept includes extensive backfilling of the mine and sealing of the waste emplacement areas. With this objective, a concrete with a salt aggregate has been developed and the feasibility of using this material for backfilling has been demonstrated.

One concern has been the level of naturally occurring long-lived radionuclides (radium and thorium) in the backfill materials. Assessments of the potential impacts of radionuclides in the backfill indicate that they do not compromise the long-term safety of the facility. A test of drift seal performance will take place during the next few years.

In conclusion, the salt concrete developed for backfilling and sealing of repositories in salt formations has proven to satisfy all requirements from pre- and post-closure considerations.

Interactions with steel waste containers

Nick Smart from Serco, UK, gave an overview of the effects of cementitious materials on the corrosion of steel during storage and disposal of various low- and intermediate-level radioactive wastes.

Steel containers are often used as an overpack for the containment of radioactive wastes and are routinely stored in an open atmosphere. Since this is an aerobic and typically humid environment, the steel containers can start to corrode whilst in storage. Steel containers often come into contact with cementitious materials (e.g. grout encapsulants, backfill). An extensive account of different steel container designs and of steel corrosion mechanisms was provided (see Appendix C). Steel corrosion rates under conditions buffered by cementitious materials have been evaluated experimentally.

The main conclusion was that the cementitious environment generally facilitates the passivation of steel materials. Several general and localised corrosion mechanisms need to be considered when evaluating the performance of steel containers in cementitious environments, and environmental thresholds can be defined and used with this aim. In addition, the consequences of the generation of gaseous hydrogen by the corrosion of carbon steel under anoxic conditions must be taken into account.

Discussion of the paper included:

Is crevice corrosion really significant in cementitious systems? Crevice corrosion is unlikely in the cementitious backfill considered because it will tend to neutralise any acidic conditions in the crevice.

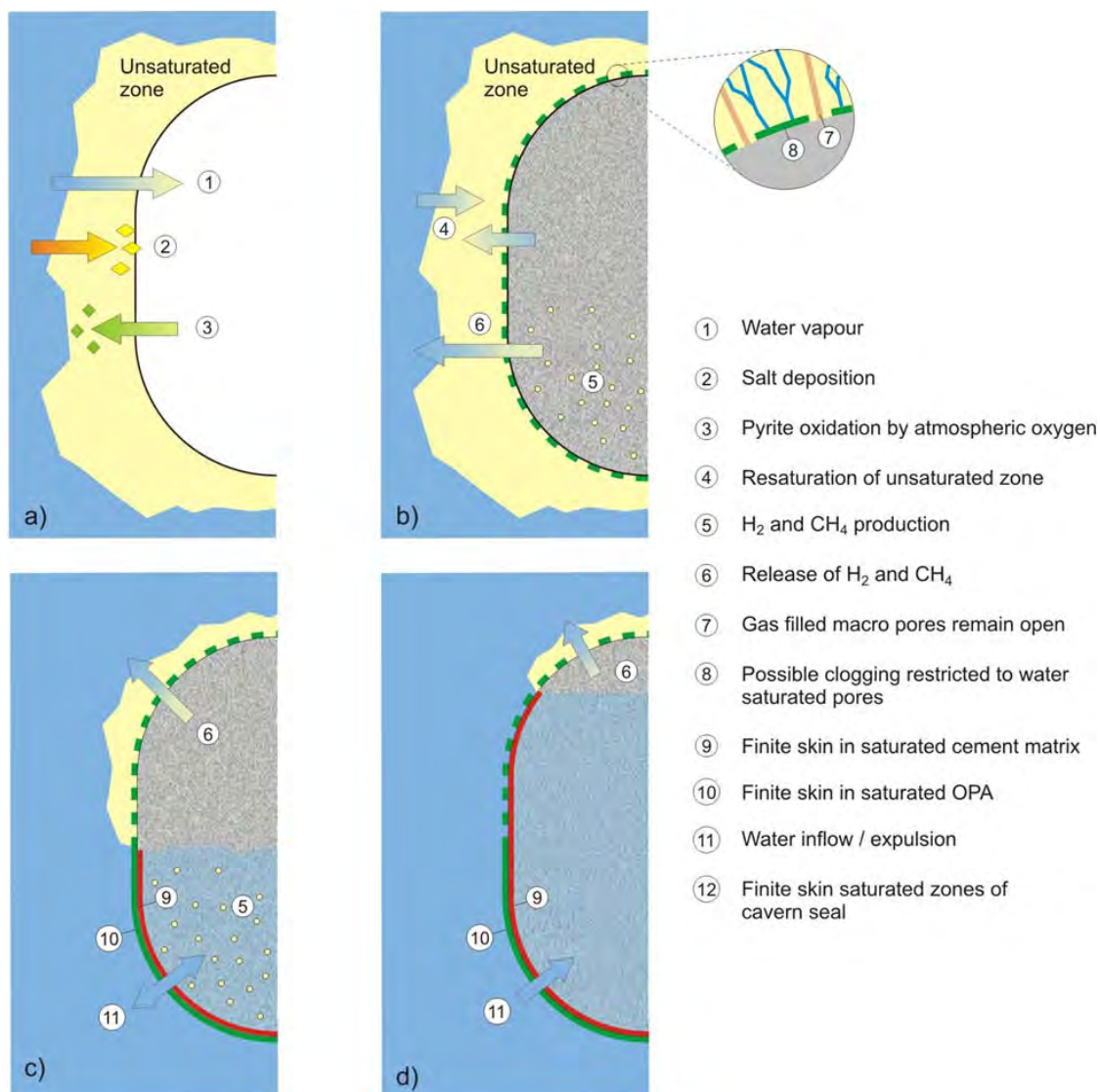
What is the role of microbially-induced corrosion (MIC) in cementitious systems? Microbes are likely to be present in a disposal facility but their effect on corrosion is uncertain.

Interactions with clay barriers - effects on gas migration

Paul Marschall from Nagra, Switzerland, described conceptual and numerical models of the evolution of a low- and intermediate-level waste repository concept in the Opalinus clay formation. In this concept, an engineered gas transport pathway is included by using gas-permeable plugs and repository seals.

In the models, an extensive set of coupled hydrochemical and hydromechanical processes are evaluated to describe gas pressure build-up and water and gas flow in the seals and in the clay formation around the repository (Figure 7). The concepts are being studied experimentally within the EC FORGE project.

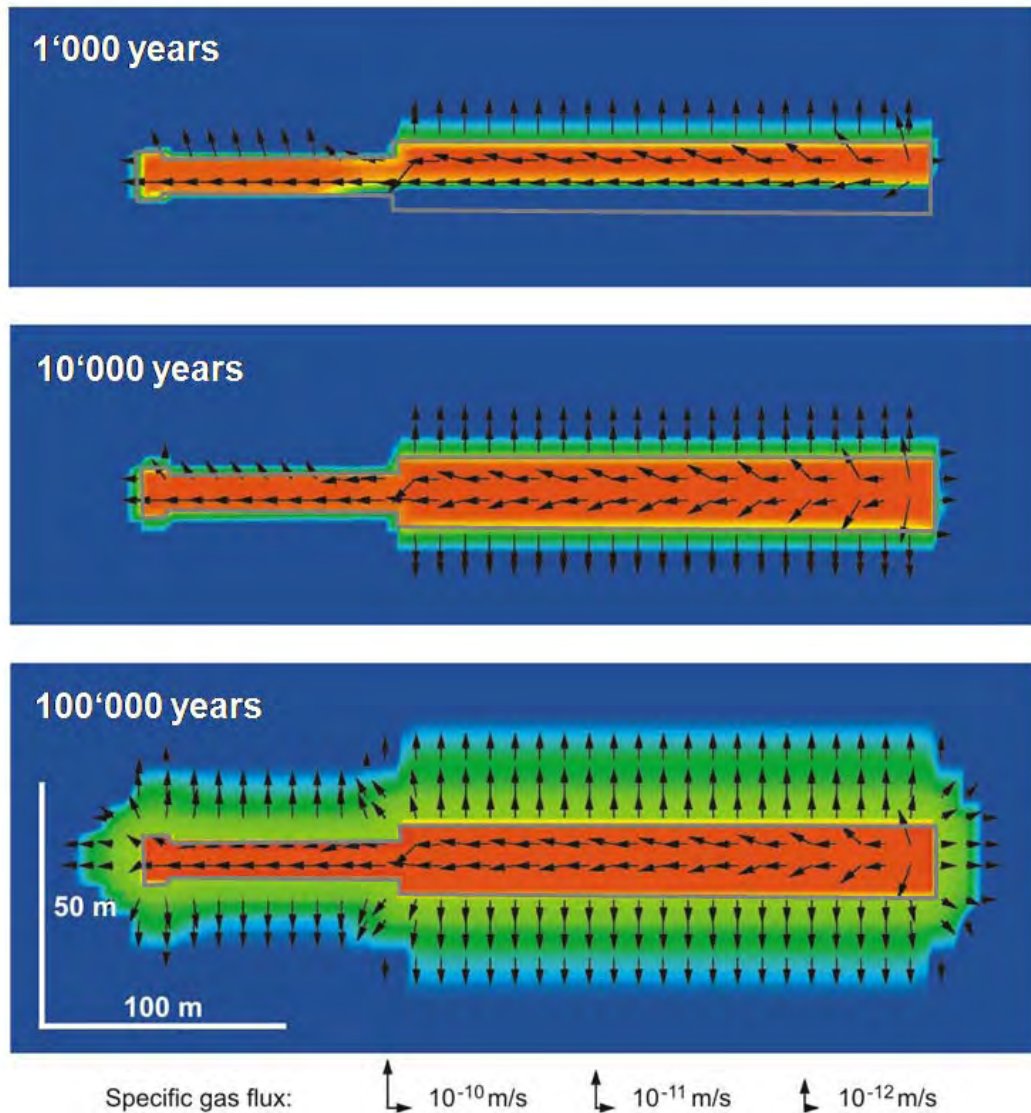
Figure 6: Conceptual model of processes at the interface of a cementitious repository and a clay host rock, including the effects of re-saturation and gas production



Simulations show the feasibility of modelling the flow and transport conditions at the cement-clay interfaces. They also show that unsaturated conditions may prevail in the backfilled disposal facility during the entire gas production phase (thousands of years; see – Figure 8), and that clogging of the cement-clay interfaces can, thus, be excluded; i.e. the engineered gas release system will function as expected.

Figure 6: Modelling results illustrating the possible saturation state of a disposal facility for low- and intermediate-level wastes developed in a clay host rock as a result of gas production.

Dark blue areas represent the fully water saturated host rock, red areas the largely gas filled disposal facility.



Discussion of the paper included:

Can you really have gas outflow and fluid inflow through a single seal at the same time as suggested by some of the modelling simulations? Yes, in some circumstances water may flow through the bottom of the seal while gas will flow through the top of the seal.

Is spatial heterogeneity in the clay important? There is a degree of spatial heterogeneity in the Opalinus clay, but because the gas flow will be channelled in the engineered part of the system, the heterogeneities in the clay do not significantly affect the results of the simulations.

How important is any feedback between the degree of water saturation and the rate of gas generation? The simulations do not couple hydraulic saturation and the gas generation rate. It is assumed instead that the surfaces of the waste and the EBS will be wet and that that rate of gas production will not be limited by the water supply. This modelling approach is considered realistic.

Key messages from Plenary Session 2

The following points summarise the main themes and outcomes of the presentations:

- Interactions with alkaline pore waters from cementitious materials probably increase the rate of HLW glass dissolution, but have little effect on the dissolution rate of spent fuel.
- In general, cementitious materials will tend to slow the corrosion of steels and copper through passivation.
- Alkaline pore waters from cementitious materials will tend to seal fractures in most host rocks due to the precipitation of minerals such as calcite and CSH.
- Chemical models are broadly satisfactory for assessing such interactions between alkaline pore waters and host rocks, but coupling these chemical models to models of the associated hydrological effects is a major challenge.
- Suitable cementitious materials have been developed for use in salt host rocks. These salt concretes typically include crushed salt as the main aggregate.
- Alkaline pore waters derived from cementitious materials have well documented negative effects on clays. Such effects have been observed in laboratory experiments, and during natural and engineered analogue studies. Although significant positive advances have been made in our ability to model these processes in the past few years, a number of uncertainties remain, especially in terms of being able to assess the hydrological consequences of such interactions.

Working Group Session 2

The second plenary session was followed by working group sessions in which the topics of the plenary were discussed in more detail. The following subsections summarise the working group discussions.

Working Group 1: Key Interaction Processes

Is there consensus on which particular interaction phenomena have low or only limited impact, and on phenomena that have potentially higher impacts?

The working group developed tables to present its findings. Tables 2, 3 and 4 relate to the interactions (via pore waters or by direct contact) of cementitious materials with HLW and spent fuel waste components, with ILW components, and with other disposal system components.

For each component considered, the group identified the interaction process considered, the timeframe within which it believed the interaction may be significant, and the reason the group believed that the interaction could affect repository safety.

In the final column of each table, the group categorised each interaction as having a high (H), medium (M) or low (L) impact, and also indicated whether this impact is expected to be detrimental (-ve) or beneficial (+ve) to the safety of a repository. The group agreed that the assessment of the impact of each interaction should ideally relate to its significance to overall repository safety, but noted that in reality this was complicated to assess and would depend upon the overall system and the specifics of repository design.

In summary:

- The effect of cementitious materials on repository safety can be detrimental or beneficial (Tables 2 to 4), depending upon the components and processes involved.
- The working group considered that overall the use of cements is positive for the repository system as a whole.
- The working group acknowledged that there are local negative impacts, but considered that these can often be mitigated.

Table 2: Cement interacting with HLW and spent fuel waste components

Cement interacting with...	Process	Timeframe	Why may it matter?	Impact on safety function (H/M/L)
Vitrified HLW	Glass dissolution	After primary overpack failure	Waste matrix lifetime	H (-ve)
Spent fuel	Fuel dissolution	After primary overpack failure	Fuel matrix lifetime	M? (-ve)
			Release of instantaneous release fraction	L (zero?)
Overpack (copper & carbon steel)	Passivation of corrosion	Varies depending upon concept	Barrier integrity (containment)	H (+ve)

Table 3: Cement interacting with ILW components

Cement interacting with...	Process	Timeframe	Why may it matter?	Impact on safety function (H/M/L)
Waste matrix (metals)	Chemical reaction	Early	Radionuclide release/gas production	H +ve (H -ve for some metals)
Waste matrix (organics)	Degradation & complexation	Early	Change in r.n. solubility/sorption	-ve
	Inhibition of microbial activity at high pH		Reduces gas production	+ve

Table 4: Cement interacting with other disposal system components

Cement interacting with...	Process	Timeframe	Why may it matter?	Impact on safety function (H/M/L)
Bentonite (buffer, backfill, plugs, seals)	Alteration of bentonite minerals	Throughout	Sealing capability (swelling, cracking)	M? (-ve) locally (but can use thicker bentonite or low-pH cement)
			Radionuclide transport parameters	+ve or -ve (locally)
Host rock	Mineral alteration (precipitation or dissolution)	Throughout	Solute transport parameters in host rock	+ve or -ve locally
			Loss of self-sealing (clay)	-ve locally
	Volume change of concrete components		Stress impacts on materials in contact (cracking etc)	-ve

Working Group 2: Upscaling

How well evolved is our ability to upscale from laboratory scales (spatial and temporal) to repository scale? How is upscaling treated in a safety case?

Many components of a repository system – including key components of the near-field such as the engineered barrier system and cementitious materials therein, and the geosphere - exhibit spatial heterogeneity. In the near field, for example, waste packages may vary in their initial contents, and there is also the potential for regions of different chemical properties to be present initially. Geosphere properties such as permeability and porosity may also vary spatially. A consideration of spatial heterogeneity is therefore required in the development of a safety case for a repository. There is also a clear need to consider the temporal evolution of conditions within the disposal system.

In general, heterogeneity in the near-field is more likely to be an issue for low- and intermediate-level waste repositories, as these tend to receive far more heterogeneous wasteforms than HLW or spent fuel repositories. Also, in general, geosphere heterogeneity is likely to be a more complex to address for repositories developed in fractured rocks than it is for repositories in clay or salt host rocks.

Upscaling is an important concern for many components of the safety case, including cementitious materials. The appropriate consideration of heterogeneity in the safety case, including any approach to upscaling, implicitly requires an associated treatment of uncertainty. An appropriate consideration of heterogeneity in the safety case can vary on a case-by-case basis according to the disposal concept.

Similarly, the significance of cementitious media to the safety case varies depending on the disposal concept and, therefore, the importance of understanding interactions of cementitious media with other repository components also varies.

Approaches to considering spatial and temporal heterogeneity in the safety case, including an appropriate approach to considering uncertainty, are well developed at a theoretical level, and have been applied in studies of the hydrogeology of a repository site (NEA 1998).

The working group concluded, therefore, that the issue is one of demonstrating the transferability and applicability of available upscaling approaches to the consideration of heterogeneity in relation to cementitious materials.

Working Group 3: Types of Cementitious Materials

What are the impacts of the different types of cementitious materials that can be used (low-pH versus high-pH; types and amounts of superplasticisers, etc)? How are these materials treated in a safety case and how can the safety case help select between the alternatives?

Table 5 identifies potential interactions involving the typical components of the EBS and the host rock with pore fluids leached from neighbouring cementitious materials. The table considers repositories for HLW, spent fuel and for low- and intermediate-level wastes. The EBS in this context comprises various combinations of a waste form (glass, spent fuel or cement), a canister (consisting in part of a steel overpack or copper shell), a bentonite buffer, and/or a backfill composed of clay, cementitious material or salt. The host rock may be a fractured crystalline rock, clay or salt.

The EBS and host rock are assumed to interact with leachates from OPC, or, alternatively, with leachates from low-pH cement blends that contain BFS, Pulverized Fly Ash (PFA) or Silica Fume (SF). Superplasticisers (SPL) may also interact with the EBS and host rock.

The interactions identified in the table were considered by the group in relation to various performance parameters underpinning safety assessments. The parameters considered were those the group believes are particularly important with regard to safety.

Other parameters, as well as coupled impacts among parameters (e.g. impacts of a degraded buffer on microbial activity and copper corrosion), could be considered in more detailed analyses of specific repository configurations. The relative importance of interactions among cementitious materials and repository components was assessed qualitatively in relation to each of the performance parameters identified in Table 5.

In accordance with the results summarised in Table 5, the conclusions drawn by the working group were as follows:

- OPC concretes and grouts are expected to have a more important, and generally adverse, impact on the EBS and near-field rock than any of the blended low-pH cements. The hyperalkaline nature of OPC leachates will, however, tend to passivate steel and copper components of the canister, which is potentially beneficial because it would tend to limit the corrosion rate of these materials.

Table 5: Possible safety-relevant impacts of various cement types on the EBS and the host rock. Relative importance of impact:

H – high, M – medium, L – low, ? – uncertain.

EBS Component/ Host rock		Performance Parameter	High-pH Systems	Low-pH systems (blends)			SPL
			OPC	BFS	PFA	SF	
Waste form	Glass	Dissolution rate	H	L	L	L	?
		Complexation	?	?	?	?	H
	Spent fuel	Dissolution rate	L?	L?	L?	L?	?
		Complexation	?	?	?	?	H
	(L/ILW)	Dissolution rate	L?	L?	L?	L?	?
		Complexation	?	?	?	?	H
Canister		Steel passivated?	Yes	No	No	No	?
		Copper passivated?	Yes	No	No	No	?
Buffer		Swelling pressure	H	L	L	L	?
		Porosity/permeability	H	L	L	L	?
		Mineralogy	H	L	L	L	?
		CEC	H	L	L	L	?
		Kd	H	L	L	L	?
		Pore fluid chemistry	H	L	L	L	?
Backfill		Clay	H	L	L	L	?
		OPC	L	M	M	M	?
		Salt	L	?	?	?	?
Host rock		Buffer capacity	H	L	L	L	?
		Porosity/permeability	H	L	L	L	?
		Mineralogy	H	L	L	L	?
		CEC	H	L	L	L	?
		Kd	H	L	L	L	?
		Pore fluid chemistry	H	L	L	L	?

- Potentially adverse impacts resulting from the interaction of hyperalkaline leachates from OPC concretes and grouts on clay minerals in the buffer, backfill and host rock may be particularly important. The group acknowledged, however, that these effects have generally been interpreted only in terms of the dissolution behaviour and thermodynamic stability of clay minerals, and that associated impacts on the mechanical and rheological properties of clay-based materials are not well understood. The group felt that OPC concretes and grouts should be avoided in repositories in which clays are present, provided this is feasible from an engineering and/or cost perspective.
- The group felt that cementitious materials will have only a minor impact on the performance of repositories in salt host rocks. The group noted, however, that the effects of low-pH cements on salt are uncertain.
- Superplasticisers may affect the complexation (and hence solubility/sorption) behaviour of radionuclides released from glass, spent fuel and cement waste forms. The effects of SPL on other safety-relevant functions of the EBS and host rock are largely unknown.

With respect to the question of how the materials are treated in a safety case, the group felt that this question should be handled differently for HLW and spent fuel repositories than for low- and intermediate-level waste repositories.

For HLW and spent fuel repositories, specific interactions such as those noted in Table 5 are usually assessed using scoping calculations or mass-balance arguments, which bound the maximum extent to which an EBS component might be degraded by interactions with cementitious leachates.

For low- and intermediate-level waste repositories, the cement waste form is treated as a chemical barrier controlling the solubility and sorption behaviour of radionuclides released from the cement matrix. The cementitious materials may also be treated as a physical barrier that limits access of released radionuclides to flowing groundwater.

In either case, the group felt that a critical assessment of all potentially negative impacts (e.g. arising from the generation and migration of a high-pH plume) is needed to enhance confidence in the results of a safety assessment.

In terms of selecting between alternatives, the group felt that models and scoping analyses can be used to identify attributes of the EBS on which to optimise performance and enhance confidence in the safety case. Specific examples of this useful relationship between safety assessment and repository design include:

- The use of scoping calculations to justify selection of an upper bound on the pH of low-pH cement leachates (i.e., the pH level below which the safety functions of the buffer would not be adversely affected).
- A geochemical analysis of the use of BFS in cementitious waste forms to establish and maintain chemically reducing conditions.
- An analysis of porosity requirements in cements needed to promote gas release.
- Scoping analyses of the minimum pH needed to limit radioelement solubilities and to optimise sorption in some ILW systems.

The following general conclusions were noted by the group with regard to the effects of cementitious materials on repository components:

- Safety assessments can provide useful feedback to guide repository design.
- Cements are engineered materials whose properties can be tailored to help optimise EBS performance and to minimise adverse impacts on other repository components.
- A better understanding is needed of the relation between chemical/mineralogical changes resulting from interactions involving cementitious materials and the EBS, and associated impacts on physical, mechanical and rheological properties.
- Although sophisticated models of cement evolution and the interaction of cement leachates with repository components are available, it is difficult to assess the accuracy of model predictions over repository-relevant time scales.
- Although it is preferable to avoid the use of OPC in repositories containing clay minerals in the buffer, backfill or host rock, there exists a large database and extensive practical experience in using OPC that can serve as a basis for developing alternative cement formulations and blends.

The group also noted that the interactions of cementitious materials with other repository components should not be considered in isolation, but rather within the broader context of other repository features, and other events and processes that will in reality occur simultaneously.

Working Group 4: Analogues

Are natural analogues of cementitious materials useful for a safety case or performance assessment analyses? What are the possibilities, benefits and drawbacks?

The working group distinguished between different types of analogue studies based on the timescales involved (Table 6). The systems studied need not always be closely analogous to a disposal facility in all respects. Examples include the cement-like rocks and highly alkaline pore waters at Maquarin in Jordan, and the ~2 000-year old cements used at Hadrian's Wall, in the UK.

Studies of natural or anthropogenic systems can be useful in that they can provide information on the processes that might occur in a disposal system, and potentially give evidence regarding the possible extent and rates of such processes.

A key advantage of studying existing natural or anthropogenic systems is that larger spatial and temporal scales can be considered than are accessible during laboratory or URL experiments. However, the initial conditions and related boundary conditions affecting these systems are often only poorly known.

Information from analogue studies may help to build confidence that performance assessment models include the relevant processes, and may also serve to provide other qualitative safety arguments.

The working group noted that studies of analogues of cementitious materials provide support for conceptual models of the alkaline plume and for the interactions of cementitious materials with other disposal system components.

To-date however, there has been little study of analogues for low-pH cements. Possible study sites in Cyprus and the Philippines were identified. It was also noted that **there are possibly more opportunities to study analogues of cements relevant to near-surface disposal than for geological disposal.**

Table 6: Characteristics of different types of analogues

Engineered analogues	Archaeological analogues	Natural analogues
Timescales <150 years	Timescales <5 000 years	Timescales : geological
More constrained in initial and boundary conditions	→	Less constrained in initial and boundary conditions
Materials are more similar to currently used materials	Less similar than currently used materials	Natural with similar chemical properties
Impact on stakeholder group: different views, dependent on audience		

Working Group 5: Interfaces

How are the interfaces between cementitious materials and surrounding repository components currently taken into account? What are the strengths and weaknesses of current treatments of such phenomena?

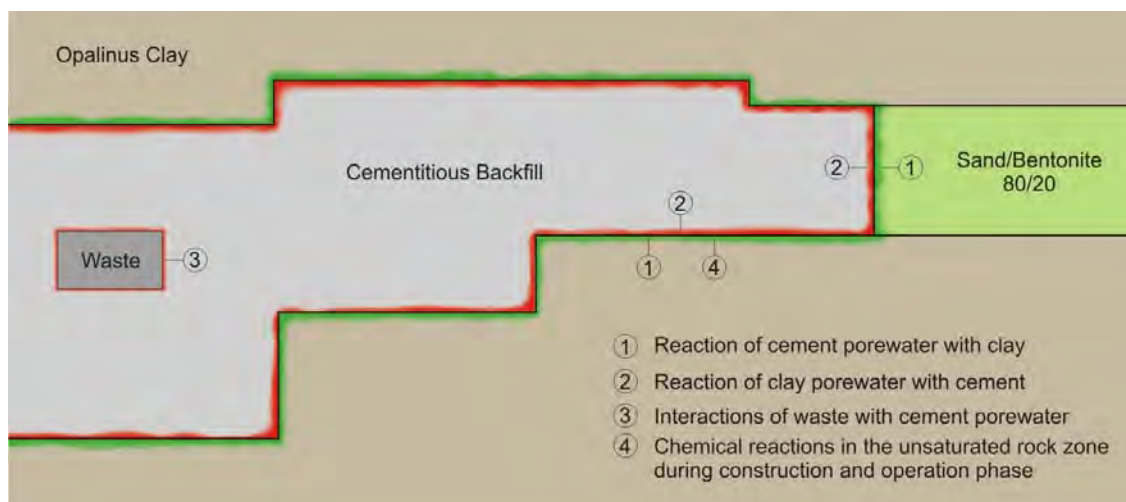
Figure 9 illustrates the types of interfaces between cementitious materials and other disposal system components considered by the working group.

The working group divided the topic into sections corresponding to the following interfaces:

- Waste/cementitious materials.
- Container/cementitious materials.
- Backfill-buffer/cementitious materials.
- Host rock/cementitious materials.

For each of these interfaces various disposal concepts were discussed.

Figure 9: Examples of interfaces between cementitious materials and other disposal system components (from Marschall et al., this workshop)



Waste/cementitious materials

ILW metal waste disposal

It was noted that the corrosive expansion of metals in ILW can be assessed/monitored by measuring the volume and timing of the associated gas production. Although simple and repository dependent, this approach was considered to be robust. The impact of the metal expansion on the cement integrity is not usually taken into account. This was felt to be possibly non-conservative as the impact on leaching of the cement matrix is ignored.

The production of ^{14}C during corrosion (especially organic ^{14}C) was also considered and it was noted that, due to uncertainty regarding the likely form of ^{14}C (e.g. as $^{14}\text{CO}_2$ or $^{14}\text{CH}_4$), it was difficult to take credit for ^{14}C retention in the cement matrix (e.g. as secondary calcite, $\text{Ca}^{14}\text{CO}_3$).

HLW disposal in clay

The group considered that the treatment by Ondraf/Niras of vitrified glass dissolution by hyperalkaline cement leachates was simple and robust. However, it was noted that, as the glass dissolves, the ensuing local acidic conditions would decrease the pH of the system, so slowing the glass dissolution rate. It was suggested, therefore, that not including this positive feedback was probably unnecessarily pessimistic.

Spent fuel disposal in clay

The current treatment, which indicates minimal dissolution of SF in hyperalkaline leachates, was also considered simple and robust. However, as above, it was felt that omitting waste-cement feedback should be reconsidered. In this case, potential increased spent fuel dissolution rates due to uranium adsorption on cement could be included.

Container/cementitious materials

ILW disposal

In most cases, performance assessments for ILW disposal have assumed instantaneous waste dissolution and that the waste container does not provide a physical barrier. The group considered that both of these assumptions were overly conservative. The group noted that a significant body of data exists on radionuclide retardation on corrosion products.

In the particular case of the Belgian ILW disposal concept, potential disruption of the host clay by gas has been explored and it is assumed that the clay will quickly reseal after decrease of the gas pressure. Radionuclide transport in the gaseous phase is assumed to be of minor importance, but it will nevertheless be further investigated.

Backfill-buffer/cementitious materials

HLW/spent fuel disposal

Bentonite buffer alteration is often treated rather simplistically in performance assessments, with simple mass balance being calculations carried out. The group accepted that the current treatments were robust, but considered them to be overly conservative. To date, little work has been done on the likely perturbations when utilising low-pH cements. In view of the considerable effort being invested in the development of low-pH cements, however, it seems that it would be sensible to begin at least some scoping studies on the interactions between low-pH cements and bentonite materials.

Scepticism was expressed regarding the pH 11 value often quoted as the level below which interactions with bentonite will be insignificant; it was felt that quantitative data to support this pH criterion were lacking.

Host rock/cementitious materials

Salt host rocks

In the current German concept for the ERAM LLW disposal facility in salt, there will be extensive backfilling with salt concrete to both stabilise the mine and seal in the waste. Whereas the NaCl-cement formulations appear to work well, mixtures with other salts are less well understood. A mass balance approach is used to assess performance of the repository which seems conservative.

Clay host rocks

As for the backfill/buffer interaction discussed above, assessments of the effects of cementitious materials on clay host rocks are usually approached by using mass balance calculations. The working group accepted that such approaches are robust, but considered that a better understanding of clay sealing mechanisms would be useful if the degree of conservatism in performance assessments was to be properly understood and possibly reduced. It was also noted that the commonly made assumption in mass balance calculations of a zone in which the clay is fully altered does not represent the obvious heterogeneity of pore clogging seen in laboratory, field and natural/engineered analogue samples.

Fractured, crystalline host rocks

Fracture sealing and the blocking of porosity, observed within short timescales, will impact on existing site hydrogeology, making accurate estimation of flow and host rock behaviour difficult. In addition, the impacts of potential fracture re-activation processes on fracture sealing are yet to be considered. Performance assessments have not therefore tended to quantify the potentially beneficial effects of fracture clogging as a result of the interaction of cementitious pore fluids with fractured host rocks.

Conclusion

In conclusion, the treatment in performance assessments of interactions between cements and other repository components was considered in general to be simple, conservative and robust. Interaction processes are not generally treated mechanistically, however, and the group considered that there is a tendency for the performance assessments to be over conservative in this regard.

Cementitious Materials in the Safety Case

Plenary Session 3

The third plenary session was designed to examine the integration of information on cementitious materials in the safety case and to consider the implications of using cementitious materials for long-term safety. The following sections summarise the papers presented and the associated discussions.

Strategic choices in the Belgian supercontainer design and its treatment in the safety case

Maarten Van Geet of Ondraf/Niras discussed various aspects relating to the selection of a supercontainer disposal concept for HLW and spent fuel disposal, including an OPC concrete buffer.

The previous Belgian reference disposal concept (SAFIR-2, Ondraf/Niras 2002) was briefly described, and it was noted that several assessments and reviews of that concept had raised questions over its feasibility, operational safety, and ability to provide containment of the wastes throughout the thermal phase, i.e., the period when temperatures in the repository will be significantly above the ambient temperature of the host rock because of radioactive decay of the wastes. In light of these findings, Ondraf/Niras worked through a process of multi-criteria options appraisal (Figure 10) with the aim of coming to a new reference concept with better characteristics.

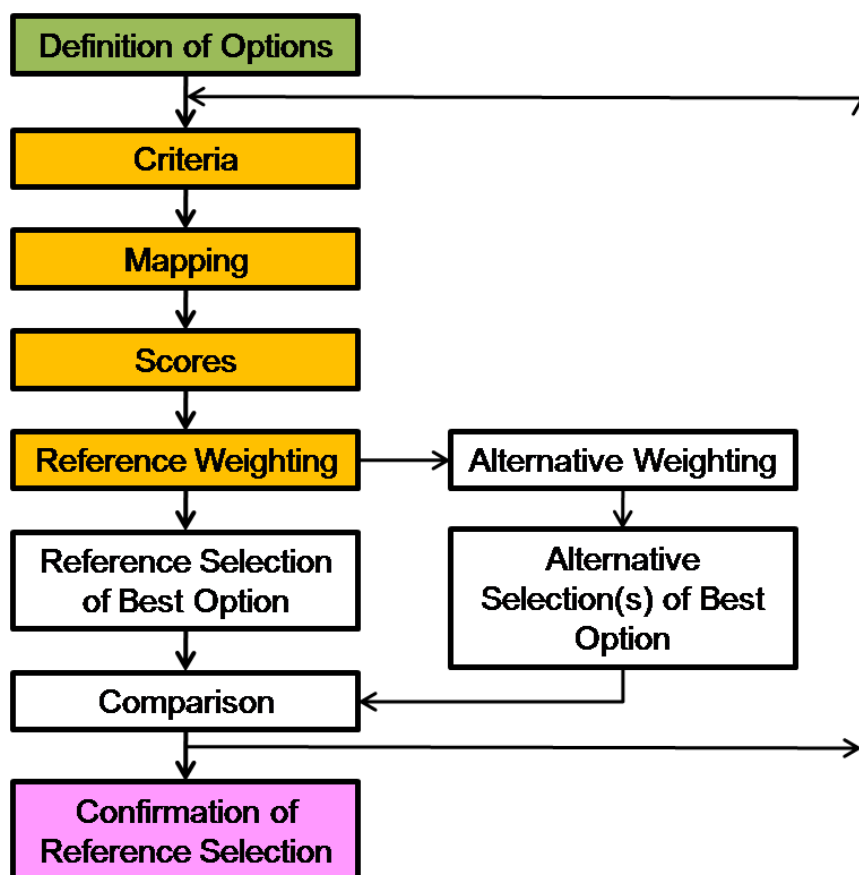
Three main types of disposal concept were considered:

A supercontainer design, in which the overpack would be emplaced in the disposal gallery as an integrated unit including a cementitious buffer. The buffer would provide radiological shielding.

- A borehole design, in which the overpack would be emplaced in a borehole perpendicular to the disposal gallery.
- A sleeve design, in which the overpack would be emplaced in a metal sleeve that would be emplaced in the disposal gallery prior to the overpack.

In the latter two concepts, separate measures would be needed to provide radiation shielding during waste transport and handling.

Several broad assessment criteria were considered; engineered robustness, host-rock perturbation, intrinsic robustness (of materials characterisation and modelling), ease of demonstration, technical operation, flexibility, and financial feasibility. The result of scoring the different design options against these criteria and various sub-criteria led to the selection of the supercontainer concept as the current reference concept and design.

Figure 10: Methodology used by Ondraf/Niras for assessing various disposal

Key reasons for this selection included:

- The requirement for watertight containment of the waste during the thermal phase, which meant adopting a design that would control overpack corrosion.
- The need to be able to characterize and model the relevant phenomena especially in the buffer. OPC concrete is a relatively well understood industrial product for which characterisation and modelling is relatively easier than for a natural product such as bentonite, a possible alternative buffer material.

In terms of safety analysis, the use of an OPC buffer provides well constrained boundary conditions for the corrosion assessment and this helps to better underpin confidence in overpack integrity during thermal phase.

If or when the overpack eventually fails, release from vitrified HLW may be faster than in the previous disposal concept, but Ondraf/Niras has used the safety case to help make a strategic choice not to rely too much on slow glass dissolution as a safety function, because in this concept glass dissolution has a minor impact on the overall safety of the system. The selection of a cementitious buffer is expected to have little effect on the rate of spent fuel dissolution. Further research is being conducted to confirm these assumptions.

Discussion of the paper included:

What was the reason for the choice of OPC for the supercontainer buffer rather than low-pH cement? The high pH environment imposed by OPC is effective in passivating the iron and steel supercontainer components against corrosion, in a way that would not

occur with low-pH cements. Even though the use of OPC brings higher alkalinity, which could cause alteration of the host rock, the amount of alteration is not significant.

Why was the multi-criteria appraisal of design options scored so evenly? The scoring was rather even because a wide range of assessment criteria was considered. However, the result from the options appraisal is robust to changes in the weightings applied to the criteria.

Safety case approach for a KBS-3 repository in crystalline rock

Barbara Pastina of Saanio & Riekkola described the approach to considering cementitious materials in a safety case for a KBS-3 repository in Finland. In this concept, cements will be used predominantly as tunnel plugs and seals.

Part of the Finnish approach has involved identifying the cement-related FEPs. For example, FEPs representing the effects of cement on spent fuel, on the canister and on radionuclide transport include:

- Fuel matrix dissolution at high pH.
- Copper corrosion at high pH.
- Radionuclide speciation and solubility at high pH.
- Radionuclide sorption and diffusion at high pH.
- Radionuclide transport due to organic materials (e.g. superplasticisers).
- Colloid formation at a high pH plume front.

FEPs representing the effects of cement on bentonite in the buffer and backfill include:

- Potential changes in swelling pressure due to mass loss, decrease in clay density, and precipitation of secondary minerals.
- Potential cracking and increase of hydraulic conductivity due to cementation.
- Increase of the cation exchange capacity due to the loss of silica from the montmorillonite structure.

Amongst the cement-related FEPs, the main concerns are related to effects on the performance of the bentonite buffer. Cement-bentonite interactions are complex, there are few experimental data, and there are significant modelling uncertainties (e.g. limited knowledge about the reactions that may occur and their rates, and the effects of temperature). Accepting the existence of various uncertainties, preliminary modelling studies performed using the TOUGHREACT code illustrate the potential for porosity reduction and clogging of porosity in bentonite affected by cementitious porewaters. The modelling also suggests that the high pH of the porewaters moving from the cementitious materials into the bentonite may be rapidly lowered as a result of reactions with the bentonite close to the cement-bentonite interface.

Taking account of the various research and modelling studies, the Finnish approach is to mitigate the negative impacts of the cementitious materials on the bentonite barriers through repository design by:

- Minimising the use of cement.
- Using low-pH cement in and near the EBS and in waste disposal areas.
- Ensuring sufficient thickness of bentonite where there is direct contact between bentonite and concrete.

Discussion of the paper included:

Why not use low-pH cements everywhere in the KBS-3 system? Only concretes near the EBS and that will remain in the repository need to be low-pH cement. Low-pH cement is a bit more expensive than OPC, but the main reason for using OPC concretes elsewhere in the facility is that is that there is more experience in their use.

Environmental safety case and cement-related issues for ILW in a co-located geological disposal facility

Simon Norris of the NDA described safety case and cement-related issues for a geological disposal facility for ILW. The Environmental Safety Case (ESC) needs to demonstrate a clear understanding of:

- The disposal facility in its geological setting.
- How the disposal system will evolve.
- How the various components of system (including cementitious materials) contribute to meeting the requirement of providing a safe long-term solution for the disposed wastes.

The ESC must include and support the key environmental safety arguments with underpinning lines of reasoning and detailed analysis, assessments and supporting evidence (including those relating to cementitious materials). Key components of the ESC are identified in Figure 11.

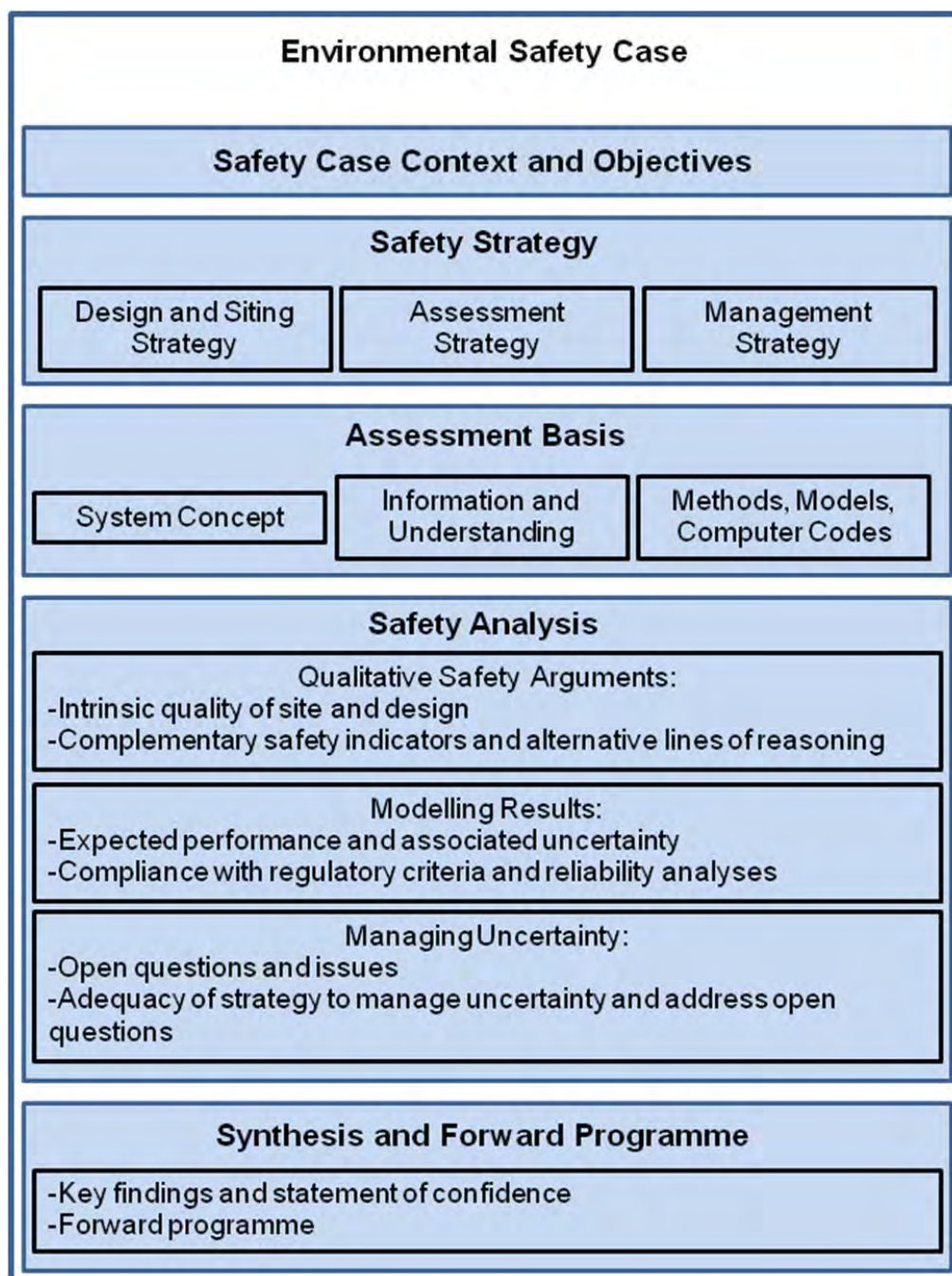
In an ILW disposal system, cementitious materials could be used in several ways:

- As in-package grouting materials and package materials.
- Backfill material.
- Shotcrete and other vault lining technologies that could be employed during construction and operation.
- Engineered seals.
- Structural materials.

Given that cementitious materials will play important roles in the disposal system - and within a general strategy for managing uncertainty - the NDA is conducting, or has recently conducted, research into the following topics:

- Assessment of the potential for interactions between disposal modules for low- and intermediate-level wastes and for HLW and spent fuel.
- The effect of possible cementitious vault liners (e.g. composed from shotcrete) on the early post-closure evolution of waste-derived gas in a geological disposal facility for low- and intermediate-level wastes.
- The evolution of cementitious backfill materials, including cracking, and related evolution of groundwater flow and chemistry in the vault environment of a geological disposal facility.
- Evidence from nature and archaeology relevant to the long-term properties of cement.
- Interaction of waste-derived gas (particularly carbon-14 bearing gas) with cementitious materials in the facility near-field.
- The choice of in-drum encapsulant, noting that for some wastes a cementitious material may not be optimal.

Figure 11: Key parts of an environmental safety case

**Discussion of the paper included:**

What are the potential impacts of cracking of cementitious materials? Cracking of the backfill is an important issue because such cracking might affect the flow of water through the backfill, the ability of the backfill to chemically condition the near-field, and the transport of radionuclides. The NDA is considering the impacts of cracking and spatial heterogeneities and is currently thinking about how to represent such effects at a vault scale. The aim is to develop better understanding of the impacts of a network of cracks through the backfill.

Plenary Discussion

A final discussion session was led by Lawrence Johnson, of Nagra, Switzerland.

It was emphasised that the safety case provides a broad approach to understanding the entire disposal system. During the early phases of safety case development, the safety case is an important tool with which to identify, assess, and manage the various design options and make choices (e.g. between the use of OPC or low-pH cements). To initiate discussion, several questions were posed relating to cement evolution, to novel cementitious materials, and to the influence of gas production in repositories.

Evolution of cements: There seems to be broad understanding of the chemical-hydrological-mechanical effects relevant to long-term safety, but can we realistically couple these in performance assessment models?

Workshop participants considered that significant progress has been made in chemical modelling of cementitious materials over recent years and that capable coupled reactive transport codes are also available. However, it was felt that the timing and impacts of cracking were uncertain and hard to include in coupled models. This may be significant in disposal systems where there is advective flow, but is less relevant for systems dominated by diffusive processes.

Uncertainties were identified related to simulating the precipitation of solid phases in reactive transport simulations. It was noted that this type of uncertainty also extends to the modelling of sorption and other surface area-dependent processes. The selection of secondary mineral phases during modelling studies can have a large effect on calculated solubilities and on the degree or extent of bentonite alteration. It was suggested that expert judgement based on knowledge of experimental results and natural systems provides the best approach for identifying the likely secondary minerals.

There was discussion of whether the results of modelling are reasonable or reliable; particularly those that suggest that over thousands of years cement pore fluids will cause alteration of only the outer few centimetres of bentonite. It was accepted that the uncertainties should be fully acknowledged, but it was also argued that the EBS can be designed so that the uncertainties are taken into account and there is confidence that sufficient unaltered bentonite will be present.

Novel materials: What further understanding do we need to bring low-pH cements to application?

It was noted that some types of low-pH cements are already being applied as 'low-heat concretes' in other industries.

There was discussion of the reactivity of low-pH cement with bentonite. Even though low-pH cements contain no free portlandite, $\text{Ca}(\text{OH})_2$, it was suggested that the remaining CSH phases would still be reactive with bentonite clay. It was also suggested that the basis for setting a pH criterion of less than 11 as the level below which low-pH cements can be used in conjunction with bentonite was not well justified. It was accepted that it is not easy to set a particular pH value criterion because the CSH and CASH phases present will buffer a range of pore water pH values from around 10.5 to approximately 11.

It was noted that in the long-term, OPC concretes evolve into materials with no free portlandite and relatively lower pore water pH values as a result of leaching. The implication of this discussion was that the justification for using low-pH cement in conjunction with clays and bentonites in HLW and spent fuel disposal systems was not so clear, particularly as the evolution of low-pH cements is less well understood than the evolution of OPC materials.

Gas production: What are the implications? What are the uncertainties, and what do we need to know?

First, it was acknowledged that gas production is probably more of an issue for low- and intermediate-level waste disposal than for HLW and spent fuel disposal, because low- and intermediate-level wastes tend to contain more cellulosic and metallic wastes that may degrade and produce gas. Again, in general terms, gas production is probably more of an issue in un-fractured host rocks, such as clays, because if a discrete gas phase is present then its migration may involve processes of pressurisation and temporary fracturing or opening of the host rock. In disposal systems in which a discrete gas phase forms, gas production might have quite significant effects on the evolution of the near-field. Groundwater may be kept out of the repository by the pressure of gases formed and the near-field may remain in a partially saturated state for long periods.

It was noted that the effects of partial saturation on cements are not well known. It was also noted that the degree of hydraulic saturation will possibly affect corrosion and gas generation rates. There is very little data on corrosion and gas production in partially saturated cementitious materials under reducing conditions.

There was discussion of whether a safety case can rely on an engineered pathway for gas release as it was suggested that there will always be some clogging effects in cementitious tunnel plugs.

There was also discussion of the degree to which it is reasonable to give separate consideration to the gas and groundwater pathways in performance assessments. The view was that, particularly for low- and intermediate-level waste disposal systems, it would be important to address at an appropriate level of detail the coupling between water flow and gas production and flow.

Conclusions

Key Points, Issues and Challenges

The various workshop discussions identified the following key points, issues and challenges.

Cementitious materials are ubiquitous in geological disposal. They have been proposed for use as roadways and floors, tunnel linings, waste conditioning matrices, waste packages, overpacks, buffers, backfills, tunnel plugs and seals, and fracture grouts.

Although some of these cementitious materials may be removed before repository closure, large quantities (e.g. several million kilograms) may remain in HLW/spent fuel repositories after closure. Even larger quantities of cementitious materials will remain in repositories for low- and intermediate-level radioactive wastes.

Although few geotechnical problems (e.g., issues of settlement, early structural failure of barriers, seepage) are expected in installing cements and concretes in geological disposal facilities, this may need to be confirmed by further underground testing and demonstration. There will also be a need to consider the variability and quality of concrete materials as supplied, and to develop procedures to verify the quality of concrete structures emplaced in geological disposal facilities.

Cementitious materials placed in a geological disposal facility will evolve and degrade over time as a result of various physico-chemical processes.

Physical degradation effects (e.g. desiccation, shrinkage, cracking) tend to lead to changes in porosity and permeability, and this may cause the materials to develop spatially heterogeneous properties that can affect patterns of water and gas flow. In detail, the relationships between permeability and porosity in these systems can be complex and uncertain. Physical degradation of cementitious materials is often not represented explicitly in safety assessments but is instead addressed through the selection of parameter values (e.g. for permeability) averaged over appropriate spatial scales. In some cases such parameter values are chosen for a series of degradation states or points in the degradation history.

There is good consensus regarding the chemical processes that occur within cementitious materials. Our understanding of OPC systems has increased significantly over the last few decades and detailed thermodynamic databases and models of the chemistry of these cements are available. Our understanding and ability to model the chemistry of low-pH cement systems has also increased in the last few years, but is less well advanced.

There are strong couplings between the chemistry of cementitious materials and the solubilities and sorption behaviour of some radionuclides, and these couplings need to be considered in performance assessment. This is usually approached through the selection of relevant solubility and sorption data, and various approaches have been taken in performance assessments to account for the effects of the chemical evolution of cementitious materials on radionuclide behaviour.

Although detailed chemical models of cementitious materials are available, it is very difficult to develop detailed coupled models that also include physical/mechanical

processes (e.g. cracking) and take account of the associated hydrological changes. The occurrence of cracking and the potential for spatially heterogeneous flow and patchy, localised chemical conditioning, leads to uncertainty in models of radionuclide transport behaviour. There may, therefore, be a need for work on upscaling the detailed knowledge of physical and chemical processes that can occur in cementitious systems. Although approaches have been proposed and applied for upscaling certain hydrological problems, these techniques have not yet been applied for considering radionuclide transport in cementitious systems at repository scales. However, it is emphasised that a complete understanding of the behaviour of cementitious materials and their interactions is not necessarily required for a robust safety case for waste disposal to be developed. The remaining uncertainties may not be significant and may be managed through appropriate disposal system design.

In geological disposal facilities for low- and intermediate-level wastes, waste degradation and metal corrosion may cause significant quantities of gas to be produced. Some recent studies suggest the possibility of using cementitious materials to form an engineered release pathway for the gas. In some host rocks (e.g. clays), gas generation may mean that the near-field of the repository is only partially hydrologically saturated for significant periods of time (thousands of years). Models of partially-saturated cementitious systems are in their infancy, and there may be important couplings between processes in such systems, including between hydraulic saturation and gas generation. Partially-saturated cementitious systems also occur in near-surface radioactive waste disposal facilities, and there may be scope for transfer of information between performance assessment programmes being conducted in these two areas.

Interactions between cementitious materials and other disposal system components tend to be localised in their effects. These effects can have positive or negative impacts. For example cementitious materials may:

- Enhance rates of vitrified HLW dissolution.
- Slow the corrosion of steel and copper by causing passivation.
- Cause localised alteration of bentonite (e.g. cementation, embrittlement).
- Lead to local alteration of the host rock (e.g. mineral dissolution and precipitation, porosity changes, clogging of fractures).

Because the interactions are local effects, they can be managed using a combination of research and design studies. The research studies are aimed at understanding the materials and quantifying the processes of interest, while the design studies are aimed at selecting suitable barrier materials and using these in appropriate combinations and masses or thicknesses so that any negative interactions are insignificant to the performance of the entire disposal system. For example, OPC is known to cause alteration of bentonite, but the chemistry of the cementitious materials, and the thickness of bentonite barriers in a repository can be designed to optimise performance.

Various solutions may exist for managing the effects of cementitious materials on neighbouring materials such as bentonite. For example, one approach might be to use low-pH cementitious materials; another might be to alter the design of the system to minimise the occurrence of interfaces between materials where interactions could occur; a third approach might be to emplace sufficient bentonite that the interactions affect only a small proportion of the barrier and are, therefore, unimportant.

Selecting a suitable design will involve various modelling studies aimed at considering effects over longer timescales than can be accessed by experiment. At a research level, models of such interactions have improved considerably over recent years but, in contrast, safety assessments still tend to represent interactions between cementitious materials and other repository components using rather simple, conservative approaches. These simple performance assessment representations may be

easier to defend, but tend to give a pessimistic view of disposal system performance. In particular, some potentially positive effects of such interactions (e.g. clogging of fractures in the host rock as a result of precipitation of cement-related minerals) have been identified but are not included in safety assessment models.

There are always uncertainties when using models to consider long periods of time, but some evidence or corroboration can be sought from studies of relevant natural and anthropogenic systems. For example, studies of natural systems, such as the cement-like rocks at Maquarin in Jordan, can provide useful information on the processes that occur in such systems. This type of information may help to build confidence that performance assessment models include the relevant effects and processes, and may also provide other qualitative safety arguments.

Uncertainty and sensitivity analyses can also be used to help build confidence that a facility will provide an acceptably safe disposal solution. Uncertainty analysis should be a central part of safety assessment. Recent advances in computing power mean that it is now reasonable to expect safety cases to include and be supported by extensive structured uncertainty and sensitivity analyses.

Overall, cementitious materials clearly fulfil important and beneficial roles in the disposal of long-lived radioactive wastes, but there are some potentially negative effects that have to be assessed and managed by using the safety case to inform disposal system design.

Workshop Achievements

The workshop was very well attended and provided:

- A valuable forum, for disposal programme managers, safety assessors and researchers to discuss the roles, use and assessment of cementitious materials in geological disposal.
- A snapshot of the 'state of the art' in the use and assessment of cementitious materials in geological waste disposal.
- Improved understanding of the roles of cementitious materials in geological disposal and the safety case.
- An opportunity for valuable sharing of experience, knowledge and lessons learnt.

The strength of interest in the topic areas covered by the workshop suggests that further such international cooperation on disposal system design and the safety case would be welcomed by the waste disposal community.

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Appendix A

WORKSHOP AGENDA

DAY 1 – 17 November 2009

09:00 – 09:30	<p>Welcome Addresses <i>ONDRAF/NIRAS, NEA</i></p> <p>Introduction: Scope and Objectives of the Workshop <i>Maarten Van Geet (ONDRAF/NIRAS, Belgium)</i></p>
09:30 – 10:15	<p>INTRODUCTORY PRESENTATION: Context for the workshop The use of cementitious materials in different national programmes: functions, similarities, differences and the main questions and interactions <i>David Bennett (TerraSalus Limited, UK)</i></p>
10:15	<p>SESSION I:</p> <p>USE AND EVOLUTION OF CEMENTITIOUS MATERIALS</p> <p><i>Chair: Jason Martino (AECL, Canada)</i> <i>Rapporteur: Roberto Pabalan (CNWRA, USA)</i></p>
10:15 – 10:45	<p>Engineering feasibility for the fabrication and emplacement of cementitious repository materials: Results from the EC-ESDRED project <i>M^a Cruz Alonso and Jose Luis García-Siñeriz (IETcc of the Spanish National Research Council, Spain)</i></p>
10:45 – 11:15	Poster session
11:15 – 11:45	<p>Compositions and uses of cementitious materials: experience from ONKALO <i>Johanna Hansen (Posiva, Finland)</i></p>
11:45 – 12:15	<p>Upscaling of mechanical and hydromechanical aspects of cementitious materials <i>Jian-Fu Shao and Nicholas Burlion (LML-University of Lille, France)</i></p>
12:15 – 13:30	Poster session
13:30 – 14:00	Chemical evolution of cementitious materials

Barbara Lothenback (EMPA, Switzerland)

14:00 – 14:30 **Implications for solubility and retention of radionuclides over long timescales**
Simon Norris and Steve Williams (NDA, UK)

14:30 – 14:45 **Introduction to the working groups**
Betsy Forinash (NEA).

14:45 **WORKING GROUP SESSION I**

14:45 – 16:45 **Parallel working group session**

16:45 – 17:30 poster session

17:30 – 18:00 **Working group reporting (5-10 minutes each)**

END OF DAY 1

DAY 2 – 18 November 2009

09:00	SESSION II:
	CROSS-CUTTING ISSUES – INTERACTION OF CEMENTITIOUS MATERIALS WITH REPOSITORY COMPONENTS
	Chair: Colin Walker (JAEA, Japan)
	Rapporteur: Russell Alexander (Bedrock Geosciences, Switzerland)
09:00 – 09:30	Interaction of cementitious materials with high-level waste (HLW) <i>Karel Lemmens (SCK•CEN, Belgium)</i>
09:30 – 10:00	Alkaline plume on crystalline rock <i>Russell Alexander (Bedrock Geosciences, Switzerland)</i>
10:00 – 10:30	Alkaline plume on clayey material <i>François Marsal (IRSN, France)</i>
10:30 – 11:00	Overview of recent and future work on material development and usage of cementitious materials in salt repositories <i>Ralk Mauke and Jürgen Wollrath (BfS); Nina Müller-Hoeppe (DBE); Dirk-Alexander Becker and Ulrich Noseck (GRS-Braunschweig); Germany</i>
11:00 – 11:30	Poster session
11:30 – 12:00	Corrosion aspects of steel radioactive waste containers in cementitious materials <i>Nick Smart (Serco, UK)</i>
12:00 – 12:30	Consequences of chemical interactions at the interface between cement and clay barriers – Potential effects on gas migration <i>Paul Marschall (Nagra, Switzerland)</i>
12:30 – 14:00	Poster session
14:00	PARALLEL WORKING GROUPS SESSION II
14:00 – 16:00	Parallel working group session
16:30 – 17:15	Poster session
17:15 – 18:00	Working group reporting (5-10 minutes each)

END OF DAY 2

DAY 3 – 19 November 2009

- 09:00 **SESSION III:**
INTEGRATION IN THE SAFETY CASE AND IMPLICATIONS FOR LONG-TERM SAFETY
Chair: *Lawrence Johnson (Nagra, Switzerland)*
Rapporteur: *David Bennett (TerraSalus Consulting, UK)*
- 09:00 – 09:30 **Strategic choices in the Belgian supercontainer design and its treatment in a safety case**
Maarten Van Geet (ONDRAF/NIRAS) and Eef Weetjens (SCK•CEN), Belgium
- 09:30 – 10:00 **Safety case approach for KBS repository in crystalline rock**
Barbara Pastina (Saanio & Riekkola Oy, Finland) and Ignasi Puigdomenech (SKB, Sweden)
- 10:00 – 10:30 **Safety case and cement-related issues for ILW repository**
Simon Norris and Steve Williams (NDA, UK)
- 11:00 – 12:00 **DISCUSSION on key issues, challenges and conclusions**
- 12:00 – 12:15 **Practical aspects concerning the optional field trip to URL**
- 12:15 – 12:30 **Closing of the workshop**

END OF WORKSHOP

Appendix B

Workshop Papers

1 – Engineering Feasibility for the Fabrication and Emplacement of Cementitious Repository Materials: Results from the EC-ESDRED Project <i>Maria CRUZ ALONSO (IETcc of the Spanish National Research Council) and Jose Luis GARCÍA SIÑERIZ (AITEMIN), Spain</i>
2 – Compositions and Use of Cementitious Materials: Experience From Onkalo <i>J ohanna HANSEN (Posiva, Finland)</i>
3 – Chemical Evolution of Cementitious Materials <i>Barbara LOTHENBACK (EMPA) and Erich WIELAND (PSI), Switzerland</i>
4 – Implications for Solubility and Retention of Radionuclides over Long Timescales <i>Steve WILLIAMS and Simon NORRIS (NDA, UK)</i>
5 – Interaction of Cementitious Materials with High-level Waste (HLW) <i>Karel LEMMENS (SCK•CEN, Belgium)</i>
6 – The Impact of a (Hyper)Alkaline Plume on (Fractured) Crystalline Rock <i>Russell ALEXANDER (Bedrock Geosciences, Switzerland)</i>
7 – Alkaline Plume on Clayey Material <i>François MARSAL (IRSN, France)</i>
8 – Overview of Recent and Future Work on Material Development and Usage of Cementitious Materials in Salt Repositories <i>Ralk MAUKE and Jürgen WOLLRATH (BfS); Nina MÜLLER-HOEPPE (DBE); Dirk-Alexander BECKER and Ulrich NOSECK (GRS-Braunschweig); Germany</i>
9 – Corrosion Aspects of Steel Radioactive Waste Containers in Cementitious Materials <i>Nick SMART (Serco, UK)</i>
10 – Consequences of Chemical Interactions at the Interface Between Cement and Clay Barriers – Potential Effects on Gas Migration <i>Paul MARSCHALL (Nagra, Switzerland)</i>
11 – Strategic Choices in the Belgian Supercontainer Design and its Treatment in a Safety Case <i>Maarten VAN GEET (ONDRAF/NIRAS) and Eef WEETJENS (SCK•CEN), Belgium</i>
12 – Safety Case Approach for KBS Repository in Crystalline Rock <i>Barbara PASTINA (Saanio & Riekkola Oy, Finland), Jarmo LEHIKOINEN (B+Tech Oy) and Ignasi PUIGDOMENECH (SKB, Sweden)</i>
13 – Environmental Safety Case and Cement-related Issues for Intermediate-level Waste in a Co-located Geological Disposal Facility <i>Simon NORRIS and Steve WILLIAMS (NDA, UK)</i>

1 - ENGINEERING FEASIBILITY FOR THE FABRICATION AND EMPLACEMENT OF CEMENTITIOUS REPOSITORY MATERIALS: RESULTS FROM THE EC-ESDRED PROJECT

Maria Cruz ALONSO (IETcc- of Spanish Research Council, Spain)
Jose Luis GARCIA-SIÑERIZ (AITEMIN, Spain)

Introduction

Cementitious materials are being proposed as main components of the alternative Engineered Barrier Systems (EBS). Concretes and mortars must play a relevant role in the future of the Geological Repository (GR). The limitation of accessibility of groundwater in GR is one requirement, because it has great influence on the chemical stability of the repository.

Concrete is going to be used during the construction for different purposes such as grouting, rock bolting, lining of tunnels and drifts, and for sealing plugs (for instance at the mouth of the disposal drift or disposal cell) and it will be also used for construction of various auxiliary structures needed for the construction and operation of the repository. Some of these uses may be temporary and the concrete may be removed before the repository closure, but an important amount of concrete will remain in the GR along its entire life.

Some of these cementitious materials are going to be in contact with the bentonite buffer, backfill material and the near-field host rock of the EBS in the GR. Over time concretes made with Ordinary Portland Cements (OPC) leached by the groundwaters will give rise to release of significant quantities of ions, mainly OH^- , K^+ , Na^+ , Ca^{+2} . The resulting leachate could have a pH as high as 13.5. The leaching water might perturb other repository materials such as the engineered barriers, the hyper-alkaline cementitious materials have shown to alter this clay barrier.

From the point of view of creating a solid safety case for a nuclear repository, it is currently impossible to predict how fast and where cement pore waters may travel during the long periods of time involved. Furthermore the hyper alkaline plume can last for a very long time (up to thousands of years) and therefore cause physicochemical transformations that could modify the radionuclide confinement properties of the disposal components.

For this reason, most of the adopted engineering construction concepts requires the use of low-pH cementitious materials, in order to avoid the high alkaline plume from the standard cementitious materials when in contact with groundwater. The accepted solution is to develop cementitious materials that generate pore waters with $\text{pH} \leq 11$, because the alteration of the EBS components is significantly reduced below this pH value.

Within ESDRED project low-pH cements were developed as an alternative to standard OPC concrete formulations for plug and rock support construction, so as to prevent or reduce the development of the hyper alkaline plume effect. On the other hand although the utilisation and performance of standard shotcrete in conventional construction works is well known, there is no experience with the workability or the performance of shotcrete formulated to obtain the low-pH products. Different aspects related to the ESDRED developments of low-pH cements for low-pH

concretes production for a GR have to be considered: 1) The definition of the general functional requirements expected for this type of concretes in specific applications. 2) The design and the properties of low-pH cements, moreover the special characteristics implied in the development and production of low-pH concretes, mainly focused on the procedure followed in the design of a specific application of low-pH cements aimed at shotcreting a low-pH concrete 3) the industrial and site production of specific low-pH shotcretes for plug and rock support.

Functional cementitious materials requirements for GR

Most of the repository concepts, irrespective of the host rock, require concrete construction in the underground repository areas and the functional requirements applicable for the different low-pH concrete applications has to be explicitly indicated, but in order to be applicable, those requirements should be connected to measurable parameters, although some desired properties could not be measured quantitatively, like stability and durability.

Obviously, the main functional requirement demanded in any type of low-pH material used in a GR is having a pore fluid pH value ≤ 11 , which is considered acceptable for preventing or reducing the alteration of the bentonite EBS. Other functional requirements are going to depend on the specific application given to the low-pH cementitious material.

But apart from the requirements needed in the specific material behaviour, those required by the specific construction method must be taken into account. The use of shotcreting has proven to be an efficient and cost saving method for rock support in underground construction. The design criteria applicable for low-pH concrete for plug and rock support applications were defined at the beginning of the project, previously to any further developing.

The main functional requirements to comply with that should be specified in every application type are: hydraulic conductivity (site specific – same order of magnitude to that of the Excavation Disturbed Zone EDZ), mechanical properties of concrete, durability (concept specific – linked to the operational life of the repository), workability and pumpability (when shotcreting), slump, peak hydration temperature, thermal conductivity (concept specific – not below that of the bentonite barrier), use of organic components (fibres or admixtures), use of other products, etc.

Regarding peak of hydration temperature and thermal properties, consideration is given during the shotcrete formulation for preventing cracks induced by heat of hydration. This is more relevant in plugs since the application of shotcrete layers within short time intervals might reduce the heat dissipation and therefore buffer the hydration temperature. Concerning thermal conductivity it is desirable that the plug has equal or higher conductivity than the bentonite buffer.

Fabrication of low-pH cementitious materials

Different cement formulations were developed within the frame of ESDRED, using conventional cement components, as OPC and mineral additions. The key properties of the low-pH were characterised. According to the characterisation results, the most suitable low-pH cements were selected to design the basic concrete composition for shotcreting, for both plug and rock support use.

The low-pH cementitious materials based on OPC must include higher contents of mineral additions, over 40%, to ensure that free portlandite is significantly reduced or even avoided. To eliminate the portlandite, mineral additions are recommended, particularly those that consume portlandite during hydration via pozzolanic reaction.

Silica based materials (silica fume or fly ash, etc.) allow the production of low-pH cementitious material; either using isolated material (binary mixes) or by mixing of several mineral blends (ternary or more blended cements). In the case of low-pH cementitious materials production, it has been determined that if OPC is used as basic cement of the low-pH blend, at least 55% of SiO₂ must be in the binder, or pozzolan blended additions above 40% have to be employed. Indeed, the composition of the blended agent has a marked effect on the pH, being SF the most effective (due to its higher silica content). Formulations with a sufficient percentage of mineral addition, > 40%, with a total SiO₂ contents > 55% show a pH below 11 after 90 days of curing.

Concrete can be seen as a composite material composed of an aggregate skeleton bound by a paste matrix. The paste itself is composed of the low-pH cement formulation, water and the chemical admixtures. As most of the physicochemical reactions occur at the paste phase, the compatibility among different constituents has to be assessed in paste evaluations, the aggregate being almost inert. Thus, the selection of the low pH concrete components is divided in two stages: Paste components, including admixtures compatibility, and aggregates proportioning.

From the Compatibility evaluation of chemical admixtures different tests have to be performed successively to determine suitable combinations of low-pH cement formulation and the admixtures to be used. It must be kept in mind that chemical admixtures are developed and optimised for “standard cements” and thus, their efficiency with special cements (low-pH) cannot be neglected. Aggregates selection is a key issue in concrete design and production as about 70 % of the concrete is made of aggregates and they strongly influence water demand, workability, pumpability and projectability of the concrete.

Main experience with respect Low-pH shotcrete plugs

The low-pH concretes designed have to fulfill with the functional requirements established for construction in underground repositories and conventional wet-stream shotcreting technique proved to be appropriate for the construction of plugs and rock support with the selected low-pH concrete. It was demonstrated that a solution for minimizing the effects of the hyper alkaline plume in the repository is now available at industrial scale. Low-pH shotcrete for plug construction provides the following improvements for the repository:

- Better compatibility of engineered materials and natural barriers due to an improved sealing material: the low-pH concrete.
- Improvement of seal/plug designs because concrete plugs could be built with no reinforcement and with no recesses excavated in the rock for competent formations (crystalline rock).
- Improvement of seal/plug construction methods and equipment because the concrete plugs could be built using the shotcreting emplacement method, which is much faster than the cast concrete, can be easily automated and could be almost continue due to the low heat release of the low-pH concrete during hardening.
- Increase of the long-term safety due to a more stable multiple barrier system (natural and engineered) thanks to the reduction of the hyper alkaline plume effect.
- Results from a short low-pH shotcrete plug constructed in a horizontal gallery in Aspö hard rock laboratory (Sweden), which was tested, to failure and thereafter dismantled and analysed, confirmed the feasibility of the selected solution and helped to determined the key parameters of the bearing capacity of a plug. A full scale, long plug demonstrator was designed and constructed in the Grimsel underground (Switzerland) which is being testing under realistic conditions.

Main experience with respect Low-pH for rock support

The main experience has been to demonstrate the feasibility of using low-pH shotcrete also for rock support, for which low pH cement is needed, but the proportions for concrete production are diverse according to the functional requirements to address. The low pH shotcrete formulation was derived from the development work implemented for low pH shotcrete for plug construction. Thus, the specific objectives carried out for the development low-pH shotcrete for rock support were related to find a formula for a workable shotcrete. The main work included was:

- The development of suitable low-pH shotcrete formulae including the selection of admixtures as superplastiziers and accelerators for industrial shotcrete application.
- Pilot testing of these low-pH shotcrete formulae for rock support
- Full scale field testing of these low-pH shotcrete formulae for rock support
- Demonstration to prove the feasibility of using low-pH shotcrete for rock support in both crystalline and clayey rock.

Although a lot of experience has been gained within ESDRED project with the use of low-pH concretes, uncertainties still remain, mainly related with, mechanism of functioning of low-pH cements with components of concrete at early ages, long term performance, durability in contact with groundwaters and environmental conditions or risk of corrosion if in contact with carbon steel, as reinforcements or fibres.

2 - COMPOSITIONS AND USE OF CEMENTITIOUS MATERIALS: EXPERIENCE FROM ONKALO

Johanna HANSEN (Posiva Oy, Olkiluoto, Finland)

Introduction

Posiva Oy, a company jointly owned by the two Finnish nuclear power companies Fortum Power and Heat Oy and Teollisuuden Voima Oyj (TVO), is responsible for the geological disposal of the spent nuclear fuel of the Loviisa and Olkiluoto power plants. The disposal facility will be a KBS-3 type repository at the depth of 400-500 metres in crystalline bedrock. Due the similar concept and bedrock type there is intensive co-operation between Posiva and SKB. The construction and operation of the repository will disturb the host rock conditions. To minimise the hydrological disturbances, such as surface water drawdown and upconing of saline groundwater, grouting is used. The impact of the grout and other cementitious materials needs to be assessed in the safety case. Consequently, it is important to document all materials during construction of the underground rock characterisation facility ONKALO, while it is intended to be part of the repository.

Time schedule for development of disposal system

The main milestones in the spent fuel disposal programme have been the Olkiluoto site selection in the Eurajoki municipality in 1999 and the Decision in Principle (DiP) by the Government in 2000 and its ratification by Finnish Parliament in spring 2001. After intensive site investigations the construction of ONKALO started in autumn 2004. As a next milestone Posiva will submit the construction license application in 2012, and thus the application is successful, the construction of the encapsulation plant and of the repository will begin in 2014-2015. The operation of the facility is scheduled to begin in 2020 after receiving the operating license. The closure of the facility will occur sometime in the 2100s, depending on the planned life time of owners nuclear power plants with a total of 12 000 tons of uranium.

ONKALO facility and the role of the ONKALO

ONKALO provides an opportunity to develop excavation techniques, and final disposal techniques in realistic conditions. It also serves as an opportunity to develop quality management practices and investigate, test and demonstrate the performance of the engineered barrier system during the next decade. The evolution of ONKALO design as well as design premises are presented in ONKALO main drawings report (Posiva, 2008).

During the excavation of ONKALO in addition to the excavation methods, the sealing actions like grouting and reinforcement of the tunnel and documentation practices are being developed. ONKALO will reach the target depth -420 meters in 2010 and thereafter excavation will continue for the characterisation and research facilities. ONKALO also helps to design the repository layout and to characterise the repository panels in greater detail. ONKALO will be later part of the repository and therefore its construction is followed by nuclear safety authorities. ONKALO consist of access tunnel and personnel, fresh air and exhaust shafts and the updated extent of subsurface facilities is described in Anttila *et al.* (2008).

Stray materials in ONKALO and in the planned repository

The first estimate on engineered and stray materials which remain in the repository in the time of closure was done before the construction of ONKALO started (Hjerpe 2004). This estimate includes all manmade materials used for construction but the altered materials like corrosion products or decomposition product during the evolution of the repository are not included. Materials with 100 % removal are not included in the estimation. The results show that the total remaining quantity will be in the range from 13 000 000 to 28 000 000 kg. Cement is the most dominating component, with about 75–85% of the total quantity. Steel, organic materials, aluminium, and zinc are other important materials. The source for cement, estimated to remain in the repository, can be found in Table 1. If steel wire mesh tunnel support is used instead of shotcrete reduces the remaining cement quantity to about half. The removal efficiency of shotcrete also influence to the result. (Hjerpe, 2004)

Table 1: Remaining quantity of stray materials during the time of closure

Material	Estimation 2004 (Hjerpe 2004)	Removal efficiency	Estimation 2007 (Hagros 2007)	Removal efficiency
Support bolts	276 241 kg	0 %	61 000 kg	0 %
Anchor bolts	18 130 kg	0 %	18 000 kg	0 %
Shotcrete with admixtures	10 991 425 kg	0 %	190 000 kg	95 %
Grouting materials	5 000 000 kg	0 %	490 000 kg	20 %
Concrete plugs	4 692 000 kg	0 %	4 700 000 kg	0 %
Miscellaneous construction	88 169 kg	98 %	88 000 kg	98 %
Floors	137 790 kg	98 %	140 000 kg	98 %
Bottom plates in deposition holes			140 000 kg	0 %

Three years later these estimates were updated (Hagros, 2007) based on a new layout and the experiences in grouting and shotcreting during construction of the ONKALO. According to the updated estimates of engineered and stray materials, the remaining amounts of cement are attached in Table 1. The scenarios have different alternatives for grouting and shotcreting and therefore the amount of cement also varies depending on the grouting and shotcreting strategies. The bottom plate of the deposition holes is reconsidered and this might be replaced with more suitable material.

In practice the total amount of introduced cement is a little above 20 000 000 kg but the remaining quantity is 6 000 000 kg, where major part comes from the deposition tunnel plugs. Estimated amount of organics in combination with cementitious materials is estimated to be 27 100 kg. The amount is quite small compared to the total amount of organic carbon in buffer and backfill which is estimated to be 1 840 000 kg to 15 140 000 kg depending on backfill materials (Hagros, 2007).

So far the length of the access tunnel in ONKALO is 3889 metres and three shafts have been raise-bored down to the -290 m. The actual use of cement for different purposes until the end of 2008 is:

- Grouting material 503 480 kg
- Shotcrete 1 671 954 kg
- Cement for anchor and support bolts 42 576 kg. (Juhola 2009)

These amounts do not correspond to the final amounts left in the repository as part of the cement (e.g. shotcrete) will be removed before closure.

Practical actions for decreasing the amount of cement

To minimize the consequences of use of cement, low pH cementitious materials and colloidal silica have been considered as alternative materials for groundwater control. Their development was initiated already in 2003. Posiva developed together with SKB and NUMO low pH grout material for sealing rock fractures (Bodén & Sievänen 2005) and analysed jointly with Nagra the long-term safety aspects of organic additives (Andersson et al. 2008). The colloidal silica grouting was tested and developed in the Äspö Hard Rock laboratory jointly with Posiva and NUMO and experiences was gained in several civil construction projects in Sweden.

As construction of the ONKALO advanced, Posiva decided that low pH grouting cement shall be mainly used from the spring 2008 onwards (Arenius et al., 2008). This decision was only valid for grouting materials because they cannot be removed at the time of closure. The shotcrete can, in principle, be removed and therefore a similar material requirement was not granted. The amount of support bolt grout and rock bolt grout was not assumed to be significant and therefore ordinary grout was preferred. The plug design for deposition tunnels was updated during 2008 and, according to the new design, the plug contains 20 000 kg cement (Haaramo & Lehtonen, 2009). Totally this makes 2 100 000 kg of cement for all plugs in deposition tunnels, which is a half of the earlier estimations, if the amount of tunnels is 105 (Posiva,2009). The plugs needed for closure have not been included in these estimations.

Conclusions

The use of cement in the repository is necessary and therefore it is important to assess their impact on long-term safety. The impact of cement on long-term safety can be minimised by developing material compositions that are not harmful (or less harmful) to the natural or engineered barriers. Though, quite intensive testing and additional experience are needed to decrease the amount of harmful components and amount of cement used without endangering the workability in expected conditions.

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3 - CHEMICAL EVOLUTION OF CEMENTITIOUS MATERIALS

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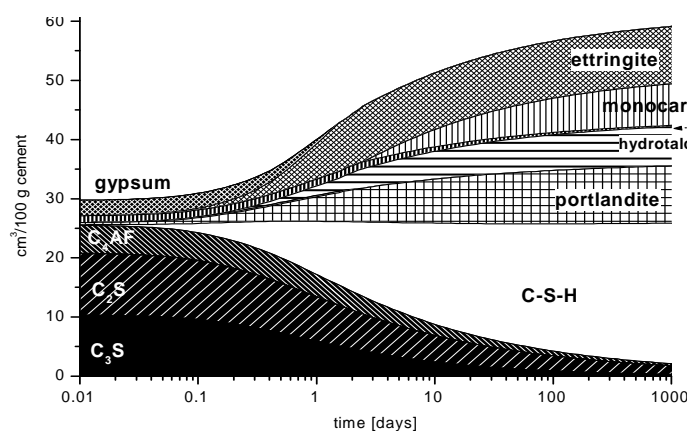
Introduction

Cementitious materials are being studied as they are important components of the engineered barrier of repositories for radioactive waste. Performance assessment takes into account that in the long term the cementitious near field undergoes major chemical changes due to the interaction with infiltrating groundwater or precipitation. Clay-based barriers as envisaged for the disposal of long-lived intermediate- and high-level radioactive waste may be locally degraded by the high pH originating from the interstitial water of the cements used for the construction of the cavern (e.g. liner etc.). In this study the potential of thermodynamic modeling of cementitious systems is discussed for assessing the influence of different parameters on the hydration and stability of cements.

Hydration of ordinary Portland cements

The processes during the hydration of Ordinary Portland cement (OPC) are well known. The main hydrate phases include C-S-H (calcium silicate hydrate), portlandite, ettringite, hydrotalcite and monocarbonate. Thermodynamic modeling coupled with kinetic equations, which describe the dissolution of the clinker as a function of time, can be used to predict the composition of hydrated cements (Lothenbach et al., 2008a, Figure 1). In the absence of limestone, monosulfate is present after longer hydration times, while in modern Portland cement, where up to 5% of limestone is generally added, ettringite and monocarbonate are formed. Furthermore, temperature influences the composition of hydrated cements (Lothenbach et al., 2008b).

Figure 1: Modelled changes during the hydration of OPC expressed as cm³/100g unhydrated cement.

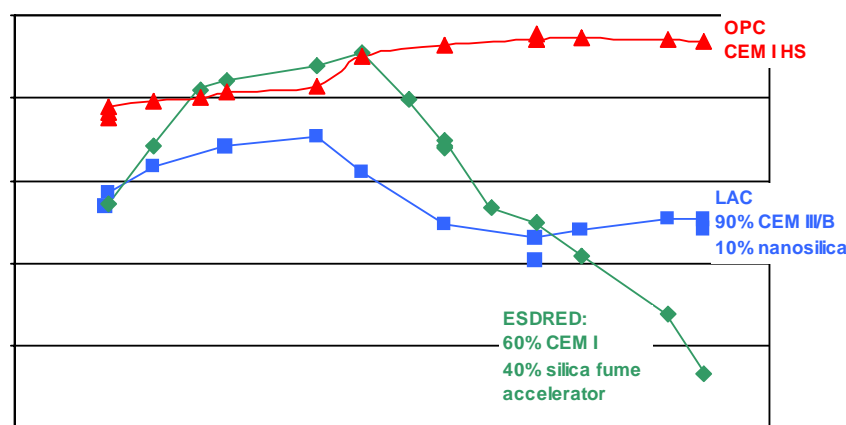


The pH values of Portland cements are generally in the range of 13-13.5. Both the pH values as well as the hydrate assemblage remain more or less stable after longer hydration times in cases where the cement is not interacting with the environment.

Hydration of blended cements

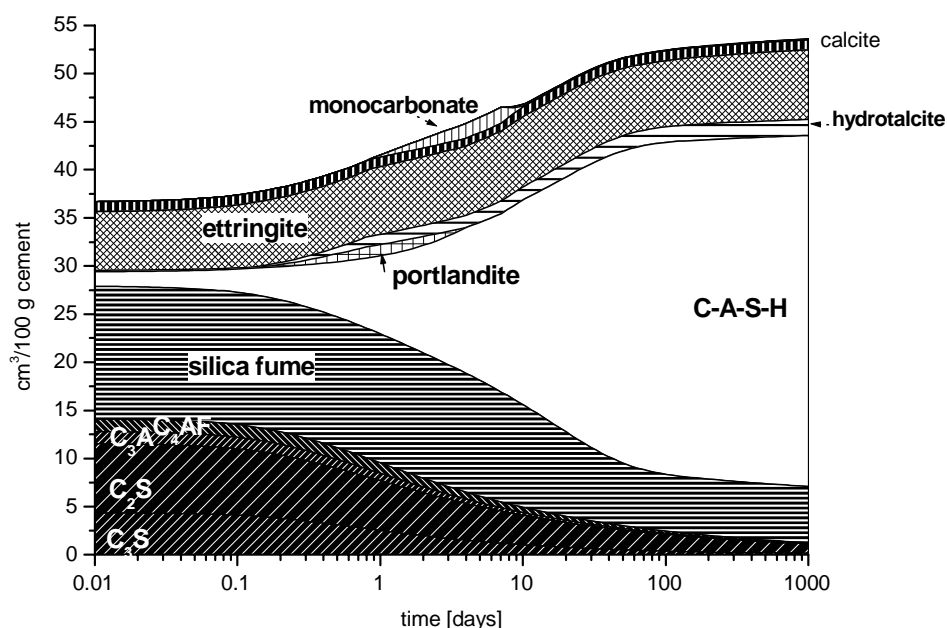
The blending of Portland cement with mineral admixtures with high silica content such as blastfurnace slag, fly ash and/or silica strongly decreases the pH of the pore solution. The resulting pH lowers with increasing silica content (Garcia Calvo *et al.*, 2009) and the pozzolanic reaction of the silica consumes the portlandite from the Portland cement. The presence or absence of portlandite affects the composition of C-S-H; in OPC a C-S-H with a high C/S is present, while silica rich blends may have a C-S-H with a C/S ratio of 1 (see below). The presence of a low C/S C-S-H leads to an enhanced uptake of alkalis as illustrated by the observed changes of pH values during the hydration of OPC, of a shotcrete mixture (ESDRED: 60% OPC, 40% silica fume, alkali-free accelerator) and a low alkali cement (LAC: 23% OPC, 67% blastfurnace slag, 10% SiO₂) in Figure 2.

Figure 2: Evolution of pH in the pore solution of an OPC, an two blended cements: ESDRED (60% OPC, 40% SiO₂) and LAC (23% OPC, 67% blastfurnace slag,, 10% SiO₂)



The presence of silica rich materials reduces not only the pH value but changes also the composition of the hydrate assemblage. After 1 year of hydration time, significant amounts of portlandite are present in the OPC (Figures 1) and high pH values in the pore solution result (Figure 2). In contrast to OPC, no portlandite is present in blends containing high amounts of silica rich materials, while ettringite may be present in pure OPC and in blended systems.

Quantification of the phase assemblage is difficult in silica rich blends as besides some ettringite the main hydration product is X-ray amorphous C-S-H. Thus, thermodynamic modeling offers an alternative to investigate changes during the hydration and to predict quantitatively the hydrate assemblage as illustrated for a slag and silica fume blended Portland cement in Figure 3. The main hydration product is a low C/S C-S-H phase intermixed with ettringite as the presence of the aluminum sulfate based accelerator leads to the fast formation of a significant amount of ettringite. The silica fume present reacts only slowly. Si NMR data indicated that after one year only half of the original amount of silica fume had reacted.

Figure 3: Modelled changes during the hydration of ESDRED

Long-term stability of Portland cements

Cementitious materials are chemically reactive and have the potential to react with the environment. For example, interaction of OPC with ground, rain or soil water, respectively, leads to a decrease of the pH of the pore solution and in the long-term to the degradation of cement (e.g. Jacques *et al.*, 2009). First portlandite and later also C-S-H, ettringite and AFm phases are leached. In particular the interaction with waters containing high sulfate concentrations causes the formation of ettringite, which results in expansion and cracking, and in the presence of carbonate, the formation of thaumasite (favoured at low temperatures). The complete deterioration of the cement due to the latter process has been observed within a few years.

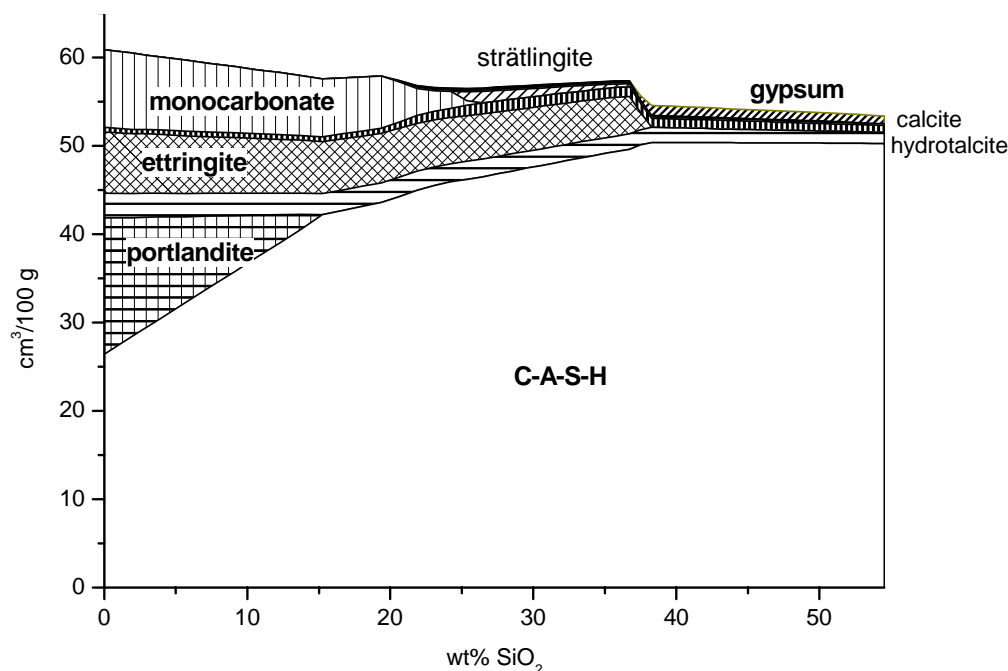
Thermodynamic modelling

Important material properties of cementitious materials such as workability, setting behavior, strength development and durability are related to the cement hydration process and to the amount and kind of hydrates formed. Thermodynamic equilibrium modeling of the interactions between solid and liquid phases in cements using geochemical speciation codes can be a tool to decipher the link between chemical composition and material properties. In the last years, more sophisticated geochemical softwares have been developed, the formation of solid solution models for various phases has been taken into account and, most importantly, the thermodynamic databases used have become more adequate as the solubility products of more and more minerals present in cementitious systems are available. The most current cement specific cement database was published in 2007/2008 (Lothenbach *et al.*, 2008b) and contains thermodynamic data valid from 0 to 100 °C for a number of cement phases. Recently, a new solid solution model for C-S-H was proposed (Kulik 2009), which is closely related to crystallographic structure of C-S-H. The latter model is not only capable of predicting the solubility and the chemical composition of the C-S-H phases, but also their average silica chain length in agreement with ^{29}Si NMR data.

Thermodynamic modeling may also be used to calculate changes in the phase assemblage and in the pore solution caused by the blending of Portland cement with SiO_2 (Figure

4). The addition of moderate amounts of SiO_2 leads to the consumption of portlandite as more C-S-H forms. The addition of even more SiO_2 results in the destabilization of monocarbonate and finally of ettringite due to the decrease in pH. Furthermore, increasing amounts of SiO_2 , and thus the formation of low Ca/Si C-S-H, lead to an increased uptake of Al in C-S-H.

Figure 4: Modelled changes in hydrated Portland cement upon blending with SiO_2



Conclusions

Thermodynamic modeling of cementitious materials enables us to quantify the composition of OPC and blended systems during the hydrations process, to decipher changes in the composition due to addition of mineral admixtures and to predict the degradation of cement in contact with the environment. Development of comprehensive thermodynamic databases for pure cement minerals and the capability of modeling solid solutions in cementitious materials are essential for future progress in this area of research.

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4 - IMPLICATIONS OF CEMENTITIOUS EVOLUTION FOR SOLUBILITY AND RETENTION OF RADIONUCLIDES OVER LONG TIMESCALES

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Introduction

Cementitious materials are used in a number of roles in the long-term management and disposal of radioactive wastes (Nirex 2001). Such materials may be present (depending on the facility design) as:

- wasteform - in-package grouting materials and package design materials;
- backfill material;
- shotcrete and other vault lining technologies that could be employed during construction and operation;
- engineered seals; and
- structural features e.g. floor slabs.

The roles of these various components in relation to the development of safety cases in the context of the management of higher activity wastes in the UK is considered in an accompanying presentation (Norris and Williams 2009). One of the roles of a cementitious backfill is to contribute to the post-closure retention of radionuclides within a disposal facility by imposing conditions under which the solubility of many elements is minimised and by providing sites for sorption from solution. Waste encapsulation grouts contribute to the containment of radionuclides within waste packages in addition to the physical containment provided by the waste container.

In the engineered barrier system (EBS) of a cement-based disposal facility the key processes affecting radionuclide behaviour after closure will be release from the wasteform through leaching and transport through the engineered barrier system. These will be influenced by solubility limitation (dissolution, precipitation/co-precipitation) and by sorption contributing to the chemical containment provided by the EBS. Resaturation of the EBS will determine the onset of release of radionuclides from a waste package. Water will eventually enter a waste package through features such as vents, where present, or due to eventual penetration of the container by corrosion. Thus, the chemical containment provided by the highly alkaline environment (and low redox conditions) plays an important role in the long-term retention of many radionuclides and a key requirement of a cementitious backfill is the ability to maintain these conditions in the long-term.

Evolution of a cement-based EBS

The evolution of the mineralogy of cementitious materials, and hence their properties contributing to physical and chemical barrier performance within the EBS, will be driven by a number of processes including (Chambers et al. 2003):

- dissolution of cements in flowing groundwater and reactions with groundwater solutes;

- transformation of metastable minerals to more stable and crystalline forms including continuing hydration and hydrothermal alteration;
- reactions between cementitious materials of different compositions (e.g. backfill and waste encapsulation grouts);
- reactions between cementitious materials, wastes and their degradation products, and non-cementitious wasteforms;
- development of spatial heterogeneity in the EBS through cracking, precipitation of new mineral and development of preferential groundwater flow.

A description of the evolution of pH within a homogeneous near field can be based on models of the dissolution of cements combined with a groundwater composition and expected flow rate. As a basis for such models the pH evolution for the leaching of a calcium hydroxide /CSH system in pure water can be broadly characterised by a period of dissolution of calcium hydroxide (approximately pH 12.5), followed by incongruent dissolution of CSH (pH decreasing from 12.5 to about 10.5) and then congruent dissolution of CSH at about pH 10.5 until the CSH is exhausted. Based on this simple description it is possible to maintain pH values of 10.5 or above for hundreds of thousands of years for representative groundwater flow rates through a homogeneous deep underground repository concept. The presence or absence of calcium hydroxide in the cement and the initial composition of the CSH gel will depend on the formulation.

In reactive groundwaters this behaviour will be modified, for example by the precipitation of magnesium hydroxide or calcium carbonate. Reactions with wastefrom grouts of different compositions from the backfill will lead to changes in mineralogical composition. Such changes can be accompanied by changes to the porosity and permeability in the affected region. Cracking within the backfill can lead to localised water flow along the cracks and preferential leaching or the deposition of reaction products. The alteration of material in the body of the cement will be influenced by the rate of migration to or from the surface of the crack. Thus the transport properties of the crack surfaces will impact on the chemical buffering of groundwater flowing along the crack and alteration of the backfill. The leaching of minerals from a cementitious backfill, their conversion to more stable and crystalline forms and the formation of new products can all alter sorption properties.

The distribution of backfill and waste in a repository will be heterogeneous and the evolution of the backfill will also display spatial and temporal heterogeneity. Different types of heterogeneity will be significant over different length scales and the timescales over which they are important will also vary. Diffusion and dispersion will lead to a trend of decreasing heterogeneity with time. The chemical containment provided by the components of the EBS is assumed to be established on a timescale that is short compared to that over which radionuclides whose behaviour is determined by the chemistry of the near field are released. Developing understanding in order to support this assumption and the expected evolution of the near field is important as part of including appropriate uncertainty in performance assessment calculations.

Radionuclide solubility and the evolution of a cement-based EBS

Having considered the processes and trends in the evolution of the EBS, the possible implications for radionuclide solubility can be considered. Key influences on solubility control will be the aqueous conditions, and hence the speciation of dissolved radionuclides, and the nature of the solid phases containing those radionuclides. "Fresh" cements generally result in pore waters with a high pH and low carbonate concentration controlled by the precipitation of calcium carbonate. Hydrolysis is an important control on the solubility under these conditions and work over several decades by a number of workers under a range of programmes has provided data to enable the solubility of the hydroxides and calcium salts of many elements to

be modelled accurately. The importance of solubility-control for individual radionuclides will depend on the total inventory of the element (and its availability) and its aqueous chemistry.

Much of the experimental data for the solubilities of phases in contact with cement-equilibrated waters comes from laboratory experiments in which the solids are amorphous or have compositions which may not be the most thermodynamically stable due to kinetics of reaction (e.g. the possible long-term formation of uranium silicates). In these cases the long-term aqueous concentration above the solid is likely to be lower than that based upon observations from laboratory experiments. Such ageing and incorporation processes are expected to be beneficial in reducing the release from the EBS. However, demonstrating such processes and obtaining robust quantitative data is challenging.

As the pH in the near field decreases over the very long-term species other than hydroxide may become important in controlling the aqueous speciation, for example carbonate is an important complexant at lower pH values. Although organic complexants such as EDTA would be expected to become more important complexants as competition from hydroxyl decreased, they would be expected to have been leached from the EBS before the pH had decreased significantly.

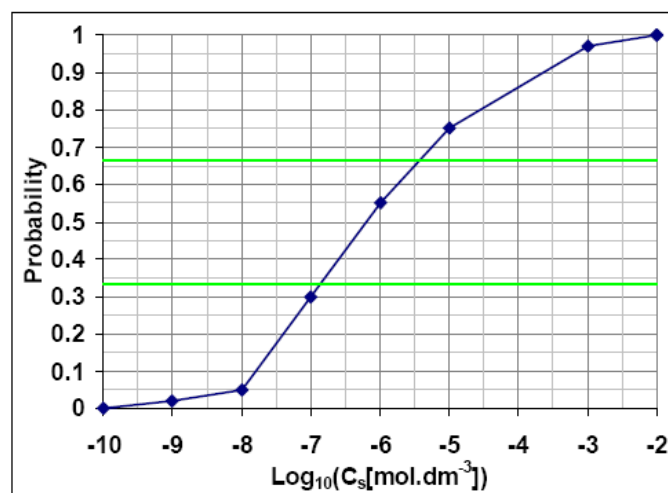
Radionuclide sorption and the evolution of a cement-based EBS

The importance of most retention/retardation processes varies from radionuclide to radionuclide. For example, some radionuclides are sorbed strongly, and consequently migrate slowly from an EBS, whereas others are sorbed very weakly. The nature and extent of sorption is determined by the speciation of radionuclide and the surface properties of the sorbing surface. In general the study of specific sorption processes is more difficult in cement systems than for single minerals and thus sorption is used as a generic term to cover all uptake processes where a radionuclide is partitioned between a cement and the solution. Most data for radionuclide sorption onto cements have been obtained on relatively young materials. However, some studies have been made for CSH gels and some leached systems which extend the data to low pH.

Treatment of uncertainty in solubility and sorption in performance assessment calculations

The objective of radionuclide solubility and sorption studies in a needs-driven research programme is to provide an understanding that is sufficient and suitable to justify the simplified representations that are made in assessment models. The EBS is a complex system that needs to be considered over very long timescales and this introduces inevitable uncertainty in the expected chemical evolution that contributes associated uncertainty in radionuclide behaviour.

In order to treat such uncertainty in performance assessment calculations it important that is represented adequately in the input data. One approach to this that has been employed in the UK programme is to undertake a formal structured data elicitation to obtain a cumulative distribution function for the parameter of interest (Phillips and Wisbey 1993). An example of a CDF for the solubility of uranium(VI) in a cementitious environment is given below (Swan and Jackson 2007).

Figure 1: Elicited CDF for solubility of uranium(VI) in pH range 9 to 12.3

An alternative approach is to review available data corresponding to the chemical conditions of interest and provide best estimate, lower bound and upper bound values based on these data. Such an approach has been used recently to obtain sorption parameters in support of performance assessment calculations for the development of a near-surface disposal facility in Belgium (Wang et al. 2009).

Conclusions

The chemical containment provided by a cementitious EBS is important in long-term post-closure performance and the general characteristics of the evolution of this EBS are understood. Research continues to address detailed aspects of evolution in order to underpin understanding of the possible impact on radionuclide behaviour. However, the EBS is a complex system that needs to be considered over very long timescales. This introduces inevitable uncertainties in radionuclide behaviour that need to be taken into account when considering input data for performance assessment calculations. These uncertainties can be captured through the use of expert groups to review available data in the context of the expected evolution of the system.

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5 - INTERACTION OF CEMENTITIOUS MATERIALS WITH HIGH-LEVEL WASTE

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Ben GIELEN and Regina VERCAUTER; (Belgian Nuclear Research Centre)

Abstract

Since a few years, the Belgian agency for radioactive waste (ONDRAF/NIRAS) has selected the *Supercontainer design* with an Ordinary Portland Cement (OPC) buffer as the reference design for geological disposal of High-Level Waste (HLW) and Spent Fuel (SF) in the Boom Clay formation [Bel 2006, Van G. 2009]. The Boom Clay beneath the Mol-Dessel nuclear zone is a reference methodological site for supporting R&D. Compared to the previous bentonite based reference design, described in detail in the final SAFIR 2 report [NEA 2003], the supercontainer will provide a highly alkaline chemical environment allowing the passivation of the surface of the overpack and the inhibition of its corrosion. The *Supercontainer* will contribute to the containment of radionuclides, but it will also have an effect on the retardation of radionuclide release from the waste and it will retard the migration of the released radionuclides.

In the *Supercontainer design*, the canisters of HLW or SF will be enclosed by a 30 mm thick carbon steel overpack and a concrete buffer about 700 mm thick. The overpack will prevent contact with the (cementitious) pore water during the thermal phase. On the other hand, once the overpack will be locally perforated, the high pH of the incoming water may have an impact on the lifetime of the vitrified waste or spent fuel. The behaviour of these waste forms in disposal conditions has been studied for several decades, but the vast majority of published data is related to the interaction with backfill or host rock materials at near-neutral pH. Very few studies have been reported for alkaline media, at pH >11. Hence, a research programme including new experiments, was started at the Belgian Nuclear Research Centre (SCK•CEN) and at INE (FZK) to assess the rate at which the radionuclides are released by the vitrified waste and spent fuel in such an environment.

The presence of concrete will have an impact on the behaviour of the vitrified HLW and spent fuel. For *vitrified HLW*, the high pH is expected to cause a faster dissolution of the glass matrix, driven by secondary phase formation. Low long-term dissolution rates, such as expected in neutral pH conditions, will probably be reached only after the formation of a sufficiently thick alteration layer separating the pristine glass from the bulk of the concrete, thus causing a pH gradient. So far, this process cannot yet be quantified well enough. For *spent fuel*, the preliminary results are not entirely consistent. The tests with spent fuel suggest that the high pH is not detrimental for the fuel stability. The tests with (doped) UO₂ suggest, however, that it may take more time to reach the threshold fuel activity where radiolytical oxidation becomes unimportant. Moreover, there are indications that the non-oxidative fuel dissolution could be accelerated at high pH by colloid formation in certain conditions. The factors affecting this colloid formation are not understood so far. Therefore it is not yet possible to assess whether this process will be relevant under in situ conditions.

The uncertainties about the present dissolution rates are still large due to the small number of data. A continuation of the programme is necessary to improve the rate estimations and to better understand the underlying mechanisms. For vitrified waste, the focus will be on the evolution at the glass/concrete interface (secondary phase formation, pH evolution...). For spent fuel, it is important to understand better the nature of the dissolution process (oxidative or non-oxidative) as a function of the fuel activity, the role of colloids, and the differences between the behaviour of alpha-doped UO_2 and real spent fuel. Tests with spent fuel pellets and hydrogen gas will be started at INE to see if hydrogen reinforces the reducing capacity enough to suppress the oxidative fuel dissolution when the alpha activity of the fuel is still high. Another important remaining uncertainty is the potential effect of concrete phases close to the fuel. This may cause sorption or precipitation of U(IV) and result in accelerated fuel dissolution. Although we expect that this process will have only a temporary effect, it needs to be quantified better. It is likely that this process will drive the slow long term fuel dissolution.

This work is performed as part of the programme of ONDRAF/NIRAS (the Belgian Agency for Radioactive Waste and Fissile Materials) on the geological disposal of high-level/long-lived radioactive waste.

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6 - THE IMPACT OF A (HYPER)ALKALINE PLUME ON (FRACTURED) CRYSTALLINE ROCK

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Introduction

As hyperalkaline cement porewaters leach out of the near-field, they may interact significantly with the repository host rock (e.g. Haworth *et al.*, 1987). In consequence, those features for which the formation was originally chosen, such as low groundwater flux and high radionuclide retardation, may deteriorate. Here, available data of relevance to the interaction of repository hyperalkaline plumes on crystalline host rocks are briefly reviewed and areas of future effort identified. As most crystalline rocks may be expected to be fractured to a greater or lesser degree, focus is on fractured systems.

Evidence

Laboratory experiments

Among the earliest experiments conducted on crystalline rock were those of Bateman *et al.* (1999), where a range of model materials and rock types (including Avrö granite and Borrowdale Volcanic Group 'fault rock') were examined. Reaction of the original rock resulted in the development of one or more of the CSH, CASH, CKSH and CK(A)SH secondary phases which resulted in a decrease in overall porosity and an increase in surface area. Note, however, that the rock samples were crushed and the system heated to 70°C.

Of perhaps more direct relevance, a hyperalkaline fluid core infiltration experiment was performed with a sample from a fracture in Nagra's Grimsel Test Site (GTS) where the fault gouge had been preserved *in situ* (Mäder *et al.* 2006). Over nine months, a gradual decrease in flow rate by a factor of 25 was observed and was attributed to clogging of flow paths in the fracture by secondary CSH precipitates due to reaction of the rock with the hyperalkaline fluids.

Field (URL) experiments

What little work that has been carried out in URLs to date has not yet been published comprehensively enough to allow full integration within this short note. The most ambitious (and successful) experiment to date has been the international HPF (Hyperalkaline Plume in Fractured Rock) project at the GTS. This long-term field experiment was carried out by injecting hyperalkaline fluids into a water-conducting shear zone along with parallel, *in situ* radionuclide transport experiments and supporting laboratory experiments (see above). Although only a short overview (Mäder *et al.* 2006) has been published to date, the full report is expected soon. Briefly, the results indicate that:

- hyperalkaline fluids cause significant dissolution of the primary mineralogy of the host rock and precipitation of secondary minerals that induce changes (including self-sealing) to the flow field
- the conceptual model (cf. Alexander and Smellie, 1998) for the likely evolution of a hyperalkaline plume in crystalline (and other) host rocks is valid

Natural analogues (NA)

The most directly relevant NA study to date was that carried out across the various sites in Jordan (see Alexander and Smellie, 1998; Pitty, 2009 and references therein for details). Although the host rock was a clay biomicrite, the data on the spatial and temporal changes to the host rock following reaction with the hyperalkaline plume (max. pH measured of 12.9) are transferable (with care) to fractured crystalline rock (and clays, see the comments in Mazurek *et al.* 2006). The main quantitative conclusions were that the conceptual model for alteration of the host rock was largely correct and that reaction will generally seal fractures (cf. HPF above). In addition, comparison of the alteration of the clay biomicrite and locally abundant basalt indicated that the secondary mineral assemblage was generally very similar. Currently, two new NA studies (Alexander *et al.* 2008; Milodowski *et al.* 2009) on low alkali cement leachate interaction with bentonites are ongoing and both are expected to produce information on reaction in fractures in the crystalline (ophiolite) basement beneath the bentonites.

Model development

Modelling of hyperalkaline fluid reaction in fractured rock began in the 1980s (e.g. Haworth *et al.* 1987) and, broadly, the present coupled calculational tools are adequate, although improvements could still be made (see comments in Soler *et al.* 2006). To date, flow and transport modelling of processes within the plume has only been attempted within the HPF project and the results were mixed, perhaps because of the highly complex nature of the experimental fracture.

A special case: grouts

As noted above, most crystalline rocks will be fractured to some degree so, to minimise groundwater ingress, some degree of fracture sealing, most probably by grouts, will be necessary. Concerns were raised (e.g. Vieno *et al.* 2003) when it was realised that several hundred tonnes of grouts could easily be required in a typical crystalline rock repository and that the hyperalkaline leachates from these grouts could impact the repository. This, in part, prompted the re-examination of previous work on low alkali cements (due to the generally lower pH of any subsequent leachate). Significant effort has recently been invested in developing low alkali grouts which, whilst still carrying out their primary role of sealing water-conducting fractures, will degrade in a manner least likely to compromise long-term repository performance (see, for example, Emmelin *et al.* 2007, Karttunen and Raivio, 2008 and references therein). In general, it is expected that these grouts will behave as expected, but open questions remain regarding their competency following fracture re-activation (either due to tectonic events or glacial offloading) and potential freeze/thaw cycles potentially penetrating as deep as 300 m at the Olkiluoto site, for example (see discussion in Alexander and Neall, 2007).

Implications to repository performance

The quantitative implications of a hyperalkaline plume on the long-term performance of repository in crystalline rock have barely been examined. Most recent assessments of potential crystalline host rocks have either simply briefly mentioned the plume (e.g. ANDRA, 2005) or have assessed the implications for the EBS, but not the host rock (e.g. Pastina and Hellä, 2006) or simply not considered it at all (e.g. JAEA, 2007). In the last case, this is understandable due to the generic nature of the assessment.

Two examples exist where preliminary assessments of the implications of the hyperalkaline plume on specific repository sites have been carried out. In the first, Alexander and Mazurek (1996) considered the likely impact on the fractured marls of the Wellenberg site in Switzerland. Focus was on application of the data collected in the Jordan NA studies and the main conclusion was that it was necessary to conduct a detailed assessment of the likely long-

term impact of gradual fracture sealing at the site due to the host rock reacting with the hyperalkaline fluids.

Vieno *et al.* (2003) assessed the likely impact on the EBS of hyperalkaline leachates (predominantly from fracture grouts) in the proposed Olkiluoto repository. The results suggested that little impact should be expected, but this was criticised by Alexander and Neall (2007) on the basis that many of the assumptions were unrealistic. Although Vieno *et al.* (2003) made use of hydrogeological data on the site, no attempt was made to assess the impact of the plume on the host rock itself and no other such studies have been reported to date.

Conclusions

Over two decades of work on various aspects of the reaction of (fractured) crystalline rocks to hyperalkaline fluids indicates that:

- the conceptual model for the evolution of a hyperalkaline plume in a crystalline host rock is largely consistent with observations from laboratory, URL and NA studies
- reactions between hyperalkaline waters and the host rock will modify the hydraulic conductivity of any fractures, significantly altering contaminant transport times and even the geometry of the flow field. Channelling effects could be significant, but this will vary from host rock to host rock
- most secondary reaction products have positive reaction volumes and thus fractures will be sealed by the precipitation of secondary phases
- (small aperture) fracture sealing occurs within short timescales (years to hundreds of years)
- the sequences of minerals predicted by coupled codes are generally very close to those observed in the hyperalkaline alteration zones, even if the specific phases cannot be represented due to a paucity of relevant thermodynamic and kinetic data

Generally, then, the phenomena associated with a hyperalkaline plume in crystalline rock can be effectively addressed by a combination of laboratory and field experiments supported by evidence from natural analogues. However, what remains clear is that the effects of the site hydrology (and tectonic/erosional processes) upon fracture sealing needs to be considered on a repository site-specific basis and this remains a challenge to PA modellers in the future. Additionally, the impact of fracture re-activation (due to tectonics or glacial unloading, for example) still needs to be considered.

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7 - ALKALINE PLUME ON CLAYEY MATERIALS

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Context and global approach

Most designs for geological disposal facilities of long-lived radioactive waste envisage the use of large amounts of concretes for mechanical support of excavated drifts and, in some cases, as containment material. Depending on the concept, these materials will be in contact with swelling clays used as engineered barriers and with the argillaceous host rock. The incoming of host rock groundwater in concretes after the sealing of drifts will induce the degradation of these materials (portlandite and CSH dissolution mainly), generating a hyperalkaline water (pH > 13 for fresh concretes, pH ~ 12.4 for evolved ones in equilibrium with portlandite, 10 < pH < 11 for old ones in equilibrium with CSH phases) in strong disequilibrium with clayey pore waters. As a result, the interaction of clayey materials with high-pH fluids may lead to a modification of their favourable hydraulic and chemical containment properties. Indeed, the migration of an alkaline plume will induce mineralogical changes that could modify the porosity, sorption properties and swelling capacity of clayey materials. Besides, the rise of pH could influence the solubility of radionuclides in clays. Therefore, the intensity and the extent of the perturbations induced by the alkaline plume must be assessed on the very long term (several hundred thousand years).

The main difficulty encountered to deal with this complex problem is to predict the evolution of clays under an alkaline perturbation on geological times. Numerical modelling enables to tackle these time scales, but should indubitably be associated with laboratory experiments and studies of engineered and natural analogues in order to better understand the mineralogical pathways and to acquire thermodynamic and kinetic data needed for the simulations, as well as to precise the evolution of transport properties of clays under an alkaline stress. The present paper addresses a review of the main outcomes from each of these subjects. A first section is devoted to laboratory experiments, such as batch, diffusion and advection experiments, giving access to time scales of about one year. Observations on engineered and natural analogues are then described, providing information between a few years and a few thousands years. A third section is dedicated to numerical modelling on the very long term. Illustrations of these types of work carried out by the scientific community are given together with the associated outcomes, with a special focus on IRSN results acquired notably on Tournemire argillite (Aveyron, France). A particular attention is given to the uncertainties already underlined in precedent reviews by Gaucher *et al.* (2006) and in the framework of the NF-PRO project (2008) concerning the reaction pathways (kinetic or thermodynamic control, reliability of data), the influence of the anionic exclusion process and the evolution of hydraulic properties (clogging, swelling capacity).

Laboratory experiments

A large number of mineralogical modifications has been observed in laboratory experiments on diverse clayey and concrete materials (various bentonite types or samples of argillaceous geological formation; pH 13-fresh concretes, pH ~ 12.4-evolved ones) in diverse conditions (dispersed, compacted samples). Most of them report the dissolution of montmorillonite, quartz

and dolomite and the precipitation of phases such as calcite, CSH and CASH. Nevertheless, the neoformation of other minerals, notably low kinetics minerals such as zeolites (high retention properties; efficient pH buffer) or illite, is also noticed but not systematically. For example, laboratory experiments performed on Tournemire argillite highlight the precipitation of K-feldspar and illite, as well as Na-zeolite (Devol-Brown *et al.*, 2007; Devol-Brown *et al.*, 2009). It is worth noting that zeolites mainly precipitate on dispersed media, except in the work of Nakayama *et al.* (2004), confirmed by Yamaguchi *et al.* (2007), which reports the formation of analcime in column experiments on compacted mixtures of bentonite and sand. Furthermore, Savage *et al.* (2007) mentioned that thermodynamic data of zeolites probably overestimate their stability.

Concerning the evolution of hydraulic properties of clays, the data are still scarce. Melkior *et al.* (2004) and Devol-Brown *et al.* (2009) confirmed the occurrence of the anionic exclusion process and a potential clogging of the porosity in diffusion experiments on geological argillite samples. Karland *et al.* (2007) observed a decrease of the swelling pressure of compacted bentonite, but only under a strong alkaline stress ($\text{pH} > 13$).

Engineered and natural analogues

Even though their transposition to radioactive waste disposal systems is not straightforward, the observations on natural analogues enable to access to transformation over long time periods (up to one hundred thousand years). Savage *et al.* (2009) notably highlighted the dissolution of montmorillonite at mildly alkaline pH ($9 < \text{pH} < 10$) over 100 ky at Searles Lake (California). Interesting mineralogical neoformations (zeolite, illite, calcite, CSH) have also been observed on Jordanian natural analogues, but their hydraulic conditions prevailing over geologic time scales are not well-known.

In comparison with natural analogues, the engineered ones present the drawback to access only to smaller time scales, but the invaluable advantage to present hydro-chemical conditions better known and close to those that could be encountered in a waste repository. Wersin *et al.* (2008) notably confirmed the occurrence of the anionic exclusion process in an in-situ experiment in Opalinus Clay (Switzerland). Tinseau *et al.* (2006) studied a 15-year vertical borehole in Tournemire sealed with concrete. Macroscopic observations showed a drastic change in the argillite texture and mineralogy at a distance of 1 cm from the concrete contact in the argillite matrix and 1.5-2 cm in decompression fractures orthogonal to the interface (see Figure 1). The experimental characterization highlighted three successive front zones. Precipitation of carbonates and ettringite occurs in the first millimetres of the concrete/argillite interface. C(A)SH and calcite precipitate in a second centimetric-scale zone, followed by a third centimetric-scale zone where calcite and possible K-feldspar overgrowth are observed. A current study on a 5-year engineered analogue in Tournemire highlights the emergence of a 5 mm-thick dark front comparable to that observed on the 15-year analogue (Techer *et al.* 2009), which tend to show that the formation of these fronts occurs progressively.

Figure 1: Observation of a centimetric perturbation front within the argillite after 15 years of argillite/concrete interactions (Tinseau, personal communication)

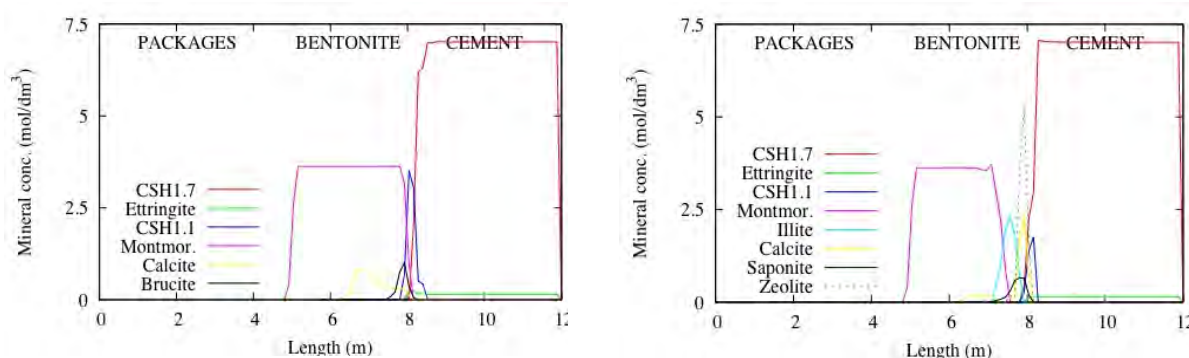


Long term modelling

Recent works in reactive transport modelling have shown that pathways under kinetic control may be of concerns. In terms of results, a pure thermodynamic approach would lead to strong disturbances in a restricted zone located near the concrete/argillite interface, whereas a kinetic approach with a similar set of minerals taken into account would globally lead to moderate disturbances on a further distance (NF-PRO, 2008; Marty *et al.* 2009). This statement has been confirmed by the modelling of the 15-year engineered analogue mentioned above with the reactive transport code HYTEC (De Windt *et al.*, 2008). Moreover, strong uncertainties remain due to the lack of reliable thermodynamic and kinetic data, notably related to zeolites and C(A)SH (Savage *et al.* 2007). In addition to this, calculations under thermodynamic control globally lead to a fast clogging of the porosity, whereas partial clogging generally occurs as an ongoing process under kinetic control of the concrete/clay systems on the very long term (see Figure 2). These uncertainties should be covered by considering both thermodynamic and kinetic approaches in reactive transport modelling. The influence of the anionic exclusion process is also not accurately well-known, which leads to another uncertainty on the diffusion coefficient, and thus on the extent of the perturbation.

It is worth noting that the modelling of the concrete alteration, instead of alkaline water only, allows a better representation of the alkaline reservoir and thus a better description of interaction processes likely to occur (diffusion of solutes through the altered concrete). In addition to this, simulations performed in the framework of NF-PRO (2008) also indicate that the near-field designs (geometry and quantity of concrete components) may significantly control the intensity and the extent of the alkaline perturbation, which means that specific calculations will still be required for each waste disposal concept.

Figure 2: Sensitivity to mineral buffering of long term calculations (low kinetic minerals not allowed and allowed to precipitate, resp. left and right). Mathieu *et al.* (2006).



Discussion

Concerning the mineralogical evolutions, a large number of laboratory experiments has been performed, providing essential information on phases likely to precipitate or dissolve due to the interaction of clayey materials with concrete fluids. However, some uncertainties still persist, notably concerning the precipitation of zeolites which are not systematically observed, particularly in compacted media. Numerical simulations highlighted the high sensitivity to the mineralogical hypotheses and a combination of both thermodynamic and kinetic approaches would be recommended in order to cover the uncertainties. Again, a consensus still exists on the need to provide accurate thermodynamic and kinetic data for numerical modelling. The occurrence of anionic exclusion, supposed to slow down the perturbation, has also been confirmed in recent studies, but its real consequence on the alkaline plume migration is still unclear.

Regarding the hydraulic properties, the diminution of the swelling pressures of compacted bentonite has been noticed. Besides, most experiments on compacted media and numerical simulations show a possible clogging of the clayey porosity. However, the influence of the alkaline plume on transport properties is difficult to assess; the clogging issue is still open, as well as the potential consequences of clayey chemical transformations on the mechanical properties of the argillite. At last, the influence of system heterogeneities, e.g. at the concrete/argillite interface, would worth further investigations.

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8 - OVERVIEW OF RECENT AND FUTURE WORK ON MATERIAL DEVELOPMENT AND USAGE OF CEMENTITIOUS MATERIALS IN SALT REPOSITORIES

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Introduction

The rock salt and potash mine Bartensleben was selected in 1970 to serve as a repository for low- and intermediate-level, mainly short-lived, radioactive waste (LILW). Located close to the village of Morsleben approximately 100 km east of Hanover the facility was named "Morsleben Repository for Radioactive Waste (Endlager für radioaktive Abfälle Morsleben – ERAM)". It was designed, constructed, and commissioned between 1972 – 78. Following studies and the successful demonstration of the disposal technologies used, the operating licence was granted in 1981. The disposal of waste was terminated on September 28, 1998. The license for operating the repository originated from the former German Democratic Republic and did not include the license for the closure of the repository. Therefore, according to the Atomic Energy Act (Atomgesetz, AtG), a license application for the closure of the repository had to be prepared by the Federal Office for Radiation Protection (BfS) who became the responsible operator of the repository after the reunification of Germany in 1990. The licensing procedure for the closure of the repository has been initiated. The closure concept comprises backfilling and sealing of the underground excavations mainly with salt concrete, a cementitious material.

Site specific conditions

Local geology

The ERAM is located in the structure of the Aller valley zone, named after the small river Aller. Tectonically, it is a fault structure, due to extension tectonics, which separates the Lappwald block and the Weferlinger Triassic block. Permian evaporate strata intruded into the fault zone and accumulated to a plug forming the now existing salt structure. The thickness of the salt body varies between 380 m and 500 m.

The salt body is characterized by an intensive folding of the layers and a high amount of anhydrite rocks, such as the main anhydrite ("Hauptanhydrit") of the Leine-formation (z3HA). The stiff anhydrite layers, broken into blocks during the flow of the plastic salt strata, stabilize the salt structure internally and lead to low convergence of mine excavations. Another feature of the deposit is the occurrence of potash seams which mainly are carnallite and kiseritic hartsalz. In general, the evaporite layers and the tectonic elements, such as folds, follow the border of the structure.

The salt leaching surface forms a more or less flat plane at a depth of approximately 140 m below mean sea level. The leaching surface displays a certain relief with depressions in some places with a proven maximum of approx. 175 m below mean sea level. The overlying cap rock has a very low hydraulic conductivity and isolates the salt structure from the aquifer system in the overlying upper Cretaceous rocks. The aquifer is overlain by unconsolidated or semi-consolidated glacial sediments. In addition, the surface cover is provided mostly by Quaternary sediments.

Mining conditions and radioactive inventory

The ERAM is a twin-mine consisting of the concessions Marie and Bartensleben. It is 5.6 km long and has a maximum width of 1.7 km. There are two access routes to the underground excavations, the shaft Bartensleben and the auxiliary shaft Marie. The 526-m-deep Bartensleben shaft connects four main levels at depths of 380 m, 420 m, 460 m, and 500 m below surface and the 522-m-deep Marie shaft connects two main levels.

Prior to waste disposal, rock salt and potash mining went on at the site for several decades. Thus, most of the mine openings are a result of salt production activities. The cavities have dimensions of up to 100 m in length, in a few cases up to 200 m, and 30 m in width and height. The overall volume of the cavities amounts to more than 8 million m³ (Figure 1), of which more than 2 million m³ have been backfilled, mainly using crushed salt.

The disposal rooms are located in the periphery of the Bartensleben claim, mostly in the western, southern and eastern fields, Fig. 1. Some amounts of short-lived waste are emplaced in the central part and the northern field. The waste is stored on the 4th level and the 5a sublevel.

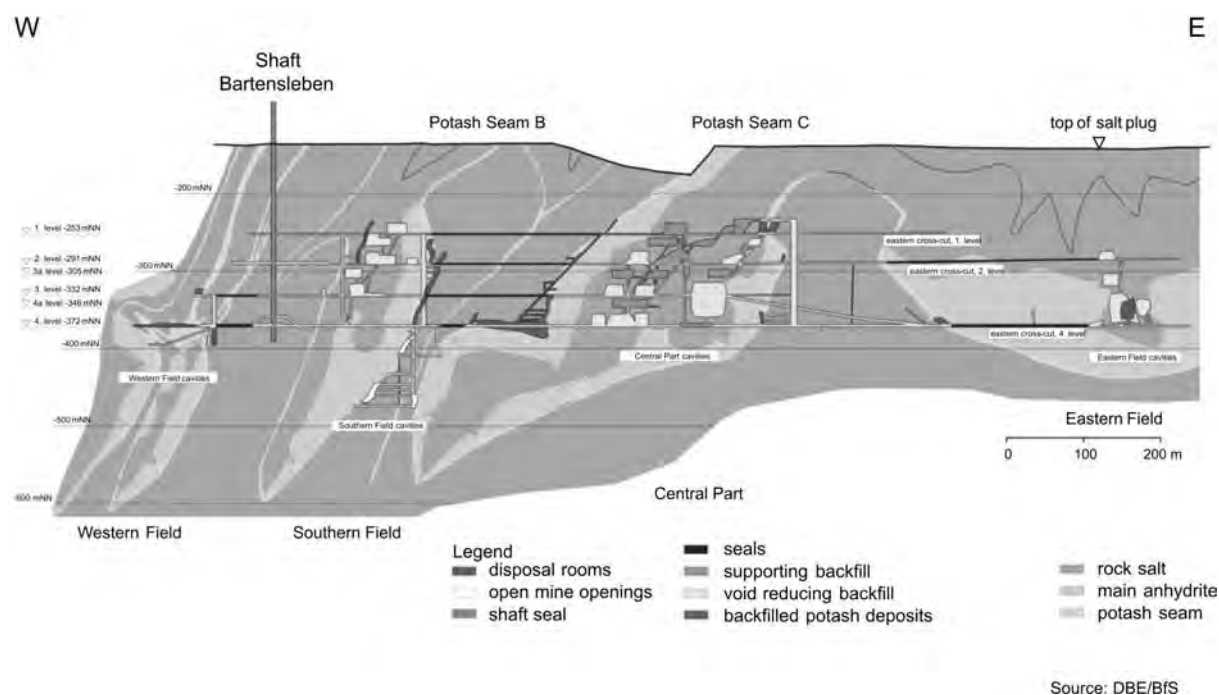
The waste originated from the operation of nuclear power plants, decommissioning of facilities and applications of radioisotopes in research, industry, and medicine. Solids and liquids as well as sealed sources were disposed of. Drum piling and dumping, as well as stacking of drums and cylindrical concrete containers were used as disposal technologies for solid waste. The liquids, mixed underground with hydraulic binders, were pumped into the storage cavities and solidified there. Altogether, a volume of about 36.800 m³ has been disposed of (approx. 28 500 m³ solids and 8 300 m³ liquids). The total activity of the waste is below $6 \cdot 10^{14}$ Bq. This includes the waste currently in interim storage at the ERAM.

Potential pathways for liquids

Concerning the safety of a repository for radioactive waste, the investigation of salt solutions as well as the detection of potential pathways is essential because brines are an effective leaching agent and have to be considered as the major transport medium of mobilized radioactive substances. Moreover, the brines may act as a corrosive medium on the binding agent of the concrete and may cause corrosion of metals. Under anaerobic conditions, the latter process results in a generation of hydrogen.

With regard to repository closure it is necessary to distinguish between enclosed reservoirs of brines trapped in rocks and inflows connected to the groundwater system. The precise investigation of active brine occurrences as well as of potential pathways is important with respect to brine inflows during the post-closure phase and the outflow of contaminated solutions. In addition to the shafts, potential pathways may occur along potash seams and inclusions of competent rock with a tendency to brittle failure, e.g. anhydrite blocks.

Figure 1: Host rock, mine openings and potential pathways for liquids



Recently, active brine inflows into the mine openings have been low. One location is situated far from the disposal areas in the Marie mine and has an inflow rate of about 10 m³/a. A dropping location with an inflow rate of about 1 m³/a is situated on the first level of the central part of the Bartensleben mine. The chemical composition of the NaCl-saturated, Mg-rich solutions has been nearly constant and proves a contact with potash salts.

Concerning potential pathways special attention has to be paid to the main anhydrite and the overlain potash seam C. These geological units connect the cap rock to the excavation damaged zone of the mine openings of the central part and may act as future pathways for liquids (Figure 1).

Operational and long-term safety objectives

The “Safety Criteria for the Disposal of Radioactive Waste in a Mine” qualitatively specify measures to be taken in order to comply with the long-term safety objectives of disposal. The long-term safety objectives generally taken into account mainly focus on radiological safety. i.e.

- protecting the biosphere against harmful effects of radionuclide release;
- avoiding criticality (not of relevance for the ERAM).

In the case of the ERAM, however, due to the large void volume classical conventional (long-term) safety objectives such as:

- limiting ground surface subsidence;
- protecting groundwater against release of conventional pollutants.

have to be considered additionally (Preuss *et al.* 2002). The safety assessments distinguish two main groups of scenarios (Preuss *et al.* 2000). In the first group of scenarios no liquid inflow into the mine openings occurs (dry repository condition) whereas in the second group of

scenarios liquids enter the mine openings and may get into contact with the radioactive waste (wet repository condition).

During the closure process operational safety has to be guaranteed as well. The related scenario is using technical words such as a so-called “non-permanent design situation”.

Operational safety includes:

- radiological occupational safety and health;
- conventional occupational safety and health.

Closure concept

According to safety measures agreed upon internationally, the multi-barrier concept is included in the closure concept, i.e. safety is not considered to be guaranteed by only one barrier, e.g. the geological formation. In general, a multi-barrier system may include the waste form, the packaging as well as backfilling and sealing measures. By this means, the waste will be isolated by a system of parallel or interlocking natural and engineered barriers.

In the case of the ERAM, tight shaft seals are planned parallel to the salt rock barrier in order to limit the volumetric flow rate of brine passing the shafts to a negligible extent. In addition, drift seals separate the main disposal areas (eastern, western and southern field) from the remaining mine openings and the potential pathways to the groundwater system existing there, e.g. the main anhydrite and potash seam C in the central part of the Bartensleben mine. One remarkable safety-relevant characteristic of the ERAM is the intact geological rock salt barrier surrounding the disposal areas. For this reason the access drifts are the relevant potential pathways for radionuclide release from the disposal areas. Thus, the drift seals are an engineered barrier of major importance.

However, the tight rock salt barrier has also to be maintained in the long term. For this reason, some of the huge cavities of the former salt production mine, whose positions are close to the top of the salt formation (salt level) or to potentially water bearing structures, have to be stabilized. In this case, simple backfill guarantees the long-term performance of the natural salt-rock barrier and it is of comparable importance as a well-performing seal.

In addition, in case of unsaturated brine intrusion, leaching effects should be minimized in such a way that no pathways to disposal areas are created by solution processes and the rock salt barrier remains intact, too.

Choice of backfill material

Next, decisive reasons are listed for choosing salt concrete as a reference backfill material:

- (1) The backfill should be similar to the natural salt environment and the existing crushed salt backfill to minimize leaching processes. As a consequence, it was necessary to include salt aggregates in the backfill material.
- (2) Due to the geomechanical situation of the central part, which is connected to the overburden and tends to brittle failure, a stiff, immediately supporting backfill material is necessary to prevent further deformation which may lead to pathway development.
- (3) As conventional occupational safety and health is not guaranteed in old huge cavities a long-distance hydraulic or pneumatic transportation system was required to avoid entering the chambers.
- (4) To guarantee radiological occupational safety and health, the potential return of contaminated circulation liquid had to be avoided.

In the following, backfill materials under discussion are listed. The requirement that was not met is given in brackets: Crushed salt (2), cemented backfill without salt components (1), magnesium oxychloride concrete with salt components (3) and backfill mixtures of brine and crushed salt (4).

The decision to use salt concrete as a reference material did not imply the exclusive use of salt concretes. As backfilling material to stabilize huge rock salt cavities mainly in the central part, however, salt concrete was identified to be optimal (Skrzyppek et al. 2000).

Plan of backfilling

When planning the closure concept every excavation was assigned to one of four backfilling categories (Köster et al. 2002). The most important is category I including cavities requiring a qualified sealing (drift seal) which will isolate the disposal areas. These excavations must be backfilled to 100% with backfill material of high quality, e.g. salt concrete M2. The basic composition of salt concrete M2 is 16.4 wt.% cement and fly ash, 13.4 wt.% water and 53.8 wt.% crushed salt. Category II includes openings that must be backfilled by more than 95% for stability reasons. The requirement of category III is an average backfill volume of 65% per mining field. The void-filling shall reduce leaching processes in case of an inflow of unsaturated brines. Category IV includes mostly inaccessible excavations in carnallite layers. A backfill volume of more than 90% shall be reached, but can hardly be verified. For this reason, only a degree of the backfilling of 50% is considered for the long-term safety analysis. The required quality of backfill material in category II – IV is less than in category I. The basic composition of salt concrete M3 applied in backfill category II-IV is 9.9 wt.% cement, 23.0 wt.% fly ash, 12.6 wt.% water and 54.5 wt.% crushed salt.

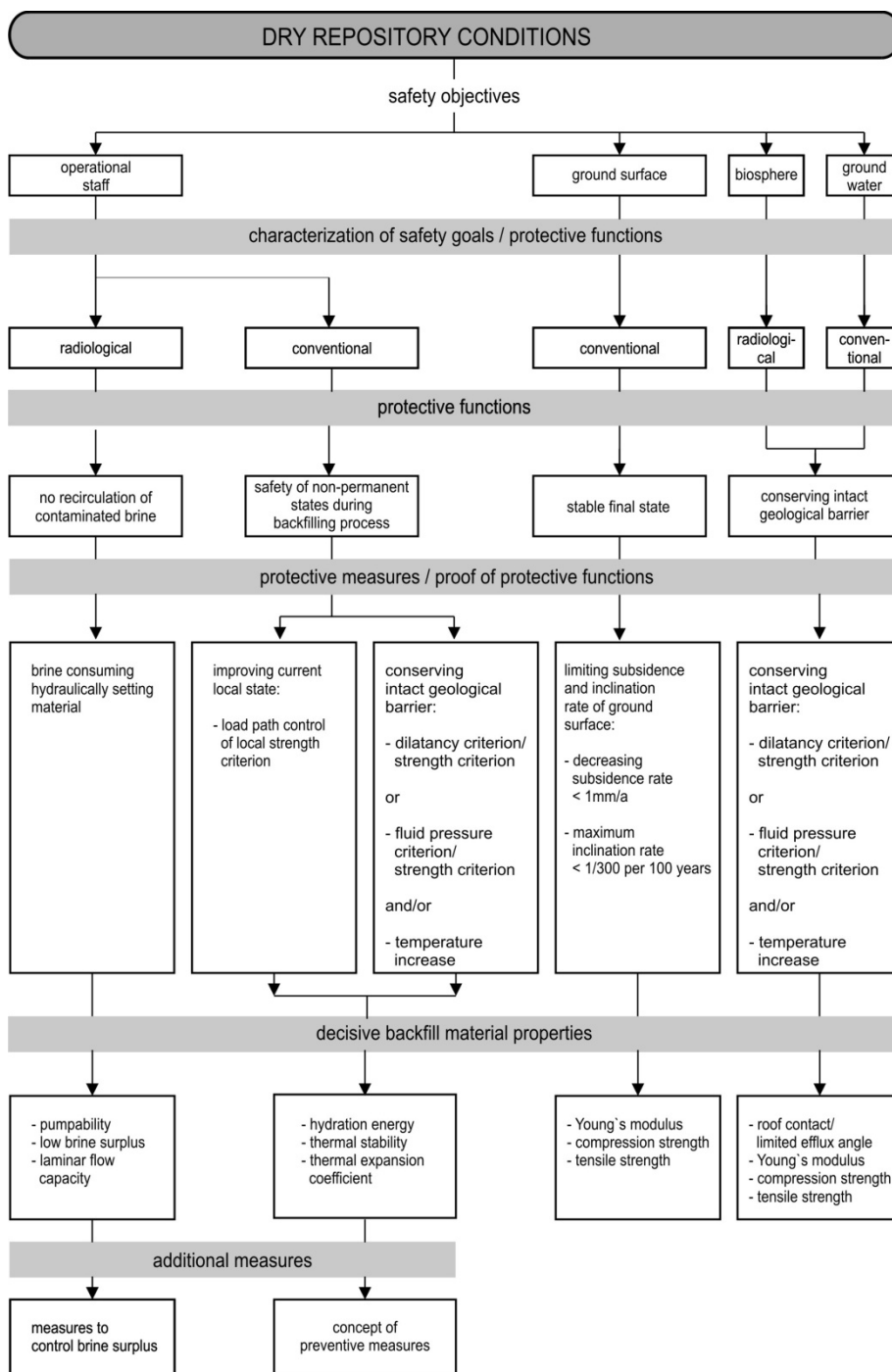
The interaction of operational and post closure safety and requirements to backfill material

With respect to backfill and sealing material, dry and wet repository conditions have to be distinguished. During the closure process and the non-permanent states in this phase, dry repository conditions are required to guarantee occupational safety. As tight shaft seals are planned, dry repository conditions will be available at least at the beginning of the post-closure phase and may continue long-term. However, as an alternative scenario, wet repository conditions cannot be excluded. In case of wet repository conditions radionuclide release must be regarded. The requirements on cementitious backfill and sealing material for both scenarios are analyzed in the following by means of flow-charts. A first draft of these flow-charts has recently been published (Preuss et al. 2000), updates are given in Figure 2 and Figure 3.

Dry repository conditions

Figure 2 shows the interactions between safety objectives and backfill material properties. Dry repository conditions are determining for stabilization measures as supporting structural safety brine pressure is not available. Groundwater and biosphere protection requirements are met automatically.

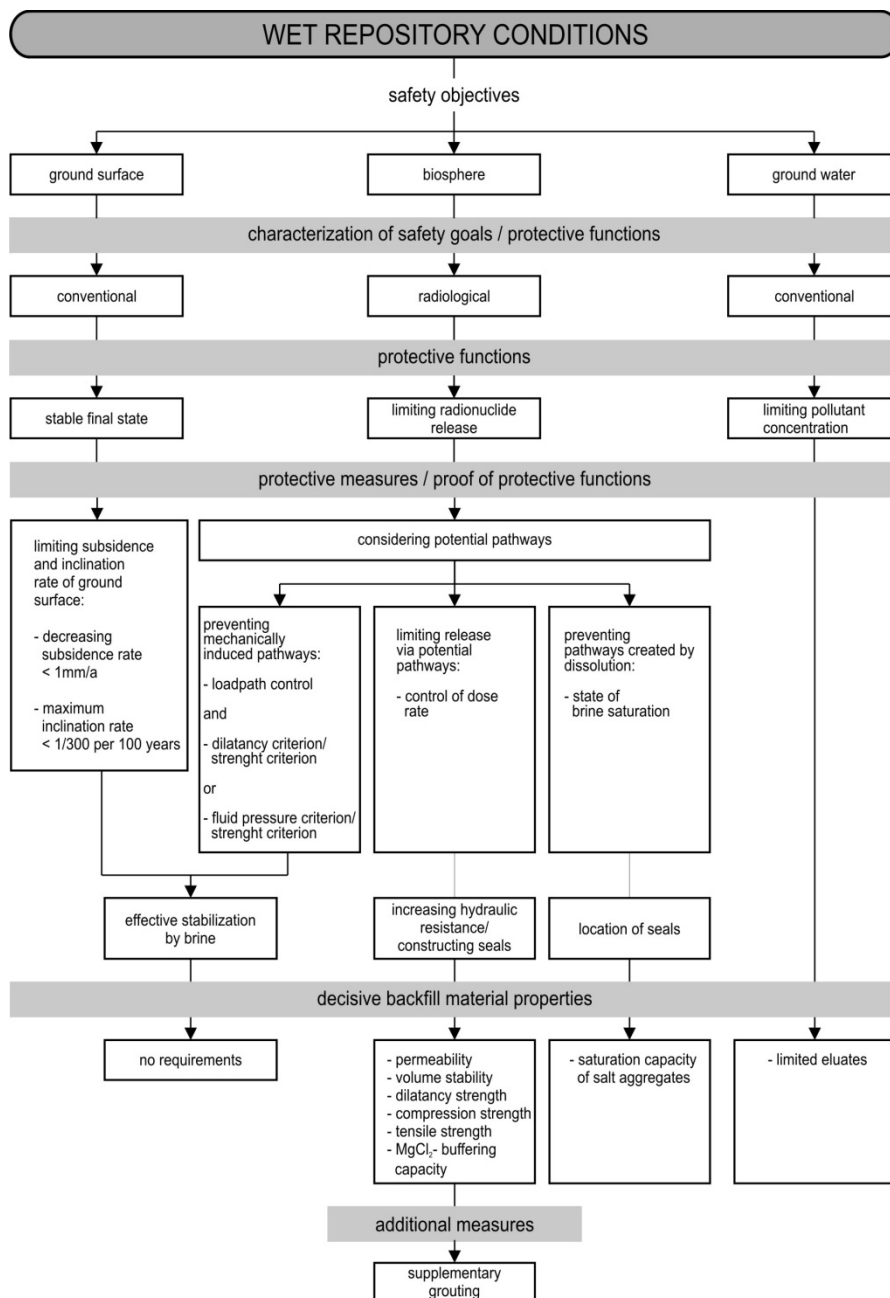
Figure 2: Linkage of safety objectives and backfill material properties under dry repository conditions



Wet repository conditions

Figure 3 shows the interactions between safety objectives and backfill material properties. Wet repository conditions are determining for groundwater and biosphere protection as radionuclides may be released. In addition, conventional pollutants may affect the groundwater. For this reason, the eluates of the backfill material are limited.

Figure 3: Linkage of safety objectives and backfill material properties under wet repository conditions



Pre-closure stabilization measures - bGZ

In November 2001, a significant roof fall occurred in the central part in a cavity of the 420-m-level, which was a restricted area due to the danger of roof falls. Numerical calculations, geotechnical surveillance, and in-situ observations showed that the risk of a progressive failure in the central part of the Morsleben repository could not be excluded which affected repository safety. Therefore, it was planned to stabilize the central part by backfilling selected cavities with salt concrete prior to the closing procedures. The stabilization measures according to the Federal Mining Act (Bundesberggesetz, BBergG) was called bGZ (bergbauliche Gefahrenabwehr-

aßnahme Zentralteil). The backfilling process started on October 8, 2003, and will be finished in 2010. Through these stabilization measures the necessary safety level is achieved up to the final closure. This measure demonstrated the technical feasibility of backfilling category II and III (Hund et al. 2004).

For the bGZ, compliance with all safety objectives for dry repository conditions had to be demonstrated to the mining authority in order to receive the licence for the bGZ. In addition, compatibility with the final closure concept had to be proven. The documents dealing with the so called “stable final state” and the groundwater protection had to be provided in order to avoid contradictions later on. Compatibility has been proven successfully.

Present status and next steps

With respect to backfill category II and III, the technical feasibility of these measures as well as their safety and compliance with long-term safety requirements have been demonstrated.

Regarding drift seals made of salt concrete (backfill category I), the conceptual planning is finished and its progress has been published in (Eilers et al. 2003, Gläß et al. 2005) as well as in the NEA EBS workshop (Mauke et al. 2003, Müller-Hoeppe et al. 2004, Herbert et al. 2005, Noseck et al. 2006, Mauke et al. 2007) extensively and is not repeated here. However, it has to be mentioned that as a next step a demonstration of drift seal performance is planned as a prototype test. A test location has already been selected. A number of small-scale and medium-scale experiments prior to prototype testing have just started including borehole sealing.

Backfill category IV is of minor interest because the requirements on the backfill quality are low. It will be discussed during the design planning stage.

Safety objectives and natural contamination of backfill materials within the context of the post-closure safety case

With regard to the post-closure safety case, salt concrete plays an important role as sealing material for emplacement areas and as filling material to reduce large void volumes in the repository. The interactions between the salt concrete seals and intruding brine (wet repository conditions) and their impact on the long-term safety assessment have been discussed in previous papers (Herbert et al. 2005, Noseck et al. 2006). Another interesting aspect related to the large volume of cementitious material emplaced in the repository is the occurrence of considerable amounts of natural radionuclides, particularly U-238 and Th-232 with their daughter nuclides. In the ERAM, the total radiotoxicity of these natural radionuclides is twice as high as that of the emplaced waste. In order to assess the effects of these radionuclides on the long-term safety consequence calculations have been performed.

For this study, relevant natural radionuclides from the thorium and uranium decay chains have been considered. These radionuclides stem from several sources. Natural radionuclides occur in salt concrete, in cemented waste forms and containers, in brown coal fly ash, in other concrete and brick constructions, in grey salt pelite, and in brine-accessible potash and rock salt deposits. The inventory of the natural radionuclides in the salt concrete is far higher than the radiotoxicity inventory of all other sources.

Important processes to be considered are dissolution of radionuclides out of the cementitious material, precipitation of secondary phases, release of contaminated brine by mechanical compaction, material corrosion, retardation of radionuclides by sorption, and radionuclide diffusion. For salt concrete two different modelling cases were considered. In case A, it was assumed that the salt concrete does not corrode but is saturated with brine from the production process, containing natural radionuclide concentrations according to their solubilities. The backfill is mechanically compacted to a certain extent, causing an outflow of

brine bearing natural radionuclides from the areas filled with salt concrete. In case B, it was assumed that the salt concrete corrodes and all radionuclides are mobilised but are subject to sorption on the corrosion residues, as corresponding experiments show high sorption values for uranium and radium.

In order to compare the results with reference values two different indicators have been calculated, namely the effective annual dose for adults according to the German Radiation Protection Ordinance and the annual drinking water dose. The results of the consequence calculations show that the maximum effective annual dose and the maximum drinking water dose for both cases are in a similar range and several orders of magnitude below the corresponding reference values. The most relevant radionuclide in all cases is Ra-226. Its mother radionuclides, especially U-238, are not directly dose-relevant but are important as a source for build-up of Ra-226.

The release of natural radionuclides is very sensitive to the sorption in the overburden of the salt dome. A parameter variation with a very pessimistic assumption of all sorption parameters reduced by a factor of ten shows a maximum dose rate less than a factor of 10 below the reference values.

Although the inventory of natural radionuclides is dominated by salt concrete, its contribution to the maximum dose plays only a subordinate role in case A. This is due to the fact that for radionuclides from brown coal fly ash and from potash and rock salt areas no solubility limits have been assumed due to the uncertainty in the geochemical conditions in these areas. In the salt concrete, where defined geochemical conditions are expected, solubility limits confine the uranium and thorium release to a fraction of less than 10^{-5} . In case B, the maximum dose originating from the salt concrete is higher, similar to the contribution of the radionuclides from the fly ash, since the release of radionuclides is not confined by solubility limits.

In reality, conditions between the cases A and B are expected. Since the overall consequences for both cases are similar, it is concluded that they describe the expected conditions precisely enough. Even though the inventory of natural radionuclides is twice as high as that of the emplaced waste, the consequences caused by natural radionuclides from the repository are very low.

Summary and Conclusion

In this paper, the closure concept for the Morsleben repository is described using cementitious materials. The conventional and radiological safety objectives are linked to backfill and sealing material properties. The consequences of the naturally occurring radionuclides of the salt concrete are negligible. Even though the Morsleben repository's radioactive inventory is low, the stabilization and sealing measures are at least equivalent to or more difficult than in a well-designed radioactive waste repository as it is a former salt production mine. Nevertheless, it is not to be handled as an old contaminated site but a regular plan approval procedure according to the German Atomic Energy Act is applied for licensing the decommissioning and closure of the repository.

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9 - CORROSION ASPECTS OF STEEL RADIOACTIVE WASTE CONTAINERS IN CEMENTITIOUS MATERIALS

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Introduction

In order to safely manage and dispose of radioactive waste it is necessary to package it in suitable containers, whether it be low level waste (LLW), intermediate level waste (ILW, large volumes, intermediate levels of radioactivity) or high level waste (HLW, small volumes of very high levels of radioactivity). The waste container forms an integral part of the waste disposal system, which normally consists of a series of engineered barriers to isolate the waste from the biosphere. Disposal concepts differ between nations, but two of the generic categories of materials that are often considered for waste containers are carbon steel and stainless steel. Corrosion is the main form of degradation that needs to be considered in assessing the safety of the waste container and the overall disposal system. Steels are often used in conjunction with cementitious materials, either in the form of grouts, which are used to encapsulate the waste materials inside the containers, or as a cementitious buffer or backfill material to surround the waste container in a geological disposal facility (GDF). For example, in the case of the GDF concept in the U.K., ILW is typically encapsulated in stainless steel containers before entering a period of storage, either above-ground in a surface store, or underground in a GDF, before finally being surrounded by a cement-based backfill material. In the case of the Belgian Supercontainer concept, HLW will be first sealed into a stainless steel container, then placed in a carbon steel overpack and surrounded by a cement-based buffer inside an outer stainless steel envelope. This complete assembly would then be emplaced in a GDF. These examples illustrate the need to understand the corrosion behaviour of both stainless steel and carbon steel in contact with cementitious materials, under conditions that are representative of the waste disposal process. The aim of this talk is to give an overview of the important corrosion processes affecting carbon steel and stainless steel in the types of cementitious material that will be encountered during waste disposal. The review makes use of experience gained by the author while working on research programmes in support of the U.K. programme on ILW disposal and the Belgian Supercontainer concept.

Nature of the cementitious environment

From a corrosion perspective the most important component of a cementitious material is the porewater that is trapped in the porespace, since any corrosion reactions will require a source of water. Cements are fine mineral powders that form a paste when they are mixed with water and harden as the hydration process occurs. The main components of ordinary Portland cement (OPC) are tri-calcium and di-calcium silicates, calcium aluminate and ferroaluminate; they are present in various ratios depending on the source of the cement. After hydration, which is an exothermic process, the main components of the solid structure are hydrated calcium sulphoaluminates and calcium silicate hydrates, which form a rigid gel (C-S-H gel). Solid $\text{Ca}(\text{OH})_2$, Portlandite, is also produced in the hydration reaction at a concentration of about 25 wt%. Although it does not contribute to the strength of the cement, the $\text{Ca}(\text{OH})_2$, together with the NaOH and KOH that are present in small amounts, have an important effect on the corrosion behaviour of metals embedded in the cement, because they control the composition of water

present in the capillary pores of the cement structure. In particular they can increase the pH of the water to values as high as 13.6. The pores have dimensions of about 10 to 50 nm if the cement paste is well hydrated, but can reach 3-5 μm if there is a high water: cement ratio or if the cement is not well hydrated. The pore sizes and the degree of interconnectivity affect the transport processes into the concrete and hence control the transport of aggressive species from the external environment to the surface of the embedded metal. Various pozzolanic materials (i.e. similar to the naturally occurring mineral 'Pozzolana'), such as pulverised fly ash (PFA), can be added to cement to produce a material with the required mechanical and physical properties. Blast furnace slag (BFS) also reacts with $\text{Ca}(\text{OH})_2$ and is used for producing cements with a fine porosity. In the U.K. a range of grout compositions have been investigated as possible encapsulants for waste in stainless steel waste containers.

In terms of corrosion, the transport properties of the cement are important. Concrete can be penetrated through its pores by gases, such as oxygen and carbon dioxide, and water containing dissolved ions, such as chloride. Transport can occur through a number of processes, such as capillary suction, permeation (due to pressure gradients), diffusion (due to concentration gradients) and electro-migration. Hence the kinetics of transport processes in concrete are determined by the environmental conditions external to the cement. The amount of water present in the cement will depend on the supply of water external to the cement (e.g. whether the concrete is fully immersed in water) or the relative humidity of the atmosphere, for example during storage of radioactive waste.

The composition of the porewater is an important factor determining the corrosion behaviour of metals exposed to cement. Porewater expression experiments show that the water is predominantly a mixture of NaOH and KOH, with a highly alkaline pH (typically in the range 12.5 to 13.5). If carbonation occurs (i.e. reaction with CO_2 in the atmosphere) this pH can fall to values as low as 9, which increases the corrosion susceptibility of steels. The corrosion resistance of both carbon steel and stainless steel is strongly affected by the pH. In addition to K^+ , Na^+ and OH^- ions, there will also be trace amounts of a range of other ions, including Al^{3+} , NH_4^+ , and sulphur species such as SO_4^{2-} , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$, particularly in BFS-based cements. Chloride ions may penetrate from the external surfaces of the cement, or from the waste material itself, and this is an important factor determining the corrosion resistance of both carbon steel and stainless steel containers during waste disposal.

Overview of corrosion of steel in cementitious materials

In the highly alkaline conditions that exist in cement, both carbon steel and stainless steel are protected against corrosion by the presence of a thin 'passive' layer. In the case of carbon steel the film is composed of a mixture of Fe(II) and Fe(III) oxy-hydroxides, whereas stainless steel is protected by a more corrosion-resistant film which is rich in chromium oxy-hydroxides. However, both types of passive film can be penetrated by reaction with aggressive species, such as chloride or thiosulphate ions. Possible sources of chloride ions during waste disposal include chloride in the waste itself, or chloride in the groundwater surrounding a GDF. In essence, the corrosion process involves two balancing electrochemical reactions. The first reaction is the electrochemical oxidation of the metal to release electrons (viz. $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$), which is balanced on the surface of the corroding metal by the reduction of either oxygen, with the consumption of electrons ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$) in oxygenated conditions, or water in anoxic conditions ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). Carbon steel is much more susceptible to chloride-induced corrosion than stainless steel because the passive film is more easily broken down than the film on stainless steel. For this reason, carbon steel tends to suffer from a more general or 'uniform' type of corrosion attack and stainless steel is more susceptible to highly localised corrosion effects. The latter are frequently categorised as pitting corrosion, crevice corrosion and stress corrosion cracking. In addition there are a number of other types of corrosion that need to be considered in assessing the applicability of carbon steel and stainless steel for use as waste container materials. These include galvanic corrosion, microbial corrosion and radiation-induced corrosion. Each type of corrosion has a potential effect on the safety aspects systems;

for example wall thinning or pitting could lead to a loss of structural strength or ultimately to loss of containment for radionuclides; similarly stress corrosion cracking could lead to a failure of lifting features and prevent safe handling practices, so it is important to assess the potential for each type of corrosion during the waste disposal process, on a case by case basis. In the talk the research that has been conducted in relation to these various types of corrosion in the context of radioactive waste disposal will be briefly reviewed, for both carbon steel and stainless steel. The environmental parameters that affect the corrosion behaviour are mainly temperature, pH of the porewater (which may vary with time due to carbonation or long-term changes in the cement chemistry), oxygen concentration, water availability and the concentration of ionic species, particularly aggressive ones such as chloride and thiosulphate. In addition corrosion susceptibility is affected by the metallurgical state and the surface condition of the metal. Much of the work that will be described in the oral presentation was carried out as part of the U.K. and Belgian research programmes.

Specific corrosion processes affecting waste containers in cementitious environments

In the absence of aggressive species such as chloride the general corrosion rate of carbon steel in cementitious environments is very low, under both oxygenated and anoxic conditions. This accounts for the durability of reinforcement bars in concrete structures. Thus the internal corrosion rates for carbon steel containers of cement-encapsulated waste during storage are expected to be very low ($<1 \mu\text{m yr}^{-1}$). In anoxic conditions, such as will be experienced post-closure in a GDF, iron corrodes anaerobically with the concomitant release of hydrogen. There has been considerable research effort expended to measure the rate of hydrogen generation by anaerobic corrosion in alkaline conditions, because the production of hydrogen may have a deleterious effect on the performance of a GDF. The carbon steel corrosion rates are low enough not to pose a long-term threat to the integrity of the containers, but the hydrogen produced could be of greater importance. Similarly, the general corrosion rate of stainless steel in cement is extremely low and in long-term tests it has not been possible to detect the generation of any hydrogen through the anaerobic corrosion of stainless steel (Smart 2004a, 2009a). The U.K. research programme took account of such factors as the surface condition, temperature, pH and chloride concentration and a similar programme of work is currently underway in support of the Belgian Supercontainer concept to measure the anaerobic corrosion rate of the carbon steel overpack surrounding the central stainless steel container (Smart, 2009b). This programme is also taking account of the possible effects of γ -radiation on the anaerobic corrosion rate of carbon steel in cementitious environments. It has been found that with clean carbon steel surfaces the corrosion rate is typically initially high (over $10 \mu\text{m yr}^{-1}$) but that it falls over a period of several thousand hours to $0.1 \mu\text{m yr}^{-1}$ or less. The corrosion product formed on carbon steel in alkaline conditions during anaerobic corrosion is normally magnetite, Fe_3O_4 .

In oxygenated conditions and in the presence of chloride ions, there is a risk of pitting corrosion of both carbon steel and stainless steel. In deoxygenated conditions the electrochemical potential of both materials (i.e. the corrosion potential) falls below the critical pitting potential and pitting does not occur. However, in the presence of oxygen both materials can suffer from pitting, the risk of which is governed mainly by the oxygen concentration, the temperature and the ratio between the concentrations of the chloride and the hydroxide ions in solution, since hydroxide acts as a pitting inhibitor. Research work carried out within the U.K. programme (Smart, 2006) has investigated the critical ranges of the $[\text{Cl}^-] : [\text{OH}^-]$ ratio for both stainless steel and carbon steel; in addition there is a considerable body of research in the literature on the factors controlling carbon steel corrosion in concrete because of its importance to the civil engineering industry. In recent years stainless steel has become an option for use as a concrete reinforcement material, where it has been found that stainless steel is resistant to corrosion in the presence of high concentrations of chloride. This has been confirmed by a long-term research programme in the U.K. on prototype stainless steel waste containers filled with waste simulant. In contrast carbon steel suffers from broad-fronted corrosion in the presence of relatively low porewater chloride concentrations (Smart, 2009a).

Crevice corrosion occurs at the junction between two mating metal surfaces, where it is possible to develop occluded cells in which localised acidic conditions can develop due to the hydrolysis of dissolved metal ions. The alkaline environment provided by a cementitious porewater has been found to inhibit the onset of crevice corrosion around the stainless steel lid flanges typical of 500 litre drums used in the U.K. (Smart, 2006).

There are a number of substances that can cause stress corrosion cracking (SCC) of both carbon steel (Smart, 2009a) and stainless steel (Smart, 2006). This process can lead to the formation of cracks at stresses considerably below the normal tensile strength of the material and this could raise concerns with regard to the handling capability of waste containers. Most attention has been focussed on the possibility of trace sulphur compounds (particularly thiosulphate in BFS-based cements) causing stress corrosion of stainless steels. For carbon steels the concentrations of aggressive species are likely to be too low in cementitious environments to cause SCC.

In some circumstances microbial activity can enhance the corrosion rate by several orders of magnitude (Smart, 2006). However, the high pH provided by cementitious environments will inhibit microbial activity and so this form of corrosion is not regarded as significant for waste containers in contact with cement, unless niches of microbial activity are allowed to develop (e.g. in voids caused by trapped gas bubbles).

Galvanic corrosion arises when dissimilar metals come into direct electrical contact within an electrolyte, such as that provided by the porewater of a cement. Research was carried out within the U.K. research programme to investigate the effect of electrically coupling a range of dissimilar metals in a cementitious medium (Smart, 2006) and a galvanic series was developed for metals in cement. This showed that the only common waste material more noble than stainless steel was graphite.

Acknowledgements

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10 - CONSEQUENCES OF CHEMICAL INTERACTIONS AT THE INTERFACE BETWEEN CEMENT AND CLAY BARRIERS – POTENTIAL EFFECTS ON GAS MIGRATION

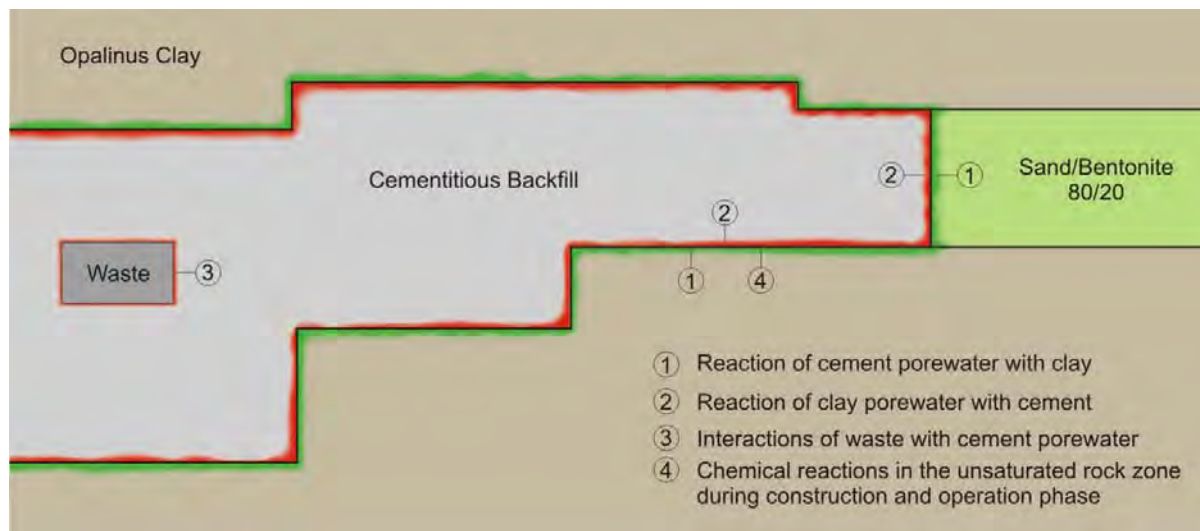
Paul MARSCHALL, (Nagra, Switzerland)

Significant amounts of gas are generated in a repository for radioactive waste. For repositories in ultra-low permeability host rock formations a demonstration is required that despite the low gas transport capacity of the geological barrier the gas can escape without impairing the long-term safety. In the context of the Swiss disposal programme for low and intermediate level waste (L/ILW), a new design option was studied, aimed at increasing the gas transport capacity of the backfilled underground structures without compromising the radionuclide retention capacity of the engineered barrier system (Nagra 2008, Senger & Ewing 2009). The concept is called “engineered gas transport system” (EGTS). It involves specially designed backfill and sealing materials such as high porosity mortars as backfill materials for the emplacement caverns and sand/bentonite mixtures with a bentonite content of 20 – 30% for backfilling other underground structures and for the seals. Numerical simulations were conducted which demonstrate the effective functioning of the EGTS concept for a range of repository configurations and parameter variants. The model calculations show clearly that an engineered gas transport system can release the gas that is produced in the emplacement caverns very efficiently through the underground structures to the backfilled access tunnel and into the adjacent rock formations. Consequently, at no point in time are excessive gas pressures to be expected in the backfilled repository system. Deviations from the expected system behaviour however, could result from the conceptual uncertainty associated with possible process couplings, such as hydrochemical interactions in the immediate vicinity of the backfilled structures. The following processes are of significance:

- Reactions of the cement water with the clay minerals of the bentonite in the cavern plugs, tunnel seal and backfill.
- Cement maturation and interaction of the cement with porewater from the host rock (“sulphate attack”).
- Interactions between waste and cement (metal corrosion, degradation of organics, sulphate attack).
- Chemical processes in the cavern near-field during the construction and operational phase (calcite precipitation, salt deposition, pyrite oxidation).

Changes in porosity and pore structures through mineral dissolution and precipitation appear primarily in the interfaces between the various repository components. The interface between the emplacement caverns and the cavern plugs plays the most significant role (Figure 1); but also of importance are the interfaces Opalinus Clay/cavern backfill as well the repository seals. The occurrence of hydrochemical interactions across the clay/cement interfaces and the associated kinetics are strongly related to the hydrodynamic evolution of the disposal system in the operational phase and the post operational phase of the repository, respectively. Reactions can occur, for all practical purposes, only in the fully saturated portion of the pore space, whereas potential self-sealing processes in the gas-filled pore space are considered unimportant.

Figure 1: Self-sealing processes resulting from hydro-chemical interactions. The formation of impermeable skin zones is considered for the interfaces host rock/cavern backfill and the contact zone between cavern backfill and cavern plug (from Nagra 2008).

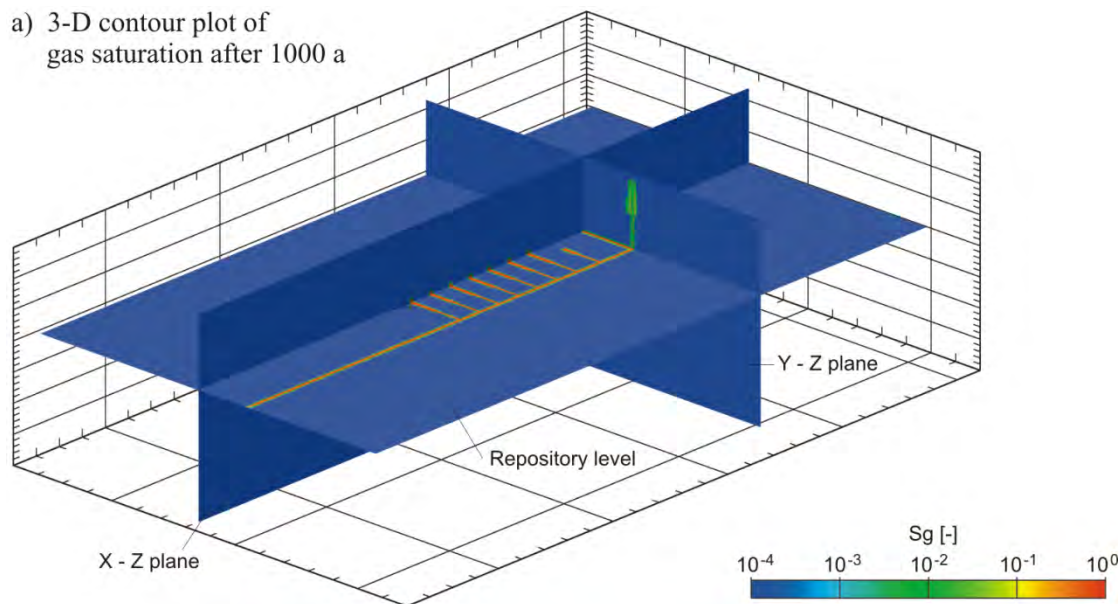


Dedicated two-phase flow simulations were conducted for studying the saturation conditions and the fluxes of gas and water in the vicinity of the underground structures (Senger & Ewing 2009). The numerical simulations provide valuable insight in the long-term evolution of the backfilled and sealed repository system. Of particular interest are the saturation conditions and the gas / water fluxes in the vicinity of the contact zones between concrete and clay based barriers, because they are setting the hydrochemical conditions for any clay/cement interactions. For the Swiss L/ILW repository concept the key conclusions with respect to the occurrence of clay-cement interactions are:

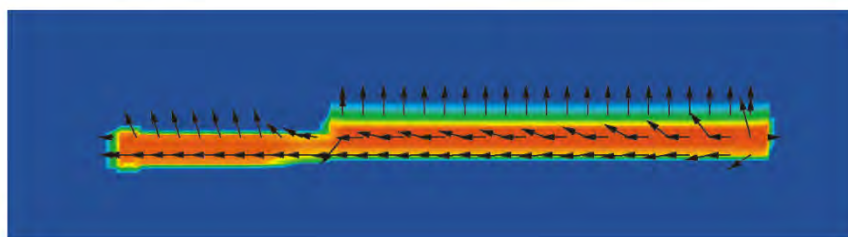
- The time scale of repository resaturation is in the order of tens of thousands to over a hundred thousand years (cf. Figure 2). For a very low permeability host rock ($k < 10^{-21} \text{ m}^2$), water consumption due to corrosion also contributes to a slowing of the resaturation process. The peak pressure is reached typically in the time frame between several 1 000 and 10 000 years.
- During the critical early post closure phase when gas overpressures develop, the backfill materials of the disposal systems and the cavern plugs are essentially dry (Figure 2). The host rock in the immediate vicinity of the underground structures is also unsaturated. In this phase it is not expected, that the gas transport capacity of the engineered gas transport path could be altered significantly by hydrochemical processes.

Figure 2: Evolution of gas saturation and specific gas flux in the vicinity of the repository (3-D overview plot and vertical cross sections through the emplacement caverns). The simulations refer to the case R_RCM01 in Nagra (2008) with a very low host rock permeability ($k_v=2 \times 10^{-21} \text{ m}^2$; $k_h=1 \times 10^{-20} \text{ m}^2$)

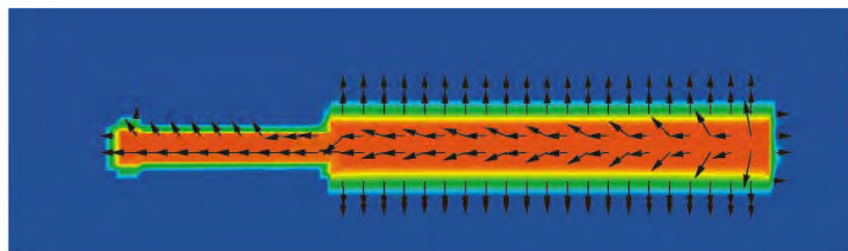
a) 3-D contour plot of gas saturation after 1000 a



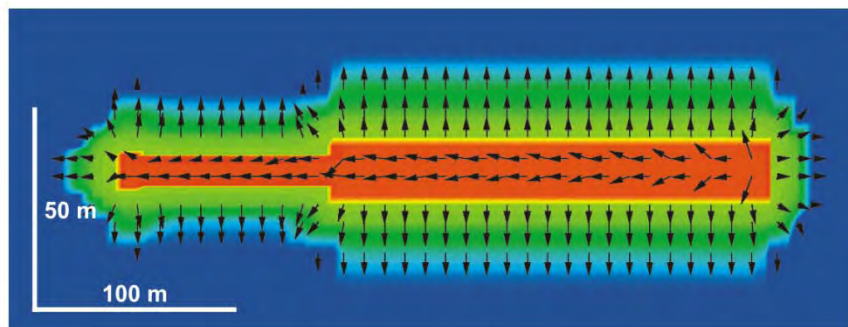
b) vertical cross-section of gas saturation after 1000 a



c) vertical cross-section of gas saturation after 10'000 a



d) vertical cross-section of gas saturation after 100'000 a

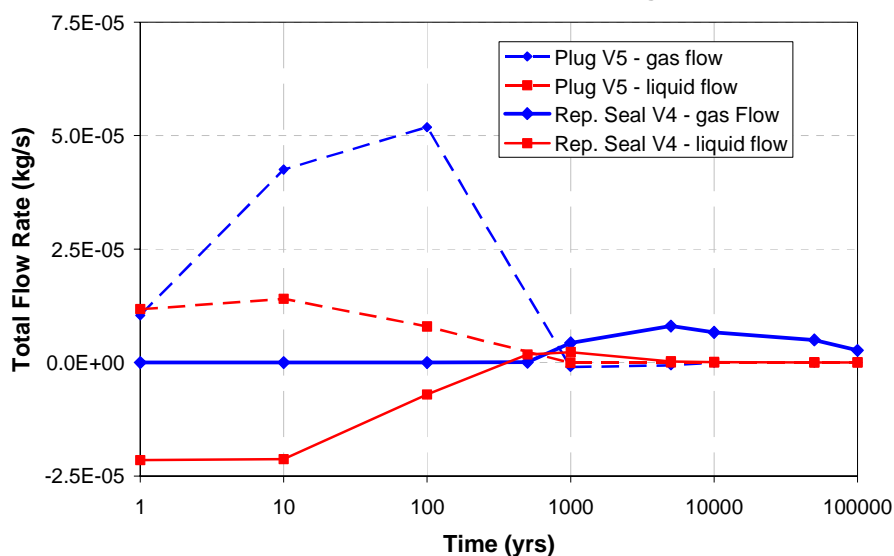


Specific gas flux: 10^{-10} m/s 10^{-11} m/s 10^{-12} m/s

Figure 2:

- Changing gas/water flow conditions are to be expected around the repository seal, which is placed at the intersection of the Opalinus Clay to the upper confining rock formation (Figure 3, solid lines). During the first 1 000 years the repository seal is saturated with groundwater from the regional aquifer system (Malm aquifer). The initial water flow rates through the seal into the repository are in the order of 0.5 m³/a. The rate reduces significantly, when gas pressure builds up in the emplacement caverns. After about 1 000 years the flow direction along the seal changes and a small amount of water is pushed out due to the increasing gas pressure. It seems important, that these changing flow conditions are taken into account in the assessment of possible cement-bentonite interactions along the repository seal.
- Similarly, changing gas/water flow conditions are to be expected around the cavern plugs, which are placed at the front end of the waste emplacement caverns (Figure 3, broken lines). During the entire gas generation phase, there is a small flow of cement water out of the emplacement caverns. This flow is driven by the gas pressure build-up in the caverns. The water saturation of the plug remains very low for the entire gas generation period. After several 100'000 years when no gas producing materials are left, a reverse flow may be expected due to the incipient resaturation of the repository.
- The on-set of a diffusion-dominated transport regime for solutes in the repository near-field begins after several 100'000 years, when the repository is fully saturated.

Figure 3: Gas and liquid flow through a cavern plug (left) and the repository seal (right), referring to run RCM03 ($k_v=1\times 10^{-21}$ m²; $k_h=5\times 10^{-20}$ m²) in Nagra (2008)



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11 - STRATEGIC CHOICES IN THE BELGIAN SUPERCONTAINER DESIGN AND ITS TREATMENT IN A SAFETY CASE

Maarten VAN GEET (ONDRAF/NIRAS) and Eef WEETJENS (SCK•CEN); Belgium

Introduction

In Belgium, geological disposal of high-level and long-lived radioactive waste in plastic clay is the reference solution for research & development (R&D) in the frame of the long-term management. Boom Clay is currently considered the reference formation for hosting a repository for this type of waste, while Ypresian clays are considered as alternative. The main safety functions that this geological disposal system should fulfil are:

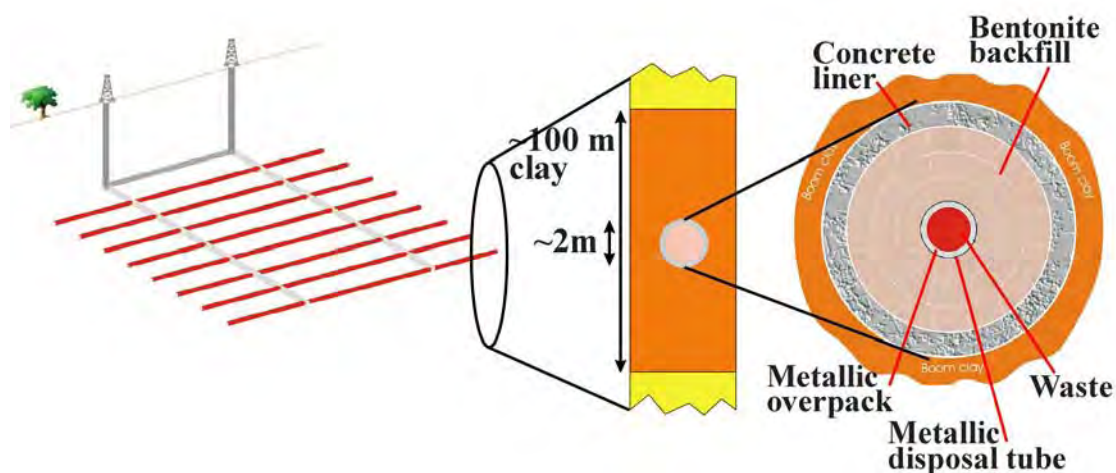
- Isolation (I): provided by the Boom Clay and its geological cover to isolate the waste from the biosphere into the far future. Furthermore, the repository is located far enough from underground areas of mineral resources to reduce the likelihood of inadvertent human intrusion, and the self-sealing capacity of the Boom Clay contributes to reducing the possible consequences of such intrusions;
- Retardation (R): Because of the favourable properties of the Boom Clay and its stability, the host formation, supported by the engineered barriers and the waste forms performs the function of delay and attenuation of the releases over extremely long periods of time;
- Engineered Containment (C): provided by the engineered barrier system during at least the thermal phase.

In recent years there has been a re-evaluation of the reference design for vitrified high-level waste and spent fuel. This paper explains the drivers of this re-evaluation, the current reference design and the implications of this so-called supercontainer design in terms of long-term radiological safety.

SAFIR 2: concept and major outcomes

In 2001, ONDRAF/NIRAS published its SAFIR 2 (Safety Assessment and Feasibility Interim Report 2) report (ONDRAF/NIRAS, 2001). The reference design used at that time for the safety assessment consisted of a network of straight galleries in the midplane of the Boom Clay at a depth of about 240 m (Figure 1). For the vitrified high-level waste and the spent fuel, the design provided multiple barriers. The primary package, surrounded by an overpack of 3 cm stainless steel, would be placed into a disposal tube made of 1 cm stainless steel. The latter was assumed to be centred in a disposal gallery, lined with concrete wedge blocks. Such a concrete liner is needed because of the limited strength of the Boom Clay host rock. The proposed backfill would be bentonite based. However, due to the limited strength of the Boom Clay itself and the in-situ lithostatic pressure of about 4.5 MPa, the swelling pressure of the bentonite should be rather limited, compared to other programmes, in order to avoid damage creation in the Boom Clay. Also, it is less crucial to have a swelling engineered barrier system that can actively recompact the excavation damaged zone (close discontinuities) as it has been shown that due to its plastic behaviour, high water content and creep, Boom Clay has the capacity to fill in voids and self-seal fractures around a purely passive support system.

Figure 1: Schematic view of the SAFIR 2 design and the SAFIR 2 layout of a geological repository in plastic clay like the Boom Clay. More details are given in the text



The main outcomes of the SAFIR 2 assessment (ONDRAF/NIRAS, 2001) and its reviews (NEA, 2003) were the following:

- Geological disposal in Boom Clay is promising;
- In the reference evolution scenario and most altered evolution scenarios, the natural barrier, the Boom Clay, is the major contributor to the overall safety.

However, this assessment and the review also highlighted possible weaknesses, namely

- The feasibility and especially the operational safety were not very clear, if not questionable;
- The engineered barrier system behaviour was rather complex and with the remaining uncertainties on near field evolution it was difficult to guarantee full containment during the thermal phase.

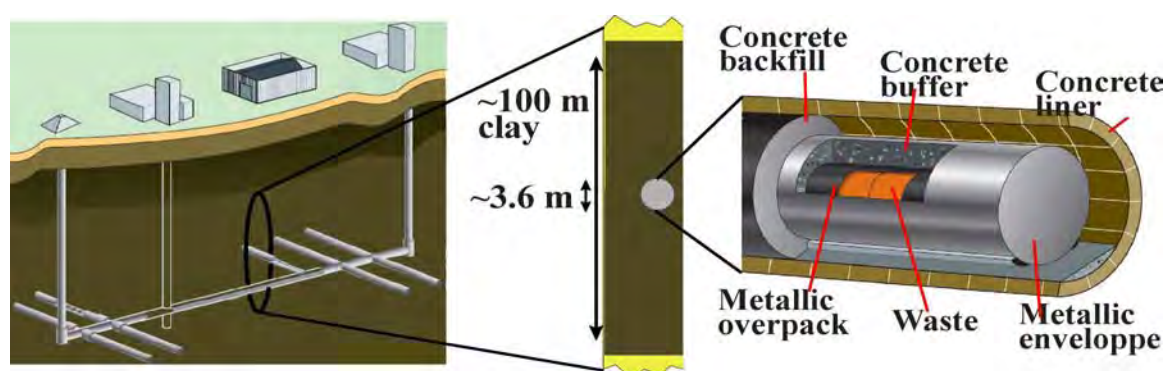
Strategic choices for re-evaluation of the concept and the resulting supercontainer design

In accordance with its safety strategy (ONDRAF/NIRAS, 2009), ONDRAF/NIRAS took the formal assessment of the SAFIR 2 report and its review as an occasion to re-evaluate the design in order to strengthen the proposed solution for long-term management of high-level waste.

A multicriteria analysis of different designs has been performed (ONDRAF/NIRAS 2004). The criteria used were related to safety reserve, host rock perturbation, intrinsic robustness, ease of demonstration, technical operation, flexibility and financial feasibility. Three alternative basic designs (supercontainer, borehole and sleeve) were elaborated. The aim of the development of a number of different designs was to establish a broad basis for justification of the selection of a reference design for the engineered barrier system (EBS). The results of this analysis showed a clear preference for the supercontainer design (Figure 2). The high-level waste and spent fuel will be placed in so-called supercontainers, consisting of a watertight carbon steel overpack of 3 cm and a massive protective concrete layer based on Ordinary Portland Cement (OPC), termed the buffer (in the order of 70 cm thick, depending on the radiological shielding needed). Optionally it might be surrounded by a stainless steel envelope of a few mm thick. Following waste emplacement, all remaining voids in the disposal galleries will be backfilled with a cement-based material. The main drivers for selecting the supercontainer design were, from a

long-term safety point of view, the formation of an engineered buffer environment around the overpack with predictable chemical conditions under which corrosion processes are very slow and well understood (contained environment) and which can be guaranteed during the thermal phase. The formation of a corrosion-protective layer of passive material on the surface of an embedded carbon steel body under the influence of a high pH environment is a well-known phenomenon and guarantees a low uniform corrosion rate (in absence of aggressive species). Moreover, it makes use of materials for which a broad experience and knowledge base exists. From an operational point of view, the supercontainer design also provides permanent shielding, which eliminates the need for remotely controlled underground operations and intrinsically better protects the workforce. In other reporting concepts, e.g. for crystalline rock, the use of cementitious materials close to high-level waste and bentonite sealing structures is avoided. However, it should be kept in mind that a concrete liner of the galleries in this case is unavoidable due to the limited strength of the Boom Clay host rock.

Figure 2: Schematic view of the current reference design, called supercontainer design, and the current reference layout of a geological repository in plastic clay like the Boom Clay. More details are given in the text



Impact of the supercontainer design on long-term safety

Ever since the re-evaluation of the reference design, the RD&D programme has been adapted accordingly and a strong interaction between phenomenologists, technologists and safety assessors has taken place. The aim is to underbuild the main drivers that have led to the choice of the supercontainer design and to evaluate the impact this design can have on long-term safety. As a consequence, in the frame of a continuous (re-)evaluation process, additional arguments in favour of the supercontainer design and some drawbacks of this design can be formulated next to the original drivers. In parallel, it is important to put this in the perspective of a systemic approach towards overall safety of the system. ONDRAF/NIRAS is preparing a safety and feasibility case 1 (SFC 1) by 2013, which should gather all arguments and evidence that illustrate that geological disposal with the current reference design is feasible and safe. At present, RD&D is ongoing and several aspects will be further scrutinized.

Corrosion

The new supercontainer design imposes better constrained boundary conditions for corrosion to better underpin the overpack integrity during the thermal phase. To this end it is important to illustrate that a high pH will be maintained in the concrete buffer during at least the thermal phase. Scoping calculations based on a local equilibrium- diffusion transport model were performed and confirmed that the Near Field will likely remain highly alkaline for a geological time span. (Wang, 2006)

Limited radionuclide (RN) release from waste form

As the chemical near field environment is now completely different compared to the SAFIR2 design, it is clear that the geochemical conditions and their evolution taking into account interactions with Boom Clay, waste and other EBS materials need to be thoroughly investigated. In this respect, dedicated research programmes have been set up to characterise the radionuclide release in the conditions, prevailing after overpack failure. Preliminary results obtained so far and qualitative arguments (contribution of K. Lemmens, this volume) indicate that:

- release from vitrified waste is faster compared to the previous concept. However, in view of long-term safety, this has little effect on the fluxes to the aquifers and doses to men. Indeed, Mallants *et al.* (2001) have shown that there is no significant contribution from the waste matrices unless their lifetime can be demonstrated convincingly to exceed several 100 thousands of years;
- for spent fuel, there is no noticeable difference in the rate of contaminant releases from the waste form for similar anaerobic conditions.

These observations are currently further being scrutinized and/or should be confirmed.

Solubility limit

The solubility of radionuclides is an additional chemical effect that limits the release from the near field for some radionuclides. When concentrations of a radionuclide species exceed a certain (pH and Eh dependent) value, that species precipitates, which limits its diffusive migration. It manifests itself where the porewater concentrations are highest, i.e. at the waste/porewater interface.

With respect to the solubility limit in the near field it is clear that the prevailing pH (and Eh) conditions of the supercontainer design need to be taken into account. However, in general terms solubilities seem to be comparable or an order of magnitude higher for fission products and comparable or order(s) of magnitude lower for actinides (ONDRAF/NIRAS, 2001 and Wang *et al.*, this volume). But compared to the SAFIR 2 design it will be important to have a focused research on RN speciation and the impact of the boundary conditions and to evaluate with the experts the confidence in the available data sets, taking into account concrete degradation.

With respect to the solubility in the far field, the difference with the SAFIR 2 concept has not changed too much, if, at least, the extent of the disturbed clay zone is not too large. Due to the significant amount of concrete used, the alkaline plume perturbation is the major topic to be evaluated [contribution of F. Marsal – this volume]. Based on current knowledge, such perturbation in clays, through which transport is diffusion controlled, remains limited (up to a few meters maximum for the supercontainer design in Boom Clay (contribution Jacques & Wang- this volume)).

Sorption capacity

The retardation of radionuclides by sorption processes plays a role along the whole pathway of the radionuclide's migration.

With respect to the near field it is again important to know the speciation of the radionuclides in the prevailing conditions after overpack failure. Substantial work on the sorption of radionuclides in concrete environment has been done, also in Belgium in the context of the surface disposal of low-level waste (contribution Wang *et al.*, this volume; contribution S. Williams, this volume). Some of this information is applicable to geological disposal as well, although important differences exist as well, e.g. oxidising (near surface) versus reducing

(geological) conditions, etc. Based on current knowledge it seems that concrete might provide some complementary sorption characteristics compared to clay, e.g. while iodine is not sorbed in clay, it may be considerably sorbed upon cement phases (contribution of J. Govaerts - this volume).

With respect to the sorption in the far field, there is not much difference with the SAFIR 2 concept provided that the extent of the disturbed zone is not too large (see above).

Conclusions

According to its safety strategy, ONDRAF/NIRAS has re-evaluated its design since the last formal safety assessment of SAFIR 2. Based on the outcome of the latter assessment, a multicriteria analysis and detailed interactions between phenomenologists, technologists and safety assessors the supercontainer design with a high pH buffer made of concrete based on Ordinary Portland Cement has been chosen as the reference design. It is believed that in this way the safety concept has been reinforced as this design should provide:

- permanent shielding during the operational phase and facilitated quality control;
- adequately understood engineered containment during the thermal phase.

Moreover this design

- is based on proven technologies and widely available, affordable materials
- has negligible negative impact on the safety functions provided by the most important barrier, the clayey host rock
- may provide complementary sorption with respect to the clay host rock for radionuclides that are mobile in clay.

On top of that, it should be kept in mind that in a case of plastic host formation, such as Boom Clay, concrete is difficult to avoid for practicality reasons (e.g. as gallery liner). However, we acknowledge that the use of concrete in this context is still fairly new and although many aspects look very promising, they still need to be scrutinised and results need to be confirmed.

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12 - SAFETY CASE APPROACH FOR A KBS-3 TYPE REPOSITORY IN CRYSTALLINE ROCK

Barbara PASTINA (Saanio & Riekkola Oy, Finland), Jarmo LEHIKONEN (B+Tech Oy, Finland), Ignasi PUIGDOMENECH (SKB, Sweden)

Introduction

Two spent fuel management organisations, SKB in Sweden and Posiva in Finland, have selected the KBS-3 method for the final disposal of spent nuclear fuel. The KBS-3 method is based on achieving long-term safety by isolating the spent fuel using multiple barriers: the spent nuclear fuel is encapsulated in a copper canister containing a cast-iron insert. The canister is surrounded by a bentonite buffer and emplaced in crystalline rock at sufficient depth to ensure effective isolation from the surface and favourable thermal, hydraulic, mechanical and chemical conditions. The selected repository sites are Olkiluoto in Finland and Forsmark in Sweden. Both sites feature a granitic host rock and reducing conditions at the planned repository depth (between 400 and 500 m).

SKB and Posiva are currently preparing to submit a construction license application for a KBS-3 type repository in 2011 and 2012, respectively. According to present plans the operational license application is scheduled for around 2018 and beginning of operations around 2020.

Cementitious materials are needed during repository construction and operation to limit the hydrogeochemical disturbances to the site and for operational safety reasons. Posiva estimated that there will be approximately 5 000 tons of cement in the KBS-3V repository at the time of closure (see J. Hansen's presentation). The inventory of cement used so far in Posiva's rock characterisation facility (ONKALO) is constantly monitored and reported and estimates of types of residual material and their inventories are regularly updated and reported (see J. Hansen's presentation).

Grouting is necessary to ensure that the main natural hydraulic pathways are not perturbed by the construction of the repository. Based on numerical modelling (Ahokas *et al.* 2006), it was determined that the risks of not using grout are greater (and the consequences more deleterious) than the risks of using it because of the effect of cement on the multi-barrier system (see below).

Safety case approach in Finland

The safety case approach in Finland has been described in the Safety Case Plan 2008 (Posiva 2008). The approach can be summarised in different steps:

- a description of the hazard presented by spent fuel, the need for safe disposal of spent fuel and the safety concept for disposal, which is a conceptual description of how safe disposal of spent fuel is achieved with the KBS-3 method and the characteristics of the Olkiluoto site.

- a description of the main components of the disposal system for which a safety case is to be made, and of how the repository will be implemented. The inventory of cement and location in the repository are taken into account in the system description.
- a description of the assessment bases, which are the scientific and technological information, understanding, models and data on which the safety assessment and safety case are based, and the methodology for carrying out safety assessment. One of the main assumptions concerning cement in the assessment bases is that the water control measures (i.e. grouting) perform as designed, that is, the main hydraulic paths of the host rock remain unchanged.
- a description of the base scenario for the evolution of a KBS-3 repository at the Olkiluoto site. In the base scenario, the cement has no impact on the system and grouting performs as designed.
- the formulation of disturbance scenarios, which include repository assessment scenarios, biosphere scenarios and human intrusion scenarios. In some of these scenarios, cement affects the performance of the buffer.
- analyses of disturbance scenarios; in reality the a perturbed buffer is modelled using modified transport parameters (e.g. distribution coefficients).
- a discussion of compliance with Finnish regulatory guidance on the long-term safety of geological disposal of spent fuel.
- a summary of the main evidence, arguments and analyses that lead to confidence in Posiva's part in the safety of a KBS-3 repository at the Olkiluoto site.
- a statement of compliance will be issued to proceed either to the submittal of the license application or to more research, including that on cement-related issues, to resolve the outstanding issues.

SKB has a similar safety case approach but there are differences mostly due to the different regulatory systems in the two countries.

Potential effects of cement on the repository's performance

According to the Finnish and Swedish approaches, long-term safety is ensured by a multi-barrier system. The main barriers to radionuclide release and transport are the canister, the buffer, the backfill and the host rock.

The central question concerning cementitious materials is to understand if and how it affects the performance of the main barriers and the transport of radionuclides. The main effect of a cementitious material is to progressively release a high-pH plume (up to $\text{pH} \approx 12$) in groundwater. The duration of the alkaline plume release is not fully known, especially with the new types of cement admixtures. High pH has a strong influence on the speciation and solubility of some elements, either decreasing (e.g. Am) or increasing (e.g. U in non-saline bentonite water) their solubility. Copper corrosion is not affected in alkaline solutions. Superplasticisers and other organic admixtures of cement as well as alternative grouting materials (e.g. colloidal silica) may also enhance radionuclide transport. Sharp pH gradients at the edge of the plume may give rise to the formation of silica colloids. The effect of cement on the host rock is to buffer the pH with minerals on the fracture surfaces as well as to seal fractures due to the formation of secondary minerals; however, both effects cannot be taken into account in the safety case because they cannot be quantified. In fact, recent modelling results show that the buffering capacity of the host rock at Olkiluoto is not as high as previously thought (Montori *et al.* 2008).

The most significant effects of cement are on the bentonite buffer (and to some extent backfill) with a potential change in swelling pressure due to mass loss (SiO_2 and montmorillonite)

and decrease in clay density, precipitation of secondary minerals, potential fissuring due to cementing processes, potential increase of hydraulic conductivity and increase of cation exchange capacity (CEC) due to the decrease of silica in the montmorillonite structure (leading to vermiculitization).

Addressing the main challenges

The main challenges are linked to the complexity of the cement/bentonite interaction mechanism and the paucity of experimental data available due to the fact that the bentonite alteration processes can be remarkably slow. Posiva and SKB are addressing the main challenges through experimental studies, modelling studies and other studies concerning the general understanding of the system's evolution in the presence of cement and also studies concerning radionuclide transport in the presence of cements or its additives.

Experimental studies on cement/bentonite interaction

The diffusion of a high pH ($\text{pH} \approx 12$) solution into bentonite porewater was studied by Karland *et al.* (2007) and further studies are ongoing in Finland (Muurinen & Carlsson 2007). Karland (2007) showed that the swelling pressure of compacted bentonite decreases at high ionic strength and high pH (Figure 1).

Muurinen and Carlsson (2007) are studying the diffusion of alkaline plume in compacted bentonite in saline groundwater (Figure 2). Although the experiment is still ongoing, Figure 2 shows that the hydroxyl ions diffuse into the bentonite and react simultaneously with the bentonite down to 10 mm from the contact solution. The capacity of the hydroxyl sites in a 10 mm layer of bentonite is too low to explain the pH change in the external solution. The probable explanation is that the silicate minerals react and consume the hydroxyl ions. The silica concentration in the external solution is low (1 – 2 mg/L), however. This indicates that the reaction products have not leached from the bentonite.

Modelling studies on cement/bentonite interaction

Modelling studies of cement-bentonite interactions have been performed by several groups (Gaucher and Blanc 2006; Trotignon *et al* 2006; Yamaguchi *et al* 2008) and references therein. In Finland modelling efforts are ongoing using the code TOUGHREACT and preliminary results have been published (Lehikoinen 2009).

Figure 1: Swelling pressure vs. density in pure montmorillonite exposed to 1 M NaCl/NaOH solutions. Effect of high ionic strength and high pH on swelling pressure.

Source: Karnland et al. 2007

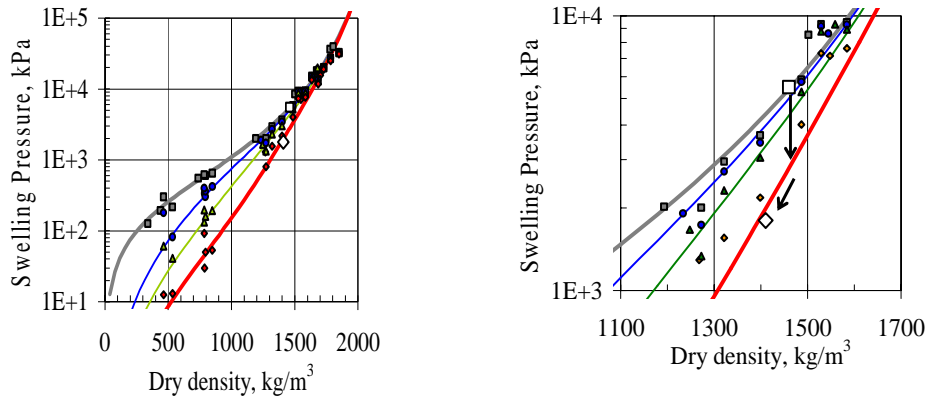
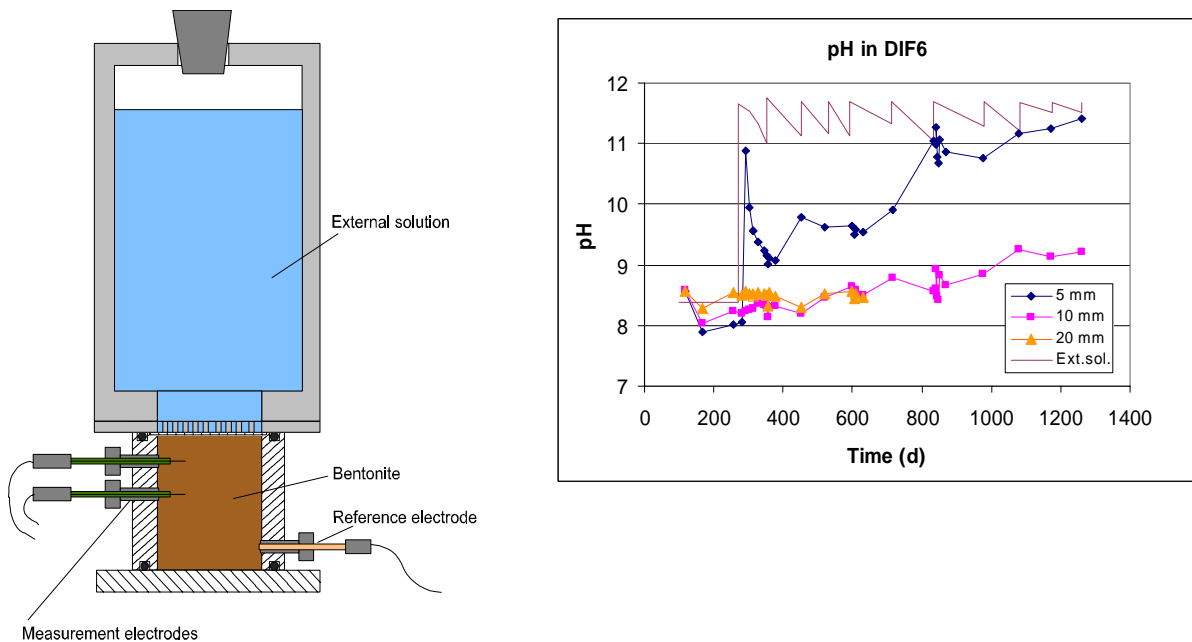


Figure 2: pH measurements at different distances in the bentonite from the high pH solution.

Source: Results up to 700 days are published in Muurinen & Carlsson (2007),

the experiment is ongoing



The modelling results show that the porosity in bentonite is expected to decrease in the proximity (few mm) to the interface between the buffer and a fracture filled with a high pH solution (Figure 3). The model shows void volume clogging but the clogs may redissolve with time. Furthermore, the time of clogging varies greatly with pH – the lower the pH, the longer the clogging takes. The model shows that the pore-fluid pH is effectively buffered at the fracture-buffer interface, but as mentioned in the previous section, experiments with pH 11.7 solutions

show diffusion of OH^- through bentonite and some buffering effect. There are several uncertainties with the current model because of the simplifications used (e.g. no temperature effect) and because of the limited knowledge about reactions and their products.

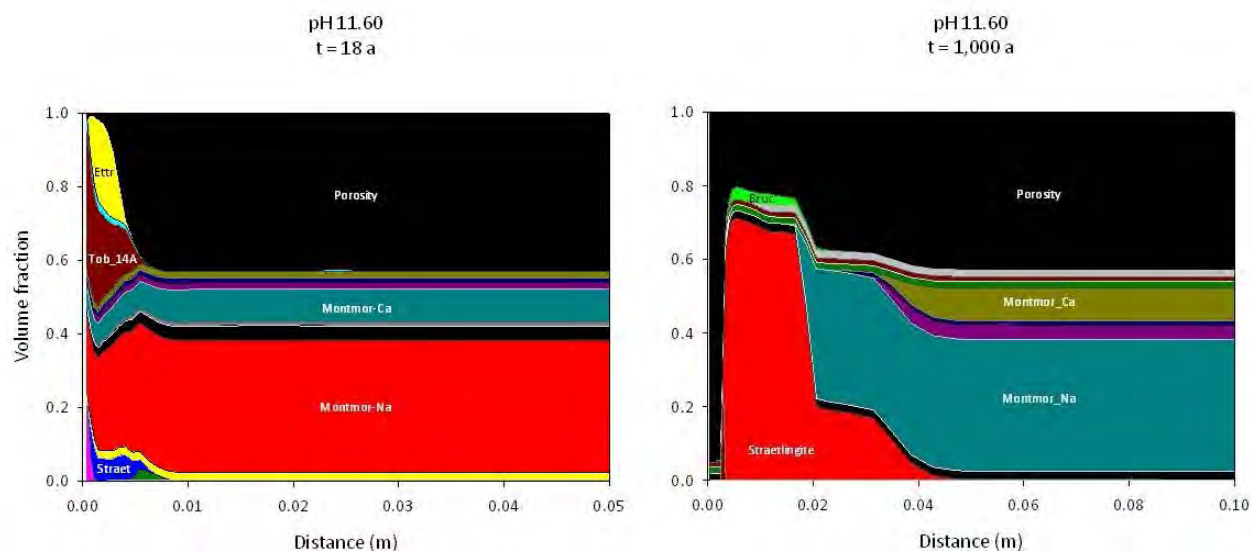
Other studies concerning the systems evolution and radionuclide transport

Posiva and SKB collaborate on several other studies concerning the understanding of the system's evolution in the presence of cement. For example the effect of superplasticisers on radionuclide transport was studied also in collaboration with NUMO (Japan). Natural analogue studies (see Alexander's presentation) and international projects concerning the effect of cement on hard rock are under way. SKB is also modelling colloid-assisted radionuclide transport.

Conclusions

The main concern that cementitious materials pose for a nuclear waste repository in crystalline rock is the potential degradation of bentonite buffer around the canisters. Both experimental and modelling studies have been performed to evaluate this. Alternative "low-pH" materials to be used in the vicinity of deposition drifts have been developed and they are being tested. Because the effects on bentonite are expected to develop only over periods of several tens of thousands of years, definite conclusions are difficult to be drawn from laboratory experiments only.

Figure 3: Chemical composition (vol. fraction) of MX-80 bentonite in contact with a fracture containing a high pH solution (pH 11.60) as a function of distance from the fracture-buffer interface (normalization to the total volume, incl. porosity). Left: composition at the time of pore clogging (18 years). Right: composition after 1,000 years of interaction omitting the initially supersaturated secondary phases. Notice the truncated extension of the spatial x-dimension to 5 cm (left) and 10 cm (right). Source: Lehtikoinen (2009)



Future efforts on the issue consist mainly in continuing the current experimental and modelling studies. The material performance of low-pH cement will also continue to be investigated. The monitoring of the pH of groundwater in the vicinity of cement sources continues and natural analogue studies are under way. A list of relevant Posiva cement-related reports is provided below.

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13 - ENVIRONMENTAL SAFETY CASE AND CEMENT-RELATED ISSUES FOR INTERMEDIATE-LEVEL WASTE IN A CO-LOCATED GEOLOGICAL DISPOSAL FACILITY

Simon NORRIS & Steve WILLIAMS (NDA) UK

Requirements of a Safety Case

In the development of a Geological Disposal Facility (GDF), safety cases will typically be developed to cover:

- Transport of waste from the site of arising to the GDF;
- Construction and operation of a GDF, including its sealing and closure;
- Post-closure period.

The subject of this presentation primarily considers the safety case for the post-closure period of a GDF, and in particular cementitious materials present in such a disposal facility, although it is noted that all safety cases will need to demonstrate consistency of approach and holistic optimisation, amongst many integration metrics.

An Environmental Safety Case (ESC), a required regulatory submission in the UK that covers the post-closure period of a GDF, is a set of claims concerning the environmental safety of a GDF for radioactive waste, substantiated by a structured collection of arguments and evidence. An ESC needs to address environmental safety during the operation of a GDF and long-term safety after wastes have been emplaced and the facility has been closed. Although the terminology used in this presentation is at times bespoke to the UK programme, the issues covered could be generically relevant to the radioactive waste management programmes that are being progressed by, for example, the international sister organisations of NDA RWMD¹. In the UK, an ESC needs to address the fundamental protection objective contained in the Guidance on Requirements for Authorisation (GRA) [Environment Agency, 2009]:

'to ensure that all disposals of solid radioactive waste to facilities on land are made in a way that protects the health and interests of people and the integrity of the environment, at the time of disposal and in the future, inspires public confidence and takes account of costs.

1. NB At present there is no selected site in the UK for GDF development, so the work of NDA-RWMD is geology-generic (i.e. we consider a range of UK-relevant geologies and have no preferred geology). This affects the choice of disposal concepts considered in our work. A GDF design that co-locates higher activity wastes, such as intermediate-level waste and high-level waste/spent fuel, in appropriate modules is being considered.

An ESC will be required to support an application for authorisation for disposals of radioactive waste at a specific site. An ESC needs to:

- Demonstrate a clear understanding of the disposal facility in its geological setting, how the disposal system will evolve, and how the various components of that system (including cementitious materials) contribute to meeting the requirement of providing a safe long-term solution for the disposed wastes;
- Set out an environmental safety strategy, the top-level description of the fundamental approach taken to demonstrate environmental safety of the system;
- Describe the key environmental safety arguments and the underpinning lines of reasoning and detailed analysis, assessments and supporting evidence (including those relating to cementitious materials).

An ESC will be a substantial submission and will include detailed information on:

- The geology, hydrogeology, geochemistry and surface environment of the chosen site and its setting;
- The characteristics of the waste including its radionuclide and materials content (including cementitious materials), treatment and packaging;
- The design and layout of the disposal facility and how it will be constructed, operated and closed;
- The basis for, and output from, computer-based models of the performance of the disposal system and its components;
- Semi-quantitative and qualitative supporting evidence that builds confidence in our claims for environmental safety.

An ESC also needs to include information on how we manage safety and how key decisions have been made, including:

- A description of our technical and management system to ensure that the GDF will be constructed, operated and closed as required;
- How the supporting work programme, including site characterisation and research activities, has been prioritised;
- How the disposal facility design has been developed and optimised, for example how choices between options for a specific site were made.

Safety Functions

A safety function – a role through which a component of the GDF contributes to safety – can be considered as relating to three principles that underpin the approach to management of radioactive waste through geological disposal, namely isolation, containment and retardation. A safety function contributes to an ESC, which itself describes:

- The overall approach to achieving safety through design of a GDF using multiple barriers;
- The main safety functions of each of the multiple barriers;
- How we use different types of evidence to build confidence in the performance of the safety barriers;
- The evidence which is applicable or available to support the arguments and confidence in the barriers.

Cementitious Materials

Cementitious materials can form a key component of a complementary multi-barrier disposal concept for a GDF, and are therefore a key issue for consideration in the analysis of post-closure performance and safety of such a facility, and in the ESC itself. Such materials consider e.g.:

- Wasteform - in-package grouting materials and package design materials;
- Backfill material;
- Shotcrete and other vault lining technologies that could be employed during construction and operation;
- Engineered seals; and
- Structural materials in the GDF environment.

The behaviour of cementitious (and other) materials needs consideration in the construction and operational safety case, as required for the pre-closure period of a GDF, and the ESC that is required for the post-closure period of a GDF. In terms of safety functions provided by components of the GDF - as can be related to cementitious materials - the following is noted:

Wasteform

The main function of the wasteform is to reduce the rate at which radionuclides can be released into pore waters/groundwater in the surrounding barriers. To fulfil this function, materials selected as wasteforms usually provide a high degree of physical **containment** and typically have some or all of the following properties:

- Low solubility under disposal conditions so that the wasteform continues to provide containment, even when contacted by groundwater and any aggressive species that may be present in groundwater;
- The ability to retain radionuclides within the wasteform effectively (i.e. to immobilise or encapsulate the waste), to minimise preferential leaching of certain species;
- Low permeability, to slow the rate at which groundwater can migrate through the wasteform matrix;
- Sufficient permeability to allow the release of waste-derived gases, to prevent over-pressurisation and damage of the wasteform.

Backfill

The backfill typically performs two main functions:

- It protects the waste package from the physical and chemical processes in the rock (i.e. it supports the **containment** function provided by the package by **isolating** it from the surrounding environment). The backfill may fulfil this function by, for example:
 - Retaining the container in the position in which it was emplaced;
 - Conducting heat generated by the waste away from the package;
 - Limiting the ingress and flow of groundwater around the package;
 - Limiting the migration of chemical and microbial species, which might enhance canister degradation, to the package surface;
 - Conditioning the chemical environment surrounding the package so that degradation processes are minimised or occur at very slow rates; and/or

- Minimising the impacts of external events such as earthquakes, by absorbing shear displacements so that they do not rupture the package.
- It slows the migration of radionuclides through the near field once a waste package has been breached (and thus provides both **containment** and **retardation**). This may be achieved by:
 - Limiting radionuclide transport through the near field by reducing the rate of porewater flow;
 - Chemically conditioning the near-field environment so that the mobility of many radionuclides is minimised; and/or
 - Providing a surface for sorption of radionuclides.

The backfill is a key component of most GDF concepts and, consequently, a detailed understanding of its long-term behaviour and how it interacts with the waste package is essential. The specific safety functions provided depend on the choice of backfill material(s) and the role of this barrier within a particular disposal system. The required characteristics of the buffer/backfill are highly dependent on the role that this barrier plays in specific disposal concepts and it is therefore difficult to define these properties at a generic level. Factors that might be considered include:

- The strength of the material;
- Its permeability to ingress by groundwater and gas;
- The surface area of the material, and its ability to provide sites for sorption processes; and/or
- The ability of the material to chemically condition the near-field environment, for example, by buffering the pH and/or the redox potential, so that it remains within a particular range over long time periods.

Engineered Seals

When a GDF is closed, the access tunnels and shafts are likely to be sealed using some form of engineered barrier. These engineered seals provide two main safety functions:

- They provide **containment** by preventing access tunnels and shafts from becoming preferential pathways for groundwater movement and radionuclide transport and release to the accessible environment; and
- They provide **isolation** by reducing the likelihood of inadvertent human intrusion.

To fulfil these safety functions, engineered seals might typically be composed of materials with a high mechanical strength, together with a low permeability and a low solubility. More than one material might be incorporated into the design of an engineered seal. In some geological environments, engineered seals may provide the safety functions described for a relatively short period of time, until the host rock takes on these functions. In other cases, engineered seals provide these safety functions over the much longer term.

Analysis of Post-closure Performance and Safety

The analysis of post-closure performance is a generic issue in an ESC, and covers cementitious materials as well as other components of and issues relating to a GDF. The main objective of the analysis of post-closure performance and safety is to demonstrate a clear understanding of the disposal system and its future evolution. The analysis considers the range of the expected evolution of the disposal system and less likely events that might affect the performance of the system. Owing to the long timescales (millions of years) that need to be

considered, there are considerable uncertainties in how the disposal system might evolve. There are three key strands to the analysis: the use of multiple lines of reasoning including qualitative safety arguments, the management of uncertainty, and quantitative modelling.

Recent and Future NDA RWMD Activities Relevant to Cementitious Materials

Recent work undertaken by NDA-RWMD relevant to the post-closure evolution of cementitious materials as could be present in a GDF includes:

- An assessment of the potential for interaction of disposal modules (e.g. ILW/LLW and HLW/SF) in a co-located GDF – this study considered the potential for the interaction of an alkaline plume developed from an evolving ILW/LLW module post-closure to interact with an evolving HLW/SF module, and conclude that such interaction can be minimized by appropriate GDF design.
- A study to assess the effect of choice of vault liner (e.g. shotcrete) on the early post-closure evolution of waste-derived gas a GDF for ILW/LLW.
- Studies to investigate evolution, including cracking, of a cementitious backfill material and how this could affect the evolution of groundwater flow and chemistry in the vault environment of a GDF.
- Consideration of evidence from nature and archaeology relevant to the long-term properties of cement.

These studies input to the consideration of cementitious materials in the ESC, and through iterative interaction with design, engineering, research and development activities allow further cementitious material-related activities to be identified and, as necessary, prioritized (note that the ESC is not always the prime driver in such considerations, as a range of stakeholders may hold differing opinions that affect the forward programme). On-going and future work as relevant to the consideration of cementitious materials in the ESC include:

- Interaction of waste-derived gas with the GDF near-field, of particular relevance with regard to carbon-14 bearing gas;
- The choice of in-drum encapsulant, noting that for some wastes a cementitious material may not be optimal.

Given their overall significance in the GDF infrastructure, and therefore in the ESC, cementitious materials will continue to be a focus of activity throughout the development and implementation of a GDF programme.

References

Environment Agency and Northern Ireland Environment Agency, Geological Disposal Facilities on Land for Solid Radioactive Wastes: Guidance on Requirements for Authorisation, February 2009.

Appendix C

Workshop Posters

#	Title	Authors
1	Experimental results on salt concrete for barrier elements made of salt concrete in a repository for radioactive waste in a salt mine	Alex-W. GUTSCH (Technical University of Braunschweig, Germany), Juergen PREUSS (Federal Office for Radiation Protection (BfS), Salzgitter, Germany), Ralf MAUKE (Federal Office for Radiation Protection (BfS), Salzgitter, Germany)
2	Natural Analogues of cement leachates: preliminary results and future opportunities from projects in the Philippines and Cyprus	Russell Alexander (Bedrock Geoscience, Auenstein, Switzerland), Carlo Arcilla (University of the Philippines, Quezon City, Philippines), Constantine Constantinou (GSD, Lefkosia, Cyprus), Naoki Fujii (RWMC, Tokyo, Japan), Margaret Honrado (University of the Philippines, Quezon City, Philippines), Hideki Kawamura (Obayashi Corporation, Tokyo, Japan), Petri Korkeakoski (Posiva, Eurajoki, Finland), Kazuki Namiki (Obayashi Corporation, Tokyo, Japan), Tony Milodowski (BGS, Keyworth, UK), Chelo Pascua (University of the Philippines, Quezon City, Philippines), Michael Rigas (GSD, Lefkosia, Cyprus), Patrik Sellin (SKB, Stockholm, Sweden), Cherry Tweed (NDA-RWMD, Harwell, UK), Edmundo Vargas (University of the Philippines, Quezon City, Philippines), Minoru Yamakawa (RWMC, Tokyo, Japan) and Ian McKinley (McKinley Consulting, Baden-Dättwil, Switzerland)
3	Assessment of the safety reserve offered by a concrete buffer in the of a geological repository in clay	Eef Weetjens, Joan Govaerts, Jan Marivoet, SCK•CEN, Mol, Belgium
4	Effect of a cement buffer on spent fuel dissolution	Thierry MENNECART (SCK•CEN), Christelle CACHOIR (SCK•CEN), Karel LEMMENS (SCK•CEN), Ben GIELEN (SCK•CEN), Regina VERCAUTER (SCK•CEN)
5	Determination of dissolution rates of vitrified high-and medium level waste in a cementitious environment	Karel Lemmens (SCK•CEN), Karine Ferrand (SCK•CEN), Ben Gielen (SCK•CEN), Regina Vercauter (SCK•CEN)
6	Accelerated hydration of high silica cements	Colin Walker (JAEA), Mikazu Yui (JAEA)
7	Development Of Low Alkalinity Cementitious Grouting Materials For A Deep Geological Repository	Kenichiro SUZUKI (Obayashi Corporation), Norihiko MIURA (Obayashi Corporation), Keishiro IRIYA (Obayashi Corporation) & Yasushi KOBAYASHI(JAEA)

8	Experimental investigation of the long term dissolution properties of a cement-based vault	E.J. Butcher (National Nuclear Laboratory), J. Borwick (National Nuclear Laboratory), A.A. Thorburn (National Nuclear Laboratory), S.J. Williams (Nuclear Decommissioning Authority Radioactive Waste Management Directorate)
9	Estimated Longevity of Reducing Environment in Grouted Systems for Radioactive Waste Disposal	Scott L. Painter and Roberto T. Pabalan, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, U.S.A.
10	Engineered analogues of cement/clay interactions in the Tournemire experimental platform (France): A couple mineralogical and geochemical approach to track tiny disturbances	Isabelle TECHER (CNRS-UMR6635, 150 rue Georges Besse, 30035 NIMES CEDEX 1, France), Pauline MICHEL (IRSN, DEI/SARG/LR2S, 92265 FONTENAY-AUX-ROSES CEDEX, France), Danièle BARTIER (CNRS-UMR5143, Muséum National d'Histoire Naturelle, 75005 PARIS, France), Elisabeth TINSEAU (IRSN, DEI/SARG/LR2S, 92265 FONTENAY-AUX-ROSES CEDEX, France), Isabelle DEVOL-BROWN (IRSN, DEI/SARG/LR2S, 92265 FONTENAY-AUX-ROSES CEDEX, France)
11	Alteration of the Tournemire argillite (France) submitted to an alkaline plume: through-diffusion and advection experiments	Isabelle DEVOL-BROWN (IRSN, DEI/SARG/LR2S, 92265 FONTENAY-AUX-ROSES CEDEX, France), Elisabeth TINSEAU (IRSN, DEI/SARG/LR2S, 92265 FONTENAY-AUX-ROSES CEDEX, France), Flore REBISCHUNG (Ecole des Mines de Paris, 77305 FONTAINEBLEAU CEDEX, France), Laurent DE WINDT (Ecole des Mines de Paris, 77305 FONTAINEBLEAU CEDEX, France), Danièle BARTIER (CNRS-UMR 5143, Muséum National d'Histoire Naturelle, 75005 PARIS, France), Sylvie MOTELLIER (CEA, DRT/LITEN/DTNM/L2T, 38054 GRENOBLE CEDEX 9, France), Isabelle TECHER (CNRS-UMR6635, 150 rue Georges Besse, 30035 NIMES CEDEX 1, France)
12	Modelling The Interaction Of An Alkaline Plume With Boom Clay At Different Scales	Diederik JACQUES (SCK•CEN), Lian WANG (SCK•CEN)
13	Space and time evolutions of cementitious components in a context of a high level and long live radwaste disposal in a deep clay formation: From phenomenological analyses to performance assessment	Isabelle MUNIER (Andra), Benoit COCHEPIN (Andra), Frédéric PLAS (Andra)
14	Mechanisms of cement leaching and degradation: Integration of neutron imaging techniques	Timothy E. PAYNE, Laurence P. ALDRIDGE, Daniel R.M. BREW, Peter J. McGLINN, (Australian Nuclear Science and Technology Organisation); Frikkie C. DE BEER, Mabuti J. RADEBE, Robert NSHIMIRIMANA (South Africa Nuclear Energy Corporation)

15	Physico-chemical impacts of cementitiously-derived calcium and silica on sodium montmorillonite	Andrew S. KINSELA (University of New South Wales, UNSW, Australia), Alice Tjitradjaja (UNSW), Richard N. Collins (UNSW), Bennett C.T. Macdonald (Australian National University, ANU), Timothy Payne (Australian Nuclear Science and Technology Organisation), Ian WHITE (ANU), T. David WAITE (UNSW)
16	Physico-chemical investigation of cement carbonation in aqueous solution in equilibrium with calcite and with a controlled CO ₂ partial pressure at 25 and 50°	Laure CHOMAT (LECBA, CEA Saclay, France), Nadia TREPY (LECBA, CEA Saclay, France), Patrick LE BESCOP (LECBA, CEA Saclay, France), Alexandre DAUZERES (LECBA, CEA Saclay, France), Corinne MONGUILLON (LECBA, CEA Saclay, France)
17	The stability of zeolites and C-S-H in the high pH reaction of bentonite	Raúl FERNÁNDEZ ^{1,*} , Jaime CUEVAS, Manuel RODRÍGUEZ ² , Raquel VIGIL DE LA VILLA ² and ³ Miguel A. CUÑADO. ¹ Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC). C/Serrano Galvache, 4. 28033 Madrid, Spain. ² Dpto. Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Campus Cantoblanco, 28049 Madrid, Spain. ³ ENRESA, C/Emilio Vargas, 7 28043 Madrid, Spain
18	Review of sorption values for the cementitious near field of a near-surface radioactive waste disposal facility	Lian WANG (SCK•CEN), Evelien MARTENS (SCK•CEN), Diederik JACQUES (SCK•CEN), Pierre DE CANNIERE (SCK•CEN), John BERRY (SERCO), Dirk MALLANTS (SCK•CEN)
19	Immobilization of Neptunium in cementitious repository environments	Jan Tits, Xavier Gaona, Rainer Dähn, Dmitry Popov, Erich Wieland
20	Benchmarking the Cemdata07 database to model chemical degradation of concrete using GEMS and PHREEQC	Diederik JACQUES (SCK•CEN), Lian WANG (SCK•CEN), Evelien MARTENS (SCK•CEN), Dirk MALLANTS (SCK•CEN)
21	Thermal and hydraulic properties of the concrete used in the ILW repository of El Cabril (Spain) preliminary laboratory tests	M.V. Villar (CIEMAT)
22	Interaction of low pH cementitious concretes with groundwaters	José Luis GARCÍA CALVO (IETcc-CSIC), María Cruz ALONSO (IETcc-CSIC), Ana HIDALGO (IETcc-CSIC), Luis FERNÁNDEZ LUCO (IECA)

1 - EXPERIMENTAL RESULTS ON SALT CONCRETE FOR BARRIER ELEMENTS MADE OF SALT CONCRETE IN A REPOSITORY FOR RADIOACTIVE WASTE IN A SALT MINE

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Juergen PREUSS (Federal Office for Radiation Protection (BfS), Salzgitter, Germany)

Ralf MAUKE (Federal Office for Radiation Protection (BfS), Salzgitter, Germany)

Introduction

The former Bartensleben rock salt mine in Germany was used as a repository for low and intermediate level radioactive waste from 1971 to 1991 and from 1994 to 1998. The repository with an overall volume of about 6 million m³ has to be closed. For the refill of the voids of the repository salt concrete is used. The concrete mixtures contain crushed salt instead of natural aggregates as the void filling material should be as similar to the salt rock as possible. Very high requirements regarding low heat development and little or even no cracking during concrete hardening had to be fulfilled even for the barrier elements made from salt concrete which separate the radioactive waste from the environment.

The salt concrete for the backfill is mixed in a plant above ground and pumped underground into the single voids of the repository with a maximal transportation rate of about 580 m³/day. For the salt concrete to be pumped underground in a tube and for the self levelling of the concrete in the voids the fresh salt concrete has an appropriate fluidity like self compacting concrete for about 2 hours without any sedimentation and no or only little bleeding in the early setting phase.

Thus, requirements for the salt concrete were set up with regard to the fluidity of the fresh concrete during the hardening process and its durability. Experimental results for material properties of the salt concrete represent the input parameter for comprehensive numerical calculations of the temperature development and thermal stresses in the massive salt concrete elements of the backfill of the voids. After the planning phase the backfilling of the repository began at the end of 2003. But this backfilling phase does not refer to the final closing of the repository.

Material Properties of Salt Concrete

Mixture of the salt concrete

The mixture of the salt concrete selected for the first backfilling stage of the repository is shown in Table 1, viz. (Gutsch et al. 2007).

Table 1. Composition of the salt concrete

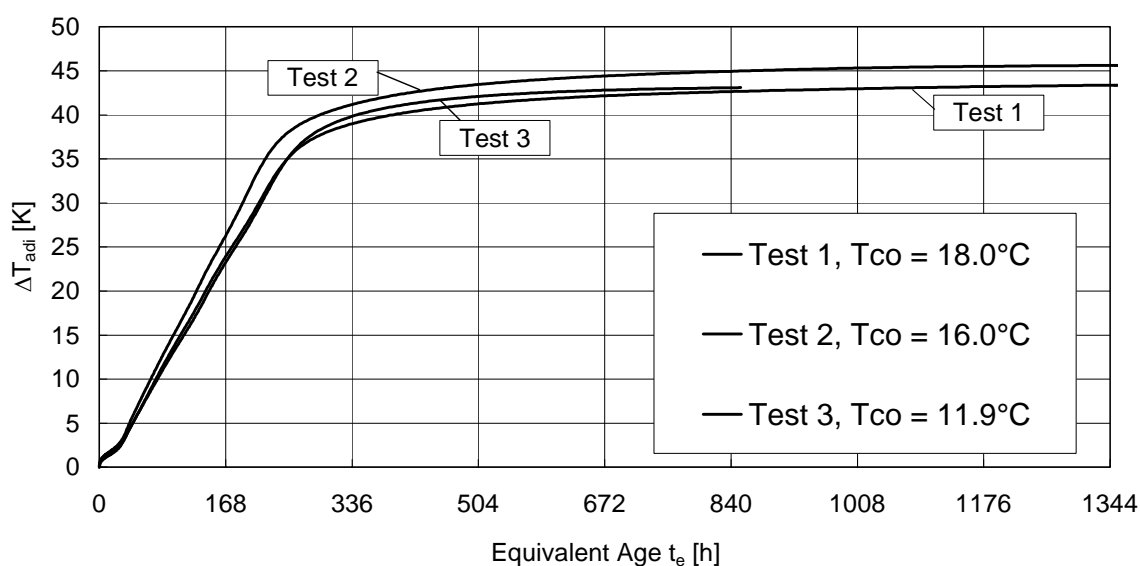
Component	Quantity	Unit
Cement CEM III/B 32.5	328	kg/m ³
Fly Ash	328	kg/m ³
Water (total)	275	kg/m ³
Salt (particle size, d = 0 - 20 mm)	1 011	kg/m ³

Thermodynamic properties

Adiabatic heat release

The heat release of the concrete during the hardening process is an important parameter for the calculation of the temperature development and thermal stresses in massive concrete structures. In laboratory tests the adiabatic heat release of the salt concrete was determined in an adiabatic calorimeter (Gutsch 1999). The results of three tests for different temperatures of fresh concrete (T_{co}) are depicted in Figure 1. The effect of the ambient temperature on the concrete hardening can be taken into account with the equivalent age t_e based on the Arrhenius function. (Gutsch 1999).

Figure 1. Heat release of salt concrete under adiabatic conditions vs. equivalent age



Thermal Dilatation, thermal conductivity and heat capacity

For the calculation of restraint stresses during the hydration process other thermodynamic material parameters such as thermal dilatation, thermal conductivity, and heat capacity are necessary.

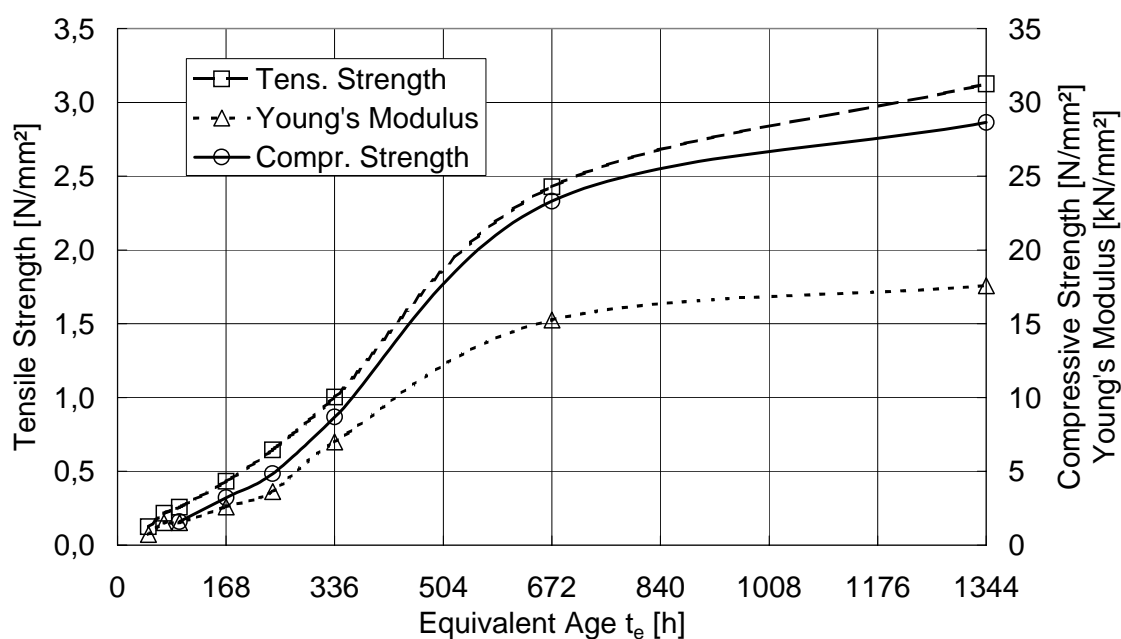
Table 2. Thermal Properties of salt concrete

Thermal property of salt concrete		Quantity	Unit
Thermal Dilatation Coefficient (+20 to +60 °C)	α_T	18-20 E-6	1/K
Heat Capacity	c	1832	kJ/(m ³ · K)
Thermal Conductivity	λ	1.14	W/(m · K)

Mechanical short term properties

The axial tensile strength and the Young's Modulus under tension were tested on cylinders (d/h = 80/250 mm) at different ages and under different thermal conditions during the hardening process. The temperature effect on the hardening was taken into consideration by the equivalent age t_e . The Young's Modulus was determined to be between 0.05 and 0.55 of the actual tensile strength f_{ct} . The compressive strength was determined on cylinders (d/h = 80/160 mm). The test results are shown in Figure 2. Each symbol in the diagram represents the mean value of six single values minimum, viz. (Gutsch et al. 2007).

Figure 2. Development of the mechanical short term properties (compressive strength, axial tensile strength, Young's Modulus under tension) vs. equivalent concrete age



Creep

Creep under tension

Tensile creep tests were performed in a temperature stress testing machine (TSTM) for different ages at first loading between $t_{e1} = 48$ h and 336 h. In the TSTM the specimen hardens under sealed and realistic temperature conditions of massive concrete structures. Curing conditions were $T = 20$ °C and 40 °C, isothermal. The specimens were sealed to prevent moisture loss. The autogenous deformations were simultaneously measured in an unloaded companion specimen. The ratio of the initial tensile stress in the creep tests to the actual tensile strength at early concrete age was $\sigma(t_1)/f_{ct}(t_e) = 0.50$, viz. (Gutsch *et al.* 2007).

Figure 3. Development of the ratio of the tensile creep deformation to initial creep stress vs. time under load.

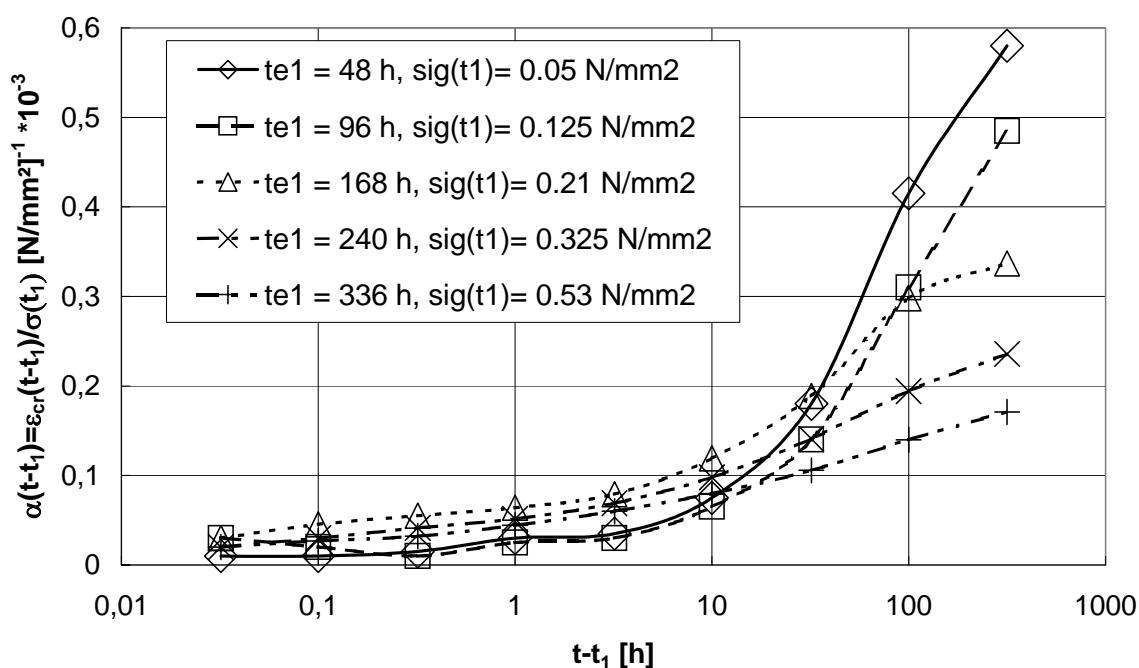


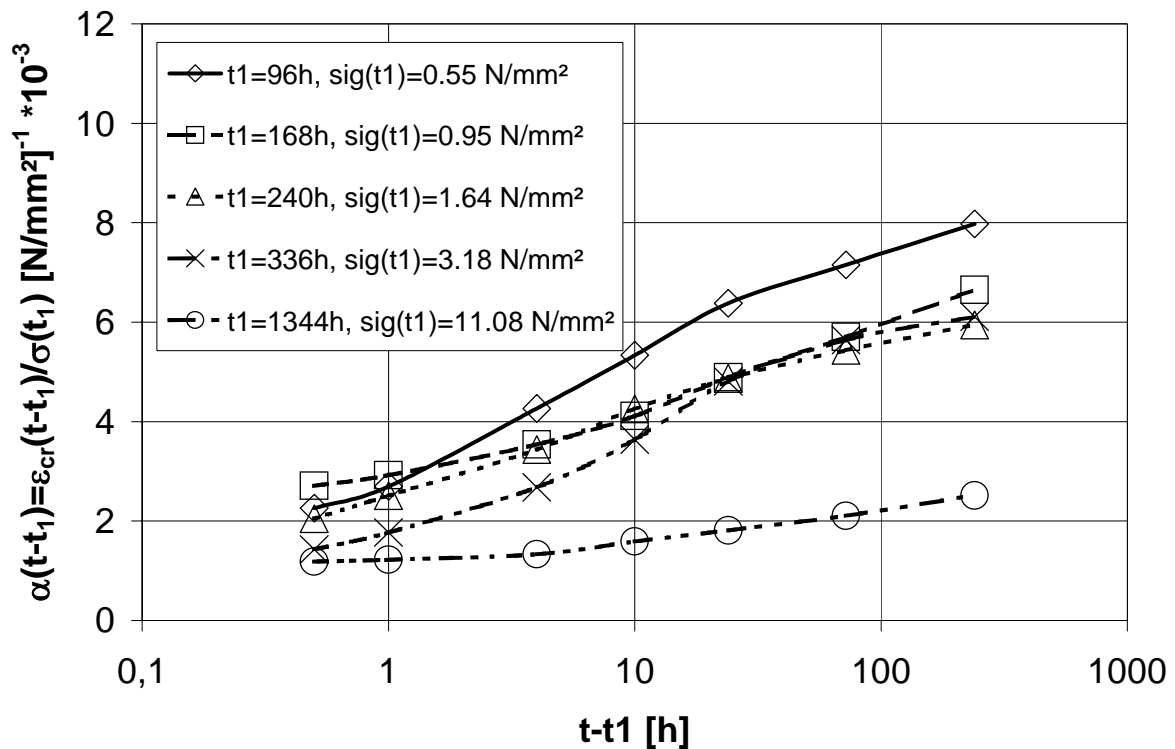
Figure 3 shows the test results of the tensile creep tests on the salt concrete for different ages at first loading. The curves represent the ratio of the tensile creep deformation $\epsilon_{cr}(t-t_1)$ to the initial tensile stress at loading $\sigma(t_1)$ vs. the time under load. Figure 3 illustrates the age dependence of the tensile creep on the age at first loading. It is comparable to the age dependence on the viscoelastic behaviour of structural concrete, (Gutsch 1999).

Creep under compression

The viscoelastic behaviour of salt concrete under compression is most important for hardened concrete (age > 28 days). However, due to the thermal stresses during the hardening process compressive stresses can arise, too. Therefore compressive creep tests were performed on early age and hardened salt concrete ($t_1 = 4$ d to 56 d). The initial stress/strength-ratio was chosen with $\sigma(t_1)/f_{cc}(t_e) = 0.28$ and 0.42 (Gutsch *et al.* 2007). Specimens were sealed during the creep tests. The load-independent deformation was measured on identical companion specimens. Results of the creep tests under compression for different ages at first loading are illustrated in Figure 4. It can be seen that the creep rate significantly depends on the age at first loading. The comparison of creep under compression (Figure 4) with the creep under tension

(Figure 3) shows a significant higher creep under compression than under tension for the same age at first loading. The ratio of creep under compression to creep under tension slightly varies with the age of the salt concrete in the range between 15 and 35.

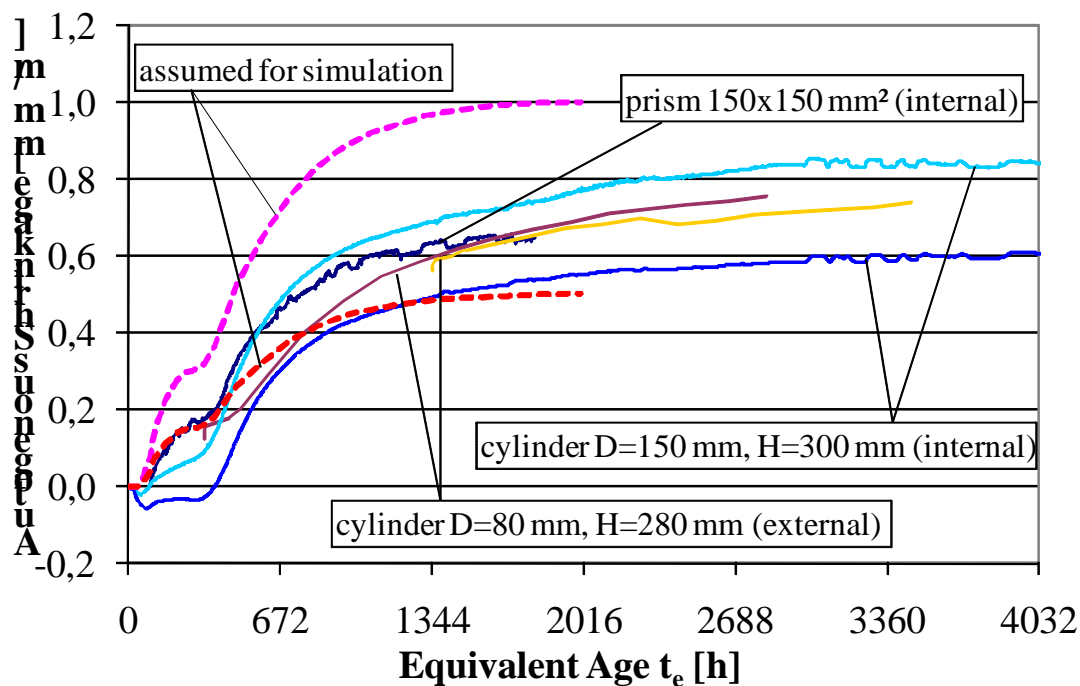
Figure 4. Development of the ratio of the compressive creep deformation to initial creep stress vs. time under load



Autogenous Shrinkage

Apart from thermal deformation also autogenous deformations might cause stresses during the hydration process in case of deformation restraint. Previously neither the water/cement-ratio of the salt concrete with $w/c = 0.83$ nor the water/binder-ratio $w/b = 0.41$ gave any indication of significant autogenous shrinkage of the salt concrete. The measured autogenous shrinkage deformations are shown in Figure 5. The results showed an autogenous shrinkage of about $\epsilon_{as,1,000} = 0.6 \text{ E-}3$ after about 1000 h and about $\epsilon_{as,1,800} = 0.7 \text{ E-}3$ after about 1800 h. In long term autogenous shrinkage tests over a period of 15,000 h (625 days) the measured autogenous deformation was $\epsilon_{as15,000} = 1.0 \text{ E-}3$. In the specimens no cracks due to autogenous shrinkage were observed.

Figure 5. Autogenous shrinkage of salt concrete, isothermal conditions $T = 20\text{ }^{\circ}\text{C}$, sealed with foil; strain measurement "internal" in the specimens and "external" on the surface of the specimens



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2 - NATURAL ANALOGUES OF CEMENT LEACHATES: PRELIMINARY RESULTS AND FUTURE OPPORTUNITIES FROM PROJECTS IN THE PHILIPPINES AND CYPRUS

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Introduction

When safe and practical implementation of deep geological repositories for radioactive waste is examined critically, it is difficult to preclude use of concrete. Nevertheless, the high pH of concrete leachates adds considerable complexity to development of robust post-closure safety assessments. This is particularly the case for designs including bentonite – which is often the most safety-critical component of the engineered barrier system. It is known, however, that bentonite is unstable in high pH environments, which has led to some repository designs that specifically

- exclude the use of concrete in any sensitive areas containing bentonite
- call for concrete removal after the operational phase
- replace conventional cement with low alkali formulations or include sacrificial buffers to reduce pH

Recently, therefore, there have been extensive efforts to better understand the interactions of hyperalkaline fluids with bentonite. The greatest challenge is bringing the information produced by laboratory (conventional and URL) and modelling studies together to form a robust safety case. This is complicated by the inherently slow kinetics of such reactions and the commonly observed persistence of metastable phases for geological time periods (for a good overview of the issues involved, see Metcalfe & Walker, 2004). Clearly, this is an area where natural analogues could play a valuable role – bridging the disparity in realism and timescales between laboratory studies and the systems represented in repository performance assessment.

As a result of a review of the available literature and contact with local experts, several sites in the Philippines and Cyprus were selected by different research groups as particularly promising for this purpose: subsequent field reconnaissance confirmed the presence of many hyperalkaline springs with pH in the range of 10-12 (McKinley *et al.*, 2008; Milodowski *et al.*, 2009). These natural analogue studies have proceeded to the stage of concept demonstration with regard to:

- Testing conceptual models of relative mineral reaction rates, the products of such reactions and their safety-relevance to the performance of the engineered barrier system
- Assessing the uncertainties associated with extrapolation of laboratory databases to realistic geological conditions and timescales
- Providing input to a range of supporting documents for safety cases, including material that facilitates communication with non-technical stakeholders

The finding that hyperalkaline springs were much more common in these locations than previously reported and their association with active gas production, intense microbial activity, contacts with Mn nodules and other relevant rocks and minerals (e.g. graphite) suggests that the analogues could be usefully expanded in terms of project goals – especially if there was increased interest of partner organisations.

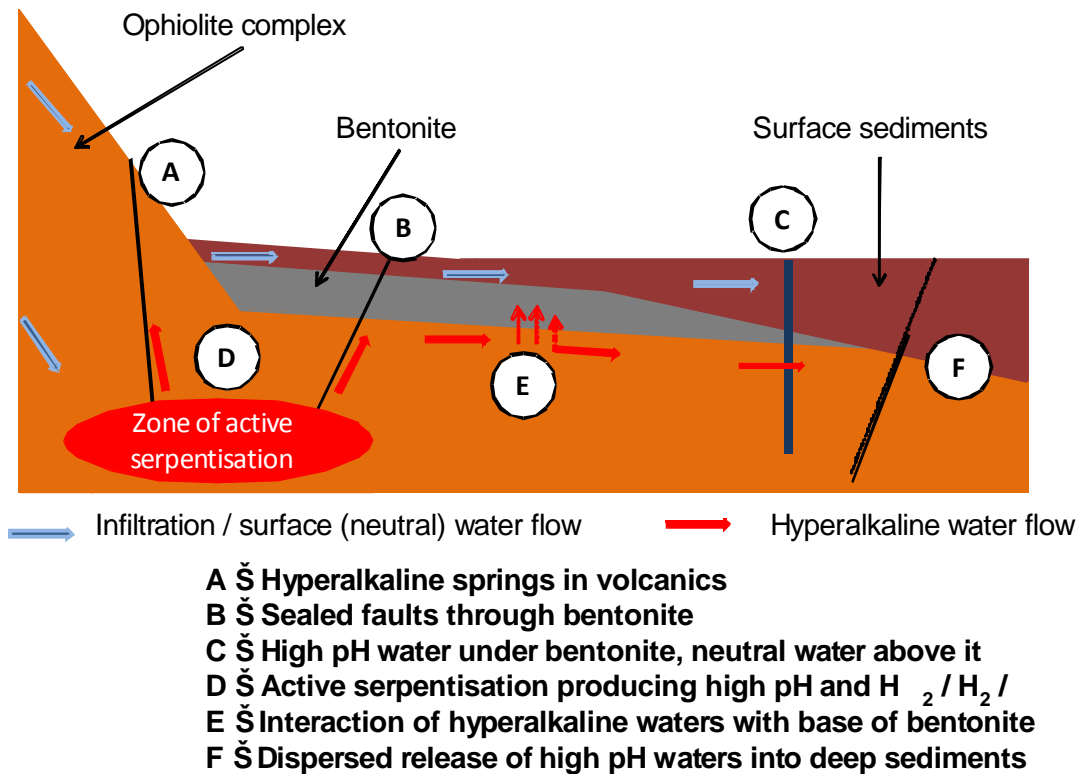
Geological setting

All hyperalkaline groundwaters studied so far in the Philippines and Cyprus originate from known ophiolite bodies. The hyperalkaline pH values (generally between pH 10 and 12) observed in the groundwaters are a product of the serpentinisation of the ophiolites, a reaction which is discussed in detail in Milodowski *et al.* (2009). The serpentinite mineral assemblages are very strongly reducing and the hyperalkaline waters are often effervescent with H₂ and/or CH₄ gas (e.g. Yamakawa *et al.*, 2009). Some of the reaction pathways are also strongly exothermic, frequently producing hydrothermal groundwaters. Despite the high pH, springs are associated with intense microbial activity and, indeed, microbial mats are often used to identify hyperalkaline seepages into lower pH surface waters.

The studies to date have focussed on sites where a bentonite, the top ‘layer’ of the ophiolite generally acts as an aquitard, isolating flow of deeper high pH waters from surface runoff (cf. Figure 1). This has been observed at both the Zambales ophiolite in the Philippines and at the Troodos ophiolite in Cyprus and means that drilling and/or trenching is required to access the site of hyperalkaline groundwater/bentonite interaction.

Figure 1: **Conceptual model of hyperalkaline groundwater/bentonite interaction**
(from Alexander *et al.*, 2008)

Conceptual model

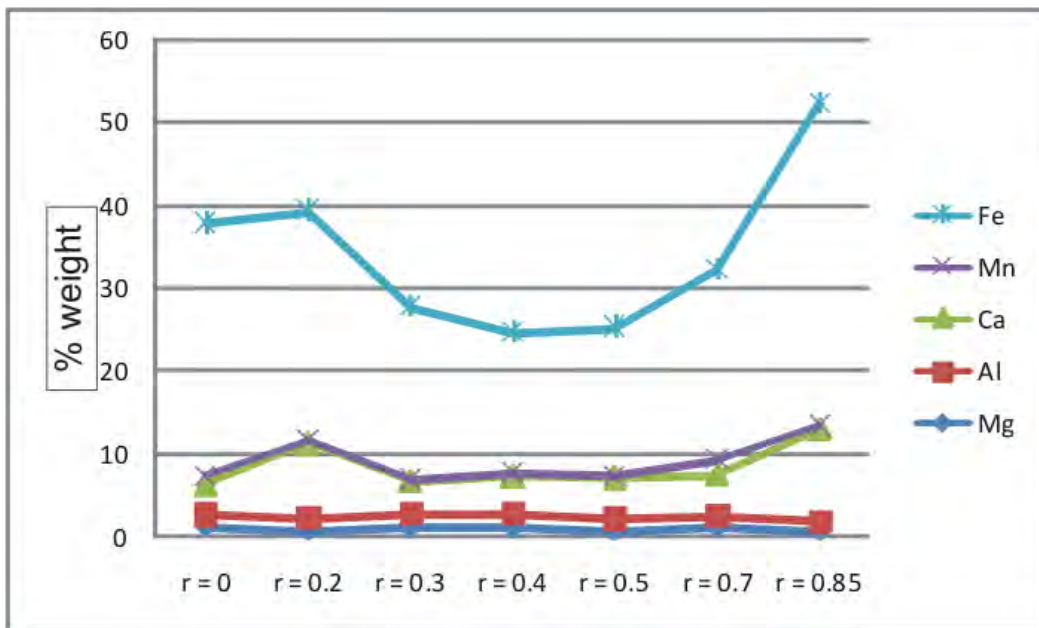
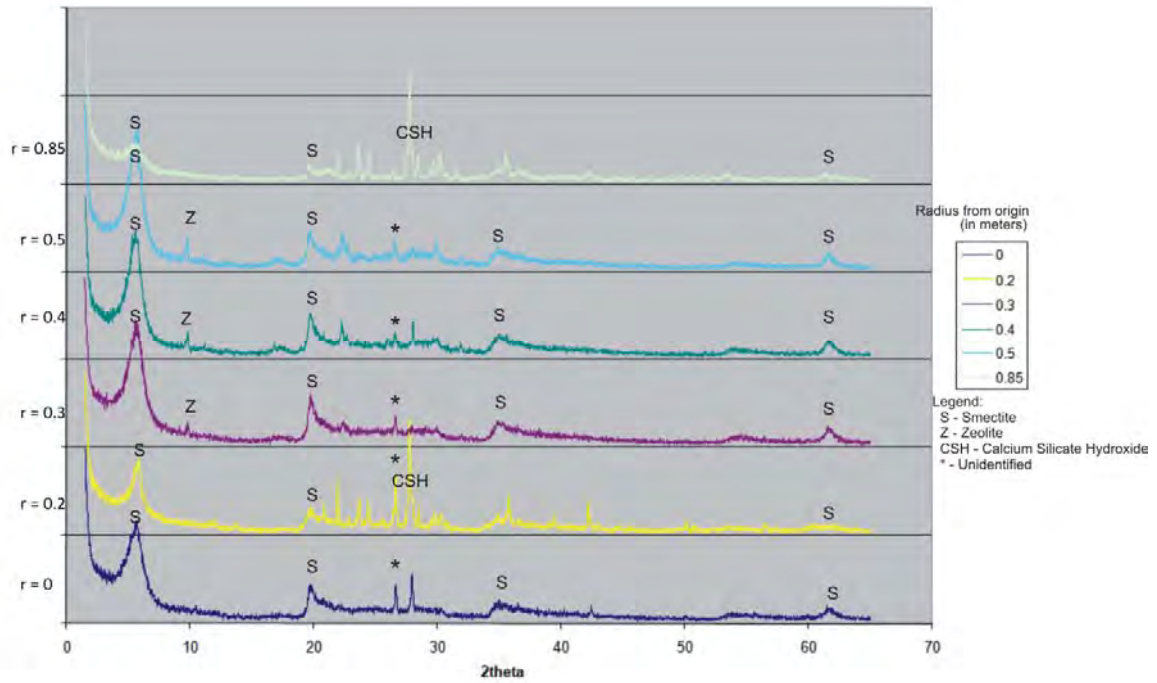


15

Preliminary results

Although still preliminary, the results from both projects indicate some degree of reaction of the bentonites in the analogue hyperalkaline cement leachates. For example, samples recovered from a sampling trench (ST1, Sailes quarry, Mangatarem, Philippines) where several metres of bentonite directly overlie pillow lavas, show that the bentonite is clearly smectitic, but zeolite, serpentine and CSH phases are also present (Figure 2). Preliminary geochemical reaction modelling suggests that the zeolites are formed from the reaction of the smectites with the hyperalkaline groundwater. Here, analcime was used as a proxy for 'zeolites' and the smectite was reacted with a hyperalkaline water produced by reaction with the underlying layered mafic to ultramafic cumulates.

Figure 2: **Mineralogy by XRD (left) and chemistry by XRF (right) of reacted material from trench ST1. On the left hand figure x-axis, the distances represent the distance away from the arbitrary sampling origin in the trench, stacked vertically for clarity (From Vargas *et al.*, 2009)**



Note also that CSH phases have been reported from other low alkali leachate analogies such as Oman but, as their stability field is $>pH10.5$, this suggests they are the product of the earliest reaction with the hyperalkaline groundwaters. Unfortunately, no samples of 'pure' non-reacted bentonite have been analysed to date and this must be a priority to allow further reaction modelling.

Perhaps more important, however, is the fact that, despite evidence of reaction, the bentonite would appear to be still acting as an aquiclude at both sites studied to date. The groundwater systems are currently underdefined, but two distinct waters have been sampled. The stable isotope signatures of the (deeper) hyperalkaline groundwater suggest an origin in the ophiolites, whereas the signatures from the neutral surface waters on top of the bentonite suggest a local origin in the bentonites (or younger sediments overlying the ophiolite), clearly showing the presence of a two-flow groundwater system in the bentonite.

Future opportunities

The results to date serve as a proof of principle and allow qualitative testing of models and databases. In order to allow more rigorous testing, samples from a wider range of hyperalkaline groundwaters (varying both in pH and salinity) would be needed. For more quantitative analysis, the more difficult issue of timescale determination must be addressed – which will require much more detailed site characterisation in order to develop a consistent model of evolution over the last Ma or so. Such characterisation will require considerable greater resources than have been available to date – but could also provide additional valuable information on post-closure safety issues associated with the use of concrete in repositories. These could include:

- Assessment of the consequences of hyperalkaline fluids on tectonic faulting in bentonite and subsequent self-healing
- Analysis of gas transport in altered and unaltered bentonite
- Evaluation of the roles of microbes and organic solutes (NB very important for low alkali cements) on mineral alteration and redox buffering in such systems
- Validation of models of radionuclide solubility speciation and sorption under high pH conditions (e.g. using source terms from Mn nodules)
- Assessing alteration processes of potentially vulnerable host rocks (e.g. tuff, non-swelling clays)
- Examining high pH stability of problem wastes (e.g. graphite).

Acknowledgements

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3 - ASSESSMENT OF THE SAFETY RESERVE OFFERED BY A CONCRETE BUFFER IN CASE OF A GEOLOGICAL REPOSITORY IN CLAY

Joan GOVAERTS, Eef WEETJENS and Jan MARIVOET (SCK•CEN, Belgium)

Introduction

Many safety evaluations of geological repositories located in a clay formation focus on the strong contribution of the natural clay barrier to the confinement of the radionuclides present in the disposed waste. Indeed, many radionuclides are strongly sorbed on clay minerals and/or have a low solubility in the geochemical conditions prevailing in a clay formation. As a consequence, only a limited number of fission and activation products, mainly anions, are expected to migrate through the natural clay barrier and reach the biosphere in a 1 million years time span.

The Belgian radioactive waste management agency, ONDRAF/NIRAS, has developed a repository concept, known as 'supercontainer concept', in which the buffer surrounding the high-level waste overpacks consists of concrete [GSL, 2005]. The gallery liner will also be made of concrete and the considered backfill material is based on cement. The clay and cement media have very contrasted chemistries that will interact and lead to a degradation of both types of material. To address this complex processes would be beyond the scope of this paper. The interested reader is therefor referred to [Wang 2006] for a detailed description of the degradation of concrete by Boom clay water and [Wang *et al.*, 2009] for more information on the alteration of the Boom clay porewater by the alkaline plume coming from the cementitious materials.

These large amounts of cementitious materials constitute an additional sorption reserve that can contribute to the long term safety of the repository. Sorption data that have been collected in the framework of the Belgian programme for the surface disposal of short-lived radioactive waste show that some anions, e.g. ^{36}Cl as chloride and ^{129}I as iodide, which are not or poorly retarded by the clay, are strongly sorbed upon concrete phases. Other mobile anions, e.g. bicarbonate containing the radioactive isotope ^{14}C , can exchange carbon isotopes with calcite phases, of which large amounts occur in the various concrete or cement-based materials used in the engineered barrier system. These phenomena result in (equivalent) sorption values which are much higher for cementitious materials than clay. Best estimate sorption values and corresponding retardation values for ^{14}C , ^{36}Cl and ^{129}I in clay and degraded cement are compared in Table 1. Also the pore diffusion coefficient is given, which is assumed to be the same in clay and concrete [ONDRAF/NIRAS, 2009].

Table1: Best estimate R_d (l/kg) values, retardation factors (RF) and pore diffusion coefficient D_p (m^2/s) for clay and degraded cement

	Degraded cement		Clay		D_p
	R_d	RF	R_d	RF	
^{14}C	5×10^3	1.1×10^5	6×10^{-2}	1.6	6.0×10^{-11}

³⁶ Cl	5×10 ⁻¹	1.1×10 ³	0	1	1.4×10 ⁻¹⁰
¹²⁹ I	1×10 ⁻¹	2.3×10 ²	0	1	1.4×10 ⁻¹⁰

Results and discussion

In the performance assessment calculations, performed with COMSOL Multiphysics [Comsol, 2008], we have simulated the dissolution of the waste matrix, the migration of radionuclides through the host clay layer, the transport and dilution of radionuclides in the aquifer overlying the host formation and transfers of radionuclides in the biosphere to man. The simulations were performed for the expected evolution scenario of the repository system; this means that it is assumed that the essential repository components will function as expected.

We evaluated if the retardation potentially provided by these cementitious materials present in the near field can give a meaningful contribution to the confinement of the mobile fission and activation products in the repository system. Four cases are considered: the first case is the reference case where no barrier function is attributed to the concrete materials (C1). The remaining three cases incorporate resp. the buffer (C2), cementitious backfill material (C3) and concrete gallery liner (C4). As far as sorption is concerned, all cementitious materials are considered to have similar sorbing potential and will be treated in the same way. This is based on the fact that most relevant concrete compositions for the disposal facility all use OPC (Ordinary Portland Cement) and calcareous aggregates in similar amounts. Therefore, the major cement phases responsible for sorption are present in comparable amounts [ONDRAF/NIRAS, 2009].

The doses via a water well pathway and activity fluxes (out of the waste package, buffer and host formation) are calculated for the four different cases. Also, two performance indicators for safety functions physical containment C (PI_C), limitation of release R1 (PI_{R1}), retardation due to migration through buffer R3_b (PI_{R3b}), and retardation due to migration through host formation R3_c (PI_{R3c}) are calculated. More information on the safety functions can be found in [ONDRAF/NIRAS, 2007]. The indicators are defined as follows [Marivoet et al., 2009]:

- $PI_C = \text{activity}_{T1} / \text{activity}_{T0}$
with: T0: time of disposal

T1: time of overpack failure
- $PI_{R1} = \text{activity}_{\text{out WP}}(t) / \text{activity}_{T1}$
with: $\text{activity}_{\text{out WP}}$: time-integrated activity flux up to time t released from waste package
- $PI_{R3b} = \text{activity}_{\text{out buffer}}(t) / \text{activity}_{\text{out WP}}(t)$
with: $\text{activity}_{\text{out buffer}}$: time-integrated activity flux up to time t released from buffer
- retardation due to migration through host formation (R3_c):
 $PI_{R3c} = \text{activity}_{\text{out HF}}(t) / \text{activity}_{\text{out buffer}}(t)$
with: $\text{activity}_{\text{out HF}}$: time-integrated activity flux up to time t released from host formation

The product of the 4 indicators defined above gives an indication of the performance of the integrated repository system (IRS):

$$PI_{IRS} = PI_C \times PI_{R1} \times PI_{R3b} \times PI_{R3c} = \text{activity}_{\text{out HF}} / \text{activity}_{T0}$$

We consider the amount of vitrified high-level waste that arises if all the spent fuel irradiated in the 7 Belgian nuclear power plants should be reprocessed; this corresponds to about 3915 vitrified HLW canisters [ONDRAF/NIRAS, 2001]. The designed lifetime of the overpack is 2 000 years and the waste matrix is assumed to dissolve at a constant rate over 10 000 years. The considered repository design is based on the supercontainer concept. The considered radionuclide inventory is based on nominal value provided by AREVA.

The results are shown in Figure 1, Figure 2 and Table 2.

Figure 1: Evolution of the ^{36}Cl (left) and ^{129}I (right) activity fluxes out of buffer and host formation for C1 (—), C2 (— —), C3 (- · -) and C4 (· · ·)

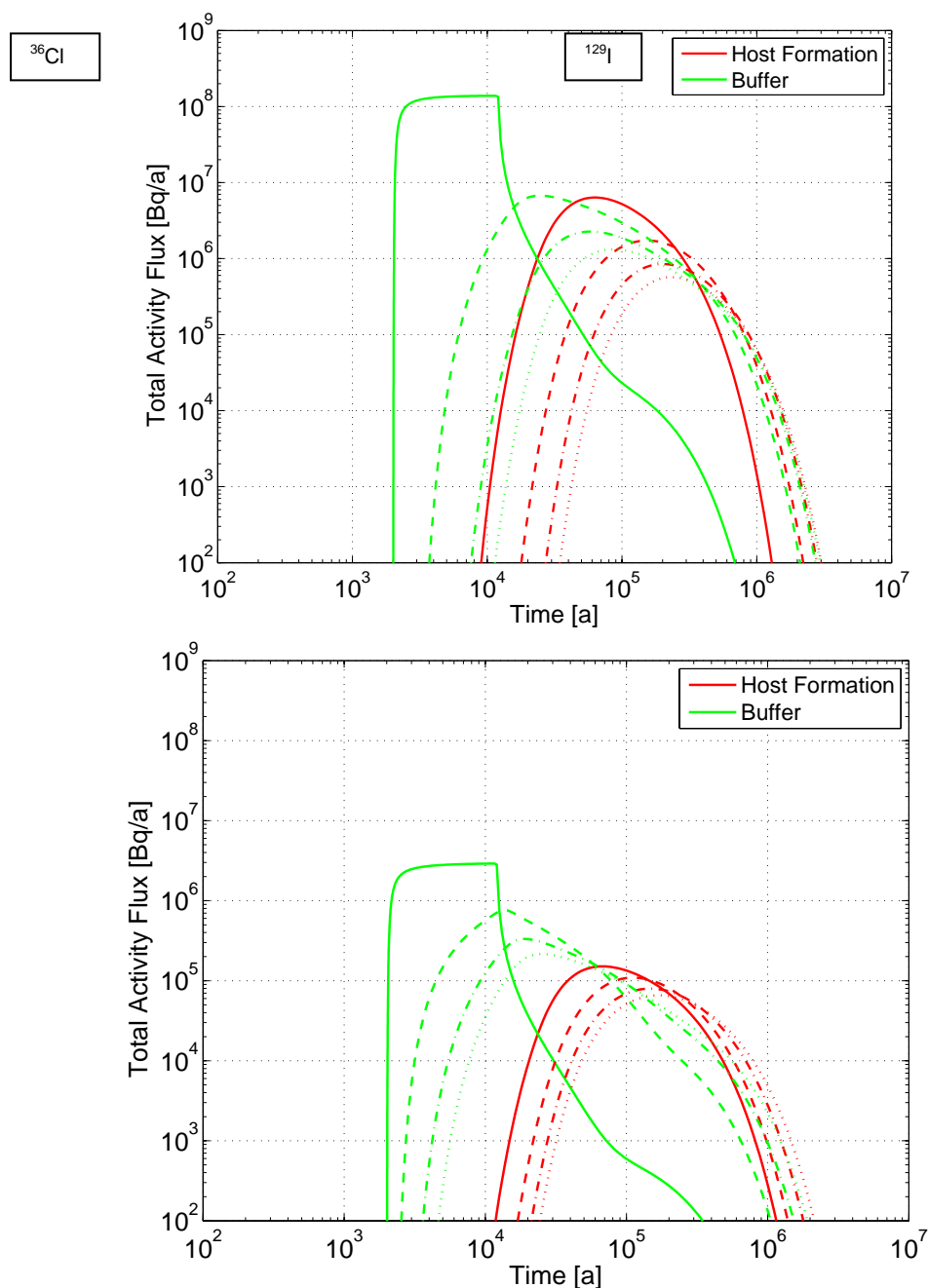


Figure 2: Evolution of the dose via a water well pathway for ^{14}C , ^{36}Cl (left) and ^{129}I (right) for C1 (—), C2 (— —), C3 (· · ·) and C4 (· · ·). As a reference, the dose limit currently considered in Belgium is 0.3 mSv/a as recommended by the ICRP [ICRP, 2000]

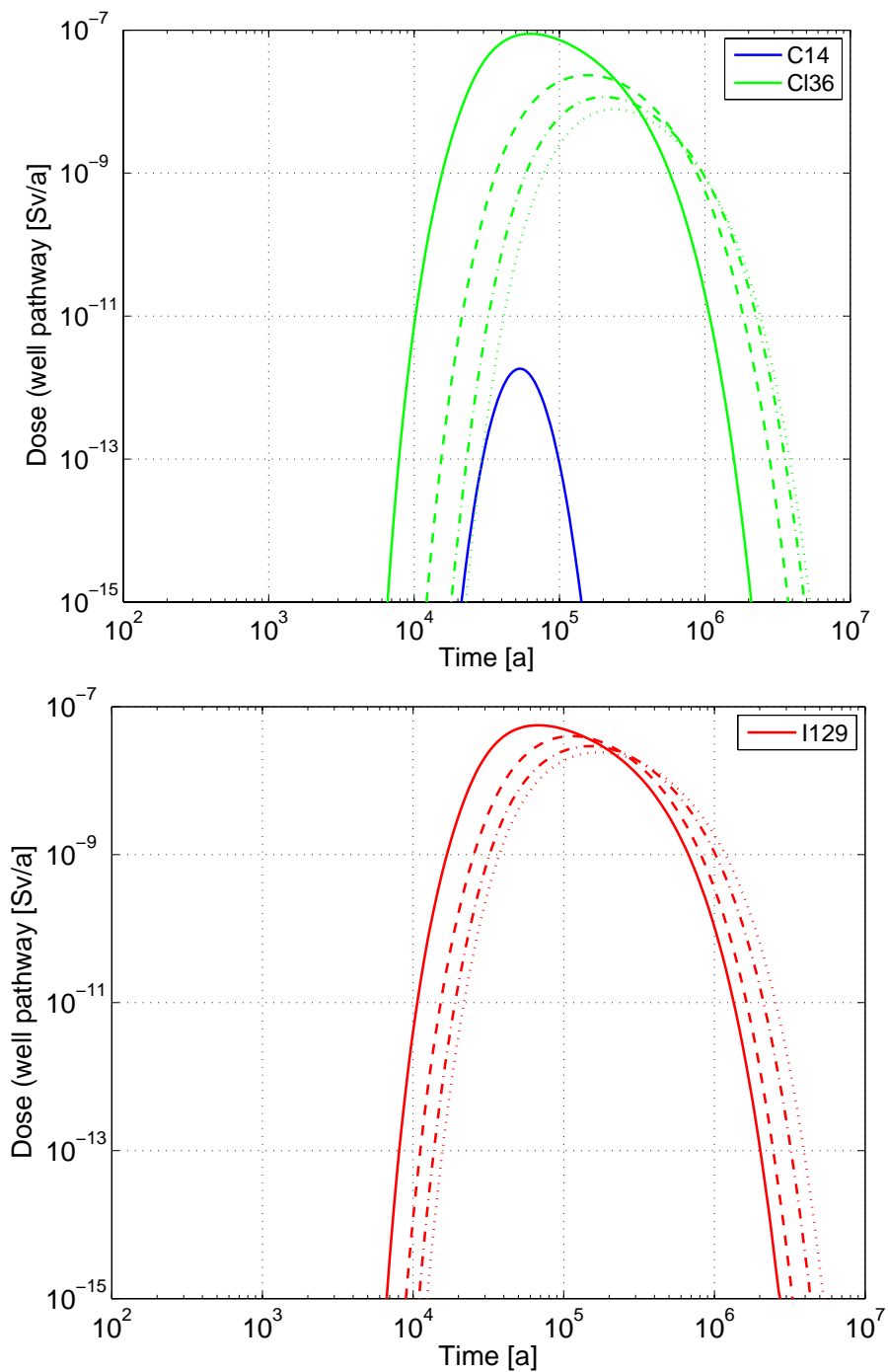


Table 2: Performance indicators for safety functions C, R1 and R3

PI	¹⁴ C					³⁶ Cl					¹²⁹ I				
	C	R1	R3b	R3c	IRS	C	R1	R3b	R3c	IRS	C	R1	R3b	R3c	IRS
C1	0.78	0.57	0.81	6.9 ×10 ⁻⁶	2.5 ×10 ⁻⁶	1.0	0.99	1.00	0.69	0.68	1.0	1.0	1.0	0.99	0.99
C2	0.78	0.58	3.6 ×10 ⁻²¹	6.9 ×10 ⁻⁶	1.1 ×10 ⁻²⁶	1.0	0.99	0.60	0.69	0.41	1.0	1.0	1.0	0.99	0.99
C3	0.78	0.58	1.1 ×10 ⁻³⁶	7.0 ×10 ⁻⁶	3.5 ×10 ⁻⁴²	1.0	0.99	0.38	0.69	0.26	1.0	1.0	0.99	0.99	0.99
C4	0.78	0.58	2.8 ×10 ⁻⁴⁶	7.1 ×10 ⁻⁶	9.2 ×10 ⁻⁵²	1.0	0.99	0.28	0.69	0.19	1.0	1.0	0.99	0.99	0.98

As can be seen on Figure, adding concrete material to the simulations has a considerable impact on the flux released from the buffer and host formation. The ¹⁴C fluxes are not shown. Due to its relatively short half-life and strong retardation on concrete, the ¹⁴C fluxes out of the different compartments are decreased to negligible quantities (< 10⁻²⁰ Bq/a) when incorporating a cement buffer. The peak of the fluxes out of the host formation of ³⁶Cl and ¹²⁹I are decreased with resp. 91% and 57% when comparing C4 to C1. Also these peaks are delayed with resp. 1.8×10⁵ and 1.2×10⁵ years, but the curves are smeared out over larger timeranges. The same conclusions can be drawn for the doses shown in Figure 2.

The influence of the concrete materials on the time integrated fluxes can be extracted from the PI's (Table 2). PI_{R1} shows a slight increase for C1 to C4, although this is only noticeable for ¹⁴C. Due to the stronger sorption in the concrete region, high liquid concentration gradients exist near the waste package boundary. This increases the diffusive flux out, leaving less time for decay inside the waste package. Hence the increased time integrated activity flux from the waste package.

PI_{R3b}, on the other hand, show a decreasing trend with increasing concrete region. This decrease, is small for ¹²⁹I, due to the long half-life and smaller retardation on concrete compared to ¹⁴C and ³⁶Cl. PI_{R3c} stays relatively constant for the three anions.

Conclusions

Performance assessment calculations have been performed to investigate if the sorption of ¹⁴C, ³⁶Cl and ¹²⁹I on the cementitious materials occurring in the near field of the repository on the diffusion would offer an extra safety reserve to deep disposal of vitrified HLW. Four cases have been studied: a reference case with no cementitious material and three cases in which the considered concrete region was subsequently extended to the buffer, backfill and gallery liner. The results show a beneficial impact on peak dose and residence time of the three radionuclides. The effect on total released fractions is very high for ¹⁴C, moderate for ³⁶Cl and small for ¹²⁹I.

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4 - EFFECT OF A CEMENT BUFFER ON SPENT FUEL DISSOLUTION

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Introduction

Since a few years, the Belgian agency for radioactive waste (ONDRAF/NIRAS) has selected the *supercontainer design* with an Ordinary Portland Cement (OPC) buffer as the reference design for geological disposal of High-Level Waste (HLW) and Spent Fuel (SF) in the Boom Clay formation. Compared to the previous bentonite based reference design [NEA 2003], the supercontainer will provide a near field environment that can be engineered to a specific design and that will offer a highly alkaline chemical environment allowing the passivation of the surface of the overpack and the inhibition of its corrosion. The *supercontainer* will contribute to the containment of radionuclides within the waste matrix, but will also have an effect on the retardation of radionuclide release from the waste and will retard the migration of the released radionuclides.

In the *supercontainer design*, the canisters of HLW or SF will be enclosed by a 30 mm thick carbon steel overpack and a 700 mm thick concrete buffer. The overpack will prevent contact with the (cementitious) pore water during the thermal phase. On the other hand, once the overpack will be locally perforated, the high pH of the incoming water may have an impact on the lifetime of the waste. Most published data and national programs are related to clayey backfill materials. Few studies are reported in alkaline media [Loida 2006, Cui 2003, Ollila 2008]. Hence, to evaluate the behavior of spent fuel (UO_2 dissolution rate and UO_2 solubility) in such an environment, a set of experiments was conducted. The objective was to estimate the spent fuel dissolution rate in *supercontainer* conditions for use in preliminary performance assessment calculations.

Experimental

Static and dynamic dissolution tests were performed. In this abstract, we will focus entirely on the static tests. These tests were performed at 25-30°C under argon atmosphere, with depleted or alpha-doped UO_2 in contact with three kinds of alkaline solutions, representative of the ageing steps of cement, and with and without metallic iron. The uranium release in solution was used to estimate the matrix dissolution rate of the UO_2 . The concentration of dissolved uranium gives the solubility of the controlling phase, which is important for the system understanding.

In most experiments, the spent fuel was simulated by depleted UO_2 (powder or pellets) representative of "old fuel". To study the influence of α -activity, some experiments were performed with α -doped UO_2 ($2.53 \times 10^8 \text{ Bq.g}^{-1} \text{UO}_2$), simulating a young PWR fuel with a burnup of 45-55 GWd/tHM, 150 years after discharge. In the doped material, ^{238}Pu was used to generate the high alpha dose and ^{233}U was used as corrosion indicator. The fuels were annealed during 6 hours at 1000°C before the beginning of the experiments. Similar tests with spent fuel were performed at INE for pH 12.5 [Loida - 2009], to see to which extent the doped UO_2 is representative of real fuel.

The static tests were performed at three fuel surface area (SA) to leachant volume (V) ratios: low SA/V (6 and 17 m⁻¹) and high SA/V (257 m⁻¹). The tests with the high SA/V were mainly dedicated to the determination of potential secondary uranium phases, but were also used to determine the dissolution rate of UO₂ at large reaction progress. The low SA/V tests were devoted mainly to the determination of the UO₂ dissolution rate.

The dissolution tests were performed with synthetic cementitious water at pH 13.5, pH 12.5 and pH 11.7. The composition of these waters (Table 1) results from the geochemical calculations of the cement pore water composition after interaction of the Boom Clay water and OPC reference concrete for a period up to around 100000 of years [Wang 2006].

For the experiments with the depleted UO₂, the total (unfiltered) uranium concentration in solution and the ultrafiltered uranium concentration (30 000 MWCO) were determined by ICP-MS every month during 18 months. After 491 days, the leachant was renewed (almost) entirely, and the sampling was continued. For the experiments with alpha doped UO₂, the dissolution of the matrix was measured by the release of the ²³³U in solution (ultrafiltered and unfiltered), using alpha spectrometry.

Other isotopes were measured as well to check the internal consistency and reliability of the measurements.

Table 1: Composition of the synthetic cementitious waters (in mol.L⁻¹)

	Na	K	Ca	Al	Si	SO ₄ ²⁻	CO ₃ ²⁻
pH 13.5	0.14	0.37	7.10 ⁻⁴ (2.5.10 ⁻⁵)	6.10 ⁻⁵	3.10 ⁻⁴	2.10 ⁻³	3.10 ⁻⁴
pH 12.5	0.016	2.10 ⁻⁴	0.015	5.10 ⁻⁶	3.10 ⁻⁶	7.10 ⁻⁶	8.10 ⁻⁶
pH 11.7	3.5.10 ⁻³		8.10 ⁻⁴			3.9.10 ⁻⁵	2.10 ⁻⁵

Results and discussion

Uranium in solution

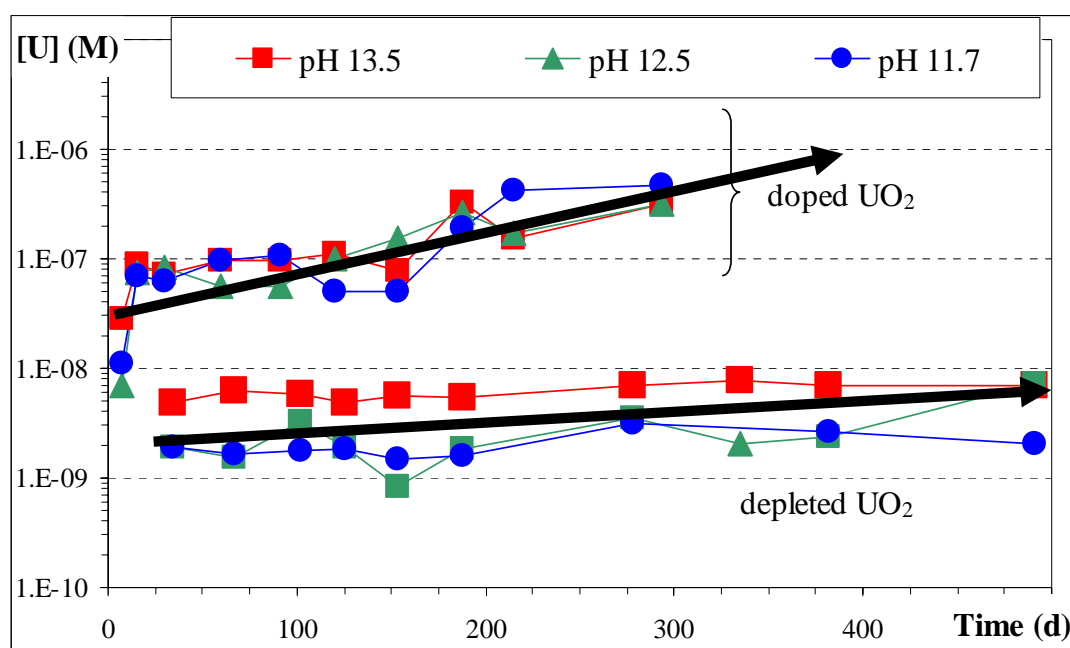
The presence of colloids is more important at high SA/V (257 m⁻¹) than at low SA/V ratio. At low SA/V (6 and 17 m⁻¹) colloids are present in negligible amount, with similar filtered and unfiltered uranium concentrations in the range 5×10⁻⁹ to 2×10⁻⁸ mol.L⁻¹. In the experiments at high SA/V, the total uranium concentrations (10⁻⁷ to 2×10⁻⁵ mol.L⁻¹) are much higher than the ultrafiltered concentrations (10⁻⁹ to 10⁻⁵ mol.L⁻¹), implying that most U is colloidal. The colloidal concentrations increased further after the solution renewal. The ultrafiltered uranium concentrations tend to increase with pH, but this is due to preoxidized U(VI), which seems to be more soluble at higher pH. The dissolved U(IV) concentration is probably not affected by the high pH. Because of the higher solubility of U(VI) phases, it is likely that the colloids consist mostly of U(IV). U speciation analyses are ongoing to confirm the presence of U(VI) and U(IV). These results suggest that the effect of the high pH on the ultrafiltered, dissolved U concentrations is not important enough to have an impact on the safety of the disposal system. Based on literature data, the U(VI) concentrations seem undersaturated with regards to Ca-uranate (CaU₂O₇·3H₂O), even when there should be enough U(VI) in the system for saturation [Meca 2008].

The presence of alpha radiation increased the total release of uranium in solution, but had less effect on the ultrafiltered concentrations. Hence the colloidal fraction increased. Compared with depleted UO₂, the total, *unfiltered* uranium concentrations increased by a factor 100 in the experiment with the low SA/V (6 m⁻¹, Fig. 1), and by a factor of at least 10 in the experiment with the high SA/V (257 m⁻¹). Although radiolysis tends to increase also the *dissolved, ultrafiltered* U

concentrations, Ca-uranate remains undersaturated at pH 13.5, but it may control U concentrations at lower pH (12.5 or 11.7).

The presence of metallic iron did not much affect the uranium concentration in solution at high pH. Both for the unfiltered and the ultrafiltered samples, the uranium concentration in solutions were about the same with or without iron. The iron appears to be a less effective chemical reductor at high pH than at neutral pH.

Figure 1: Evolution of total dissolved U concentrations for the tests at SA/V of 6 m^{-1} . The concentrations are higher, and increase faster for the doped UO_2 than for the depleted UO_2 , but no effect of the presence of redox control. The long term increase is used to estimate the long term matrix dissolution rate by linear regression



Dissolution rates

The dissolution rate was calculated, based on the total uranium concentration in solution. This gives a high initial rate, which is biased by preoxidation. The long term rate is much lower, and was estimated by means of a linear regression of the long term (total) uranium concentrations (Figure 1).

The long term dissolution rates are higher at pH 13.5 than at lower pH. To be conservative, but also because pH 13.5 may be realistic under in-situ conditions, we base the preliminary estimations of the matrix dissolution rate on the rates measured at this high pH. The rates at lower pH were not much lower. For the performance assessment calculations, a source and an expert range are proposed (Table 2). The source range is the range in which we expect the actual rate to lie with high probability. The expert range is a narrower subset of this range based on expert judgment.

The proposed source range for depleted UO_2 is similar to the range of rates for neutral pH in anoxic or mildly reducing conditions. The alpha effect on the dissolution rate is, however, much stronger in cementitious water at high pH than in reducing clay water at neutral pH [Salah 2006]. The dissolution rate of α -doped UO_2 is much higher than for depleted UO_2 (Figure 1), but roughly

in the same range as the dissolution rate measured for real spent fuel in similar conditions [Loida 2009]. So α -doped UO_2 can in a first approximation be used to estimate the dissolution rate of real spent fuel at high pH, although some differences occur. Secondary phases were observed only for the real spent fuel, whereas colloid formation was observed only for the depleted and alpha doped UO_2 .

Table 2: Source range and expert range for the depleted and doped UO_2 in *supercontainer* conditions

Dissolution rate ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)	Depleted UO_2 (very low alpha activity)	Doped UO_2 (High alpha activity)
Source range minimum	0.2	37
Source range maximum	14	>1900
Expert range minimum	1	37
Expert range maximum	2.6	>1900

Conclusion

For depleted UO_2 , simulating old spent fuel, the dissolution rate at high pH seems to be similar to the rate at more neutral pH. Alpha radiation seems, however, to accelerate the dissolution rate more at high pH than at neutral pH, even in reducing conditions (in the presence of metallic iron). This may cause a relatively fast oxidative fuel dissolution in the first stage, when the alpha activity is still high. It may take more time to reach the threshold alpha activity, under which oxidation is completely compensated by reductive processes. H_2 formed by anaerobic overpack corrosion may help to suppress the dissolution rate in this stage. The massive colloidal formation observed in certain test conditions with UO_2 may also indicate an acceleration of the chemical (non-oxidative) fuel dissolution at high pH. On the other hand, the dissolution rates obtained with real spent fuel do not suggest a negative impact of pH 12.5 [Loida 2009]. The uncertainties of our present dissolution rates are, however, still large due to the small number of tests and data. The dissolution rates are considered as preliminary rates and the experiments are still ongoing. The direct effect of concrete on the fuel dissolution was not yet studied.

Work performed as part of the programme on geological disposal of high-level/long-lived radioactive waste that is carried out by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and Fissile Materials."

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5 - DETERMINATION OF DISSOLUTION RATES OF VITRIFIED HIGH- AND MEDIUM LEVEL WASTE IN A CEMENTITIOUS ENVIRONMENT

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Introduction

Since a few years, the Belgian agency for radioactive waste (ONDRAF/NIRAS) has selected the *supercontainer design* with Ordinary Portland Cement (OPC) buffer as the reference design for geological disposal of vitrified High-Level Waste (HLW) and Spent Fuel (SF) in the Boom Clay formation. Compared to the previous bentonite based reference design described in detail in the main SAFIR 2 report (NEA 2003), the *supercontainer* will provide a near field environment that can be engineered to a specific design and that will offer a highly alkaline chemical environment allowing the passivation of the surface of the overpack and the inhibition of its corrosion. The *supercontainer* will contribute to the containment of radionuclides within the waste matrix, but will also have an effect on the retardation of radionuclide release from the waste and will retard the migration of the released radionuclides.

In the *supercontainer design*, the canisters of HLW or SF will be enclosed by a 30 mm thick carbon steel overpack and a 700 mm thick concrete buffer. The overpack will prevent contact with (alkaline) pore water during the thermal phase. On the other hand, once the overpack will be perforated, the high pH of the incoming water may have an impact on the lifetime of the vitrified waste. Most published data and national programs are related to clayey backfill materials. Few studies are reported for alkaline media (Gin 2001). Hence, to evaluate the durability of the glass matrix in such an environment, a set of experiments was conducted. This should result in the determination of a range of glass dissolution rates that can be used in the performance assessment calculations.

Experimental

Most experiments were performed at 30°C and at pH 13.5, corresponding to the conditions at the glass surface expected after the thermal stage. In these experiments, simulated, inactive SON68 (R7T7) glass and SM539 HE 540-12 (PAMELA) glass were used. The second glass contains a higher Al₂O₃ weight % (20 %, vs. 4.9% for SON68).

Dynamic experiments

Dynamic tests were conducted at 30°C in contact with a 0.1M and 1M KOH solution, giving a pH around 13 or 14. In these experiments, the conditions were less realistic but they allowed to determine the maximum rate of glass dissolution ('forward rate' of dissolution). Indeed, all leached glass components are continuously removed, so the affinity for further glass dissolution remains high, and the formation of protective layers is unlikely.

Some dynamic tests were also performed in a synthetic cementitious water at pH 13.5 (denominated YCWCa). The target composition of the YCWCa solution was obtained by modelling (Wang 2006). It simulates the pore water composition in the cement buffer in the first period after the thermal stage. The composition of the YCWCa used for the experiments is given in table 1. From these experiments, the initial rates of dissolution were determined (similar to the forward rate for the tests in KOH solutions).

In the dynamic experiments, the glass powder was placed in a PolyTetraFluoroEthylene cell with a small volume (360 mm³) to reach rapidly the steady-state silicon concentration. Samples were taken at intervals of 40 minutes during 9 hours and diluted with ultrapure water. The monomeric silicon concentration was measured by UV/Visible spectrophotometry according to the blue β -silicomolybdenum method.

Table 1: **Composition of the synthetic cementitious water at pH 13.5 (YCWCa)**

Element	Al	Ca	K	Mg	Na	Si	SO ₄ ²⁻
Concentration in mol.L ⁻¹	<7x10 ⁻⁶	3.9x10 ⁻⁴	3.3x10 ⁻¹	<4x10 ⁻⁷	1.4x10 ⁻¹	1.9x10 ⁻⁴	9x10 ⁻⁴

Static experiments

The more realistic static tests were conducted at 30°C in a mixture of cement powder and YCWCa solution at pH 13.5. PolyPropylene bottles containing 7.5 gram of glass (125-250 μ m), 4 glass coupons (placed in the solution on a magnetic floating stirrer), 7.5 gram of Portland cement powder (400-500 μ m) and a cement cube (1.1 x 1.1 x 1.1 cm) were placed in an incubator at 30°C in a glove box under Ar atmosphere with < 1 vppm O₂. Samples of the supernatant solution were taken regularly and analyzed for Si, B, Na, Mg, Ca, Li, K, Al, Mo and Fe by ICP-AES or ICP-MS. The sulphate and chloride concentrations were determined by Ion Chromatography. Each time a sample was taken, a glass coupon was removed simultaneously for mass loss determination. At the end of the experiments, the cement powder and the glass powder were separated from the solution by centrifugation and dried at room temperature. "Blank" experiments containing only cement powder and YCWCa were also performed. To better understand the results of the static tests with cement, similar static experiments without cement were carried out.

Results and discussion

Dynamic experiments

In the dynamic tests with the SON68 glass in the KOH solutions, the forward rate of dissolution increased slightly between pH 13 and 14, from 0.17 to 0.35 g.m⁻².d⁻¹. However, for the SM539 glass, the forward rate was 4.5 times higher at pH 14 than at pH 13. It increased from 0.35 to 1.6 g.m⁻².d⁻¹. This is probably due to the easier hydrolysis of the Al-O bonds at the highest pH. In the dynamic experiments with the synthetic cementitious solution at pH 13.5 (YCWCa), the initial dissolution rates were around 0.03 g.m⁻².d⁻¹ for the SON68 glass and 0.36 g.m⁻².d⁻¹ for the SM539 glass. The value for the SM539 glass at pH 13 is similar to the value obtained in the KOH solution. However, in the case of the SON68 glass, this value is around 5.6 times lower. This suggests that, for SON68, the presence of Ca in the cement water, suppresses the dissolution rate.

Static experiments

In presence of cement

The experiments at 30°C in presence of cement were performed for durations up to 556 days. The high pH did not change much in spite of the significant glass dissolution, because it was buffered by the cement. It showed a small decrease (up to 0.2 units for SON68, up to 0.4 units for SM539), but came back to the initial value near the end of the test.

For the SM539 glass, the dissolution rate calculated from the mass loss of the coupons was quite constant. A regression rate of $0.23 \text{ g.m}^{-2}.\text{d}^{-1}$ was determined. This value was close to the initial rate of $0.36 \text{ g.m}^{-2}.\text{d}^{-1}$ measured in the YCWCa solution in the dynamic set-up. It was slightly lower, probably because the pH was slightly lower than 13.5. For the SON68 glass, rates between 0.025 and $0.082 \text{ g.m}^{-2}.\text{d}^{-1}$ were determined, this is also close to the initial rate in the dynamic tests ($0.03 \text{ g.m}^{-2}.\text{d}^{-1}$).

The Ca concentrations were stable in the blank solutions (without glass) but decreased upon contact with the glass. This decrease was stronger for the SM539 glass. This was probably due to the formation of secondary phases. The Si and Al concentrations were very low in the blank tests and increased in presence of glass, this increase being higher for the SM539 glass. These concentrations were controlled by the cement/glass interaction.

SM539 and SON68 glass coupons were observed by Optical Microscopy. Needle-shaped and spherical particles were visible on the SM539 glass surface. However, no secondary phases were observed on the SON68 glass surface. The glass/cement powders were also analyzed by XRD. The SON68/cement sample showed the same peaks as the Ordinary Portland Cement used as reference. It contained Portlandite $\text{Ca}(\text{OH})_2$, calcite $\text{Ca}(\text{CO}_3)$, Calcium Aluminum Silicate Hydroxide (CASH), calcium silicate Ca_3SiO_5 (CS) and Calcium Aluminum Iron Oxide (CAFO). There was no evidence for new crystalline phases. The XRD pattern for the SM539/cement sample showed two changes relative to the blank cement. The CS peaks at 2.74 \AA and 2.77 \AA was replaced by a CASH peak suggesting that the CS phase was transformed into a CASH phase due to the Al leaching from the SM539 glass. A peak at 14 \AA characteristic of the tobermorite also appeared.

Without cement

In the static experiments at 30°C without cement, the dissolution rate decreased with time. The initial and final dissolution rates calculated from the normalized loss of boron were similar for the SON68 glass and the SM539 glass. They were around $0.0064 \text{ g.m}^{-2}.\text{d}^{-1}$ and $0.0049 \text{ g.m}^{-2}.\text{d}^{-1}$. These relatively low dissolution rates explain why the pH was constant. A steady-state Si concentration was observed for the SM539 glass suggesting saturation and control by a secondary phase, whereas the Si concentration continued to increase for the SON68 glass suggesting a kinetic control.

The Ca concentration showed a strong initial decrease suggesting sorption or secondary phase formation on the glass surface. After an initial increase of the Al concentrations, constant concentrations were reached, which decreased again for the SM539 glass. This suggests Al saturation or oversaturation in these conditions. The Al is assumed to be in equilibrium with the gel or secondary phases in the alteration layer. Regardless of the glass, the Na concentrations increased.

Glass coupons and glass powders were observed by Scanning Electron Microscopy. After 313 days, an alteration layer depleted in Na, highly enriched in Si, Ca and slightly enriched in Al, Fe and Ti was observed on the SM539 glass surface. There were no clear crystalline phases, but spherical particles were observed, which are probably crystalline phases in formation.

Compared to the alteration layer, these particles contain less K and Ca and more Al and Si. For the SON68 glass, the surface is enriched in Al, Si, Ca, Fe, Zn and Nd.

Influence of the cement on the glass dissolution rate

In the experiments without cement, the Si and Al concentrations were high and the dissolution rates were low. In presence of cement, the Si and Al concentrations were very low and the rates were high. Apparently, the cement is a sink for Si and Al due to sorption and/or precipitation. It thus keeps the dissolution rate high for both glasses. Without cement, the Ca concentration (below the detection limit) and the dissolution rates were low. In the experiments with cement, the Ca concentration and the dissolution rate were high. Apparently, the favourable effect of the high Ca concentration which may stabilize the gel was not sufficient to counter the negative effect of Al and Si sorption on the cement.

Conclusion

Glass leaching tests were performed at 30°C in cementitious water at pH 13.5 with or without cement. These experiments have allowed to propose a pessimistic range of dissolution rates of 0.025-0.082 g.m⁻².d⁻¹ for the SON68 glass and 0.2-0.3 g.m⁻².d⁻¹ for the SM539 glass. These rates can be used as preliminary values in performance assessment calculations. It was shown that the presence of cement maintains the dissolution rate at the high initial rate, because it acts as a sink for Si and Al. The mechanism responsible for the fixation of Si and Al on the cement seems to depend on the glass composition. For SM539, there is ample evidence for secondary phase formation. For SON68, there is no such evidence, and the fixation mechanisms is not clear (amorphous phases, sorption ...). Because the pH, and Si, Ca and Al concentrations were stable in the tests with cement, in spite of the continuous glass dissolution, the dissolution rate may remain constant for a long time. So there is no clear evidence for the existence of a lower long term rate, although this can be expected at sufficient reaction progress. The proposed dissolution rates are considerably higher than the long term rate observed in neutral pH conditions, which are expected to be lower than 10⁻⁴ g.m⁻².d⁻¹.

In the future, the dissolution processes will be studied more in detail, using a.o. SEM-EDS, SIMS and more XRD analyses. The main objective is to verify if a lower long term rate can be expected in more realistic conditions. Therefore, tests with large percolation cells and monolithic cement plugs will be performed. Moreover, the contribution of the internal glass surface due to the cracks in the glass block will be studied. In these cracks, the pH, and hence the dissolution rate, is expected to be much lower than on the outside of the glass block.

Acknowledgements

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6 - ACCELERATED HYDRATION OF HIGH SILICA CEMENTS

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Introduction

Current Japanese designs for high level radioactive waste (HLW) repositories anticipate the use of both bentonite and cement based materials. Bentonite is to be used as a buffer and backfill material and provides a physical barrier to impede both the migration of radionuclides in the event of a HLW canister failure and the ingress of invasive groundwaters. Cementitious materials are to be used in the construction of the repository, but their role in containing the HLW is only secondary.

Fractures in the host rock will require grouting to improve mechanical stability and retard the ingress of groundwater during the construction phase of the HLW repository. Grouting is problematic because of the small aperture of some of the fractures, which can be of the order of a few microns or less. Using hydrated Ordinary Portland Cement (OPC) as a grouting material is undesirable because the associated high pH buffer ($12.5 \leq \text{pH} < 13.7$) will have an undisputed detrimental effect on the performance of the bentonite buffer and backfill and of the host rock by changing its porosity. Instead, hydrated low pH cement (LopHC) grouting materials are being developed to provide a $\text{pH} \leq 11$ (Bodén and Sievänen, 2005) to reduce these detrimental effects. LopHC grouting materials use mixtures of superfine OPC (SOPC) clinker and silica fume (SF), and are referred to here as high silica cements (HSC). Presently, the mixture ratios being investigated for grouting materials are 30 – 50 wt % OPC clinker and 70 – 50 wt % SF with the addition of up to 3 wt % superplasticizer (SP) and high water/cement (w/c) ratios in the region of 1.0 – 2.0.

It is well known that the hydration of OPC with the addition of SF lowers the pH of the porewater by the reaction with OH^- ions as SF dissolves, the consumption of portlandite (CH) to form more C-S-H gel and by lowering the Ca/Si ratio in the C-S-H gel (Massazza, 1998). However, there are very few comprehensive studies in the literature concerned with the mineralogy and solution chemistry of such high additions of SF to OPC, to say nothing of SOPC. Recent experimental studies (Codina *et al.*, 2008; Garcia *et al.*, 2007; Mihara *et al.*, 1997) have investigated different OPC/SF mixture proportions, w/c ratios, curing times and temperatures, making direct comparisons of the reported mineralogy and solution chemistry impractical.

The focus of the present study was to therefore identify the development of the unhydrated and hydrated mineral assemblage and the solution chemistry during the hydration of HSC. Since hydration experiments of cementitious materials are notably slow, a ball mill was used to accelerate hydration. This was done for two reasons. Firstly, to develop a method to rapidly hydrate cement based materials without the need for higher temperatures, which can alter the mineral assemblage, and secondly, to ensure that the end point of hydration was reached in a reasonable time frame and so to realize the final mineralogy and solution chemistry of hydrated HSC.

Materials and Methods

The starting materials for the accelerated HSC experiments were a low alkali SOPC ($\text{K}_2\text{O} + \text{Na}_2\text{O} = 0.6 \text{ wt } \%$, $1 - 15 \mu\text{m}$, $1071 \text{ m}^2 \text{ kg}^{-1}$), Elkem SF Microsilica940U (modal particle size = $0.15 \mu\text{m}$,

18380 m² kg⁻¹), Mighty 150R SP (naphthalene sulphonate type), and deionized water (18 MΩ cm). The composition of the SOPC clinker and SF are shown with a calculated normative SOPC clinker mineralogy in Table 1. SOPC was used as a reference material since its mineralogy and solution chemistry is relatively well known (see (Lothenbach and Winnefeld, 2006)) and three mixture proportions of HSC were investigated using SOPC/SF ratios of 50/50, 40/60 and 30/70, detailed in Table 1. Slurries of SOPC and HSC were made using 600 g of cement, containing 3 wt % SP, and 2.4 L of water, giving a w/c = 4. Although this w/c is unrealistically high and arguably in the realm of leaching as opposed to hydration, it facilitated the recovery of samples for subsequent analyses.

Table 2: **1. Oxide composition of SOPC (wt %) and SF (wt %). 2. Normative SOPC clinker mineralogy, \underline{c} = CO₂, \underline{s} = SO₃. 3. Experimental mixture proportions of HSC. CS components are C3S, C2S and SF. SOPC was used as a reference material. sp/c = superplasticizer/cement ratio. w/c = water/cement ratio.**

1. SOPC and SF composition			2. Normative SOPC clinker mineralogy			
Oxide	SOPC (wt %)	SF (wt %)	Mineral	(wt %)	Mineral	(wt %)
SiO ₂	20.3	96.1	C3S	48.7	C \underline{c}	4.6
Al ₂ O ₃	5.4	0.5	C2S	22.6	C \underline{s} H _x	3.4
Fe ₂ O ₃	2.7	0.2	C3A	9.9	M	1.3
CaO	63.4	0.1	C4AF	8.4	K+N(\underline{s})	1.0
MgO	1.2	0.4				
K ₂ O	0.4	0.9				
Na ₂ O	0.2	0.2				
SO ₃	2.4	0.1				
CO ₂	2.0	-				
Total	98.0	98.5				

3. Experimental mixture proportions					
Cement	Binding ratio (wt %)		Ca/Si in CS components	sp/c (g/g)	w/c (ml/g)
	SOPC	SF			
SOPC	100	0	2.6	18/600	2400/600
HSC55	50	50	0.5	18/600	2400/600
HSC46	40	60	0.3	18/600	2400/600
HSC37	30	70	0.2	18/600	2400/600

The slurry was placed in a 5 L ball mill and the head space replaced with argon to minimize carbonation during the hydration process. The ball mill was run continuously throughout the experiment duration and slurry samples were taken after 1, 3, 5, 7, and 10 days and 2, 3, 4, 5, 6, 7, and 8 weeks. The subsequent handling and treatment of all slurry samples was undertaken in sealed flasks or in an argon atmosphere prior to analyses. Slurry samples were centrifuged and the liquid phase filtered through 0.2 μm filters into separate sealable flasks. The solid phase was rinsed with acetone to remove excess water prior to analysis by powder XRD and FE-SEM. The pH of the liquid phase was measured under argon using a combined pH electrode calibrated against pH standards of 7, 9, 12.6, and 13, before being acidified with 0.2 % nitric acid from 2-fold to 200-fold dilutions ready for determinations of K, Na, Ca, Si, Al, S, Mg, and Fe concentrations in solution by ICP-AES analysis.

Results and Discussion

The solid phase evolution of the primary SOPC clinker phases and hydrated mineral assemblage for SOPC and HSC formulations as determined by powder XRD is shown in Table 2. The phases identified for SOPC were consistent with those identified by Lothenbach and Winnefeld (2006) for OPC, except that the SOPC clinker phases were consumed within 7 days using a ball mill to accelerate hydration as opposed to still being present after 1 year of passive hydration. Ball milling therefore seems a practical method to accelerate the hydration of cement based materials at room temperature.

Increasing the quantity of SF in the HSC resulted in the primary SOPC clinker phases being consumed more rapidly, after 1 day for HSC37 with the exception of C2S, which persisted for 5 days. The most noticeable difference in the solid phases was in the hydrated mineral assemblage where for HSC55, CH was consumed after 7 days and the AFm phase(s) (including C₄AH₁₃ and monocarbonate) were lost after 2 weeks leaving just C-S-H gel and ettringite (AFt) as the final hydration products. In HSC46 and HSC37, CH and the AFm phase(s) were consumed more rapidly, with CH being lost before the complete hydration of C2S. AFt also disappeared, leaving just C-S-H gel as the final hydration product of HSC46 and HSC37.

Table 3: Solid phase evolution as determined by XRD. O = Present, X = Not present. d = days, w = weeks.

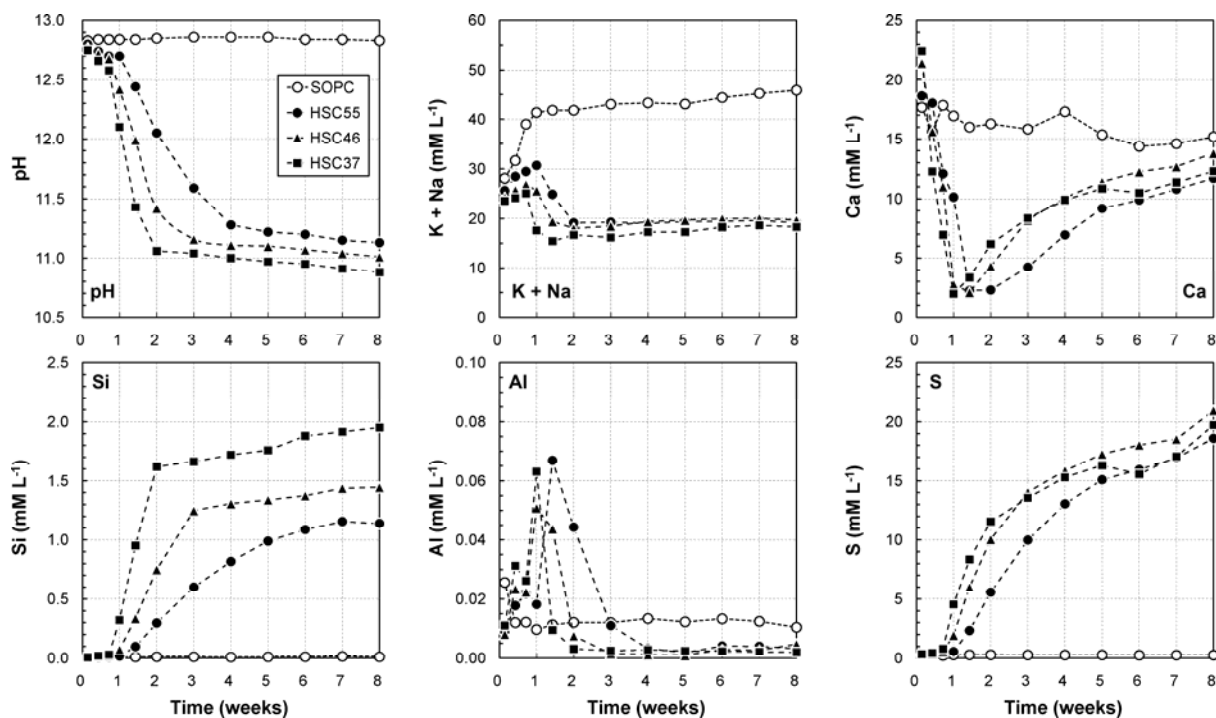
Time	SOPC							HSC55							HSC46							HSC37										
	C3S	C2S	C3A	C4AF	CH	C-S-H	AFt	AFm	C3S	C2S	C3A	C4AF	CH	C-S-H	AFt	AFm	C3S	C2S	C3A	C4AF	CH	C-S-H	AFt	AFm	C3S	C2S	C3A	C4AF	CH	C-S-H	AFt	AFm
1 d	O	O	O	O	O	O	O	X	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
3 d	O	O	O	O	O	O	O	O	X	O	X	O	O	O	O	O	X	O	X	O	O	O	O	O	X	O	X	O	O	O	O	O
5 d	X	O	X	O	O	O	O	O	X	O	X	X	O	O	O	X	O	X	X	O	O	O	O	X	O	X	X	O	O	O	O	
7 d	X	O	X	X	O	O	O	O	X	O	X	X	O	O	O	X	O	X	X	X	O	O	O	X	O	X	X	X	O	O	O	
10 d	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	O	
2 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
3 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
4 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
5 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
6 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
7 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	
8 w	X	X	X	X	O	O	O	O	X	X	X	X	X	O	O	X	X	X	X	X	O	O	X	X	X	X	X	X	X	O	X	

Mass balance calculations result in C-S-H gel forming ≥ 80 wt % of hydrated HSC. C-S-H gels of decreasing Ca/Si ratio increasingly accommodate other cations (Hong and Glasser, 1999; Richardson and Groves, 1993) and so it may be possible that C-S-H gel really is the final hydration product of HSC46 and HSC37, albeit with a substantial component of foreign ions and the charge balance and solubility issues this implies. The viability of this mechanism is the subject of ongoing research. However, perhaps a simpler explanation is derived from the ball milling method used, which resulted in ≈ 70 % reduction in grain size as the hydration of SOPC and HSC progressed. This reduction in grain size was manifest in the XRD patterns by a 90 % drop in the intensity of the reflections, meaning that the minor minerals, such as AFt and/or the AFm phase(s), could still be present, but that they were lost in the noise of the XRD pattern.

The liquid phase evolution in terms of the pH and solution composition is shown in Figure 1. Concentrations of Mg and Fe were consistently below the detection limits of the instrument, 0.002 and 0.0009 mM L⁻¹, respectively, for all analyses. The data shown for SOPC are consistent with known data for OPC having undergone some degree of leaching, given that a w/c ratio = 4 was used in the experiments, whereby K + Na are high enough to still influence the pH and partially suppress the solubility of CH. While the pH and concentrations of elements remain fairly constant for SOPC, the same cannot be said for the HSC formulations. These behave like SOPC while CH is still present, but change markedly once it is lost. The pH falls from 12.7 to

approximately 11 in all cases, but more rapidly with an increasing SF content. Attaining the target $\text{pH} \leq 11$ appears to be only practicable using HSC37. The Ca concentration falls to a minimum after 1 week when the Si concentration begins to increase and was an expected consequence of the pozzolanic reaction of the SOPC with the SF. Comparing the concentrations of Ca and Si with solubility data from the C-S-H system ((Walker *et al.*, 2007) and references therein) and the final $\text{pH} = 11$, is consistent with a Ca/Si ratio = 0.6 – 0.9 in the C-S-H gel; also supported by thermodynamic calculations using the GEMS2 and PHREEQC codes that predict a Ca/Si ≈ 0.83 for these HSC formulations. This Ca/Si ratio range is higher than the Ca/Si ratio of the CS components in the raw materials (Table 1), implying that SF is still present in excess. The Ca/Si ratio of the C-S-H gel and amount of excess SF could be calculated if the Ca/Si ratio corresponding to SF saturation was known with more certainty, since it lies somewhere between a Ca/Si ratio = 0.4 – 0.7. The changes in Ca and Si concentrations appear to be a week ahead of the corresponding drop in pH, which may be a result of the K+Na concentrations in solution. After a week, the K+Na and Al concentrations decrease while the Ca and S concentrations increase. As already mentioned, C-S-H gel can increasingly accommodate other cations in their structure as their Ca/Si ratio is lowered and so the decrease in K+Na concentrations may be a result of this mechanism since there is no (known) alkali solid phase buffer. The decrease in Al concentration is a likely consequence of the precipitation of an Al bearing solid, perhaps as $\text{Al}(\text{OH})_{3(\text{am})}$, gibbsite or kaolinite. The increase in Ca and S concentrations however, is a likely result of the dissolution of AFt at $\text{pH} = 11$ and/or its conversion to gypsum, observed at $\text{pH} = 10.7$ by (Myneni *et al.*, 1998). HSC formulations may therefore release an initial high Ca and S plume in its subsequent leaching by groundwater.

Figure 1: Solution pH and composition evolution



Ongoing research is to support the above interpretations with geochemical modelling and an experimental program is underway to leach these hydrated SOPC and HSC formulations in pure water to again assess the development of their mineralogy and solution chemistries.

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7 - DEVELOPMENT OF LOW ALKALINE CEMENTITIOUS GROUTING MATERIALS FOR A DEEP GEOLOGICAL REPOSITORY

Kenichiro SUZUKI (Obayashi Corporation), Norihiko MIURA (Obayashi Corporation), Keishiro IRIYA (Obayashi Corporation) and Yasushi KOBAYASHI (JAEA), Japan

Introduction

In order to reduce uncertainties of long-term safety assessment for a High Level radioactive Waste (HLW) repository system, low alkaline cementitious grouting materials has been studied. The pH of the leachate from the grouting material is targeted to be below 11.0, since the degradation of the bentonite buffer and host rock is limited.

The current work focused on the effects of pozzolanic reactions to reduce pH and the development of low alkaline cementitious injection materials in which super-micro ordinary Portland cement (SOPC) was partially replaced by silica fume (SF), micro silica (MS) and fly ash (FA).

Grouting of rock masses deep underground requires a good knowledge of the basic properties of the grouting material such as strength, resistance to segregation, fluidity, and etc. Furthermore, it is vitally important to realize how the grouting material will respond to a high injection pressure into the fracture. Thus, in order to understand the penetrability of different low alkaline cement mixes and to observe their flow behavior through the fracture, injection tests were conducted by using a simulated model fracture of 2 m diameter made from parallel plates of acrylic acid resin and stainless steel.

Experimental results of the basic properties for selecting suitable materials and that of injecting into a simulated fracture to assess the grouting performance are described in this study.

Basic Property Tests and Suitable Mix Proportions

Selection for Mix Proportions

According to the target values in the flowchart shown in Figure 1, 10 different mixes of SOPC, SF, MS and FA were selected with the addition of a superplasticizer (SP). Basic property tests of all 10 of the cement mixtures were investigated experimentally as described by the following:

Strength

Several mix proportions were subjected to fall-cone tests and uniaxial compression tests. The results demonstrated that water binder (cement + pozzolan) ratios in weight = 1.0 - 2.0, and SOPC/SF/MS/FA ratios of 5/5/0/0 and 4/5/1/0 were suitable mix proportions. The desired early age strength, shear strength and compressive strength development were achieved. Compressive and shear strength are shown in Figure 2.

Resistance to Segregation

All the mix proportions had a low bleeding ratio under the target value of 2 %. Under high pressurized condition, 2.0MPa, more bleeding was observed.

Fluidity

Rheological properties such as the plastic viscosity and yield value were measured with a rheometer after 30 minutes of mixing the materials. Rheological properties of selected 10 mix are shown in Figure 3. Although 50 mPa · s is generally required as a target viscosity, 100 is set in this study. Lower viscosity is difficult in low alkaline grout due to fine particle such as silica fume.

Given the required properties described above, 10 mix proportions with a SP were found to be the most promising and suitable for grouting.

Figure 1: Flowchart of selection criteria for suitable mix proportions

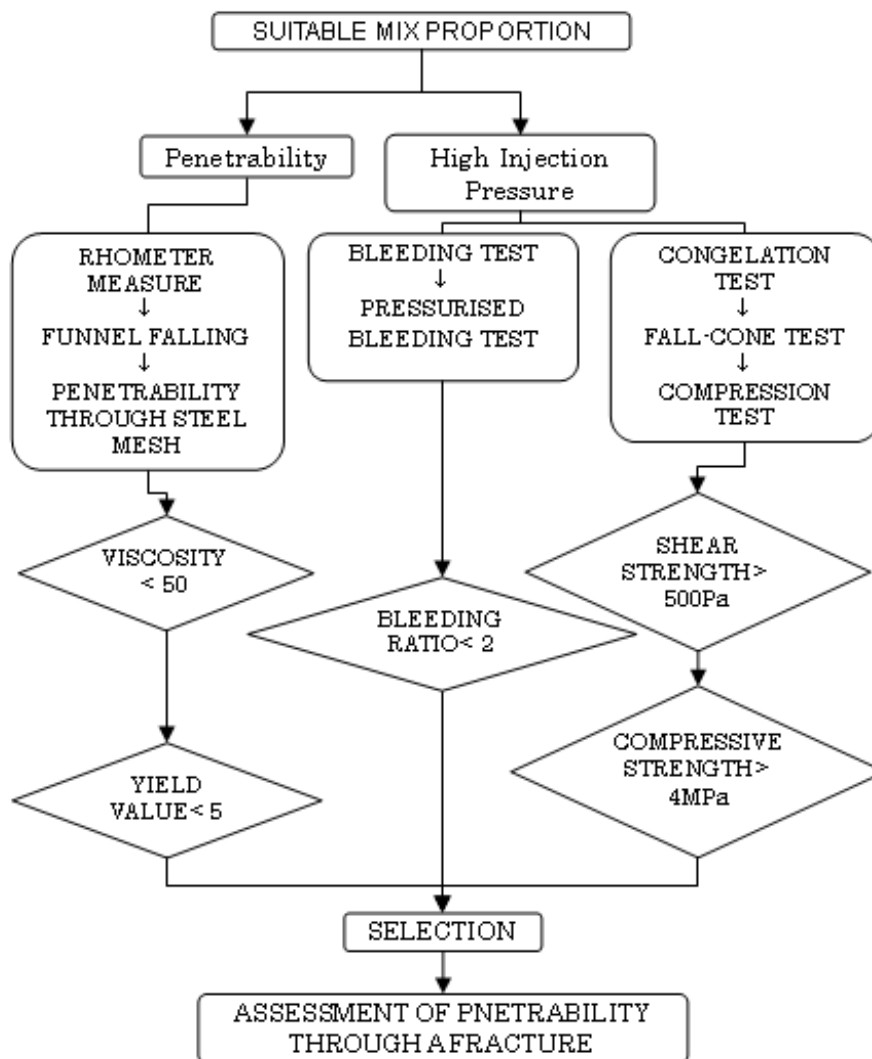


Figure 2: Compressive and shear strength of selected 10 mix proportions (Red line:Target value)

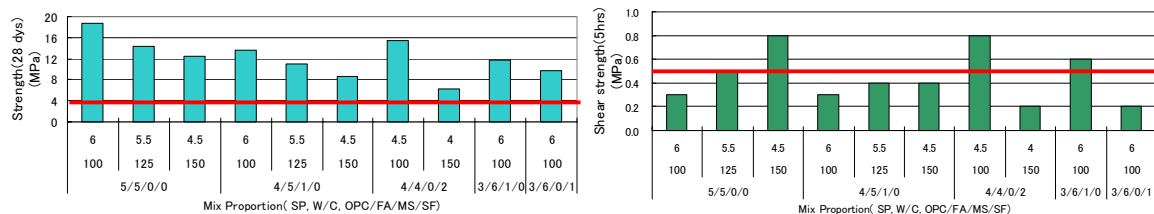
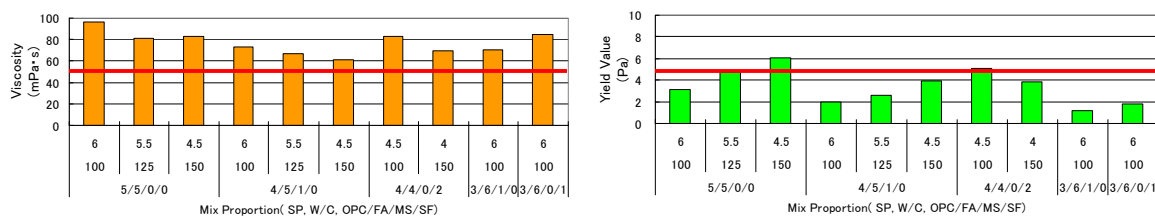


Figure 3: Rheological properties of selected 10 mix proportions (Red line:Target value)



Penetration Test Using a Simulated Model Fracture

Test Equipment and Procedures

The overall setup is shown in Plate 1. To directly observe the penetrating behavior of the cementitious materials, the upper surface disk is an acrylic acid resin of 2 m diameter and 5 cm thickness and the lower surface disk is steel and of the same dimensions. The aperture is controlled by a spacer. Against the high injection pressure, a confining steel frame of 70mm thickness is connected to the lower steel disk by 48 bolts.

The used grouting system consisted of:

- mixer: High shear Colloidal Mixer (TOYOSYOJI Co., Ltd. attached inverter. Maximum rev speed 2,100 rpm)
- agitator: 40 liter tank with stirring fan
- pump: servo-controlled injection pressure, maximum 10 liter per minute
- measurements: injection grout volume and pressure at the outside the injection hole, pressure distribution in the model fracture by 12 pressure sensors installed in the lower steel disk, continuous digital images of all the tests taken by CCD camera set 3 m above the simulated model fracture.

Testing Procedure and Cases

The testing procedure of the grout includes:

- Apertures of the simulated fracture were created with thin plate spacers having 0.1mm, 0.05 mm, and 0.02 mm thickness. Water injection tests were done prior to each grout injection test to assess the quantity of water leaking from the system, thereby confirming the constancy of the test equipment and the reliability of the results.

- Effects of injection pressure, three cases of injection pressure such as 0.1 MPa, 1.0 MPa, and 2.0 MPa were done.

Radial flow through the model fracture was observed by CCD camera and measured injection volume and pressure and pressure in the fracture.

**Plate 1: Overall Experimental setup.
Birds-eye view of the Parallel Plate Fracture Model and Experimental System**



Test Results

In order to know how the grout propagates and spreads in the model fracture, we show observational results of the typical two cases, in which one had complete penetration of grout throughout the entire fracture (Plate 2) and another case in which penetration was limited (Plate 3). The ratio of SOPC/SF/MS/FA in these tests was 5/5/0/0 and 3/6/1/0, respectively. The flow behavior through the model fracture was determined by pressure sensors installed in the lower steel disk, the results of which are shown in Figures 2 and 3. These results were obtained under the same conditions; a fracture aperture of 0.05 mm and an injection pressure of 2.0 MPa. Penetration into the fracture progressed mainly during the increasing injection pressure stage (< 80 seconds) followed by a decline in inflow and pressure during the constant injection pressure stage (> 80 second). It is proposed that friction loss and deformation of the fracture near the injection hole had a large effect on the injected grout. Furthermore, Newtonian fluids and the transient consistency properties of grouts will also have to be considered to predict grout propagation and spread.

Recommendation Proportion

In order to assess grouting performance into the fractured rock, 10 mix proportions were selected based on the basic properties such as strength, resistance to segregation, and fluidity and subjected to the injection tests into a simulated fracture. In the experimental investigations, penetration into the fracture of all the mixtures progressed mainly during the increasing injection pressure and the ratios of SOPC/SF/MS/FA = 5/5/0/0 was more penetrable than the other mix proportions. And it is recommended that water binder ratio can be decided to fulfill the required strength. In this study, 100% at minimum W/B is applicable to inject the required small fissure.

Therefore, it is recommended that the ratio of SOPC/SF/MS/FA is 5/5/0/0 and W/B is 100% as a suitable proportion of low alkalinity cementitious grouting material.

Acknowledgement

This work is one of the activities within the project funded by the Ministry of Economy, Trade and Industry of Japan. The authors express their gratitude to Dr. Colin Walker for his review input.

Plate 2: **Complete penetration of grout** Plate 3: **Limited infilling of the model fracture through the model fracture**



Figure 2: **Examples of the relation between time and inflow rate, injection pressure, and pressure in the fracture OPC/SF/SS/FA/(W/B)=5/5/0/0/150, fracture aperture=0.05 mm**

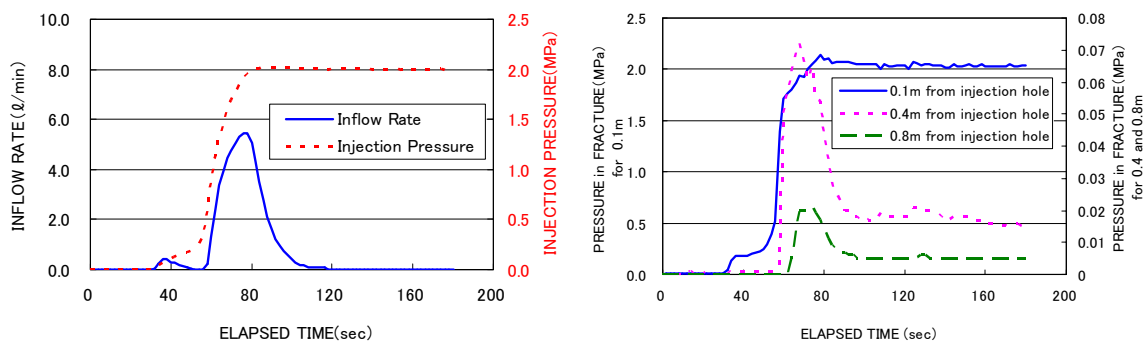
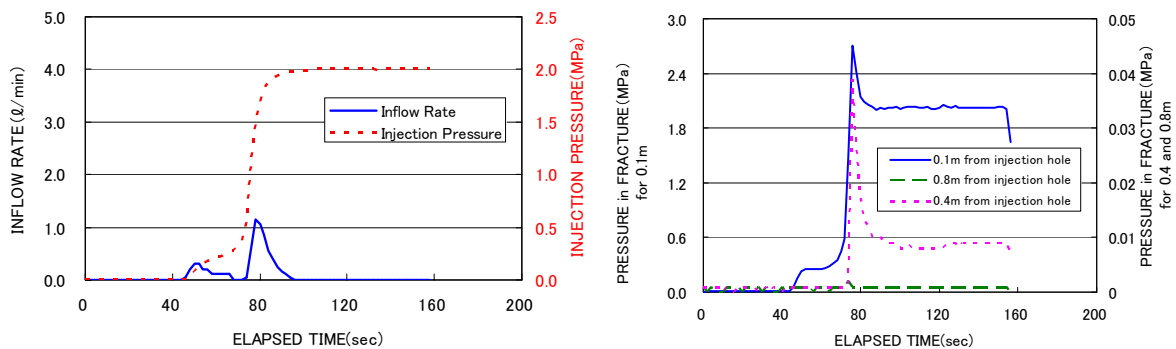


Figure 3: **Examples of the relation between time and inflow rate, injection pressure, and pressure in the fracture OPC/SF/SS/FA/(W/B)=3/5/1/0/100, fracture aperture=0.05mm**



8 - EXPERIMENTAL INVESTIGATION OF THE LONG TERM DISSOLUTION PROPERTIES OF A CEMENT-BASED VAULT BACKFILL

E.J. BUTCHER (National Nuclear Laboratory), J. BORWICK (National Nuclear Laboratory), A.A. THORBURN (National Nuclear Laboratory), S.J. WILLIAMS (Nuclear Decommissioning Authority Radioactive Waste Management Directorate)

Abstract

Government policy in the UK is for geological disposal of higher activity radioactive waste. The Nuclear Decommissioning Authority is responsible for implementation of a Geological Disposal Facility (GDF) through its Radioactive Waste Management Directorate. One concept for the long-term management of packages of intermediate-level radioactive waste (ILW) is to place them in underground vaults in a GDF. After the packaged waste is placed in the vault it is planned to fill the space around the waste packages with a cement-based backfill prior to closure of the facility. The currently specified backfill is the NRVB. This is porous and is designed to provide an alkaline environment in which the mobility of radionuclides is reduced.

The NRVB is composed of a blend of Portland cement, limestone flour and hydrated lime and in principle, there is sufficient alkaline material within the NRVB to maintain alkaline conditions until up to at least 1000 NRVB volumes of groundwater have passed through the repository. However, no experimental studies have investigated the full leaching of NRVB until essentially only the calcium carbonate content remains. Those studies which have been carried out indicate that the buffering behaviour is altered under saline conditions.

Leaching trials are therefore ongoing at the UK National Nuclear Laboratory (NNL) to investigate the dissolution of NRVB until pH values typical of calcium carbonate are achieved. The objective of this work is to determine the buffering capacity of samples of the NRVB, and to allow the sequential release of the alkalinity from the intact samples to be monitored.

Leaching is being performed utilising three leachants; deionised water and two saline solutions. Trials have been performed in duplicate for each leachant to allow an initial assessment to be made of the reproducibility of the data produced.

In order to simulate the conditions expected in the GDF the approach being used in the trials is a flow through experiment utilising a flexible wall permeameter. The configuration of the permeability cell is shown in Figure 1.

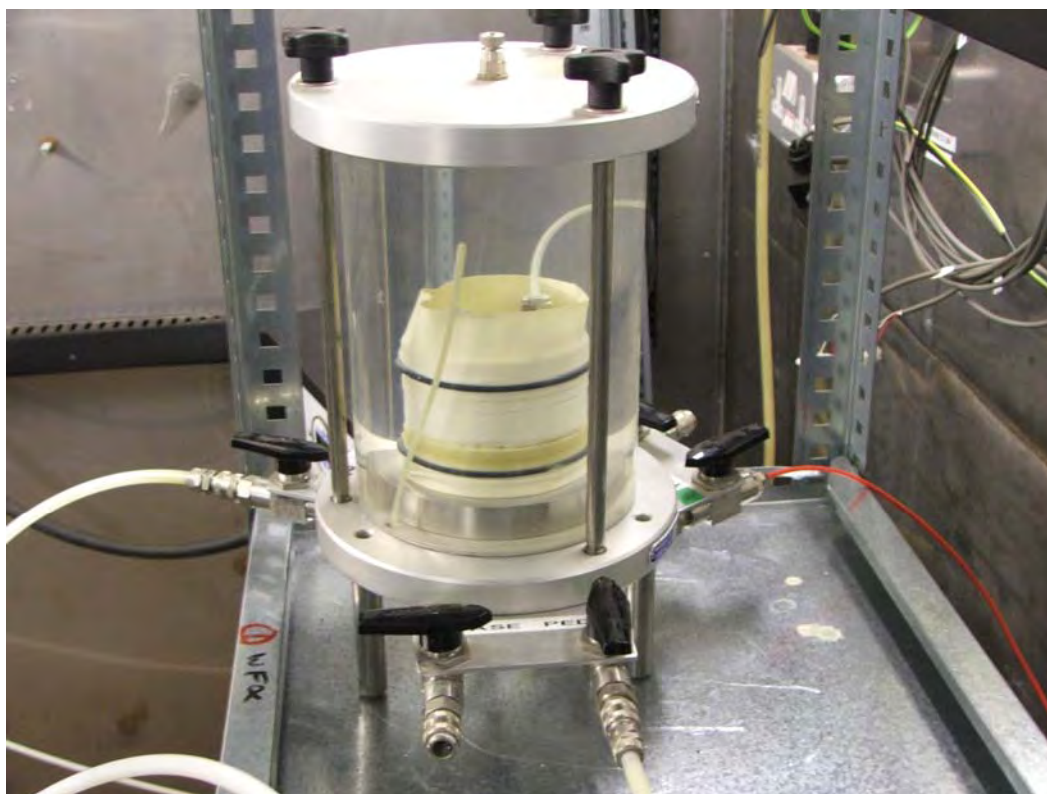
In order to assess the leaching in the environment expected to be present in the GDF the temperature is controlled at 35°C, the long-term temperature which it is expected will be achieved in the post-closure environment. This has been achieved by installing the equipment within a temperature-controlled cell.

The experimental approach has the following benefits:

- The use of equipment designed specifically for this purpose.

- Flow rates can be monitored and if necessary adjusted, to maintain optimum values, ensuring that dissolution/diffusion kinetics do not affect the outcome, and the experiment can be completed within the desired timescale.
- The use of intact samples is more realistic than crushed samples, in which fresh surfaces are created and mineralogical changes may occur as an experimental artefact.
- A flow through test allows accurate measurement of the volume of groundwater which has had direct contact with the internal surfaces of the NRVB.
- Groundwater flow in a repository is likely to create preferential flow paths, mineralogical changes and may not access closed porosity, a flow through experiment should provide some indication of the significance of this.
- The temperature is representative of repository conditions, and therefore solubility and mineralogy will be as realistic as possible.

Figure1: Permeability Equipment



Results

Figure 1: pH Data for leaching performed with Deionised Water

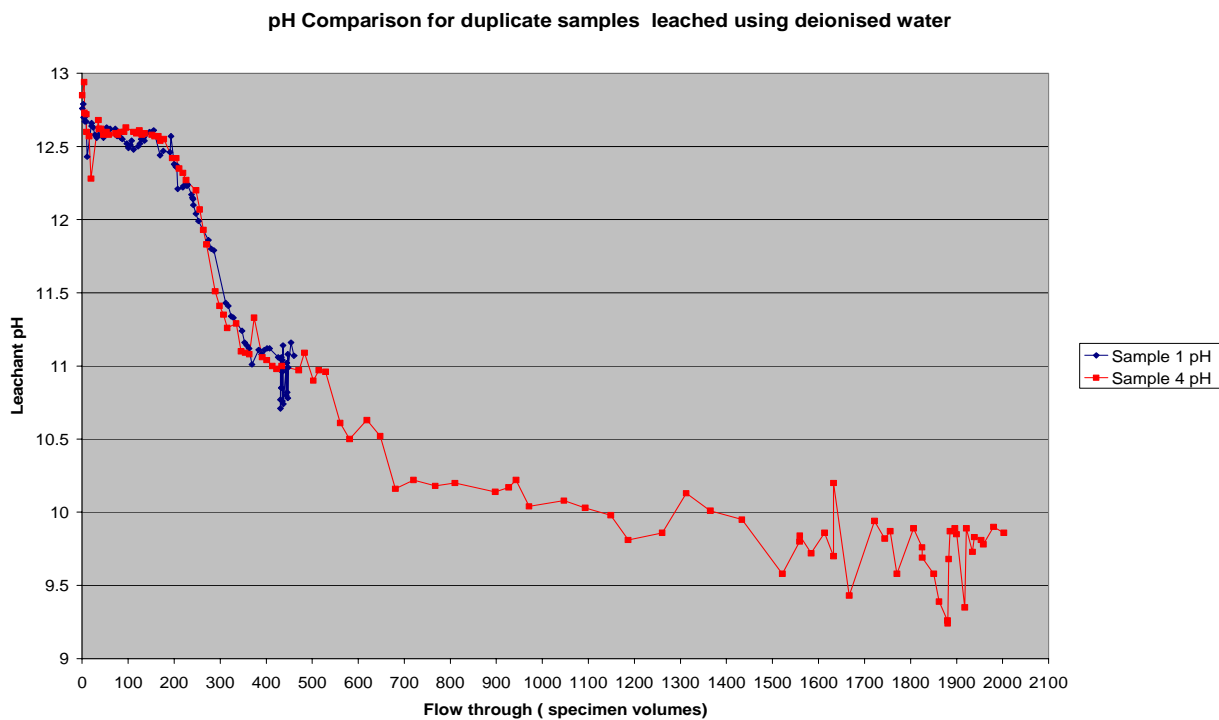
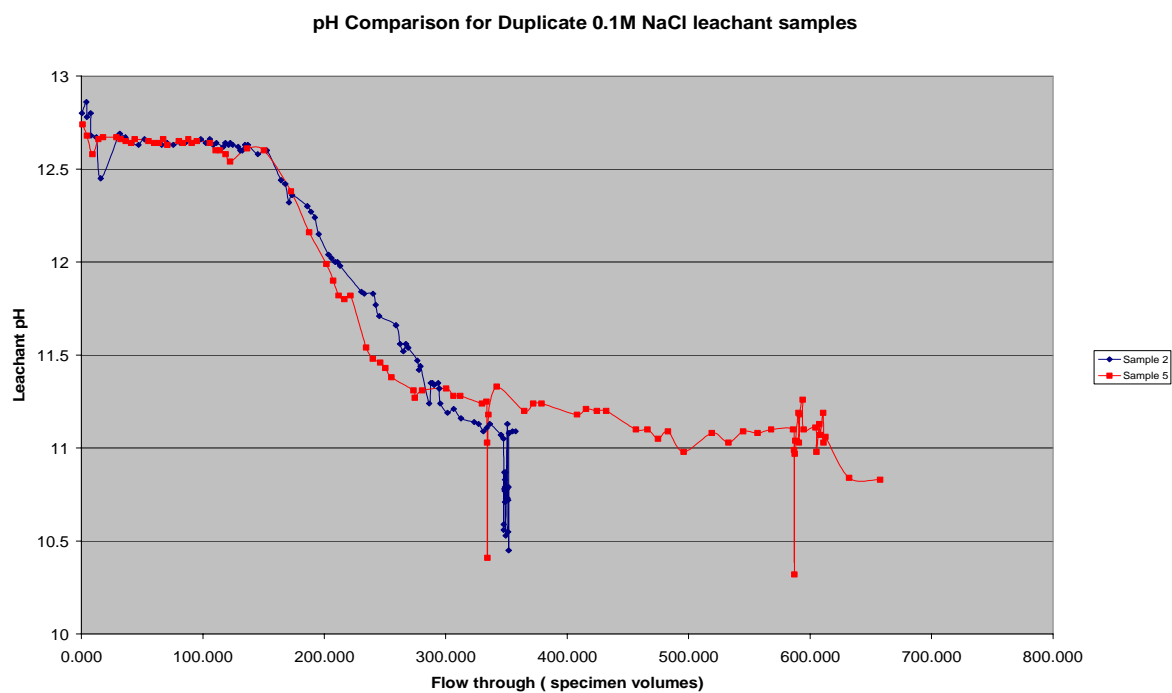


Figure 2: pH Data for leaching performed with 0.1M NaCl Solution



Discussion

While these trials are ongoing there are a number of observations which can be made based on the data generated to date:

- All of the samples show the leaching curves of a pH greater than 12.5 initially, relating to the solubilisation and leaching of the alkali metals. This is followed by a period of leaching during which the pH remains relatively constant at ~ 12.4, which is expected to relate to buffering by portlandite and CSH dissolution. The pH is then observed to show a gradual reduction after the portlandite has been leached and the buffering of the pH is maintained by CSH. Similar results for cement only samples have been reported by Glasser previously.¹
- Variation in flow rates observed between replicate samples is observed, resulting in larger leachant/leachate flow through replicate samples which have been on test at the same pressure for comparable times. This is illustrated for the deionised water (Figure 1) and 0.1M NaCl (Figure 2) leached samples. This variability in permeability is consistent with work summarised other researchers, who have studied permeability testing of concrete samples². This indicated that coefficients of variation in the range of 44 to 52% were recorded for a range concrete samples, all tested using the same method.
- The effect of the variation in flow rate is that replicate samples, leaching of which started at the same time, have been exposed to significantly different degrees of leaching expressed in terms of the volume of leachant which has passed through the NRVB samples. However comparison of the leachate pH data between the replicates after the same volumes of leachate have been collected through each sample shows good agreement in the pH data.
- An experimental observation from the 0.1M NaCl solution trials (Figure 2) are the two lower pH samples which are observed at approximately 330 and 590 volumes. Examination of the complete data set, including flow rates and observations concerning the operation of the flow cells indicated that these two samples correlate with the equipment becoming blocked due to the formation of the corrosion product. This corrosion product was observed to be a brown gelatinous materials and was attributed to the corrosion of components within the permeameter equipment. A possible interpretation of this data is that the corrosion product removes hydroxide from solution during its formation and reduces the pH of the remaining leachate.
- The permeability cell equipment used for the trial allows the pressure applied to the leaching solutions to be varied, if required as the trials progress. Therefore where an increase in flow rates through the sample has been observed, as the cementitious components are leached, leaching pressures have been reduced to allow lower flow rates (which are closer the achieving chemical equilibrium) to be maintained.

Conclusions

- These trials are ongoing, however the data produced to date are consistent with previous work on cementitious material leaching. The flow rates are being adjusted by varying the leachant pressure if required, in order to maintain conditions which are close to

¹. Glasser F.P., Progress in the Immobilization of Radioactive Waste in Cement, Cem. Conc. Res, Vol 22, 1992, pp201-216

². Hooton, R.D., What is Needed in a Permeability Test for Evaluation of Concrete Quality, Pore Structure and Permeability in Cementitious Materials, L.R Roberts and J.P. Skalny Eds, Materials Research Society Symposium Proceedings, vol. 137, 1988, pp141-149

equilibrium. This is one of the advantages of the use of the permeability cell equipment which gives the flexibility change flow rates without disturbance of the backfill sample,

- The flow through approach has allowed data to be generated to assess leaching and alkalinity release of the backfill material under flow thorough conditions which are comparable to those which may occur in a potential geological disposal facility.

9 - ESTIMATED LONGEVITY OF REDUCING ENVIRONMENT IN GROUTED SYSTEMS FOR RADIOACTIVE WASTE DISPOSAL

Scott PAINTER and Roberto PABALAN (Center for Nuclear Waste Regulatory Analyses)

Introduction

A key factor determining the release and transport of redox-sensitive radioelements (e.g., technetium, selenium) from grouted, near-surface, low-activity waste disposal facilities at U.S. Department of Energy (DOE) sites is the redox potential of the cement-based material. At DOE low-activity waste disposal sites, blast furnace slag is added to the grout formulation to impose an initially reducing chemical condition on the grouted system. Sulfide species are released into the pore fluid upon slag hydration, predominantly as S^{2-} , which impose a strongly reducing redox potential on the system and chemically bind some radioelements as insoluble species. Significant uncertainty exists regarding the long-term persistence of the reducing capabilities of the slag-bearing grout and its long-term effect on radionuclide release and transport.

The objective of this study is to estimate how long reducing conditions could persist in near-surface, slag-bearing grouted systems for radioactive waste disposal. The oxidant of most concern is oxygen—in the gas phase or dissolved in infiltrating water—which could react with the blast furnace slag and decrease the grout reductive capacity. The study used a numerical model to simulate oxygen transport in fractures and porous grout and to assess the lifetime of reducing conditions for a range of hydrological conditions, fracturing scenarios, and grout parameter values.

Computational Approach

The evolution of the oxygen concentration in the grout is modeled by coupling one-dimensional advection–dispersion in a partially saturated fracture with one-dimensional diffusion into a fully saturated porous grout. The oxidation–reduction reaction is written as an effective reaction that consumes oxygen (O_2) and grout-reducing equivalents (R) and produces oxidized grout (RO_2):



The oxygen conservation equation in the fractures is given by

$$\phi_f S_l \frac{\partial C_l}{\partial t} + \phi_f S_g \frac{\partial C_g}{\partial t} + \frac{\partial}{\partial z} (\Omega_l + \Omega_g) = -\psi_{F \rightarrow M} \quad (2)$$

where

ϕ_f — fracture internal porosity (1 for open fracture with no sediment)

S_l, S_g — liquid and gas saturation in the fracture

- C_l, C_g — liquid- and gas-phase oxygen concentration [meq e⁻/m³]
 Ω_l, Ω_g — liquid- and gas-phase fluxes in fracture [meq e⁻/(m²·yr)]
 $\psi_{F \rightarrow M}$ — fracture-to-matrix oxygen transfer rate [meq e⁻/(m³·yr)]
 t — time [yr]
 z — vertical distance through the fracture [m]
 b — fracture aperture [m]

In the grout matrix,

$$\phi \frac{\partial C'}{\partial t} - \phi D_e \frac{\partial^2 C'}{\partial x^2} = -kC'R\rho_{grout} \quad (3a) \qquad \frac{\partial R}{\partial t} = -kC'R \quad (3b)$$

where

- ϕ — matrix porosity
 ρ_{grout} — bulk density of the grout [kg/m³]
 D_e — effective diffusion coefficient in the matrix [m²/yr]
 C' — oxygen concentration in matrix pore water [meq e⁻/m³]
 k — grout oxidation rate constant [m³/(yr·meq e⁻)]
 R — grout reductive capacity [meq e⁻/kg]
 x — coordinate direction perpendicular to the fracture [m]

The boundary and initial conditions are:

$$\left. \frac{\partial C'}{\partial x} \right|_{x=l/2} = 0 \quad (4a) \qquad C_l(z, t=0) = 0 \quad (4e)$$

$$C'(x=0, z, t) = C_l(z, t) \quad (4b) \qquad C'(x, z, t=0) = 0 \quad (4f)$$

$$C_l(z=0, t) = C_0 \quad (4c) \qquad R_0(x, z, t=0) = R_0 \quad (4g)$$

$$C_l(z=L, t) = C_0 \quad (4d)$$

where ℓ is the fracture spacing. The partial differential equations are solved using the NDSolve routine of the Mathematica™ software.

Calculated Oxygen Concentration in Fracture Versus Depth

Oxygen concentrations versus depth along the fracture were calculated at different times for different combinations of fracture aperture, spacing, and hydraulic conductivity, including open fractures and wide fractures filled with sediment (parameters listed in Table 1). The results are shown in Figure 1. In all cases, the oxygen concentration in the fracture closely tracks the boundary condition because gas phase oxygen diffusion in the partially saturated fracture is fast relative to diffusive loss to the fully saturated porous grout matrix. In other words, gas phase diffusion is the important transport process supplying oxygen to the fractures. Diffusion in the grout is the rate-limiting process, and gas phase diffusion and liquid phase advection are sufficient to keep the fracture supplied with oxygen.

Matrix Diffusion-Only Model

Because oxygen diffusion in the grout is the rate-limiting process, the longevity of a reducing environment in grouted systems can be studied using a diffusion-only model. In this simplified approach, the oxygen concentration within fractures is described as a boundary condition for a one-dimensional diffusion model. The governing equation is the same as Eqn. (3), with the following boundary and initial conditions:

$$\left. \frac{\partial C'}{\partial x} \right|_{x=\ell/2} = 0 \quad (5a) \qquad C'(x, z, t = 0) = 0 \quad (5c)$$

$$C'(x = 0, z, t) = C_0 \quad (5b) \qquad R_0(x, z, t = 0) = R_0 \quad (5d)$$

The calculated oxygen concentrations in the grout pore space and reductant concentrations versus distance from the fracture wall are shown in Figure 2 at four different times. The oxidation reactions occur in a narrow front that migrates slowly away from the fracture.

Conclusions

For a wide range of hydrological conditions, oxygen concentrations in through-going vertical fractures and conduits in subsurface vaults and tanks are expected to be maintained at or near the levels of the surrounding soil by a combination of gas phase diffusion and liquid phase advection. The relatively slow rate of diffusion in the pore space of the intact grout is the rate-limiting process for oxygen loss to the oxidation reaction. Given the long timeframes of interest in performance assessments, it is concluded that transport processes in the fracture can easily resupply the fractures with oxygen from the surrounding soil.

Given that diffusion in the pore space of intact grout material is the rate-limiting process for grout oxidation, detailed process-level models coupling fracture transport with matrix diffusion and chemical reactions can be avoided. Instead, simpler models coupling oxygen diffusion and grout oxidation reaction can be used, with fractures representing internal boundary conditions with specified oxygen concentrations.

Acknowledgment

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Table1. Parameter values used in modeling oxygen concentration in fractures (see Figure 1)

Modeling Case	Fracture Aperture, b (mm)	Fracture Spacing, ℓ (m)	Fracture Hydraulic Conductivity, k_f (m/s)	Fracture Porosity, ϕ_f (-)	Calculated Saturation in Fracture, S_f
A	0.3	0.3	7.5×10^{-3}	1.0	0.15
B	0.1	0.3	7.5×10^{-3}	1.0	0.28
C	0.1	1.0	7.5×10^{-3}	1.0	0.43
D	0.1	2.0	7.5×10^{-3}	1.0	0.57
E	0.1	5.0	7.5×10^{-3}	1.0	0.87
F	10	5.0	10^{-4} (sediment filled)	0.25	0.31
G	10	20	10^{-4} (sediment filled)	0.25	0.58
H	10	5.0	10^{-5} (sediment filled)	0.25	0.80
$D_e = 1.58 \times 10^{-5} \text{ m}^2/\text{yr}$ $R_0 = 49.8 \text{ meq e}^-/\text{kg}$ $k = 10^{-3} \text{ m}^3/(\text{yr meq e}^-)$ $\rho_{\text{grout}} = 1,700 \text{ kg/m}^3$ $\phi = 0.46$ $C_0 = 1,000 \text{ meq e}^-/\text{m}^3$ $q_{in} = 0.4 \text{ m/yr}$ (Darcy velocity at top of reducing grout)					

Figure 1. Calculated oxygen concentration in vertical fractures versus depth modeled using a coupled fracture advection–dispersion and matrix diffusion model. The red, green, and blue curves are the results after 5, 10, and 100 years, respectively. The green curves are hidden behind the blue curves in Figures 1(d) to 1(h). The key point is that the oxygen concentration in the fracture stays very close to that of the surrounding soil ($1,000 \text{ meq e}^-/\text{m}^3$). Table 1 lists the parameter values used in the calculations.

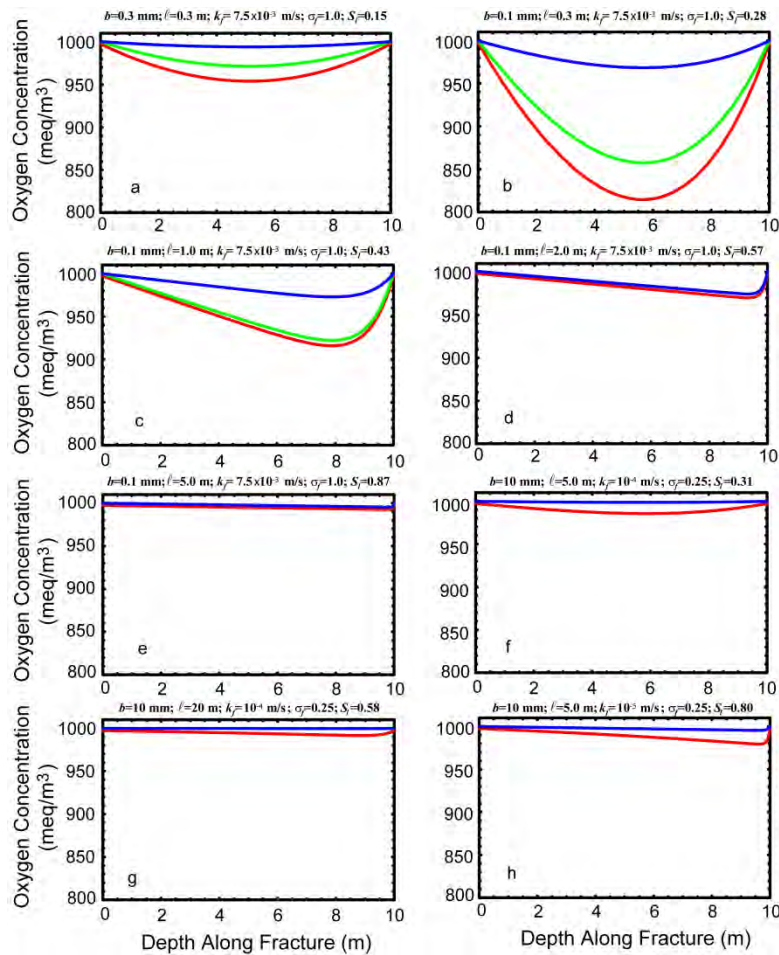
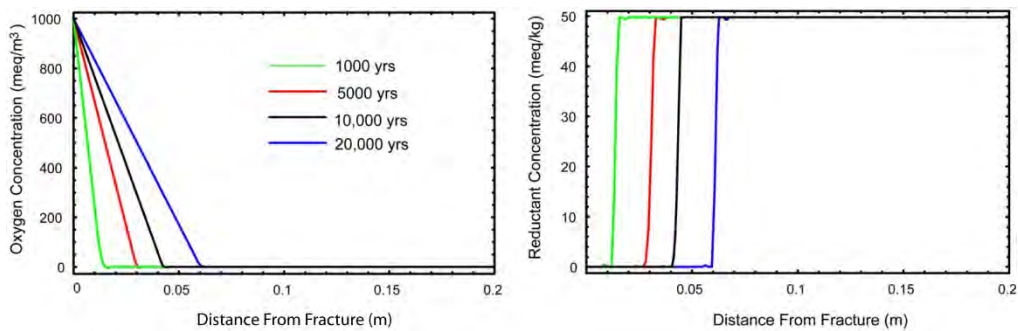


Figure 2. Oxygen and reductant concentration versus distance from the fracture calculated by a matrix diffusion/reaction model.



10 - ENGINEERED ANALOGUES OF CEMENT/CLAY INTERACTIONS IN THE TOURNEMIRE EXPERIMENTAL PLATFORM (FRANCE): A COUPLED MINERALOGICAL AND GEOCHEMICAL APPROACH TO TRACK TINY DISTURBANCES

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In France, the concept of a geological disposal of high-activity and long-lived nuclear wastes requires the use of concrete and cement-bearing materials as building structures or as waste containment packages, in conjunction with clayey barriers (e.g., compacted bentonite as an engineered barrier and/or argillite-type rocks as a geological barrier). The concrete degradation will produce high-pH fluid (pH >13) that will be in disequilibrium with the geological setting environment (argillite porewater pH being close to neutral). Understanding and modeling of such perturbations on confinement properties over a long term is thus a key issue of performance assessments. Numerous studies have been dedicated these last decades to cement / clay interaction understanding based on laboratory experiments, modeling and/or natural/engineered analogues observations (see Gaucher & Blanc, 2006 and references therein for synthesis). These studies were predominantly focused on mineralogical approaches and clues regarding the cement/clay interactions and can be gained by relating mineralogical and geochemical characterizations (isotopic approaches particularly).

Since 2008, a French scientific research group, TRASSE, constituted by the Institute for Radioprotection and Nuclear Safety (IRSN) and the Scientific Research National Center (CNRS) supports investigations on radionuclide transfer in soils and ecosystems, including the knowledge of confinement barrier effects. In this framework, a scientific program has been especially established to better understand the high-pH fluids / clay interactions through a mineralogical and geochemical study of three engineered analogues available by means of the IRSN Tournemire experimental platform. This platform, located in Aveyron (France), is based on a tunnel, excavated between 1882 and 1886 through Domerian marls and Toarcian argillites, and is dedicated since 1990 to multidisciplinary research programs. Different contexts presenting the argillite formation in contact with a cementitious material are encountered and are linked to its historical construction and scientific evolution. These rare examples of cement/clay contacts maintained over time scales ranging from a few years to a hundred of years are studied as engineered analogues of a deep geological storage. This approach is moreover completed by experiments (diffusion and advection) performed in laboratory over shorter time and smaller space scales in order to discriminate and control the major parameters involved in such interactions (refer to the poster Devol-Brown et al., this session).

This poster displays the scientific program developed on three engineered analogues of the Tournemire experimental platform:

- (1) **The tunnel walls** were recovered by lime after excavation. Lime is yet in contact with the argillite in various hydro-geological environments (water-circulation zones and dry zones) and its interaction with the argillite can be studied over a duration of more than 120 years;
- (2) **A concreted exploration borehole**: four exploration boreholes were drilled in 1990 from the basement of the tunnel for hydrogeological measurements and then filled with concrete and cement. These cementitious materials are presently in contact with the Toarcian argillites for 17-18 years. Over-drilling of a selected borehole provides a 15-20 years old cement / clay engineered analogue (ref. Tinseau *et al.*, 2006, 2008)
- (3) **The 2003 galleries**: two experimental research galleries were excavated in 2003, perpendicularly to the tunnel and walls were then covered by several centimetres of different concrete formulations. A Portland (CPA/CEM I) and a CHF (CEM III) cement were used and formulated with calcareous or siliceous rubbles (Figure 1). For each configuration, concrete and argillite in contact were collected by dry drilling.

The first step of the study concerned the dry drilling method to collect properly without damage the cement / argillite interface in the 'galleries 2003 engineered analogues'. The method used allowed the collection of four cores showing a good surface contact between the two different materials (Figure 1). Two cores were collected close to the tunnel EDZ (ABGP2 and ABGS2); two ones far from it (ABGP1 and ABGS1) (Figure 1). No water-circulations were suspected in the four core contexts.

The macroscopic observations displayed a 1 to 4.5 mm dark front in the argillite at the immediate contact with the concrete. The first observations pointed out a thicker 'dark front' at the contact with the Portland siliceous concrete (4.5 mm) than at the contact with the CHF or Portland calcareous concretes. This dark front can be compared to those observed on the DM engineered analogue (a 15 years analogue; Tinseau *et al.*, 2008; Techer *et al.*, 2008) which have been characterized by low porosity values and C-S-H phases. This macroscopic observation leads us thus to expect high-pH fluid percolation in the first few millimetres in contact with the concrete in 2003 galleries. To valid this hypothesis, mineralogical (XRD, TEM) and Sr isotopic geochemical characterizations were performed on the four cores. First, the Sr-isotopic composition of the Toarcian argillite was defined in sample collected at more than 5 cm from the concrete, in order to get a reference. The data revealed classical and well known composition (Figure 2) for the clayey rock. The Sr isotopic composition of the concretes was then determined in samples collected at the direct contact with the argillite: the cementitious materials displayed high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to the clayey rock ones (Figure 2). Close to this material, in the dark front, argillite displayed Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios) very close to 'reference' ones but however slightly and significantly higher ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios are given with an analytical error of $\pm 5.10^{-6}$), indicating a slight chemical disturbance in this millimetric zone which may be linked with the neoformation of CaCO_3 or C-S-H phases from cementitious fluids. This disturbance was not high enough to be observed on the XRD patterns of the whole rocks or on the $< 2\mu\text{m}$ fractions. Nevertheless, SEM observations showed massive precipitation of calcite (Figure 3) and possible precipitation of rare C-S-H phases. Complementary observations and isotopic measurements (Sr, C, O) are in progress to precise the degree, nature and extension of the secondary phases neoformation.

Figure 1: Schematic representation of the 2003 galleries (main and secondary galleries) of the Tournemire experimental Platform showing the four wall concrete coverings (names of the four cores added). Photography of the concrete/argillite interface in the ABGP1 borehole

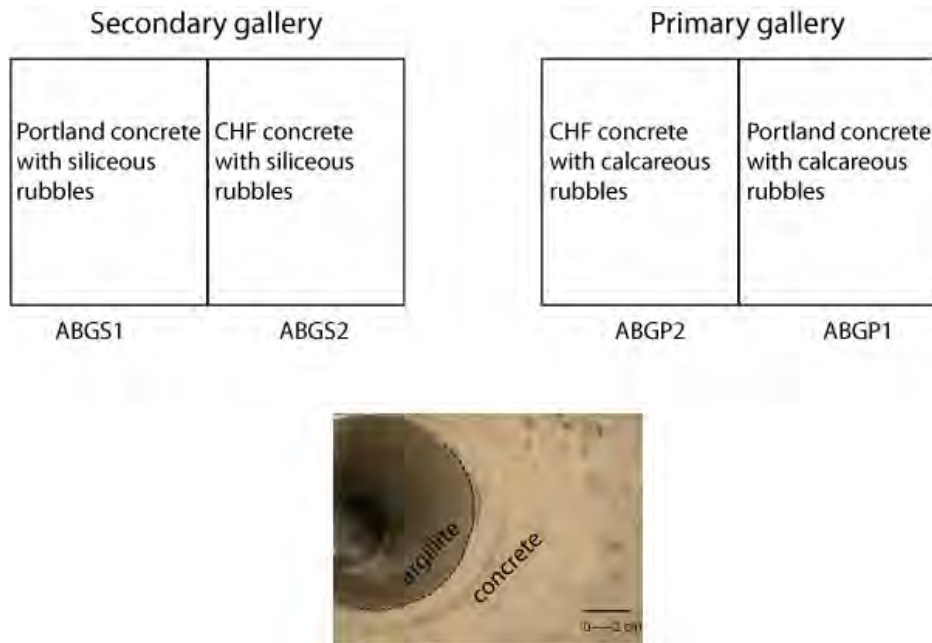


Figure 2: Sr isotopic compositions of the Toarcian argillites and the Portland calcareous concrete (surface) collected along the ABGP1 core: heterogeneity of the cementitious material explained by the variability of calcareous rubbles; slight ⁸⁷Sr enrichment in the 2 mm thick argillite 'dark front'

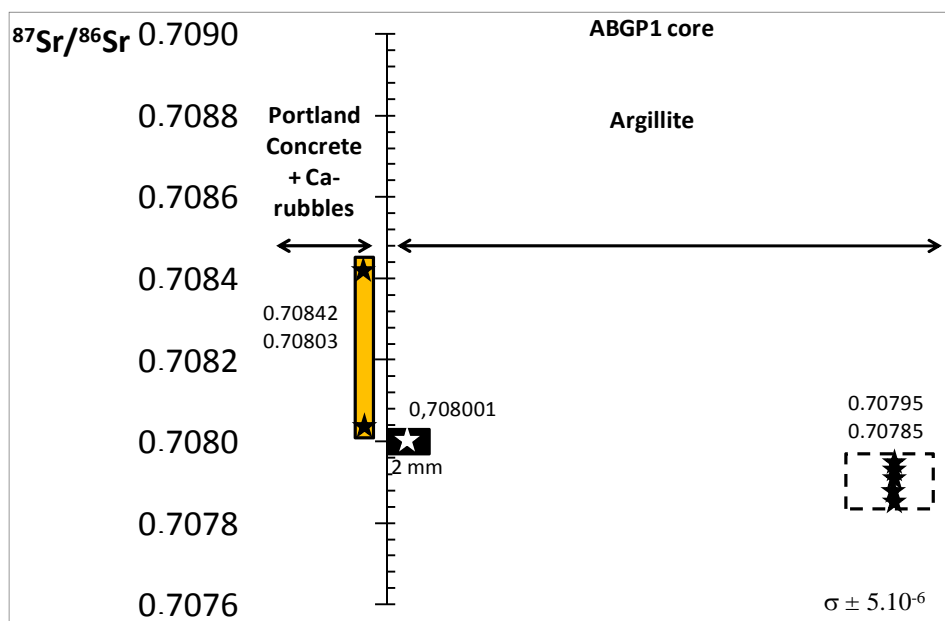
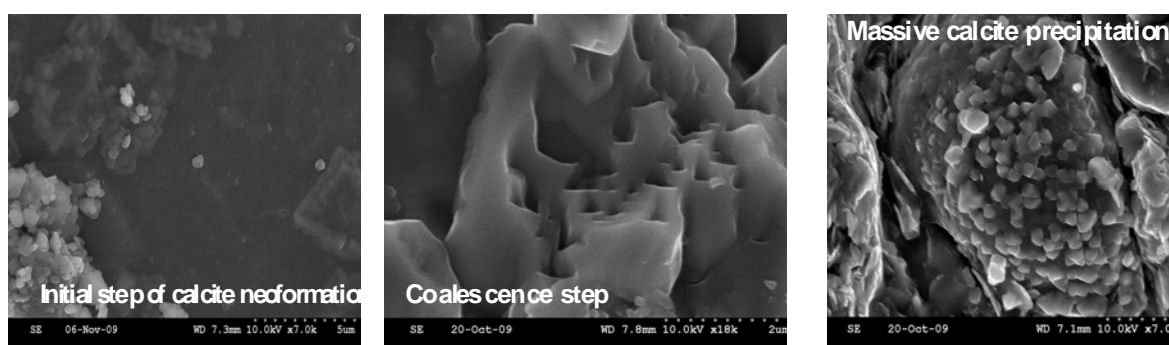


Figure 3: SEM images from the dark front zone



Keywords: alkaline plume, cement, clay, isotopes.

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11 - ALTERATION OF THE TOURNEMIRE ARGILLITE (FRANCE) SUBMITTED TO AN ALKALINE PLUME: THROUGH-DIFFUSION AND ADVECTION EXPERIMENTS

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The alkaline disturbance of clayey rocks in contact with cementitious materials is an important point in safety performance studies for the potential storage of high-level radioactive wastes in deep geological formations in France. High-pH plumes arising from cementitious leachates are known to alter the mineral assemblage of clayey formations selected to play the role of natural barriers for radioactive waste repositories. Dissolution of constitutive minerals such as smectite and precipitation of secondary phases such as feldspar and zeolite have been reported [1]. These mineral changes are suspected to have a significant effect upon diffusive transport properties, either enhancing or decreasing the mudrock ability for radioelement confinement. For instance, experiments performed under alkaline conditions have shown a decrease in water diffusion fluxes and an increase in cation fluxes [2].

Therefore the short and long term behaviour of the clayey rock in the geological barrier must be evaluated and understood. In this purpose, the Institute for Radioprotection and Nuclear Safety (IRSN) and the Scientific Research National Center (CNRS) have developed a research program based on argillites of the Tournemire experimental platform (France). This program, integrated in the TRASSE Research Group, aims at describing, among others items, the modifications of Toarcian argillites in contact with cementitious materials over various time scales (from a few years to a hundred of years).

The Tournemire experimental platform of IRSN in Aveyron is based on a tunnel and several galleries. The tunnel was excavated between 1882 and 1886 through Domerian marls and Toarcian argillites. Its walls were recovered by lime that is yet in contact with the argillites.

The program associated to the study of the engineered analogues provided by the Tournemire experimental platform is presented in this congress (See poster X Bartier *et al*, this session).

In parallel, lab experiments (diffusion and advection) are performed in smaller time (1 year) and space scale to control some parameters and complete engineered analogues results.

This poster aims at detailing the scientific program developed on diffusion lab samples (1) and advection lab samples (2):

(1) This diffusion study was designed to provide better understanding of the phenomena that govern diffusion processes during the transient phase between site and alkaline conditions. Experiments involving the use of “through-diffusion” cells [2,3] were performed to reproduce the effect of an alkaline plume through different types of Tournemire clayey materials. Two kinds of synthetic alkaline fluids aiming to mimic a fresh concrete pore water (N1) or a moderately degraded concrete pore water (N2) and three kinds of sliced rock materials (no fractured, with an

opened fracture or with a tectonic fracture filled with calcite) were investigated for the diffusion of both water and major cations (Tab. 1).

An equilibration procedure was required to i) resaturate the rock with water and ii) force its equilibration with a synthetic solution prior to diffusion experiments. Then tritiated water (HTO) considered as a reference species was introduced in the upstream reservoir in order to deduce the HTO diffusion coefficient through each sample. The process for alkaline fluid diffusions was then somewhat different from the so-called “through-diffusion” process: in these experiments, steady chemical conditions were maintained in the upstream reservoir filled with synthetic alkaline fluids (N1 or N2) while the downstream reservoir, initially filled with a synthetic site solution, was left free of any particular constraint. At last, tritiated water was introduced in the upstream reservoir in order to deduce the evolution of diffusion coefficients for HTO after alkaline fluid diffusion.

(2) The advection study was designed to evaluate the influence of an advective hydraulic regimen on the interaction argillite/alkaline fluid in comparison with the diffusive one. Two advection experiments were performed with an equilibrated synthetic water and then a synthetic fresh concrete fluid (N1) through fractured sliced samples under a pressure of 26 bars (Tab. 1). A significant flow rate is observed in the first case (cell 2) even though no flow is observed in the second one (cell 3).

In all experiments, pH and concentrations (cations, anions) were monitored in time. Mineralogical and petrographical analyses (XRD, SEM, TEM) of the argillite cores were performed before and after the experiments for characterizing the mineral alterations and their potential role on the alkaline plume migration. The advection experiments were modeled with the reactive transport code HYTEC by simulating aqueous chemistry, cation exchange and kinetically-controlled dissolution/precipitation processes.

Table 1: **Experimental characteristics of diffusion and advection experiments**

Diffusion experiments				
N° Cell	Sliced rock material		1rst phase	2nde phase
	Strat. orientation	Structure		
1	0°	No fracture	N1/site	N2/N1
2	0°	Opened fracture	N1/site	N2/N1
3	60°	Large tectonic fracture filled with calcite	N1/site	N2/N1
4	0°	Thin tectonic fracture filled with calcite	N1/site	
5	0°	No fracture	N2/site	
6	0°	Opened fracture	N2/site	
7	0°	Large tectonic fracture filled with calcite	N2/site	
8	60°	Large tectonic fracture filled with calcite	N2/site	
Advection experiments				
2	0°	Opened fractures	N1	
3	0°	Opened fractures	N1	

X/X: upstream reservoir/downstream reservoir initial conditions (kept constant in the upstream reservoir)

Site: synthetic site solution ([Na] = 12.5 mM, [K] = 0.14 mM, [Ca] = 0.37 mM, [Mg] = 0.29 mM, [Cl] = 9.3 mM, [SO₄] = 0.21 mM, [F] = 0.23 mM, pH = 8.4)

N1: synthetic fresh concrete fluid ([Na] = 80 mM, [K] = 100 mM, [Ca] = 1 mM, pH = 13.12)

N2: synthetic moderately degraded concrete fluid ([Na] = 8 mM, [K] = 10 mM, [Ca] = 30 mM, pH = 12.73)

For diffusion experiments, the main conclusions are the following:

- HTO diffusion coefficients during the alkaline diffusion processes: decrease of 25-30 % during the N1 diffusion process and then of 60-70 % during N2 (Tab. 2).

Table 2: Evolution of De(HTO) before and after diffusion experiments

	Unfractured sample	Samples with opened fracture	Samples with calcite-filled fracture
N1/site			
De(HTO) initial (m ² .s ⁻¹)	(2.62 ± 0.12)10 ⁻¹¹	(2.80 ± 0.14)10 ⁻¹¹	(2.17 ± 0.09)10 ⁻¹¹
De(HTO) final (m ² .s ⁻¹)	(1.92 ± 0.08)10 ⁻¹¹	(2.04 ± 0.10)10 ⁻¹¹	(1.42 ± 0.06)10 ⁻¹¹
N2/N1			
De(HTO) initial (m ² .s ⁻¹)	(1.92 ± 0.08)10 ⁻¹¹	(2.04 ± 0.10)10 ⁻¹¹	(1.42 ± 0.06)10 ⁻¹¹
De(HTO) final (m ² .s ⁻¹)	(7.89 ± 0.34)10 ⁻¹²	(8.24 ± 0.34)10 ⁻¹²	(4.78 ± 0.18)10 ⁻¹²

- Precipitation phenomena are less intense during the N1 diffusion process than N2: the alkaline plume induces calcite precipitation and CSH neoformation.
- No significant differences between the phenomena observed in unfractured and fractured clayey samples show that discontinuities are readily sealed by the swelling property of the clayey rock when fully hydrated.
- The tectonic fractured-zone slices show larger heterogeneity than the samples without discontinuities: the occurrence of calcite and pyrite veins in this zone plays a role in the diffusion process.

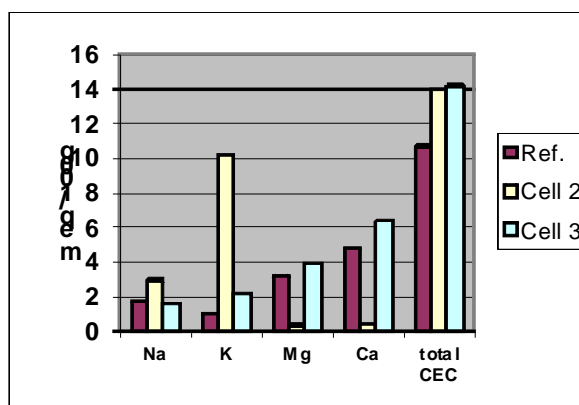
For advection experiments, samples analyses after N1 fluid advection show:

- In the case of cell 2, the fluid is abundant, its flow rate varies with time (~ 12 ml/d) and its chemical composition evolves until it reaches that of the input alkaline solution N1. No fluid recovered in the case of cell 3.
- No significant mineralogical differences between cells 2 and 3 by XRD, SEM, TEM analyses: fractures are preferential zones for neoformations such as calcite, potassic feldspars, CASH, and rare Na-zeolites (confirmed by modeling).
- No significant difference between cationic exchange capacity of cells 2 and 3: maybe an artificial increase resulting from the CASH dissolution at neutral pH (Fig. 1)
- Significant difference between cationic distribution of cells 2 and 3: if the cell 3 one is very close to the initial state, the cell 2 one shows a Na and K concentration increase in parallel to a Mg and Ca decrease (confirmed by modeling) (Fig. 1).
- In the case of the cell 2, (i) the alkaline plume applied under an advective hydraulic regimen induces a deep mineralogical evolution of the argillite, (ii) the initial fracturation state is two important to allow a sealing phenomenon. Whereas in the case of the cell 3, a diffusive regimen seems occur probably in reason of a low fracturation

state combined with a low advective pressure so (i) the alkaline plume is less intense inducing less mineralogical disturbances nevertheless (ii) resaturation and neoformations located on fractures induce a sealing phenomenon.

- Modelling results correctly fits the evolution over time of chemistry and cation exchange population. Likewise the modelling of 15 year-old analogues at Tournemire [4], kinetics of dissolution and precipitation is found to be necessary for a better reproduction of the experimental observations in the argillite samples compared to thermodynamic equilibrium. Modelling shows no significant evolution of the porosity for both cells 2 and 3.

Figure 1: **Major cation concentrations and CEC before and after advection experiments**



Keywords: alkaline, diffusion, advection, fracture.

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12 - MODELLING THE INTERACTION OF THE ALKALINE PLUME WITH BOOM CLAY AT DIFFERENT SCALES

Diederik JACQUES and Lian WANG (SCK•CEN, Belgium)

Introduction and objectives

In Belgium, Boom Clay is studied as a potential host formation for geological disposal of high-level radioactive waste. The current reference design of the engineered barrier system ('supercontainer design') plans to use a considerable amount of cementitious materials as construction material, buffer and backfill. Diffusion of the alkaline pore fluids from the concrete engineered barriers to the Boom Clay may change the retention properties of the Boom Clay in the vicinity of the engineered barriers- Boom Clay interface. The objectives of this work are to (i) model the breakthrough curves obtained from leaching small undisturbed Boom Clay cores with young concrete water (high Na and K content, pH 13.5), and (ii) simulate the possible extent of Boom Clay alterations owing to interactions with alkaline fluids for a period of 100000 y. For both objectives, the reactive transport code PHREEQC is used.

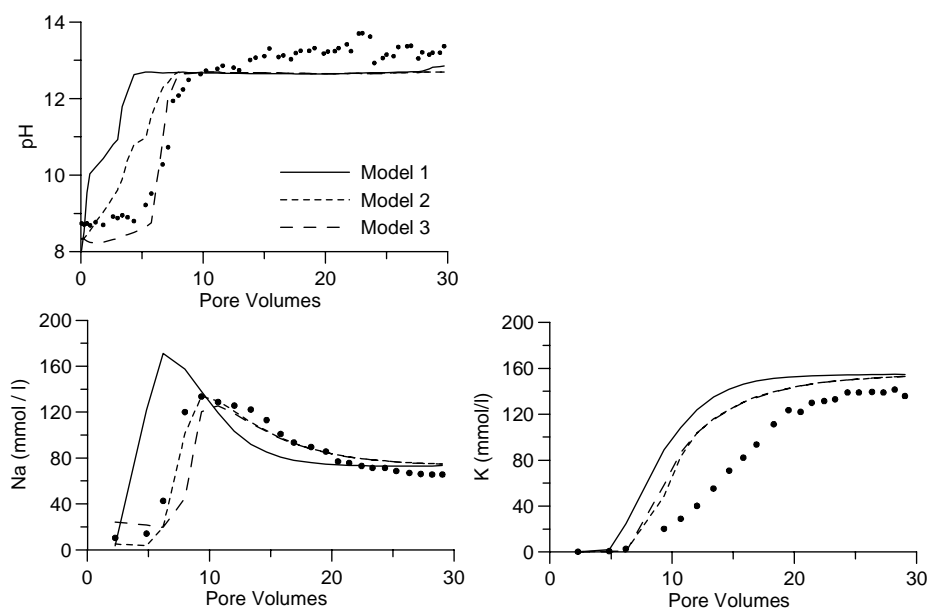
Laboratory-scale modelling

Drill cores of Boom Clay with a diameter of 38 mm and a length of 32 mm were confined between two stainless steel filters (same diameter and a thickness of 2 mm). Synthetic young concrete water (pH 13.5 and rich of K and Na) was percolated through the cores for a period up to 3 years. pH and concentration of different elements were measured in the outflow. Wang *et al.* (2009) described in detail the experimental conditions and results.

The solid-phase model of Boom Clay applied in this study is based on a simplified Boom Clay mineralogy (quartz, montmorillonite, kaolinite, illite and calcite). Kinetic dissolution is assumed for the first four minerals, whereas calcite is assumed in equilibrium. A list of possible secondary minerals considered in modelling is taken from literature and these minerals are assumed to be in equilibrium. The dissolution of the primary minerals is thus considered to be the rate-limiting step. Three sorption models are used to describe the interactions of cations originating from cementitious pore water with the Boom Clay. Model 1 uses cation exchange reactions in which proton exchange with clay is neglected. Model 2 assumes an increased cation exchange capacity with increasing pH due mainly to proton release from natural organic matter. Model 3 extends model 2 with surface complexation reactions of protons on amphoteric surface hydroxyl groups at clay edges.

Results (Figure 1) show that model 1 fails to buffer the high pH, even by using a cation exchange capacity much higher than the measured one. Model 2 describes the Na-outflow fairly well with acceptable parameter values (indicating that cation exchange is the dominating process controlling the Na behaviour within the time of experiment), but pH buffering and K-breakthrough simulations differ considerably from the observations. Model 3 gives the best performance and shows that the proton complexation on the clay surfaces contributes significantly to the pH-buffering capability of the Boom Clay.

Figure 1: Measured (dots) and simulated outflow of pH (top), Na (bottom left) and K (bottom right) for the percolation experiments with young concrete water. Simulations are shown for model 1, 2 and 3 for pH, and with model 3 for Na and K.



Long term modelling

Model approach

The diffusion of an alkaline plume is simulated for a period up to 10^5 years with the PHREEQC-2.12 geochemical code (Parkhurst and Appelo, 1999) using the *lnl.dat* database with minor adaptations for some cement phases. To account for the mass balance and variations in the composition of the alkaline plume with time, the concrete material in the near field is explicitly included in the model. The concrete material is located between 0.22 m and 1.62 m from the centre of a radial simulation geometry. The steel components in the supercontainer design are ignored, and an initial homogeneous concrete material was assumed.

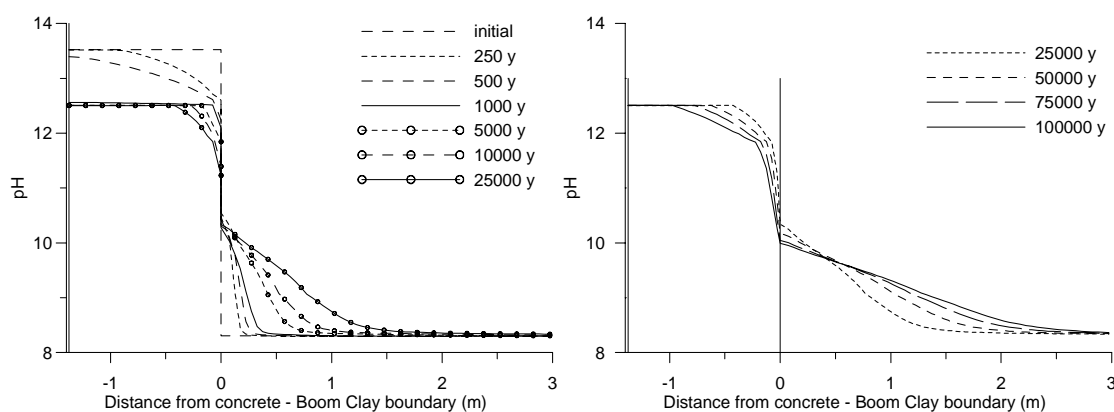
A reference model is defined including five minerals representing the Boom Clay mineralogy (quartz, kaolinite, illite, Na-montmorillonite, and calcite), a pH-independent (clay minerals) and dependent (organic matter) cation exchange complex and surface acidity reactions on the illite and Na-montmorillonite (after Bradbury *et al.*, 2005). All mineralogical reactions are assumed to be in equilibrium. In addition to the reference case, other simulations assess the sensitivity of the capacities of the exchange and surface sites, the initial amount of primary minerals (plus and minus 25%) and the value of the diffusion coefficient in Boom Clay (five times smaller and larger than the current best estimate). In addition, some alternative model formulations for the Boom Clay mineralogy and the choice of the secondary phases are tested.

In all these simulations, there is no feedback of mineral precipitation and dissolution to changes in porosity and, subsequent, diffusion coefficient. For example, clogging of the pore space in the concrete due to calcite precipitation will certainly have an effect on the diffusion of elements in and out the concrete. Nevertheless, the current simulations will give an idea of the possible extent of the alkaline plume perturbation in the Boom Clay.

Results and discussion

Figure 2 shows the pH evolution in the reference model. Within the first 1000 years, the Na- and K-oxides in the concrete are depleted resulting in a pH decrease from 13.5 to 12.5. Portlandite is completely depleted up to 0.3 and 1.0 m from the concrete – Boom Clay interface after 25000 and 10^5 years, respectively (pH is smaller than 12.5). At the concrete – Boom Clay interface, a substantial amount of calcite is precipitated (data not shown). Overall, the disturbance of the Boom Clay by the diffusion of an alkaline plume is limited up to 0.4 – 1.2 m from the concrete – Boom Clay boundary after 25000 years (for different model formulations) and up to 2.0 – 2.5 m after 10^5 years (for the reference case). After 25000 years, the volume occupied by minerals has increased by at most 15 percent for the reference case (taken into account the parameter uncertainty) and at most 25 percent for the different model formulations.

Figure 2: pH evolution near the concrete – Boom Clay boundary for the reference model (vertical line indicates the concrete – Boom Clay interface).



Parameters defining the capacities of the cation exchange complexes or the surface acidity sites have no effect on the extent of changes in pH. The initial amount of the primary minerals has a slightly larger effect, especially kaolinite. The most crucial parameter is the diffusion coefficient. Although this parameter is relatively well defined for undisturbed Boom Clay, it is still an uncertain parameter with respect to the altered Boom Clay by an alkaline plume. The pore diffusion coefficient depends on the porosity of the porous medium and the alkaline plume may trigger processes that could alter the porosity. However, these effects were not taken into account in the present simulations.

The selection of mineral reactions and sequence is a crucial factor for assessing the spatial extent of the alkaline plume perturbation. Decreasing (e.g., neglecting exchange and surface acidity reactions or allowing primary minerals only to dissolve) or increasing (adding dolomite-dis as a primary mineral) the total buffer capacity in the model increases or decreases the spatial extent of the disturbed zone, respectively. By adding dolomite-dis as a primary mineral increases the buffer capacity significantly, since it acts as an additional source of CO_2 . The Boom Clay mineralogical model for buffering the pCO_2 in the clay (De Craen et al., 2004) is the most efficient in buffering the alkaline plume. The disturbed zone is limited up to 0.4 m after 25 000 y.

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Acknowledgements

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13 - SPACE AND TIME EVOLUTIONS OF CEMENTITIOUS COMPONENTS IN A CONTEXT OF A HIGH LEVEL AND LONG-LIVED RADIOACTIVE WASTE DISPOSAL IN A DEEP CLAY FORMATION: FROM PHENOMENOLOGICAL ANALYSES TO PERFORMANCE ASSESSMENT

Isabelle MUNIER, Benoit COCHEPIN and Frédéric PLAS (Andra, France)

Introduction

Cement is an important material considered as part of many engineering components for High Level and Long-lived (HLLL) radioactive waste disposal in a deep clay formation: Intermediate Level and Long-lived (ILLL) disposal packages, embedding matrix of some ILLL primary containers, support base of drift/access ramp seals, plug of HLLL waste disposal cell, slabs/liner of ILLL waste disposal cell/drifts and access ramp... These different components play specific roles for operating safety and/or post-closure safety.

In an integrated overview of the phenomenological evolution of a waste repository, cementitious materials cannot be considered as generic. According to the clay host rock characteristics and the types of radioactive waste, cementitious components will be submitted to specific phenomenological evolutions in term of thermal (T), hydraulic (H), mechanical (M), chemical (C) and radiological (R) processes that could be independent or coupled, sequenced or concomitant.

Based on design concepts in relation with cement types, this paper draws the map of the phenomenological evolutions of the various cementitious components focusing on processes involved, specificities, similarities, time and space scales in relation with the safety functions they have to fulfil. Indeed, Andra settled an integrated approach from the phenomenological analysis of waste disposal THMCR evolutions to performance assessment in order to ensure a total coherence of each step till the safety assessment.

This integrated approach has been elaborated and applied for the Andra's "Dossier 2005". At that time, several phenomenological simulations of the THMCR radioactive waste disposal components evolution have been conducted in order to assess their behaviour in time and space. The stress was put on the hydraulic evolution with the desaturation/resaturation period of the structure.

In the frame of filing the repository licence application scheduled for 2014, the same approach is conducted from the phenomenological analysis to the safety assessment going through performance assessment.

Phenomenological approach

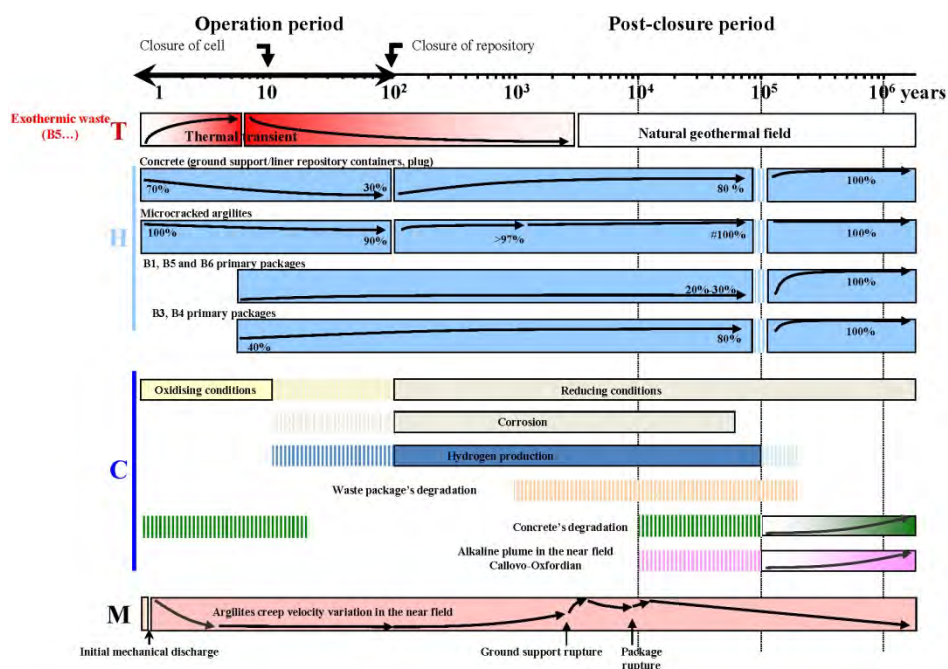
The major processes affecting cementitious components are highlighted considering operating and post-closure periods. For example, the kinetics of chemical phenomena depends on environmental conditions, and more specifically, on the water availability, and thus, on the time period considered. In that context, the THMCR phenomenological evolution of the whole

disposal is considered in order to explore the domains of the phenomenological evolution of cementitious materials.

To illustrate this approach, the case of the cementitious components of an ILL waste disposal cell is presented. The stress will be done on their mechanical and chemical evolutions with time, both processes being related to the hydraulic and temperature conditions of the cell.

The analysis of cement components of the ILL cell submitted to THMC processes takes place in a specific Andra's tool, the Phenomenological Analysis of Repository Situations (PARS). This analysis is a space-time description of the various phenomena affecting the repository's components and their environment. Each disposal component evolution is split up into various situations corresponding to a specific time and space interval within which a few major phenomena dominate. Each situation details the THMC processes impacting the component. Among other sources of quantification such as natural analogous, these analyses use the numerical simulations to demonstrate the time and space extents of these processes. The synthesis of all of these analysis elements allows the drawing of a synthetic view of each disposal component evolution (Figure 1).

Figure 1: Chronogram of main phenomenological processes for ILL waste disposal cell (Andra's "Dossier 2005")



Hydraulic and thermal conditions

Before sealing the disposal cells, environmental conditions are controlled by the air ventilation which fixes the hygrometric and temperature conditions. According to the absent or poor exothermicity of waste, cell hygrometry would be in the range between 25% and 40%, and the ventilation air temperature from 23°C (the natural rock temperature) up to 40°C. Ventilation leads thus to a non-negligible desaturation of cementitious components and host rock near field.

After the cell sealing, hygrometry (and temperature in case of exothermic ILL waste) rises due to the ventilation stop. The near field and the cementitious structure components begin then their resaturation. The hydrogen produced by the anoxic steel corrosion delays the cell resaturation but the air hygrometry till increases up to 100%. The complete cell resaturation

needs about hundred thousand of years. The thermal transient period affecting the exothermic waste cell components lasts few tens of years before decreasing down to the initial host rock thermal conditions.

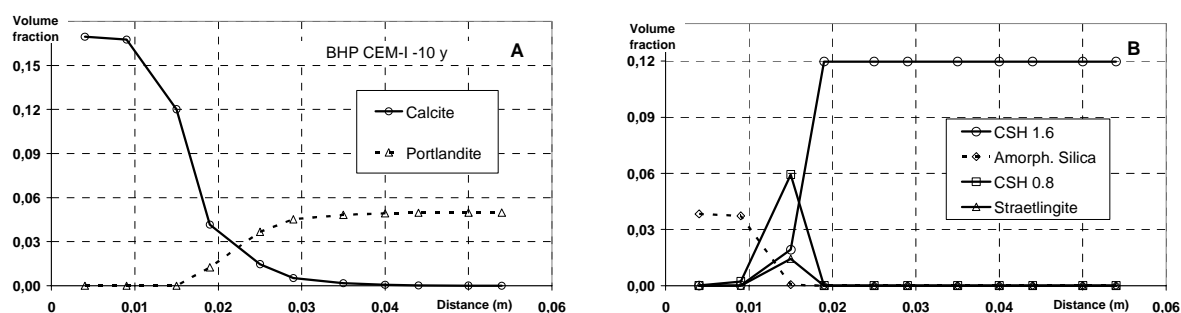
These thermal and hydraulic conditions drive the chemical and mechanical processes undergone by the cementitious material of ground support/liner and disposal packages.

Chemical evolution

The cementitious components of the ILL cell are submitted to several chemical processes among which carbonation and hydrolysis. These two phenomena concern different components and occur at two different scales of time and space. Indeed, carbonation rather affects cementitious material in contact with the ventilation air, i.e. the waste packages and the slab/liner intrados, and hydrolysis concerns the slab/liner extrados during the post-closure period.

Biphasic reactive-transport simulations have been settled in order to achieve a quantitative evaluation of the carbonation extent over period of time inaccessible to the experiment (Figure 2). The resaturation limits strongly the development of atmospheric carbonation, due to the concomitant need of pore water and carbon dioxide. Thus, in dry condition, the carbonation of cementitious components remains partial and reaches only few centimetres or decimetres in depth. After the closure and the stop of the air ventilation, the cement carbonation still continues until the complete carbon dioxide consumption.

Figure 2: BHP CEM-I waste package - (A): Calcite/Portlandite, (B): CSH (along a half section of the waste package wall) (Trotignon *et al.*, 2009)



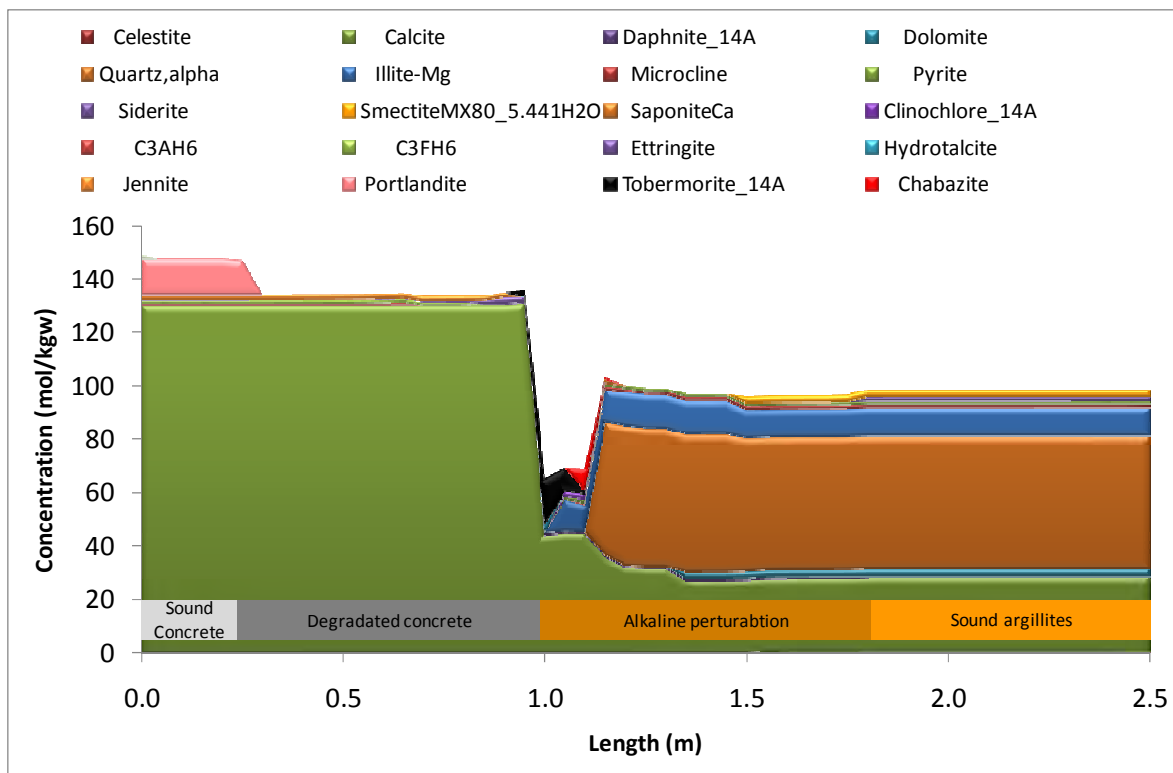
During the operating period, the hydrolysis of the cementitious coating in contact with the host rock is also limited to a small thickness (few centimetres scale) due to a poor water availability from the unsaturated clay. After the cell closure, the cement hydrolysis at the liner/clay interface develops with the increase of the water availability. The cement degradation starts from the cement liner extrados toward the waste packages. The extent of the cement hydrolysis is mainly driven by diffusion processes imposed by the Callovo-Oxfordian hydraulics. The several carried out simulations indicate a degradation extent of utmost few decimetres over 100 000 years (Figure 3). Thus, the water reaching the disposal packages, the embedding matrix and the primary packages remains a cement pore water during hundreds of thousands of years preventing thus the cement matrix of these components from hydrolysis.

Mechanical evolution

The mechanical processes affecting the ILL cells follow a different sequence. During the operating period, the main process is the loading of the ground support/liner by the host rock

(few MPa). The loading is small due to the desaturation of the clay which slows down the clay creep rate. The disposal packages are only submitted to their own weight.

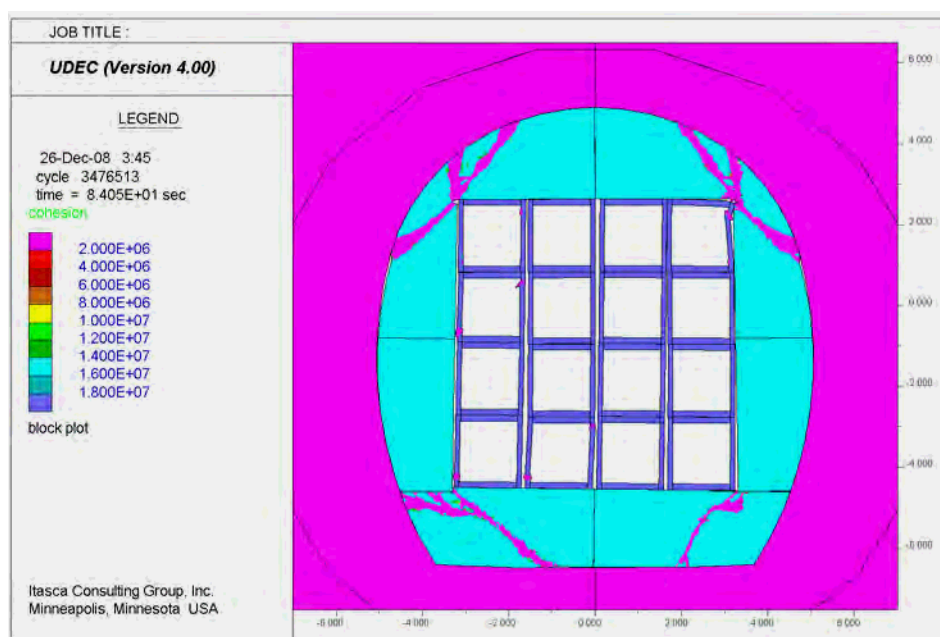
Figure 3: Alkaline perturbation and concrete degradation at the interface between argillites and liner after 100 000 years



From the first tens to one hundred years after the closure of the engineered structure and the start of the host rock near-field resaturation, the clay achieves sufficiently high degrees of saturation to reactivate the creep. The clay creep and swelling thus increase the loading on liner, resulting in stresses increase. These stresses involve displacements in the liner and lead to the concrete rupture. The liner fracture induces a loading on the disposal packages, which in turn get fractured. The actual simulations of the mechanical loading of the ILL disposal cell components show the fracture scheme after 5 000 years (Figure 4). It is to note that during this length of time, the ground support/liner mechanical properties are not reduced by chemical degradation.

Thus, the chemical and mechanical processes which affect the different cementitious components of the ILL cell do not evolve in the same space and time context. Indeed, the chemical processes develop at long term (> 10 000 years) whereas the mechanical processes take place at medium term (few hundreds of years – few thousands of years). The consequences of these two processes also impact different scales of length. Chemical degradation concerns essentially the components interfaces (at most few decimetres scale) whereas the consequences of the mechanical processes may be observed at longer distance (metric scale), especially considering the ground support/liner loading and fracturing.

Figure 4: Cracking pattern based on cohesion contour in the reference case, 5,000 years (Damjanac & Billaux, 2009)



Safety and performance assessment approach

Once elaborated the picture of the chemical and mechanical evolutions of the different cementitious components of an ILL waste disposal cell, the way these components fulfil the safety functions has to be verified by considering the maps of phenomenological evolution and their uncertainties.

These functions are derived from the principal function of a repository, which consists in “to protect humans and the environment from the dispersal of radionuclides” and are specific to the disposal operating or post-closure periods. Different safety functions dedicated to the cementitious components of an ILL waste disposal cell can be considered (Table 1).

The different cementitious components of the ILL cell are concerned by these functions according to different ways depending essentially on which properties, chemical or mechanical, are used to fulfil the functions.

The performance assessment simulations program is designed to make the link between the complexity of the chemical and mechanical phenomenological evolutions of the cementitious components and the necessarily simplified representations used in safety assessment. These simulations make then possible to evaluate how these simplifications may impact the radionuclide transfer representation and to evaluate the effects of uncertainties, whatever they are (numeric, conceptual...).

Chemical evolution

The previous results of the reactive-transport simulations allow us to draw a phenomenological map of the chemical evolution of the ILL disposal cell cementitious components over time. These elements of quantification are then translated into parameters required for performance assessment. Then, the time and space evolutions of the two main parameters rendering the radionuclide transfer (distribution coefficient (Kd) and solubility limit

(SL)) are deduced from the phenomenological simulations and then used in performance and safety simulations.

Table 1: **Some safety functions and associated required properties of cementitious components**

Functions	Periods	Components	Properties required	Processes modifying	
Maintaining the mechanical stability of storage structures	Operating	Slab/Liner	Mechanical strength	Clay creep	
				Cement hydrolysis...	
Allowing the retrievability of waste packages	Operating	Disposal package	Mechanical strength	Loading of disposal packages	
				Loading of liner	
				Gas overpressure...	
Resisting to the perturbations induced by gas production	Operating	Disposal package	Mechanical strength	Gas overpressure...	
Preserving the confinement properties of the host rock	Operating	Slab/Liner	Mechanical strength (limiting EDZ formation)	Clay creep Cement hydrolysis...	
	Post-closure	Slab/Liner	Chemical properties (limiting alkaline plume)	Water circulation Temperature...	
Limiting the release of radionuclide and immobilising them within the repository		Slab/Liner	Chemical properties (radionuclides retention)	Water circulation	
				Temperature...	
	Post-closure	Disposal package	Mechanical strength (waste geometry preservation)	Chemical properties (radionuclides retention)	Water circulation
				Temperature...	Loading of disposal packages
				Loading of liner	
				Gas overpressure...	
	Embedding matrix	Chemical properties (radionuclides retention)	Water circulation Temperature Degradation products of the waste...		

For example, the pH space and time evolution during the liner degradation has been evaluated in the frame of Andra's "Dossier 2005" (Andra, 2005). Thus, areas characterized by specific degradation states of the cement (sound, altered, degraded) have been deduced from this evaluation at four successive time steps. At each of these states were associated the specific retention properties of ⁷⁹Se (Figure 5) (Pepin et al., 2007, Pepin et al., 2009). These simplifications allow to simulate the transfer of this radionuclide at the scale of the entire cell and to perform an uncertainty analysis, as well as a multi-parameters sensitivity analysis. Through specific indicators, this study enabled to obtain the partial rank correlation coefficient (PRCC) and the rank sensitivity indicator between each input data with correlated uncertainties (Figure 6).

Figure 5: Way of considering geochemistry (Kd, SL) in ranges of times for a concrete material (around waste domain) (Pepin et al., 2009)

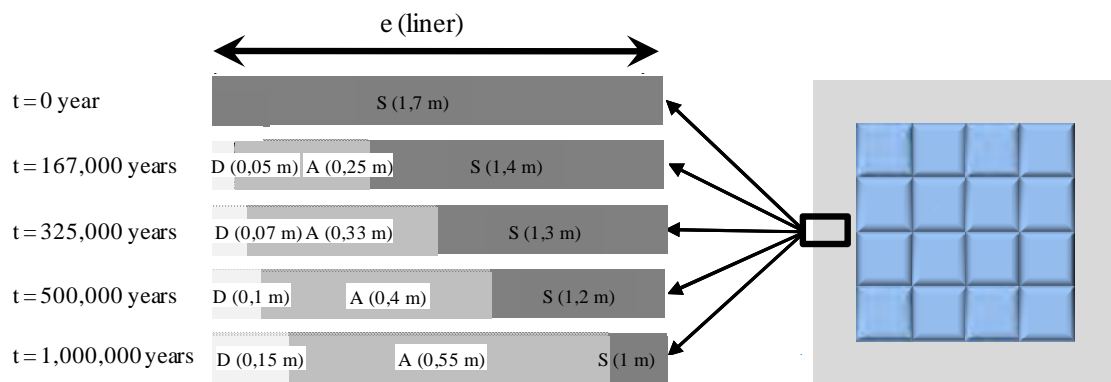
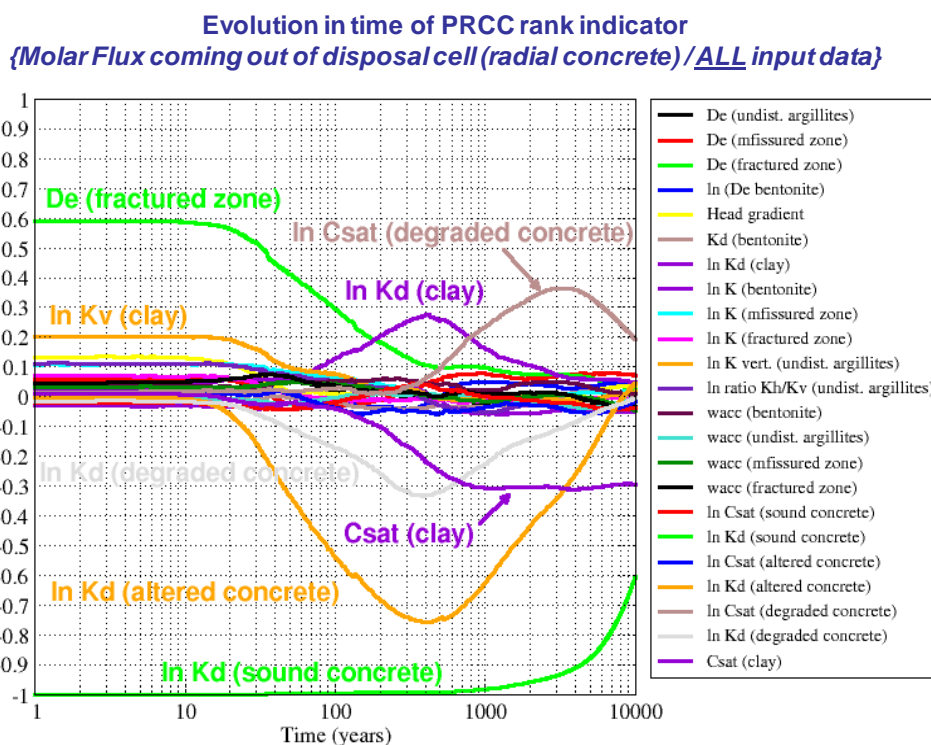


Figure 6: Evolution in time of PRCC for all input data - Molar rate coming out of ILLL disposal cell (radial concrete) – ⁷⁹Se (Pepin et al., 2009)



This approach allows us to refine the approach we used in the Andra's "Dossier 2005", in which the chemical degradation of the cementitious liner was not explicitly taken into account. Indeed, since the chemical degradation of the cementitious slab/liner is driven, among other, by the hydraulic properties of the host rock and by their own, which depend on their mechanical integrity (see below), it was considered a unique value of K_d and SL for the whole slab/liner during the post closure period. These values have been chosen as the most prejudicial for the radionuclides transfer among those characterising the different degradation state of the concrete. This reasoning enables on one hand not to take into account the mechanical and then the hydraulic properties evolution of the slab/liner and, on the other hand, to set aside the uncertainties of the fronts development resulting from the concrete chemical degradation.

Mechanical evolution

The phenomenological evolution of the cell components mechanical behaviour indicates the appearance of fracture within few thousands of years. This evolution involves the degradation of the hydraulic properties of the concrete components (permeability, diffusion coefficient...).

In the performance analysis, the mechanical processes are not taken into account as such but through the variation of hydraulic parameters. Thus, the analysis conducted in the Andra's "Dossier 2005" considered the concrete components with degraded hydraulic properties (diffusion coefficient of water into water, permeability of sand) from the beginning of the post-closure. These radical choices allowed to disregard the uncertainties of the fracture instance time by neglecting the transient step before mechanical evolution of the cell.

Conclusion

The analyses conducted above on the waste disposal functioning gives us crucial information concerning the key parameters which drive the ILL cell components evolution in a low permeability host rock and allow us to precise the role of the different cementitious components of the ILL cell in the safety of the waste disposal and in which way they can achieve this role. Thus, during the operating period, the mechanical strength of the cementitious components is the major property used to maintain the integrity of the waste package and to limit the host rock deformations. During the post-closure period, the chemical properties are the most required since it governs the radionuclides retention near the waste.

Moreover, for the ILL cell, the main interest of the cement formulation concerns essentially its set up (optimization...) and not the long term, because the chemistry of the cement is used to buffer and homogenize the chemical specificities of the different waste at the scale of the cell. This is not the case for other cementitious components of storage in contact with bentonite (plug, seals), in which the chemical degradation of bentonite is expected to be limited. In that case, specific cements such as low pH concrete are studied.

The research on the mechanical, chemical and hydraulic properties of concrete (and clay) and on coupling has to be developed in order to limit at most the uncertainties of the different processes involved (clay creep rate and saturation, chemical degradation, hydraulic resaturation of the cell...). Our numeric tool have also to be developed in such way they can integrate, for example, a higher complexity and refinement in the time and space evolution of input parameters.

These researches will help to derive the safety margin according to the waste specificities and to proportion cementitious components, especially considering the need to maintain or not their mechanical properties after the disposal closure.

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14 - MECHANISMS OF CEMENT LEACHING AND DEGRADATION - INTEGRATION OF NEUTRON IMAGING TECHNIQUES

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Introduction

Cementitious material is a commonly used wasteform for low and intermediate level radioactive waste, and comprises a major part of both structural components and barriers in many repository concepts. When exposed to water, cement-based barriers and wasteforms are expected to degrade by mechanisms involving both chemical and structural changes.

The research program addresses several aspects of these processes, including the leaching of the wasteforms, water transport properties, as well as the effect of high pH cement leachates on the chemical and physical properties of surrounding materials (including clay barriers and host regolith materials). The current paper emphasises the role of diverse characterisation techniques, particularly the integration of neutron based methods in elucidating the physical properties of cementitious materials and their effect on water transport.

SEM studies of wasteform durability

A standard method of studying nuclear wasteforms involves sectioning the material and examination with electron microscopy. As part of our research program, we investigated the aqueous durability of a possible candidate wasteform for Australian radioactive waste. A series of medium term (up to 92 months) durability tests, without leachate replacement, was conducted on samples of this wasteform. The wasteform was made from cement, ground granulated blast furnace slag and a simulated waste liquor. The wasteform was an inhomogeneous mixture containing calcite, a calcium silicate hydrate phase, hydrotalcite and unreacted slag particles.

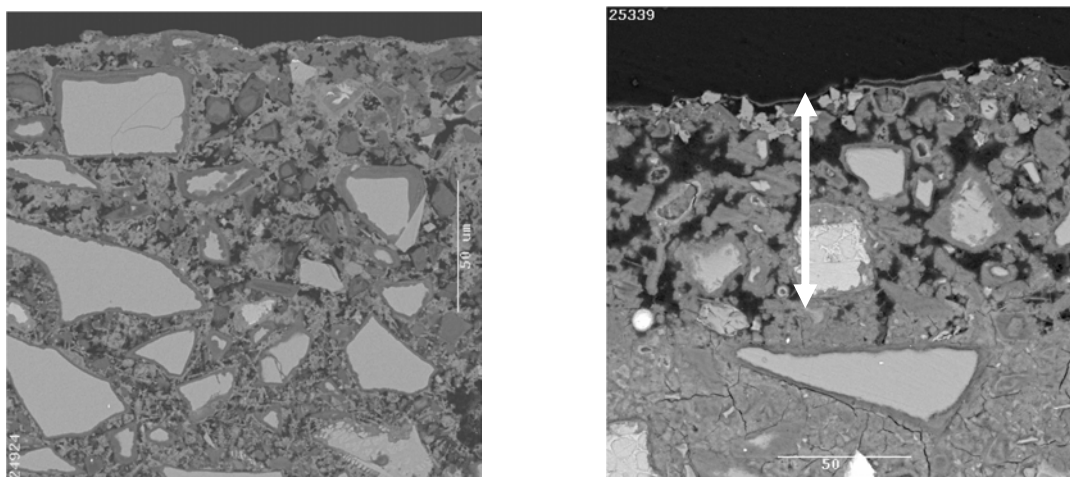
The unleached samples were white in colour on the surface, but dark grey and mottled on the interior. Optical microscopy showed the white surface layer on the cement cylinders was approximately 800µm deep. The surface of the samples was smooth with no signs of cracking. After leaching, irrespective of the leaching period (1, 3, 6 or 92 months), the specimens exhibited cracking on the surface and a deterioration of their structural integrity.

Scanning Electron Microscopy (SEM), incorporating Energy Dispersive X-ray Spectrometry (EDS), was used to characterize the unleached specimens and those leached for 92 months. SEM/EDS showed a high degree of inhomogeneity in the wasteform (see Figure 1). EDS analysis was variable and the back-scattered electron images divided components into three groups - unreacted slag, reacted slag and cement matrix (including calcite). From a wasteform point of view, the matrix is the primary phase for waste encapsulation thus the focus of the SEM/EDS investigations.

The cement specimen leached for 92 months exhibited corrosion to a variable depth, on average about 80 µm (see Figure 1). Analysis by EDS was carried out on a few areas within the

altered zone, and distal to the zone for comparison of elemental composition. The most notable feature was the decrease in Ca content within the corroded zone, dropping on average by about 10 wt% compared to that in the unaltered zone. The Ca content within the unaltered zone was similar to that of the matrix in the unleached wasteform. Concentrations of Al and Si in the leached cement matrix (both within and outside the altered zone) were not significantly different from that of the unleached wasteform. These observations reflect a dissolution front which leaves behind a zone of decalcified CSH surrounding an uncorroded core [1].

Figure 1: SEM photomicrographs of unleached (left image) and leached (right image) specimens (both x500 magnification). Composition is primarily slag particles in a cement matrix. Porosity caused by leaching evident to a depth of about 80 μm (shown by white arrow).



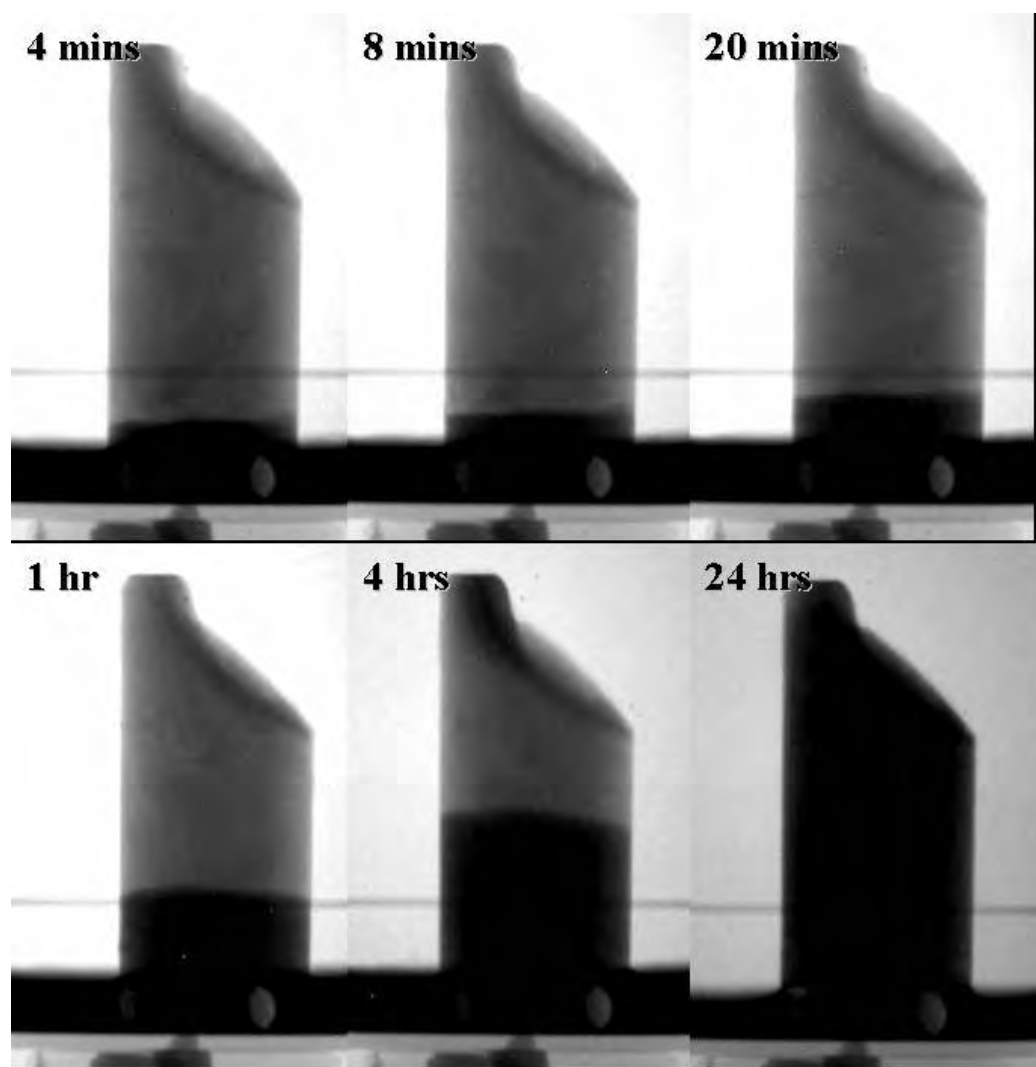
Water ingress properties determined by neutron radiography

The technique of neutron radiography provides a non-destructive method to quantify water movement in cement, and enables comparisons between cementitious materials having different compositional and structural/physical properties. We investigated the applicability of this technique to a number of samples of interest in the present study, including cement pastes and several mortars with water:cement ratios (w:c) of 0.42 and 0.80. Neutron Radiography (NRad) provides similar images to X-ray radiography, but whereas X-ray attenuation is dependent on atomic number, neutrons are efficiently attenuated by specific elements, particularly hydrogen rich materials such as water or organic matter. The visibility of water is a key attribute for our current application.

In each case, samples were covered in aluminium tape except for one end-face to facilitate water transport in one direction only. The cylinders were partially immersed to a depth of about 2 mm so that the uncovered face was in constant contact with tap water at room temperature. At pre-defined time intervals, samples were removed from the water, weighed and transferred to the NRad facility to collect radiographic data. The facility equipment was arranged so that the sample remained partially immersed during data acquisition. The NRad facility has been described elsewhere [2] and in a single neutron radiograph the images came from a 5 second exposure time with a spatial resolution of 0.094 mm/pixel. Water contents were computed from the image using procedures already published [3].

A time series of neutron radiographs for one of the mortar samples (w:c = 0.80) is given in Figure 2, showing the progressive ingress of water within the sample. These data can be used to compute sorptivity relationships as has been discussed previously [4].

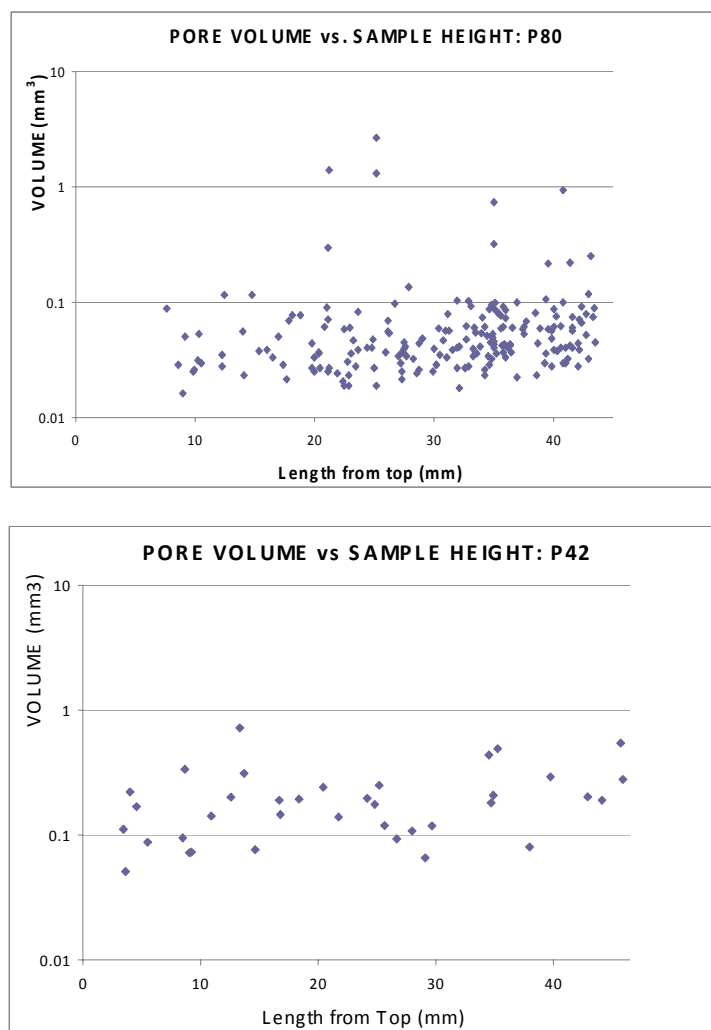
Figure 2: Neutron radiographs depicting water front movement as a function of time through the mortar with w:c of 0.80.



Neutron tomography measurements of pore volume distributions

Neutron tomography provided cross-sectional images of the cement samples from transmission data, obtained by irradiating each sample from many different directions. In the present work, the macro-pore distributions were constructed using the neutron tomography data. Figure 3 presents macro-pore volume distribution graphs as a function of depth within the sample for the two cement pastes studied (w:c = 0.42 and 0.80 respectively). In these figures, each data point indicates a detected pore with the indicated volume. Thus the density of points reflects the number of pores and their spread indicates the size distribution. The plots show the relationship of higher porosity with higher water content of the cement paste.

Figure 3. Pore volume distribution of samples as determined by neutron tomography. Note the observed differences between the two samples reflecting the effect of the w:c ratio



Summary

The physical properties of cementitious materials (both wasteforms and barriers) are critical in determining the long-term behaviour of nuclear waste repositories. Chemical leaching tests and analyses by techniques such as electron microscopy can be augmented by neutron radiography and tomography. These methods provide a useful non-destructive method of determining properties related to water transport in cementitious materials, in particular the sorptivity and pore size distribution.

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15 - PHYSICO-CHEMICAL IMPACTS OF CEMENTITIOUSLY-DERIVED CALCIUM AND SILICA ON SODIUM MONTMORILLONITE

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Introduction

The storage of nuclear waste frequently involves the construction of a concrete encasement adjacent to an engineered clay barrier, which can expose the swelling clay to elevated concentrations of certain cations (particularly calcium) and very high alkalinity (pH 10 - 13). These conditions have the capacity to degrade the integrity of the clay layer and, as such, it is necessary to fully understand the effects of all possible biogeochemical interactions involved. In this study, the changes in hydraulic conductivities and other physico-chemical properties of Na-montmorillonite assemblages under the influence of both highly alkaline (pH 9 and 12) conditions and elevated concentrations of calcium and silica are examined.

Methods

Na-montmorillonite suspensions & filtration experimental method

Colloidal montmorillonite suspensions were prepared from a naturally-sourced Australian bentonite which was dispersed in MilliQ water and size-fractionated by centrifugation before mixing with NaCl (to 1 molL⁻¹). No chemical pre-treatment of the clay was employed with the end product being a homo-ionic Na-montmorillonite suspension. The stock suspensions were stored at 4°C until used. All subsequent experiments were performed on ten-fold Milli-Q dilutions of Na-montmorillonite gel which had solid contents of ~ 9 g/L. Natural pH was ~8.9, with adjustments made with micro litre additions of concentrated NaOH and HCl.

A constant pressure filtration method was employed to examine the hydraulic properties of the Na-montmorillonite using the rigorous method developed by Smiles (1986; 2000). By differentiating the liquid flow relative to the solid phase, the cumulative outflow and cake moisture contents can be used to calculate the material hydraulic conductivity, contingent on the matric potential. Further details on the implementation of this methodology for the characterisation of swelling clay materials can be found in Santiwong *et al.* (2008a; 2008b). Fresh Na-montmorillonite suspensions were made from concentrated stock gels for each salt concentration and pH condition to avoid any ageing effects. A summary of the different feed suspensions used for the filtration experiments is given in Table 1.

Filtration experiments were performed on 50 mL volumes of feed suspensions dispensed into a Perspex filtration cell, designed to pass through a membrane (\varnothing 0.044 m) at its base. The membrane used for all filtration experiments was a micro filtration membrane with an average pore size of 0.22 μ m (DURAPORE®, Millipore) and was chosen to ensure the complete retention of clay and other solid particles on the feed-side of the membrane. Cumulative permeate outflow was measured using an electronic balance connected to a computer for instantaneous logging.

After each filtration run, both wet and dry weights of the filter cakes were determined, with the dry cakes weighed after > 48 hrs at 105°C.

Table 1: **Various treatment conditions of the montmorillonite suspensions**

Feed conditions	pH	Suspension Concentrations		
		Na (mM)	Ca (mM)	SiO ₃ (mM)
1	9	100	--	--
2	12	100	--	--
3	9	100	50	--
4	12	100	50	--
5	9	100	--	10
6	12	100	--	10
7	9	100	50	10
8	12	100	50	10

Further physico-chemical characterisation techniques

Electrophoresis measurements were performed using a Zetasizer Nano ZS (Malvern Instruments). Measurements of electrophoretic mobilities were made within folded capillary cells, with the ionic strength calculated simultaneously. All electrophoresis measurements were made on suspensions that were mixed > 24 hrs previously, in order to ensure equilibrium had been attained. Scanning electron microscopy (SEM) of the various montmorillonite assemblages were performed using the cryo-snap preparation process detailed in Santiwong *et al.* (2008b). Briefly, small strips of fresh filtered montmorillonite cakes were momentarily immersed in liquid-N₂, after which they could be snapped to produce an untouched edge that could be imaged using a non-cryogenic / high-vacuum (normal) stage. All SEM images were performed on an XL 30 CP SEM (Philips) at 15 kV.

Results & Discussion

Hydraulic Properties

A summary of the hydraulic properties across the eight feed suspensions is contained in Table 2. The results show a ~ 65-fold variation in hydraulic conductivity between the highest conducting sample (pH = 12 + 50 mM calcium + 10 mM silica) and the lowest conducting sample (pH = 12) at 5 kPa. The moisture ratios also showed large discrepancies between samples, although not consistent with the hydraulic conductivities.

Table 2: **Summarised void (or moisture) ratio and hydraulic conductivity (at 5 kPa)**

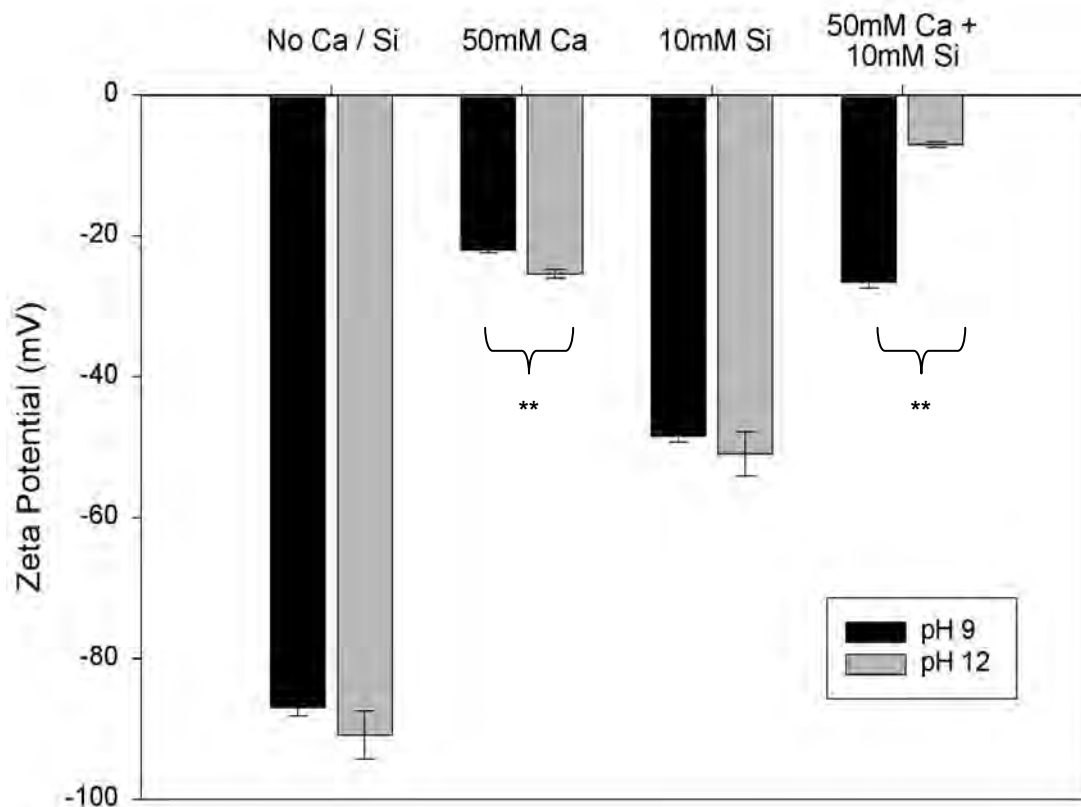
Ca	Si	Void Ratio (m ⁻³ / m ⁻³)		<i>k</i> (mm day ⁻¹)	
		pH 9	pH 12	pH 9	pH 12
--	--	44.4	56.5	3.78	3.47
50mM	--	47.2	31.8	100.92	192.37
--	10mM	72.0	56.1	6.31	2.55
50mM	10mM	106.1	88.8	116.68	179.76

Further physico-chemical characterisation

The zeta potential values obtained for the different additions of calcium and silica showed little variation between the paired pH values (9 & 12), except for the combined 50 mM calcium and 10 mM silica sample and, to a lesser extent, between the 50 mM calcium samples (Figure 1). However, there were significant differences between the unmodified sample and addition of 50mM calcium, 10mM silica and combined calcium / silica samples at their respective pH ($P < 0.05$). The large contrast in values upon the addition of 50 mM calcium is indicative of a significant compression of the electrical double layer.

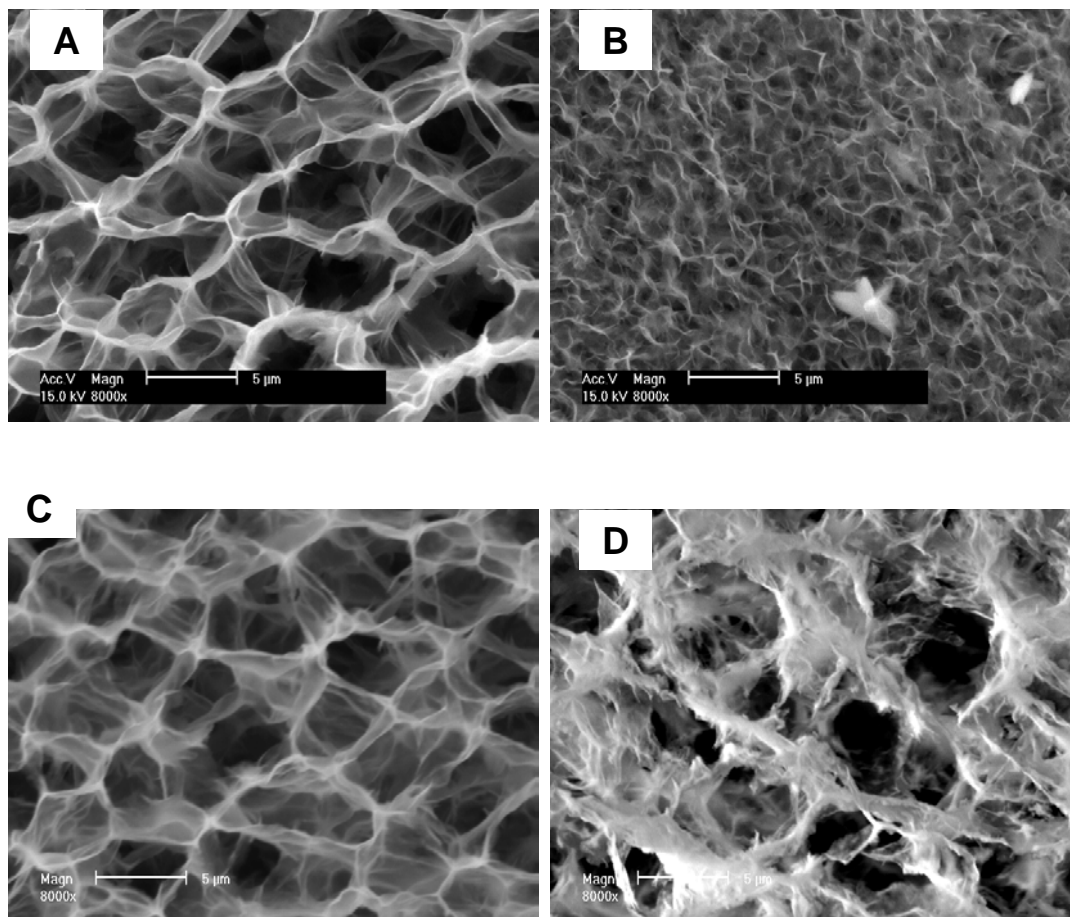
The SEM micrographs (Figure 2) show a dramatic difference in pore size and in their overall

Figure 1: **Zeta potential for all eight Na-montmorillonite suspensions** (** $P < 0.05$)



structural assemblage between the various filter cakes. The Na-montmorillonite without calcium or silica (Figure 2A), along with the 10 mM silica sample (Figure 2C), displayed the largest pore size of the samples (2 to 5 μm) despite being previously shown to have the lowest hydraulic conductivity. Conversely, the samples with the highest hydraulic conductivity, those with additions of calcium, exhibited a much smaller pore network (Figures 2B and D).

Figure 2: SEM micrographs of the filter cakes; A) the unaltered Na-montmorillonite, B) with 50 mM calcium, C) with 10 mM silica, and D) with 50 mM calcium and 10 mM silica. All cakes were prepared at pH 12, and under the applied pressure of 20 kPa. The scale bar in all images is 5 μm (8000 x magnification)



Along with the strongly negative zeta potential measurements (Figure 1), edge-face attraction under these conditions is not expected, with repulsion being the dominant mode of interaction. In terms of the orientation of the repulsive assemblage (i.e. edge-edge or face-face), the SEM micrograph of the unaltered alkaline montmorillonite (Figure 2A), resembles a macro-scale structure with pore sizes in the order of 2 to 5 μm . Previous research on dilute swelling clay suspensions has shown the position of lowest potential energy is likely to be edge-edge contact (M'Ewen and Mould 1957), although work by Benna and colleagues (1999) on purified Na-montmorillonite at high pH, suggested a card-house structure of edge-edge, edge-face and face-face repulsion.

The presence of the Ca^{2+} ions promotes the contraction of the electric double layer, as shown by the significant increase in zeta potential (Figure 1), effectively reducing the size of individual tactoids. It follows that the addition of calcium also reduces inter-tactoid repulsion, minimising pore-space and consolidating the filter cake assemblage. Lagaly and colleagues have reported that calcium ions promote the development of face-face contacts and the associated formation of quasicrystalline, band-like structures (e.g. Brandenburg and Lagaly 1988). The SEM micrograph shows a substantial reduction in pore size (Figure 2B), which corresponded to an enhanced movement of water. This would suggest that the sizes of the individual pore-spaces do not reflect the hydraulic conductivity of a Na-montmorillonite gel, but rather the forces acting on the water and the overall meso-structure are more determining factors.

The influence of silica alone appears to have had little impact on the hydraulic properties and structural assemblage of the clay; although an insufficient equilibration time for complete polymerisation to occur may have been a contributing factor to this result. Contrastingly, when in combination with Ca^{2+} , we see physico-chemical changes to the suspensions that cannot be accounted by the divalent calcium alone. Owing to its polymeric properties (a factor enhanced by interlinking Ca^{2+}), the negatively charged dissolved silica is able to form a more stable diffuse layer, most likely through bridging associations between the tactoids, as seen in Figure 2D. The differing zeta potential values between pH 9 and 12 could be due to the mono-/divalent transition of silica (pK_a 9.91; Falcone 1982), with the divalent silicate further enhancing the influence of the electrical double layer.

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16 - PHYSICO-CHEMICAL INVESTIGATION OF CEMENT CARBONATION IN AQUEOUS SOLUTION IN EQUILIBRIUM WITH CALCITE AND WITH A CONTROLLED CO₂ PARTIAL PRESSURE AT 25 AND 50°C

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Introduction

In the framework of radioactive waste geological disposal, structural concretes have to be adapted to underground chemical conditions (Andra, 2005). A limited impact on the environment is also required. Ordinary Portland Cement, CEM I type, are characterized by high pH (higher than 13) which could produce an alkaline plume in the repository near-field. To avoid this issue, new cementitious binders, called low pH, were designed (pH lower than 11). In contact with a rock-clay formation, cement mineralogy will evaluate due to combined various chemical degradations: leaching, carbonation, chloride and sulfate attacks. The different types of interaction between clay materials and cementitious materials were studied by experimental approach (Read *and al.*, 2001; Kurashige *and al.*, 2007) and modelling approach (Trotignon *and al.*, 2006). For concrete in water saturated medium, it's believed that carbonation will have a major impact on the interaction between concrete and the geological medium. So, to understand the complex degradation of the cement paste in that context, it's interesting to study a simplified system such as degradation in carbonated water solution. This solution must be at equilibrium with a CO₂ partial pressure 30 times higher than the atmospheric pCO₂, to reproduce underground natural conditions of Callovo-Oxfordian clayey rock of Bure (France). The study's aim is to compare the behaviour of the new low pH material (CEM I + silica fume + fly ashes) with a CEM I cement paste, both of them being submitted to carbonation in aqueous solution in equilibrium with calcite and with a pCO₂ equal to 1.32 kPa (1.3 10⁻² atm). Two different temperatures, 25 and 50°C, are considered. To realize these experiments, two different original types of devices were developed. This study was carried out thank to the financial support of the Andra.

Experimental procedure

Materials

Two types of materials are studied. The first one is a cement paste prepared by mixing an ordinary portland cement with distilled water with a ratio of 0.4 (w/c). The cement employed is a French cement type CEM I 52.5 PM ES CP2 (Lafarge). The composition of the OPC used is presented in Table 1. After a 6 years curing period under water, slice (= 7 cm/ h= 2 cm) were sawn from the cement paste specimens. The periphery is protected from degradation thank to an unreactive resin.

Table 1: Chemical composition of the OPC cement used for CEM I cement paste (all values are in mass %)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	Total
20.9	3.2	4.6	65.1	0.6	2.76	0.1	0.6	0.6	1.1	99.56

The second one is a new low pH material prepared by mixing CEM I cement (37.5 % in mass), fly ash (30 % in mass), silica fume (32.5 % in mass) with distilled water with a ratio of 0.4 (Codina *and al.*, 2008). The cement employed was a French cement type CEM I 52.5 N CE PM-ES-CP2 (Lafarge). The compositions of the CEM I cement, the fly ash and the silica fume used are presented in Table 2.

Table 2: Chemical composition of the CEM I cement, the fly ash (FA) and the silica fume (SF) used for low pH material (all values are in mass %)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	Total
CEM I	22.2	2.9	2.6	66.8	0.9	2.2	0.2	0.2	0.2	1.5	99.5
FA	51.5	11.6	0.6	5.1	1.8	0.7	0.4	1.3	1.0	4.8	98.9
SF	96.3	<0.2	0.1	0.5	<0.2	0.2	<0.2	0.3	0.1	2.2	99.8

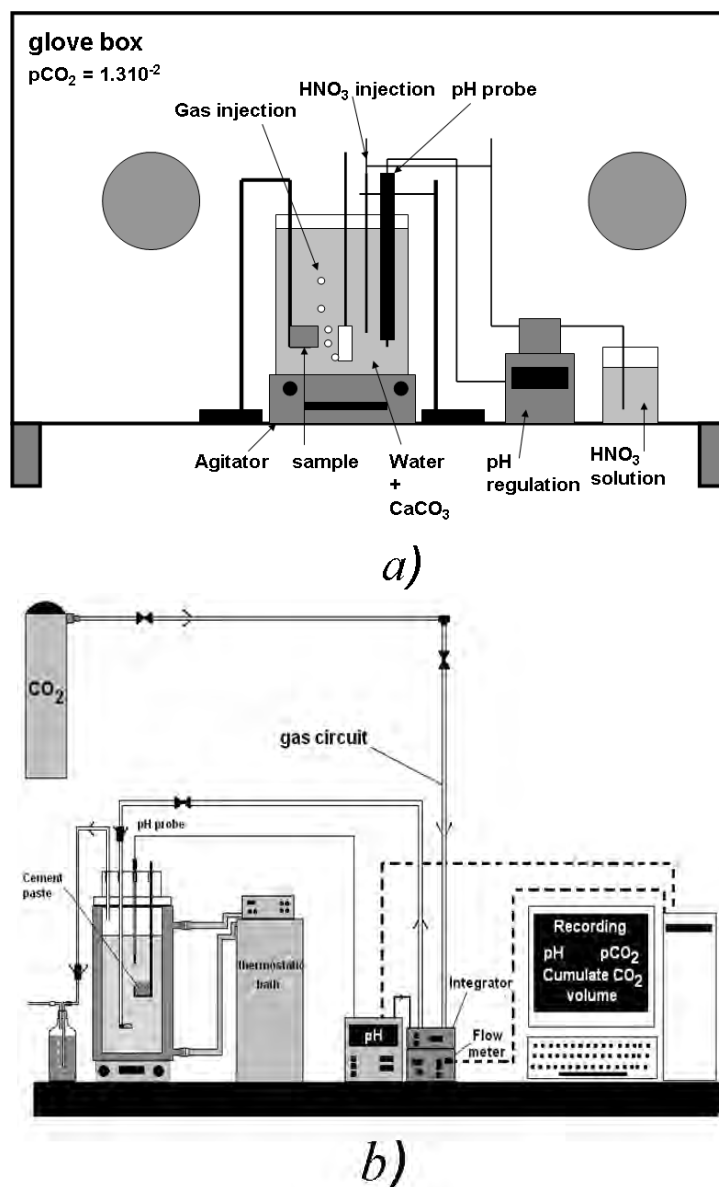
After a 6 months curing period under water, slice ($= 7 \text{ cm} / h = 2 \text{ cm}$) were sawn from the cement paste specimens. The periphery is protected from degradation thank to an unreactive resin.

Procedures

The aggressive solution is an aqueous solution in equilibrium with calcite and with a $p\text{CO}_2$ equal to 1.32 kPa ($1.3 \cdot 10^{-2} \text{ atm}$). Theses conditions control the pH of the aggressive solution. The theoretical pH is 7.2 and 7.22 at respectively 25°C and 50°C. Two original types of devices were developed. The first one was used for the experiments at 25°C (Figure 1.a). It consists of a glove box in which the $p\text{CO}_2$ is held to 1.32 kPa ($1.3 \cdot 10^{-2} \text{ atm}$), thank to a mix of CO₂ and N₂. The possible pH increase above the pH reference (7.3), in the leaching reactor, could be compensated by addition of HNO₃ solution.

The second type of devices is used for experiments at 50°C (figure 1. b). In that case, the pH and $p\text{CO}_2$ are maintained constant, in the leaching reactor, during the experiment using CO₂ flow-meter controlled by pH regulator (Dauzères *and al.*, 2009).

Figure 1: Experimental devices used to achieve the carbonation of cement paste in aqueous solution in equilibrium with calcite and with a $p\text{CO}_2$ equals to 1.32 kPa ($1.310 \cdot 10^{-2}$ atm) at 25°C (a) and 50°C (b)



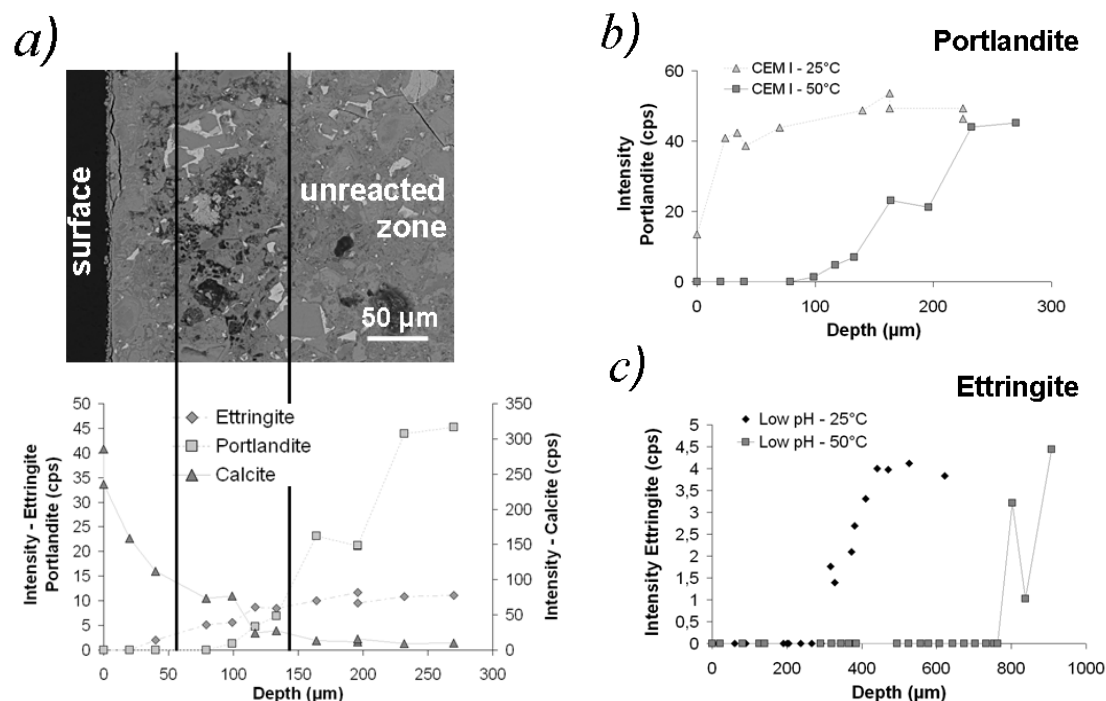
Cement pastes are immersed in the solution for one month in 1.8 or 4 litres for experiments at respectively 25°C or 50°C. The leaching solution is renewed periodically.

Results

The major information is given by solid analysis: XRD and SEM. The mineralogical evolution inside the degraded material is studied thanks to XRD analysis. A diffraction diagram is made at different depths relative to the initial surface, by polishing the sample. The results are presented with the intensity of the principal peak of the phase of interest versus the depth at which the diagram is made. The interatomic spacing associated to the peak considered is 9.72, 4.9 and 3.03 Å for respectively ettringite, portlandite and calcite.

Figure 2: Solid analysis on CEM I cement paste (a and b) and of low pH materials (c) leached in an aqueous solution in equilibrium with calcite and a $p\text{CO}_2$ equals to 1.32 kPa (1.310^{-2} atm).

Comparison with SEM observation and XRD analyses is made for the degradation experiment on CEM I cement paste at 50°C (a). XRD analyses for the experiments at 25°C and 50°C is presented for CEM I cement paste (b) and low pH material (c).



Portlandite and ettringite leaching and calcite precipitation close to the surface are the phenomena observed for CEM I paste (Figure 2. a). These observations confirm anterior ones (Richet *and al.*, 2004). The comparison of SEM observation and XRD analyses, for a CEM I paste degraded at 50°C, show that calcite precipitation is associated to pore clogging. The densified microstructure zone, due to calcite precipitation, is followed by a micro-porous zone, due to portlandite dissolution. Beside, exogenous calcite crust formation is observed. A 30 and 240 μm depth degraded zone, characterized by the portlandite dissolution, is identified at respectively 25°C and 50°C (Figure 2. b). This observation is compatible with previous hydrolysis studies in temperature (Peycelon *and al.*, 2006).

The XRD analyses is more difficult with low pH paste because the latter contains few crystallized phase. There is no portlandite detected due to the high content of pozzolanic material. Nevertheless, calcite precipitation and ettringite dissolution (Figure 2. c) on the whole altered layer are the transformations witnessed. As for CEM I paste, the temperature increase from 25°C to 50°C induces a deeper degraded zone. The low pH binder shows a degraded thickness much higher than the CEM I paste. Indeed, the CEM I pastes are more reactive to carbonation and a carbonated surface layer is quickly formed. This carbonated surface layer seems to limit the transport process. Precipitation of calcite inhibiting cementitious materials degradation was observed in rich hydrogencarbonate solution (Kurashige *and al.*, 2007). The difficulties of XRD analysis of low pH material show the necessity to use another solid technical characterisation such as SEM to quantify the CaO/SiO₂ ratio (C/S) in the degraded zone.

Conclusion

Carbonation seems to have a major influence on the interaction between concrete and the geological medium. To study the carbonation of cement paste in an aqueous solution in equilibrium with calcite and a CO₂ partial pressure equals to 1.32 kPa ($1.3 \cdot 10^{-2}$ atm), two original devices were developed. The behaviour of the new low pH material (CEM I + silica fume + fly ashes) and a CEM I cement paste is studied at two different temperatures: 25 and 50°C. For CEM I paste, portlandite dissolution front informs on the degraded zone depth. The precipitation of calcite at the surface induces the pore clogging and the formation of a densified microstructure zone at the surface. Low pH material present a degraded zone deeper compared to CEM I paste. The same phenomenology is observed at 25 and 50°C, but at 50°C, the degraded zone thickness is greater.

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17 - THE STABILITY OF ZEOLITES AND C-S-H IN THE HIGH pH REACTION OF BENTONITE

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Cement-bentonite interactions will occur in deep geological repositories for high level radioactive waste. We performed laboratory experiments in order to constrain some previous geochemical and mineralogical uncertainties in the formation of secondary minerals in the high pH reaction of FEBEX bentonite at moderate temperatures.

The reactivity of a Mg-homoionic FEBEX bentonite was studied at 25, 60 and 90 °C in batch reactors using two solutions representative of short and long time evolution stages of cement degradation. These were a “young” cement water (YCW or K-Na-OH solution) and an evolved cement water (ECW or Ca(OH)₂-saturated solution) controlled by portlandite dissolution. They were periodically renewed in order to maintain a constant pH regime for a period of almost 2 years. A Mg-saturated bentonite was mixed with the alkaline solution, either YCW or ECW, at a solid/solution mass ratio of 1:5. Aqueous chemistry, mineralogy, microstructural and crystallochemical parameters were studied for the reaction.

The main phases obtained in the reaction with YCW, were K-zeolites, mainly chabazite (60 °C) or merlinoite (90 °C), Figure 1. No significant reaction was detected in the 25 °C experiments. The chemical compositions of chabazite and merlinoite obtained in the YCW experiments at 60 and 90 °C exhibit Si/Al ratios close to 2:1, similar to those reported in previous studies (Dohahoe *et al.*, 1990a; Skofteland *et al.*, 2001; Yakubovich *et al.*, 2005). In order to account for the thermodynamic variables considering the crystallochemical characteristics of the minerals found in this study, two calculations were carried out: 1) a theoretical approach consisting of the calculation at 25 °C and 1 bar of the apparent Gibbs free energy of formation ($\Delta G_{f,298.15}^{\circ}$) and enthalpy of formation ($\Delta H_{f,298.15}^{\circ}$) from the sum of the polyhedral contributions (Chermak and Rimstidt, 1989); and 2) the use of experimental thermochemical data ($\Delta H_{f,298.15}^{\circ}$) obtained for synthetic chabazite and merlinoite of variable compositions.

The method derived from the sum of polyhedral contributions (approach 1) does not show good agreement between the experimental data and the theoretical equilibrium of zeolites but with the use of regression methods (approach 2), Figure 2, the calculated constants indicate a close agreement with favourable conditions for merlinoite formation at 60 – 90 °C. Chabazite is metastable in the whole range of temperatures (Figure 2). As established by Skofteland *et al.* (2001), K is preferentially stabilised in the buckled eight rings of merlinoite, which form a perfect nest for the potassium ion. The favoured potassium site in chabazite is also occupied by many other cations (Yakubovich *et al.*, 1999; Smith *et al.*, 1989; Shim *et al.*, 1999).

Figure 1: Formation of merlinoite at the expense of chabazite observed at 90 °C by SEM in the 5- to 50- μm fraction

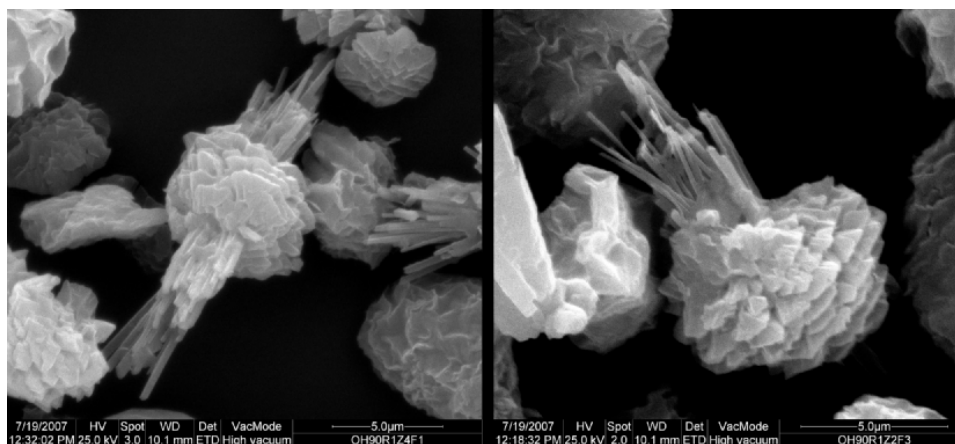
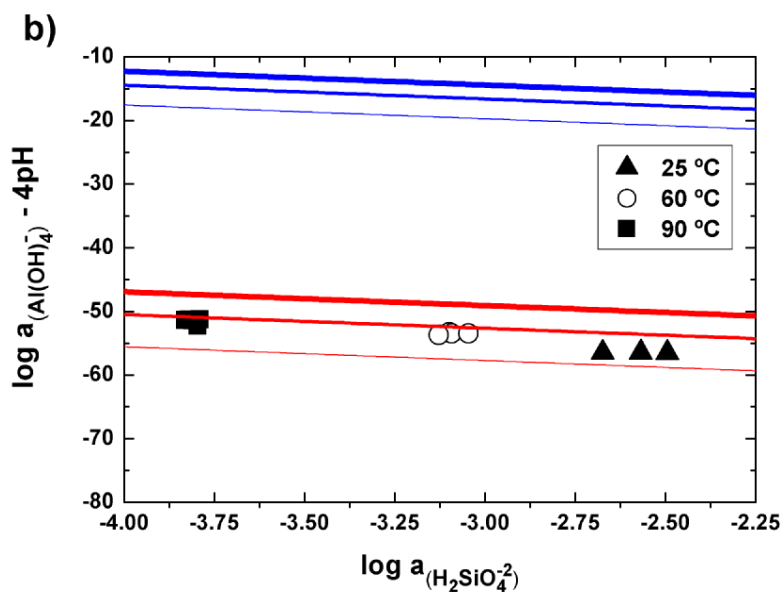


Figure 2: Solubility diagrams as a function of temperature for the 5- to 50- μm fraction of chabazite (blue) and merlinoite (red).



Zeolite occurrence has been observed as one of the main characteristics in the hyperalkaline reaction of FEBEX bentonite (sodium and potassium hydroxide solutions in the presence or absence of portlandite). This is relevant in order to constrain the reactivity of the clay barrier in the repository. It has been observed that the type of zeolites formed depends mainly on the chemical composition of the aqueous solution, the pH and temperature of the reaction and the amount of zeolite formed over the time of treatment. In addition, the type of alkaline cation favours the crystallisation sequence (Vigil de la Villa *et al.*, 2001). One novelty of the present work with respect to earlier studies is that the pH was maintained at high and almost constant values (12.8 – 13.5) over the reaction time. Under these conditions, chabazite precipitates in addition to phillipsite at 60 °C, while merlinoite is the favoured zeolite at 90 °C.

The results demonstrate that zeolites are likely to form at very high pH values when the aqueous Ca concentration is low. The general consensus is that C-(A)-S-H phases form in the cement – bentonite interface at a higher pH than zeolites (Savage *et al.*, 2007).

The compilation of data obtained in the present work and previous studies (Vigil de la Villa *et al.*, 2001; Ramírez *et al.*, 2002a; Sánchez *et al.*, 2006) on the alkaline reaction of FEBEX bentonite in batch experiments confirm that the rise in temperature at similar hydroxide activity values is the main controlling factor in the formation of zeolites. However, the type of zeolite is clearly controlled by the type and concentration of the alkaline solution. See Table 1.

Table 1: **Zeolite occurrence as a function of temperature, type of solution, final pH (measured at room temperature) and calculated hydroxide activity. The Si/Al mole ratio in the zeolite composition is indicated in parenthesis and the hydroxide activity within brackets. phil = phillipsite; ac = analcime; ch = chabazite and m = merlinoite. N.A. = Not Accomplished.**

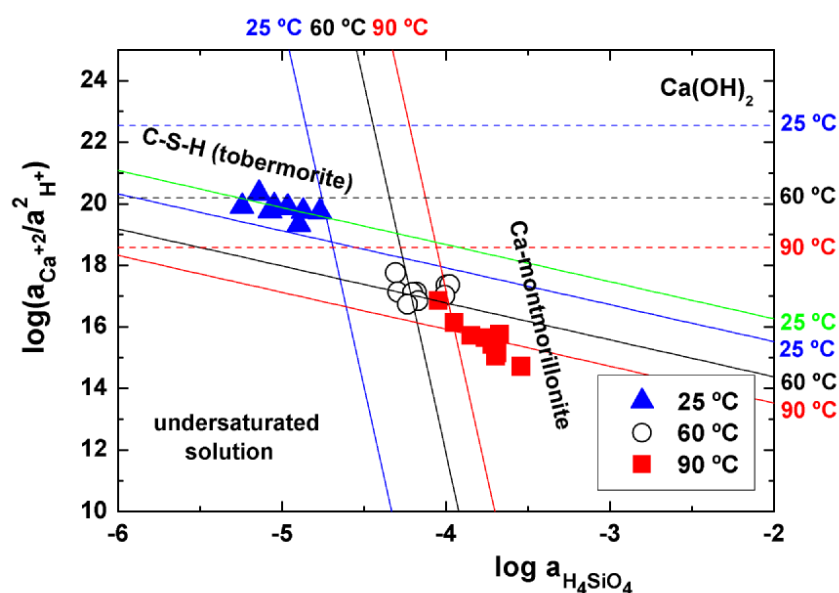
	KOH dominant solutions			NaOH solutions			
T (°C) / pH [a_{OH^-}]	13.5	13	12.5 – 12	12	11 – 10.5	10 – 9.5	9
25 – 35	-	-	phil (1.9) [3.2E-1]	-	-	-	-
60 – 75	ch / m-phil (2.1) [2.6E-1]	-	phil (2.0) [3.2E-1]	phil (2) [3.2E-1]	-	-	-
90	-	ch (2.1) / m (2.2) [2.5E-1]	phil (2.2) [3.2E-1]	phil / ac (2.2- 2.3) [3.1E-1]	-	-	-
125	N.A.	N.A.	N.A.	-	ac (2.5) [2.9E-1]	ac (2.6) [1.6E-1 – 7.1E-2]	-
200	N.A.	N.A.	N.A.	-	-	ac (2.8) [3.8E-2]	ac (2.9) [5.1E-3]

In the ECW experiments, the slow montmorillonite dissolution reaction observed at pH values near 11 indicate a possible equilibrium between montmorillonite and the reaction products (C-S-H type phases) of the alkaline reaction $Ca(OH)_2$ – bentonite. Taking into account the possible presence of low crystalline C-S-H phases in this experiment, we thermodynamically evaluated the chemical stability of the experimental solutions in the system portlandite – Ca-montmorillonite – tobermorite-11Å (as a thermodynamically stable approach for a low Ca/Si ratio C-S-H phase), using the EQ3/6 database (Wolery, 1992). At 60 and 90 °C, the experimental aqueous activities agree with the equilibrium between tobermorite and montmorillonite in a portlandite unsaturated solution and support the assumption of precipitation of a crystalline

phase, but at 25 °C, the equilibrium is not yet reached, Figure 3. Nevertheless, the scientific literature shows a wide range of chemical compositions and thermodynamic constants for the C-S-H and therefore, the interpretation of the equilibrium modelling with respect to the experimental aqueous compositions is highly dependent on the thermodynamic data used. In order to evaluate the robustness of the C-S-H role in the equilibrium model, a C-S-H tobermorite-type phase, for which the thermodynamic properties were calculated by Kulik and Kersten (2001) at standard conditions (25 °C, 1 bar), was also evaluated. Equilibrium activity calculations fit, at 25 °C, better with CSH than with the tobermorite-11Å from EQ3/6, and then predict equilibrium conditions controlled by C-S-H (amorphous) precipitation.

Finally, we should remark that zeolites are shown likely to form at very high pH, low Ca concentration and in batch conditions. For the case of compacted bentonite experiments just traces of zeolites were found at the cement-concrete interface (EC project NF-PRO) and tend to indicate that such mineral formation may not occur significantly in compacted media.

Figure 3: Activity diagram showing the equilibrium conditions in the system $\text{SiO}_2\text{-CaO-H}_2\text{O}$ for the experimental data as a function of temperature (the green line represents the equilibrium of the C-S-H tobermorite-type phase calculated by Kulik and Kersten, 2001).



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18 - REVIEW OF SORPTION VALUES FOR THE CEMENTITIOUS NEAR FIELD OF A NEAR-SURFACE RADIOACTIVE WASTE DISPOSAL FACILITY

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This paper reports part of the documentation being assembled by ONDRAF/NIRAS to support the safety assessment of the near-surface disposal of short-lived low and intermediate level waste (LILW-SL) or category A waste at Dessel, Belgium. The aim of this study was to establish a sorption database of critical radionuclides and chemotoxic elements on concrete through literature review and data selection with the support of an international panel of experts (for details see Wang et al., 2009). The database compiles sorption values in the form of distribution coefficients (K_d values) or distribution ratios (R_d values) for radionuclides sorption on cementitious materials. The database is to be used in safety assessment calculations to quantify the retardation of safety relevant radionuclides in the cementitious near field. Sorption values were critically reviewed and selected for both reducing and oxidizing conditions. Therefore, the resulting sorption values are also applicable to geological disposal studies. To support the evaluation of sorption values, solubility of concerned elements was also discussed.

The data base contains sorption values for sixteen elements that need to be considered in detailed impact calculations for the near-surface disposal facility of Dessel. Mainly based on literature data, best estimate sorption values in addition to upper and lower bound values were determined. The basic data consider sorption on cementitious materials made from benchmark cement, which is pure Ordinary Portland cement without effects of organic additives, high concentrations of chloride or other ions. Effects of organics and other perturbing components are also discussed. The geochemical evolution of the cementitious near field was also addressed, as this provides valuable information on the evolution of the cement pore water composition and the mineral composition of concrete, required for developing site-specific and chemical condition dependent sorption data. Four characteristic degradation states of concrete were defined and sorption data for each state were selected.

A considerable part of the scientific basis for each of these topics was established at meetings of a Panel of Experts who reviewed work on each topic carried out by SCK•CEN and also provided advice and additional information. The strategy comprised a structured approach, using expert evaluation where relevant literature data exist, and expert estimation of K_d or R_d values on the basis of analogue information where no relevant literature data are available. To justify the selected sorption values, it is emphasized throughout this study that selected sorption values should be supported, to the greatest extent possible, by scientific arguments and process understanding.

To be able to perform a defensible long-term safety assessment of the Dessel near-surface disposal facility, a scientific basis is needed to quantify the safety function R3 (retardation of contaminant migration as defined by ONDRAF/NIRAS, De Preter, 2007) and its long-term evolution. Such basis should cover the following topics:

- Chemical degradation mechanisms and evolution of chemical conditions governed by the degradation of cementitious engineered barrier components;

- Selection of K_d as a function of cement degradation state;
- Evaluation of K_d variation possibly related to the evolution of cement composition;
- Geochemical evolutionary path (evolution of pH, Eh, dissolved major ions, amount of minerals) which defines a varying chemical condition under which sorption values are required;
- Impact of organics and their potential degradation products on radionuclide behaviour;
- Impact of other potentially perturbing components.

The modus operandi of the Expert Panel meetings is briefly summarized as follows: the panel of international experts was providing guidance to the initial sorption review performed by SCK•CEN; the review was first checked for:

- *reliability*: The panel agreed that they must be fully aware how reliable the data are that they are using. Several issues were discussed:
 - It was generally agreed that data from batch experiments are preferable. Data from through-flow experiments are a second choice. It was noted that there may be a distinction between what is scientifically best, (maybe batch R_d values) and what some stakeholders may see as best (maybe through-flow experiments). However, it was stressed that priority should be given to scientific aspects to achieve a data base that reflects the best scientific understanding.
 - Experts pointed out that it is essential for traceability and defensibility to clearly separate what has been used for K_d derivation from any further supporting arguments and "conservatism". For example: K_d for a given radioelement may be selected only on the basis of batch data from simplified systems to arrive at a "best" and most reliable estimate. If this selection can be further supported by transport data in complex systems closer to repository conditions, then that is fine - but this must not be mixed in with the actual selection process.
 - It was stressed that the experts must be aware of the implicit assumptions involved in the K_d approach. One of the implicit assumptions regarding K_d is reversibility. It was noted that hydrated cement systems are fairly special in this sense, because (at least within many experimental setups) the sorbing solid is undergoing alterations while sorption is taking place (this can lead to incorporation of radionuclides). However, one should be careful to distinguish this from non-reversibility of the actual sorption reaction: apparent non-reversibility in sorption in a cement system may be due to the variation of the sorbing phase in cement and may have nothing to do with irreversible sorption in the thermodynamic sense.
 - There were concerns raised over the use of thermodynamic data in linear free-energy models. However it was suggested that some thermodynamic modelling would be necessary and would provide supporting information.
- *appropriateness for the Dessel disposal facility* (relevant cement systems, or more general, relevant solid phases, ...). It was highlighted that cement systems are highly reactive and will be affected by, for example, leaching. They behave differently to other less reactive systems, for example, clays. It was also noted that chemical conditions within a near-surface facility could be heterogeneous and the degree of water saturation in concrete could vary;
- *data quality*: a detailed review on the experimental procedure was carried out to ensure the reliability of the sorption values reported (any influence of solubility, i.e., concerned elements are really sorbed but not removed by precipitation, solid to liquid ratio used for sorption measurement, cement is a strong sorbent so the detection limit to the

measurement of radionuclide concentration must be sufficient to determine reliable K_d , i.e., experimental window), etc.;

- *time frames*: The number of time frames to use was discussed. It was decided that all four states of cement degradation should be considered as these were proportional to time, although the constants of proportionality were not exactly known;
- *heterogeneity*: It was noted that there are several types of heterogeneity that need to be considered. These include:
 - stable and radioactive isotopes of the same element need to be considered. The distribution of radioactive and non-radioactive wastes over the facility might be important in view of isotopic dilution;
 - organics within the waste packages and the potential impact of their degradation products on radionuclide sorption and migration in concrete;
 - wastes containing high chloride concentrations and the effect on sorption ;
 - degree of water saturation, which may well be different for different components within the repository. There was agreement among experts that water held in the interstitial pores in the cement gel may not have the same thermodynamic properties as bulk water, and therefore sorption values derived from bulk water experiments may not be applicable to gel pores;
- *completeness* (have all relevant data been considered?).

For each species, possible mechanisms explaining the sorption processes were discussed, thereby seeking consistency among chemically-similar species. For each element best estimate sorption values were derived for each of the four pH states, together with upper and lower bound values. For some elements insufficient data were available to allow best estimate values to be determined. In such cases, a chemical analogue was used where possible. Experts noted that there is a danger that large data sets that typically display a large scatter are given large error ranges (or upper and lower bounds), whereas small data sets with comparatively smaller scatter are given smaller error ranges. The error ranges indicated in this study should therefore be cautiously used, as their derivation is more driven by visual analysis of summary data plots rather than a statistical approach. The summary of best estimate sorption values for benchmark cement is shown in Table 4 for the four States of concrete degradation (for the reference temperature 25°C):

- *State 1*: pH greater than 12.5 at the early state of concrete degradation due to the presence of high concentrations of alkalis (Na and K);
- *State 2*: characterised by a pH around 12.5 controlled by the solubility of portlandite;
- *State 3*: a pH around 12.5 - 10.5 regulated by the equilibrium of C-S-H with the infiltrated water from the surrounding non-cementitious materials;
- *State 4*: the subsequent state with pH < 10.5 controlled by calcite (CaCO₃).

The current review is based largely on existing and well-accepted compilations including those from Wieland and Van Loon 2002 and Bradbury and Van Loon 1998, but tries to improve in terms of the following aspects:

- *Recent state-of-the-art data*: our review included new data and provided improved understanding about sorption mechanisms on cement established since the publication of existing data compilations;
- *Detailed and site specific near field geochemical conditions*: site specific information such as chemical compositions of rain waters, local soil and engineering cover materials and the interactions between soil and rain waters are considered in establishing the relevant geochemical boundary conditions for the selection of sorption values;

- *Sorption values for all stages of cement degradation:* the majority of the existing compilations deals with situations for deep geological disposal of radioactive waste, where only the initial state of cement degradation is relevant because of a very slow water flow and mineral dissolution/precipitation. For the near surface disposal facility at Dessel, the rate of water infiltration could be higher once the concrete engineered barriers have degraded physically/mechanically. In such case, cement degradation would proceed faster also, hence sorption values for highly degraded cement materials at later stages of cement degradation are also relevant. The current review therefore evaluated sorption values for all 4 stages of cement degradation;
- *Judgement of an international panel of experts:* unlike the majority of existing data compilations, the selected sorption values in the current review are endorsed by an international panel consisting of the following experts:
 - E. Giffaut (ANDRA, France)
 - M. Ochs (BMG, Switzerland)
 - C. Gallé and V. Blin (CEA Saclay, France)
 - B. Schwyn (NAGRA, Switzerland)
 - A. Hooper (Alan Hooper Consulting Ltd, UK)
 - S. Williams (NDA-RWMD, UK)
 - E. Wieland (PSI, Switzerland)
 - J. Berry and D. Lever (Serco, UK)
 - F. Glasser (University of Aberdeen, UK)

Table 4: Selected best estimate R_d (l/kg) values as function of cement degradation state.
^s inorganic carbon. i.d. = insufficient data. For Ni site-specific cement data were used to calculate R_d for States I, II, and III (bold face). Values between parentheses are for high chloride background concentrations

Element		State I	State II	State III	State IV
Cl		2×10^1 (1)	5×10^1 (1)	2×10^1 (1)	0 (0)
I		1×10^0 (1)	1×10^1 (1)	1×10^0 (1)	4×10^{-1} (0)
Nb		5×10^4	5×10^4	5×10^4	5×10^2
Ni		6.5×10^1	4×10^2	4×10^2	5×10^0
Ra		3×10^2	1×10^2	8×10^2	10^0
Sr		1×10^2	3×10^1	1×10^2	10^0
Cs		i.d.	2×10^0	2×10^1	i.d.
Th		3×10^4	3×10^4	3×10^4	3×10^4
U	U(IV)	3×10^4	3×10^4	3×10^4	3×10^4
	U(VI)	2×10^3	3×10^4	3×10^4	5×10^1
Pu	Pu(IV)	5×10^3	3×10^4	3×10^4	3×10^2
	Pu(VI)	2×10^3	3×10^4	3×10^4	5×10^1
Np	Np(IV)	3×10^4	3×10^4	3×10^4	3×10^2
	Np(V)	i.d.	i.d.	i.d.	i.d.
Pa	Pa(IV)	3×10^4	3×10^4	3×10^4	3×10^4
	Pa(V)	1×10^4	1×10^4	1×10^4	3×10^2
Am		1×10^4	1×10^4	1×10^4	1×10^4
C ^s		2×10^3	5×10^3	2×10^3	i.d.
H		0	0	0	0
Tc	Tc(IV)	3×10^3	3×10^3	3×10^3	i.d.
	Tc(VII)	1	1	1	1

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Acknowledgement

This work has been performed as part of the project on disposal of category A waste – short-lived low and intermediate level waste (LILW-SL) – that is carried out by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and enriched Fissile Materials.

Disclaimer

The findings and conclusions in this paper are those of the authors and do not necessarily represent the official position of ONDRAF/NIRAS. The work presented in this paper was more particularly carried out as preparatory work to a future license application file for a near surface disposal facility at Dessel to be submitted by ONDRAF/NIRAS to the FANC. Therefore, the results in this paper have not yet undergone regulatory review nor approval by the FANC. Furthermore, it is not excluded that further developments and refinements of the work presented in this paper will be included in the future license application file.

19 - IMMOBILIZATION OF NP IN CEMENTITIOUS REPOSITORY ENVIRONMENTS

Jan Tits, Xavier Gaona, Rainer Dähn, Dmitry Popov and Erich Wieland
(Laboratory for Waste Management, Paul Scherrer Institut, Villigen, Switzerland)

Introduction

In many nuclear waste disposal concepts, the use of cementitious materials is foreseen to immobilize long-lived intermediate level wastes (ILW). ILW may contain significant amounts of Neptunium-237, which constitutes a potential hazard to the environment due to its long half-life ($2.14 \cdot 10^6$ years). Predicting the release of Np from a cement-based repository requires an adequate understanding of its interaction with the main sorbing components of hardened cement paste (HCP). The redox chemistry of Np under hyperalkaline conditions, its solubility as well as the mechanisms controlling its uptake by cementitious materials are still poorly understood (Wieland & Van Loon, 2003). Both Np(IV) and Np(V) are expected to exist under repository conditions: Np(V) prevails in the early stage after repository closure, while Np(IV) becomes stable in a later stage after depletion of the oxygen and development of reducing conditions.

The present study focuses on the uptake of Np(IV/V) by cementitious materials using a combination of wet chemistry experiments and synchrotron-based spectroscopic and diffraction techniques. The combination of both sources of information can provide key inputs for a final mechanistic interpretation with a sound thermodynamic background, therefore improving long-term predictions of Np behaviour in cement-based repositories.

Wet chemistry studies

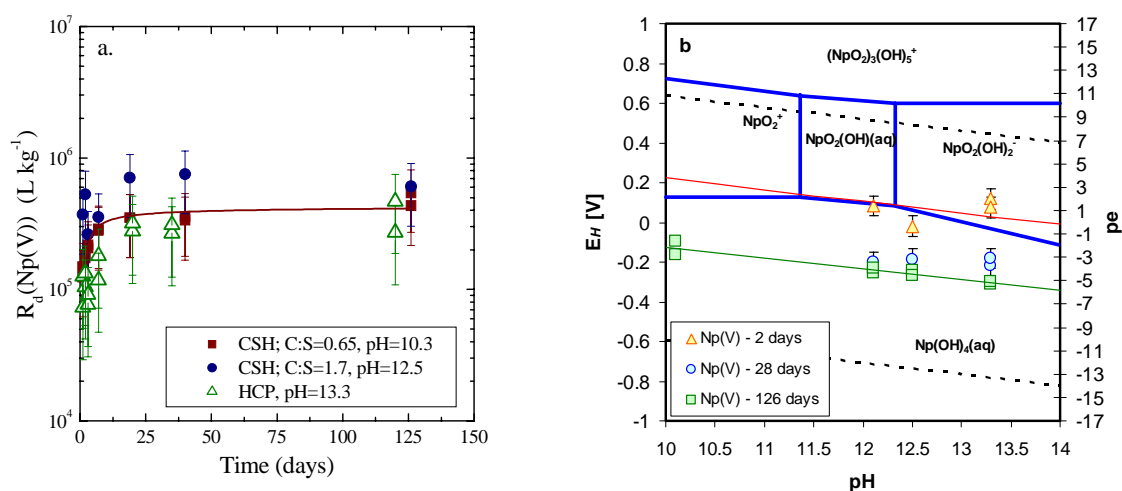
In the cementitious environment of an ILW repository, sorption processes are expected to dominate the chemistry of Np. Nevertheless, the assessment of Np solubility in such an environment is a necessary requirement to achieve a complete understanding of the system.

Solubility tests from oversaturation were set-up with Np(V) under anoxic conditions using a) an artificial cement pore water (ACW) with high alkali content and $\text{pH}=13.3$, reflecting the pore water composition of a fresh hardened cement paste, and b) a 10^{-4} M $\text{Ca}(\text{OH})_2$ solution ($\text{pH}=10.3$), reflecting the pore water composition of a degraded hardened cement paste controlled by the C-S-H solubility. Thermodynamic calculations indicated that both systems were undersaturated with respect to $\text{NpO}_2\text{OH}(\text{fresh})$. Consistently with these calculations, no Np(V) precipitation was observed in the 10^{-4} M $\text{Ca}(\text{OH})_2$ solution in the concentration range $5 \cdot 10^{-8}$ M $\leq [\text{Np}] \leq 10^{-4}$ M. Nonetheless, precipitation of an unknown Np(V) solid phase was observed in ACW at $[\text{Np}] \geq 6 \cdot 10^{-7}$ M. This finding suggests the possible formation of ternary Ca-Np(V)-OH phases (i.e. $\text{Ca}_{0.5}\text{NpO}_2(\text{OH})_2$ or $\text{CaNpO}_2(\text{OH})_3$), which have been previously described in Altmaier *et al.* (2008). The precipitation of these phases is clearly favoured at higher pH and Ca concentrations (as is the case in ACW). Further investigations are on-going to verify this hypothesis and to develop thermodynamic data for these phases.

Np(V) uptake by C-S-H phases (both in ACW and alkali-free solutions) and HCP was investigated under anoxic conditions. Sorption kinetic tests indicated that Np sorption reaches

equilibrium after approximately 20 days. Figure 1a shows that the measured sorption values (R_d) were very high. Based on the effective charge of the NpO_2^+ cation ($E_{\text{eff}} = 2.3$) (Fanghänel and Neck, 2002), a sorption behaviour similar to divalent cations with R_d values ranging from 10^3 to 10^4 L kg^{-1} was expected. Figure 1b shows a gradual and significant decrease of the E_H with time for all the suspensions of Np(V) and C-S-H/HCP. The predominance diagram in Figure 1b further shows that, according to the measured E_H , Np(IV) is the stable redox species in the C-S-H suspensions after a reaction time of 126 days. This observation suggests that Np(V) was reduced to Np(IV) during the sorption process, which would also be consistent with the higher R_d values expected for the +IV redox state ($E_{\text{eff}} = 4$). Further studies are on-going with the aim of verifying the reduction of Np(V) during sorption on cementitious materials.

Figure 1. Np(V) sorption kinetics on C-S-H phases (C:S = 0.65 and 1.82) in alkali-free solution at pH 10.3 and 12.5 and on HCP in ACW at pH 13.3. a) R_d values. b) Predominance diagram of Np for $+1V \leq E_H \leq -1V$ and $10 \leq \text{pH} \leq 14$. Squares/circles/triangles correspond to E_H measurements



Thermodynamic modeling

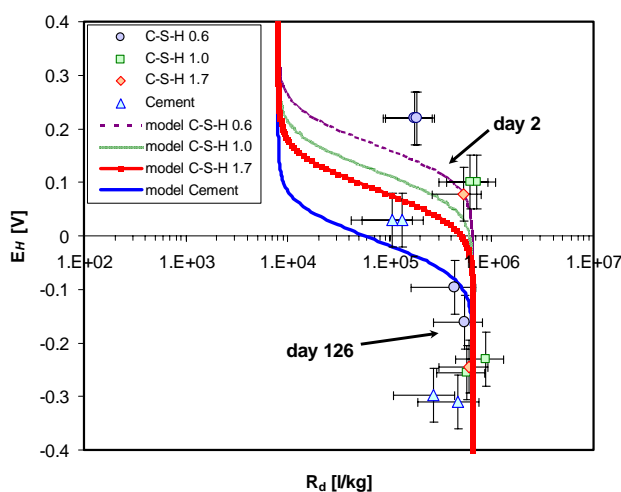
The wet chemistry data allow a mechanistic interpretation of the Np(V) uptake by cementitious materials on the assumption that Np(IV) was formed. Assuming thermodynamic equilibrium after 126 days and accounting for the reducing E_H values measured, most of the aqueous Np (> 99.99%) in the four systems studied is expected to be in the +IV redox state. Similarly, taking into account the high amount of Np taken up by the solid, the very low concentration in solution and the very reducing conditions, the sorbed Np is expected to be predominantly in the +IV state as well. Thus, the predominance of Np(IV) in both aqueous and solid phases suggests that the R_d values measured under equilibrium conditions reflect the sorption behaviour of Np(IV).

Thermodynamic equilibrium at a given pH- E_H value further implies that Np(IV)/Np(V) ratios are fixed and, in the case of aqueous species, known. Therefore, it is possible to define a mechanism where the uptake of Np(V) by a surface “>” is coupled to the reduction to Np(IV). On the assumption that Np(IV) surface species (>Np(OH)_{4(ads)}) are the same in all experiments, three reactions can be defined according to the aqueous speciation of Np(V) at different pH values:

- rx. 1.** $\text{NpO}_2^+ + 2\text{H}_2\text{O} + 1\text{e}^- + > = >\text{Np(OH)}_{4(\text{ads})}$; (C-S-H C:S=0.6, pH=10.1)
- rx. 2.** $\text{NpO}_2(\text{OH})(\text{aq}) + \text{H}^+ + \text{H}_2\text{O} + 1\text{e}^- + > = >\text{Np(OH)}_{4(\text{ads})}$; (C-S-H C:S=1, pH=12.1)
- rx. 3.** $\text{NpO}_2(\text{OH})_2^- + 2\text{H}^+ + 1\text{e}^- + > = >\text{Np(OH)}_{4(\text{ads})}$; (C-S-H C:S=1.6/cement, pH=12.5/13.3)

Reactions rx.1, rx. 2 and rx. 3 are characterized by E_H° and rG° (correlated with $\log K$). Under non-standard conditions, E_H° is related to the experimental E_H through the Nernst equation. The above proposed mechanism is able to adequately explain experimental wet chemistry data, both in terms of E_H and R_d values (Figure 2). The model was developed by assuming an R_d [Np(V)] $\sim 10^4$ L kg⁻¹, which would correspond to the sorption of a cation with $E_{\text{eff}} \sim 2$. It is also worth mentioning that observations on E_H and R_d at shorter times (2 days) suggest a weaker sorption, which would be consistent with the presence of Np(V). Synchrotron-based experiments are foreseen to check the possibility of $>\text{Np}(\text{OH})_{4(\text{ads})}$ formation.

Figure 2. **Experimental data and modeling exercise for E_H dependence with R_d for Np(V) uptake by C-S-H phases and cement**



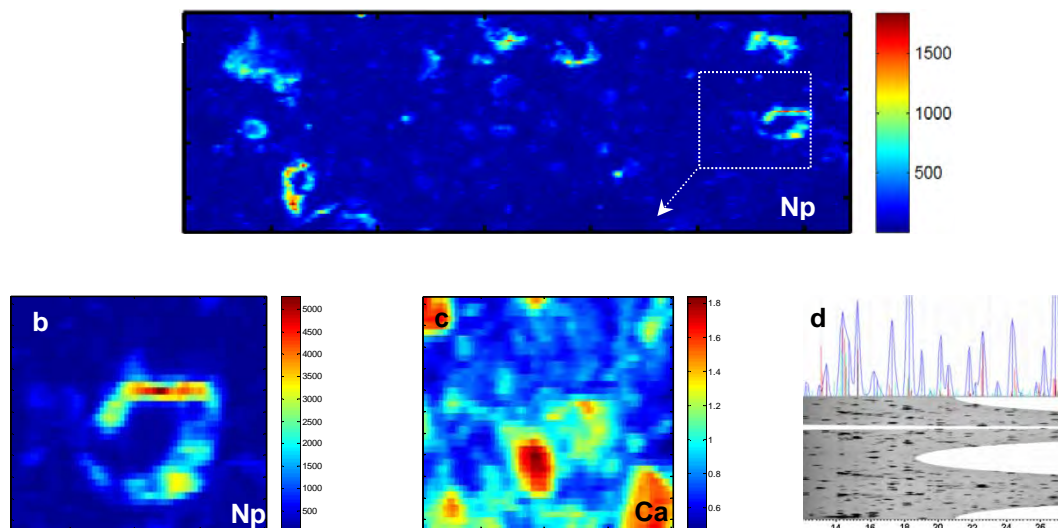
Synchrotron-based studies

Synchrotron-based (micro-)spectroscopic and micro-diffraction techniques provide information on the coordination environment of Np both from a macro- (bulk studies) and a microscopic perspective, depending on the size of the beam and the set-up of the experimental station.

Bulk-EXAFS data provide information on the redox state and coordination sphere of Np in C-S-H and HCP samples. The main difference between the EXAFS spectra of Np(IV) and Np(V) arise from the splitting of the neighboring oxygen shell, which was observed for Np(V) (i.e., axial and equatorial oxygens) as a result of the neptunyl ($[\text{O}=\text{Np}=\text{O}]^+$) structure, but not for Np(IV). Further, Np(IV)-O distances were found to be longer (e.g., Antonio *et al.* 2001; Denecke *et al.* 2005; Hennig *et al.* 2009). Preliminary experiments with Np doped C-S-H phases confirm the feasibility of Np redox determination by EXAFS.

Obtaining information at the micro-scale is particularly important in complex systems, such as cement, which exhibit a high degree of heterogeneity. In this context, a first set of micro-spectroscopic and micro-diffraction measurements were conducted on Np(IV) doped cement thin sections (~ 50 nm thickness) on the microXAS beamline at the SLS (Switzerland). Micro-XRF mappings showed that Np(IV) tends to accumulate around Ca-rich particles in the cement matrix (Figures 3a, b, c). Micro-XRD measurements on one Np(IV) spot further showed that Np(IV) is mainly present in amorphous state. Micro-XRD identified the Ca-rich particle as a mixture of clinker minerals (Figure 3d). The environment of Ca-rich clinker minerals is considered to be a highly reactive region, where C-S-H phases form. Note that the wet chemistry experiments also indicated a strong interaction of Np (presumably in the +IV redox state) with C-S-H phases. A new series of micro-spectroscopic and micro-XRD investigations are foreseen.

Figure 3: Micro-XRF mappings of a Np(IV) doped Portland cement thin section. Fluorescence signals of $L_{III}[Np]$ (a, b) and Ca (c) collected at 13650-14020 eV and 3420-4040 eV, respectively; d) Identification of crystalline components of a Ca-'hot-spot'; bottom: composite image collected within 90° of angular range (x axis: 2θ angle; y axis: azimuth). Each pixel contents value of the composite image is the maximal one within all of the pixels of the same coordinates; top: integrated intensities. The strongest diffraction lines correspond to C_3S (red) and C_2S (green)



Conclusions

The experimental results from this study suggest that Np(V) is not redox-stable in cementitious environments in contact with C-S-H phases, and Np(V) sorption is coupled with Np(V)/Np(IV) reduction. The uptake mechanism can be successfully modelled by considering a coupled sorption-reduction process.

Bulk-XAS measurements will allow the determination of the redox state as well as the coordination environment of sorbed Np species in the next phase of this study. Micro-spectroscopic and micro-diffraction techniques can provide relevant information on the cement phases involved in the process of Np sorption by cementitious materials.

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20 - BENCHMARKING THE CEMDATA07 DATABASE TO MODEL CHEMICAL DEGRADATION OF CONCRETE USING GEMS AND PHREEQC

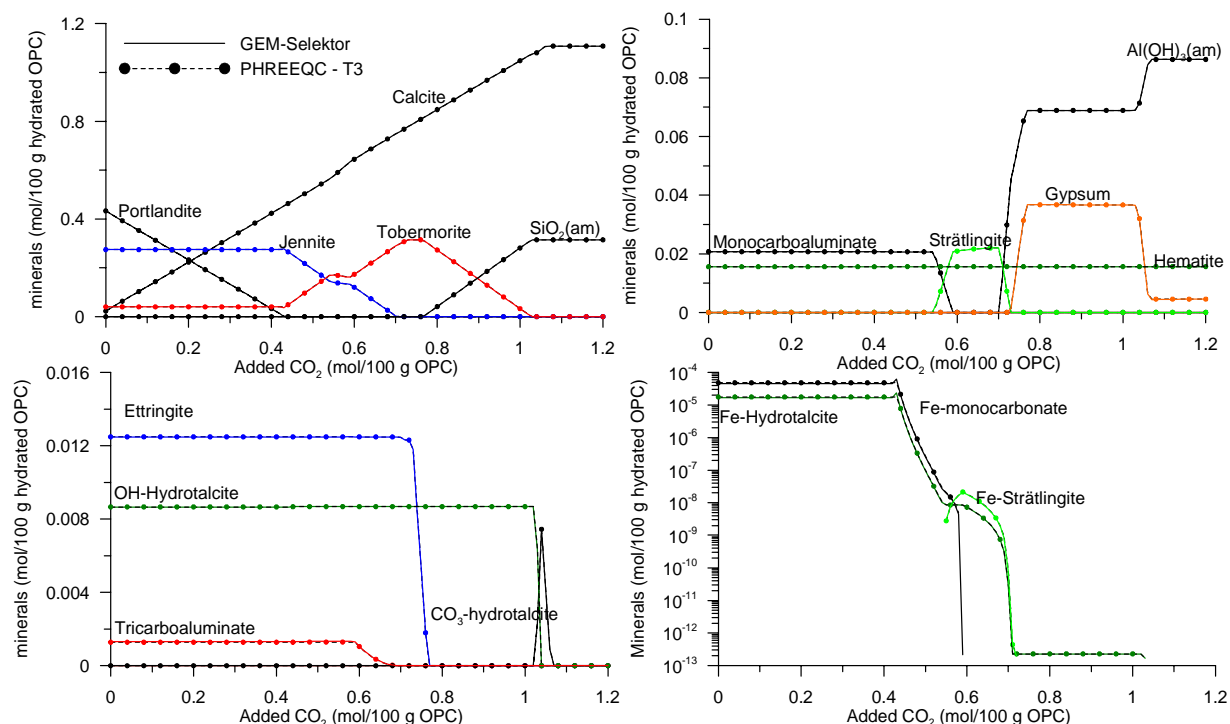
Diederik JACQUES, Lian WANG, Evelien MARTENS and Dirk MALLANTS
(SCK•CEN, Belgium)

Thermodynamic equilibrium modelling of degradation of cement and concrete systems by chemically detrimental reactions as carbonation, sulphate attack and decalcification or leaching processes requires a consistent thermodynamic database with the relevant aqueous species, cement minerals and hydrates. The recent and consistent database CEMDATA07 (Matschei *et al.* 2007; Lothenbach *et al.* 2008) is used as the basis in the studies of the Belgian near-surface disposal concept being developed by ONDRAF/NIRAS. Several cement hydrates for ordinary Portland cement systems (OPC) are included in the databases such as a solid solution model for the calcium silicium hydrates (C-S-H phases), AFm phases (as monocarboaluminate, strätlingite), AFt phase (ettringite and tricarboaluminate), hydrogarnet, and hydrotalcite. The database is consistent with the thermodynamic data in the Nagra/PSI-Thermodynamic Database. When used with the GEMS thermodynamic code (Kulik 2007), thermodynamic modelling can be performed at temperatures different from the standard temperature of 25°C. GEMS calculates thermodynamic equilibrium by minimizing the Gibbs free energy of the system. As such, it also provides information of the change in Gibbs free energy of formation at the target temperature.

Alternatively, thermodynamic equilibrium can also be calculated by solving a nonlinear system of mass balance equations and mass action equations, as is done in PHREEQC (Parkhurst and Appelo 1999). For this method, mass action constants (K) are needed at the target temperature. These can be obtained by the relation between the mass action constant and the change in Gibbs free energy of reaction. The latter is calculated as the sum of the change in Gibbs free energy of formation multiplied by the stoichiometric coefficients in the reaction equation. A PHREEQC-database for the cement systems at temperatures different from 25°C is derived from the thermodynamic parameters and models from GEMS. For each reaction $\log K$ as a function of temperature is described by a three-term polynomial expression. Thermodynamic properties as the change in enthalpy, entropy and heat capacity of reaction are used to calculate these parameters. Excellent agreement was obtained between the PHREEQC-based three-term expression with fitted coefficients and the original relationships obtained from GEMS to describe the temperature dependency of the $\log K$ values.

A number of benchmark simulations using PHREEQC and GEM-Selektor were done to verify the implementation of the CEMDATA07 database in PHREEQC-databases. Simulations address a series of reactions that are relevant to the assessment of long-term cement and concrete durability. Verification calculations were performed for different systems with increasing complexity: CaO-SiO₂-CO₂, CaO-Al₂O₃-SO₃-CO₂, and CaO-SiO₂-Al₂O₃-Fe₂O₃-MgO-SO₃-CO₂. Three types of chemical degradation processes were simulated: (1) carbonation by adding CO₂ to the bulk composition, (2) sulphate attack by adding SO₃ to the bulk composition, and (3) decalcification/leaching by putting the cement solid phase sequentially in contact with pure water. An excellent agreement between the simulations with GEMS and PHREEQC was obtained (Figure 1).

Figure 1: Solid composition during carbonation (CO₂ added to Ordinary Portland Cement, OPC) simulated with GEMS and PHREEQC at 25C. Each graph plots a different group of cement minerals



In the most complex system (CaO-SiO₂-Al₂O₃-Fe₂O₃-MgO-SO₃-CO₂), reaction equations describing the major mineralogical changes were derived. Most pertinent observations are as follows:

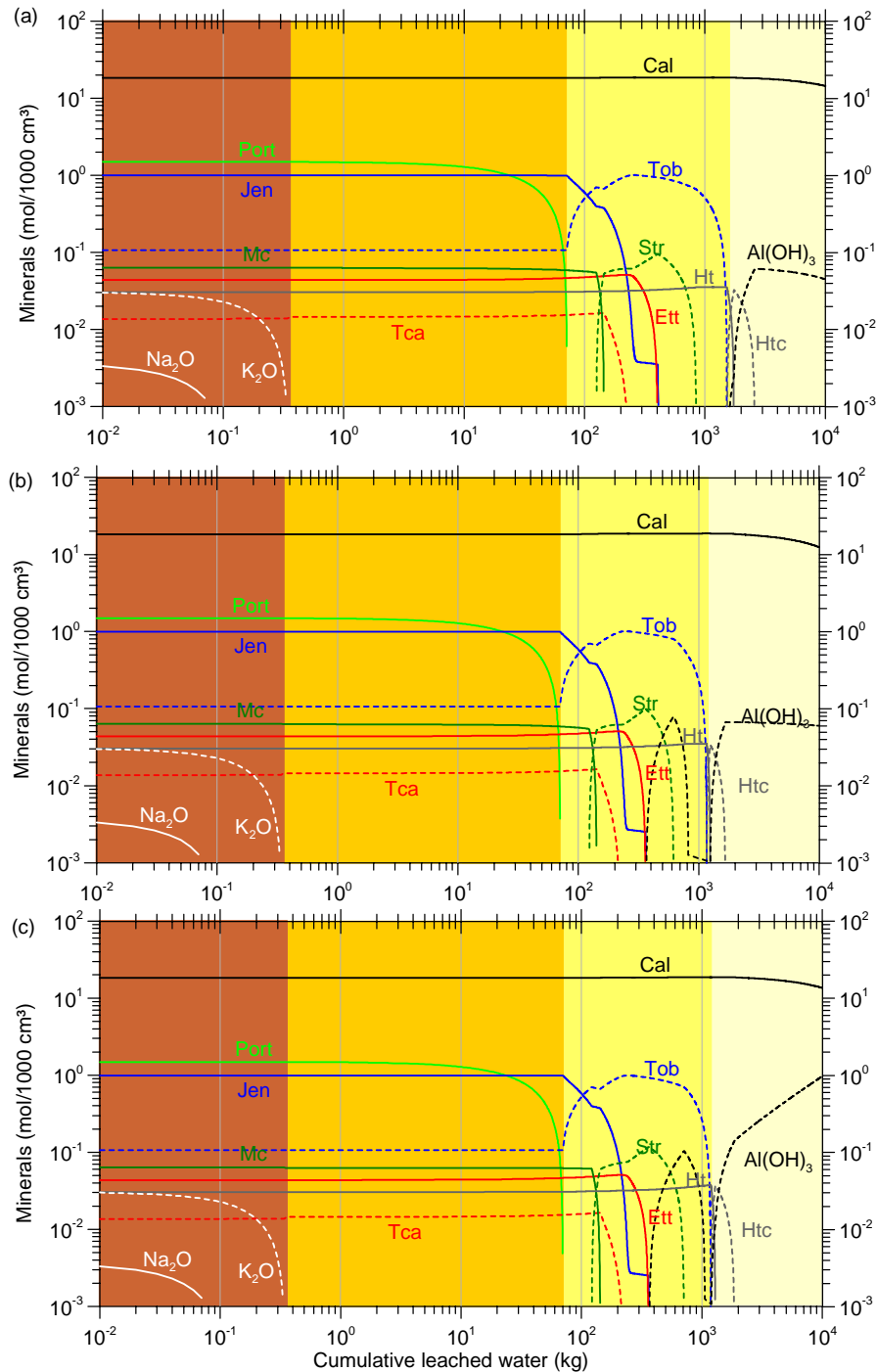
- Carbonation leads to the formation of calcite. Ca is then supplied by dissolution of the different phases in the following overall sequence: portlandite, jennite in the C-S-H phase (*decalcification*), dissolution of the AFm (monocarboaluminate, secondary strätlingite) and AFt (ettringite, tricarboaluminate) phases, tobermorite in the C-S-H phase and hydrotalcites. Besides calcite, also SiO₂(am), Al(OH)₃(am) and gypsum are present after the carbonation.
- The sulphate attack leads to the formation of gypsum in the following overall sequence: transformation of the aluminium-bearing, sulphate-free minerals (monocarboaluminate, OH-hydrotalcite) into ettringite, portlandite dissolution, dissolution of jennite in C-S-H phase (*decalcification*), dissolution of ettringite, dissolution of tobermorite in the C-S-H phase, dissolution of hydrotalcites and calcite dissolution. Besides gypsum, also SiO₂(am) and Al(OH)₃(am) are present after sulphate attack.
- The same overall sequence is present during leaching, but without the formation of stable phases: most important reactions include portlandite dissolution, jennite dissolution, AFm and AFt dissolution, tobermorite dissolution, calcite dissolution, and hydrotalcite dissolution.

Two decalcification/leaching processes are described: (1) leaching of cement with Boom Clay water, and (2) leaching of concrete with rain and soil water.

The leaching with Boom Clay water is simulated both with PHREEQC and GEMS. The agreement between both simulations was excellent. The main sequence of reaction equations

during leaching with Boom Clay pore water was a combination of decalcification and carbonation.

Figure 2: Geochemical changes during leaching of 1000 cm³ concrete with (a) Rain water – bulk deposition, (b) Soil water – CO₂, and (c) Soil water – gibbsite at 10°C. Port: Portlandite, Jen: Jennite-like end member, Tob: Tobemorite-like end member, Mc: Monocarboaluminate, Ca: Calcite, Str: Strätlingite, Tca: Tricarboaluminate, Ett: Ettringite, Ht: OH-hydrotalcite, Htc: CO₃-hydrotalcite. Colours indicate degradation state: Brown: State 1 (pH controlled by Na and K), Orange: State 2 (pH controlled by portlandite), Yellow: State 3 (pH controlled by C-S-H, Afm and Aft), Light Yellow: State 4 (pH controlled by calcite)



Once the implementation of the CEMDATA07 database in the PHREEQC database was verified, an application was developed that considered the assessment of long-term geochemical evolution of a concrete-based disposal facility. For a near-surface disposal facility, concrete components may come in contact with rain water (during the operational phase prior to capping) and soil water (during after capping with a multi-layer soil cover). The typical four degradation states of concrete degradation were quantified in terms of pore-water and solid phase evolution during the leaching of concrete with rain and soil water (Figure 2). From the four states identified, State 3 is chemically the most complex one and concerns the dissolution of AFm, AFt and C-S-H phases. These cement phases do not dissolve in a successive manner, but in a more complex way, e.g. transforming first the AFm phase monocarboaluminate in strätlingite, followed by ettringite dissolution and followed by strätlingite dissolution (see Figure 1, from Jacques *et al.* 2009). Biological activity, increasing the inorganic carbon concentration in the pore water, has a negative effect on concrete durability: the concrete needs less water to degrade to state III. Soil weathering products (case with gibbsite) only have a slight buffering effect and thus, a small positive effect on concrete durability.

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Acknowledgement

This present work has been performed as part of the project on disposal of low and intermediate level waste – short lived (LILW-SL) that is carried out by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and enriched Fissile Materials.

Disclaimer

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21 - THERMAL AND HYDRAULIC PROPERTIES OF THE CONCRETE USED IN THE ILW REPOSITORY OF EL CABRIL (SPAIN). PRELIMINARY LABORATORY TESTS

María Victoria VILLAR (CIEMAT, Spain)

Introduction

In most countries the final disposal of low and intermediate-level radioactive waste is performed on surface or near-surface facilities, in which concrete is frequently used as a barrier. This work is a contribution to the understanding of the behaviour of concrete barriers in surface disposal facilities, in particular in the Spanish disposal facility of El Cabril, where the waste containers are placed inside concrete cells. The durability of concrete and its mechanical properties are intrinsically bound to moisture transport effects, especially when it is subjected to repeated wetting and drying regimes, and that is why a detailed thermo-hydraulic characterisation is necessary to model its behaviour.

The concrete used in this experimental work has been cast in El Cabril following the procedures used to manufacture the disposal cells. It has a characteristic strength of 350 kp/cm² and uses ordinary Portland cement, resistant to sulphates and seawater, with a water/cement ratio of 0.43. Its average pore size is 0.03 µm (Zuloaga 2008).

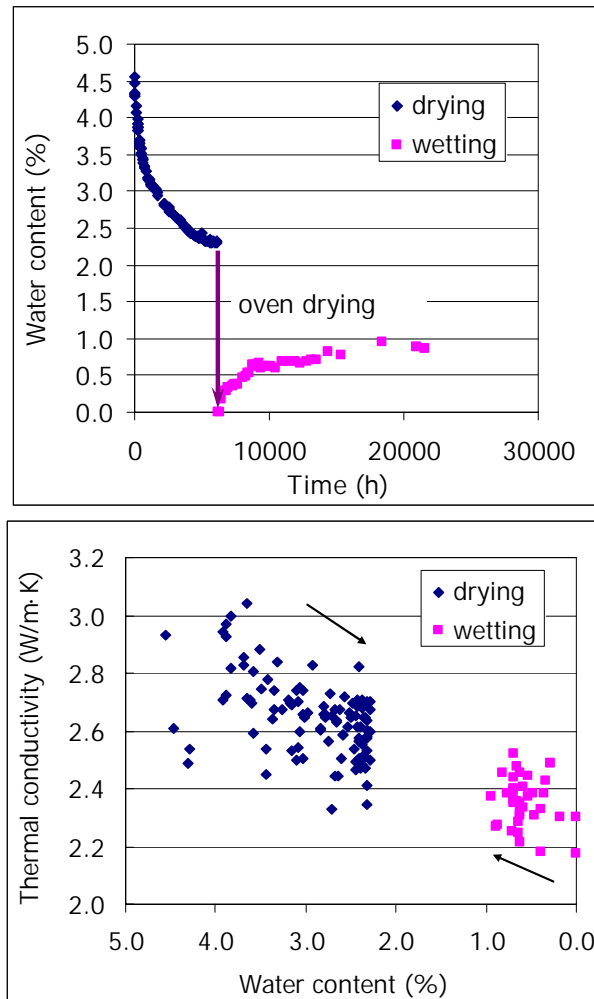
In addition to the determination of the thermal conductivity of concrete as a function of water content, a hydraulic characterisation –including determination of saturated permeability, permeability to gas for different degrees of saturation and water retention curves– is being performed in the laboratory and the results obtained so far are presented below.

Thermal conductivity

The superficial thermal conductivity of several saturated concrete blocks has been measured at room temperature using the hot wire transient method. The average value obtained is 2.7±0.3 W/m·K.

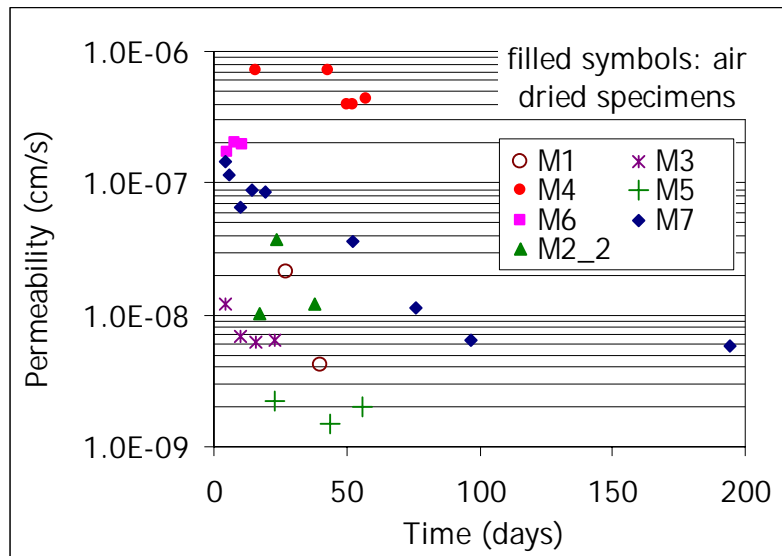
Also, the thermal conductivity of a 4-kg concrete block was periodically measured as it dried at laboratory conditions from an initial water content of 4.6 percent. It took nine months for the water content of the block to stabilise. This final water content, as determined by oven-drying at 110°C, was 2.3 percent, which would be the equilibrium water content for a suction of 116 MPa, corresponding to the average relative humidity and temperature in the laboratory. The thermal conductivity of the oven dried concrete was on average 2.3 W/m·K. Afterwards, the block was left to stabilise again under laboratory conditions and its thermal conductivity was also periodically measured. The water content reached during air drying before drying in the oven was not recovered, nor was the thermal conductivity (Figure 1), which highlights the hysteretic behaviour of concrete thermal and hydraulic properties.

Figure 1: Evolution of water content and thermal conductivity of a concrete block under laboratory conditions (wetting took place after oven drying)

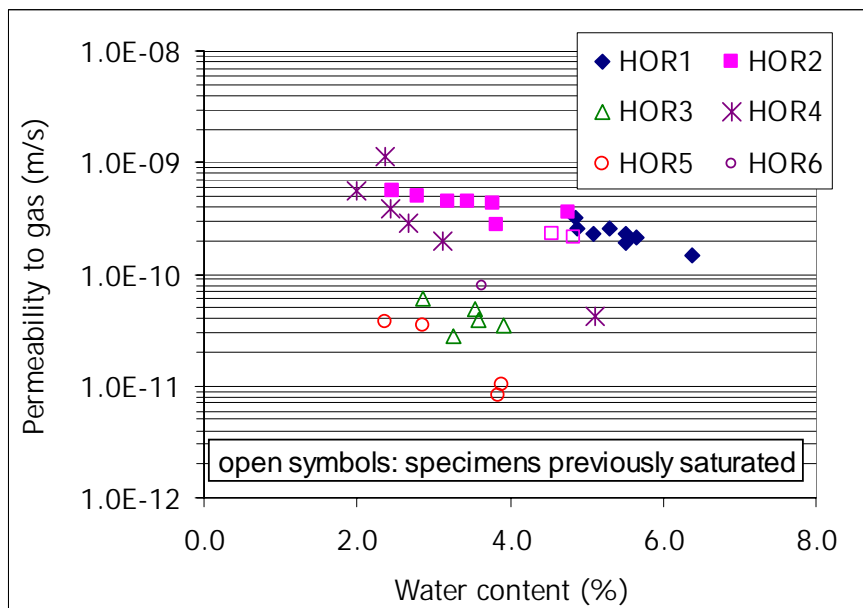


Water permeability

The saturated hydraulic conductivity of cylindrical concrete samples of diameters 3.5 or 5.0 cm and heights between 4 and 6 cm has been measured in a constant head permeameter by applying an average hydraulic gradient of 187. The specimens were previously saturated with deionised water. It has been observed that it takes several days for the value of permeability to stabilise, as shown in Figure 2. The average preliminary value obtained so far is $4.1 \cdot 10^{-11}$ m/s, for an average concrete dry density of 2.28 ± 0.02 g/cm³ and a water content of 6.0 ± 0.2 percent. Some samples were tested after being air dried and later saturated, and they have higher permeabilities, the average value being $1.3 \cdot 10^{-9}$ m/s, for an average concrete dry density of 2.29 ± 0.02 g/cm³ and a water content of 6.3 ± 0.4 percent.

Figure 2: Preliminary saturated water permeability of several concrete specimens**Gas permeability**

The permeability of concrete specimens of different water content has been measured using as fluid nitrogen gas injected at a pressure of about 0.1 MPa in a variable head permeameter. The preliminary results obtained are shown in Figure 3. As expected, the permeability decreases with water content, since the effective porosity also decreases due to the blocking caused by water. In addition, the specimens that had been previously saturated have lower permeabilities.

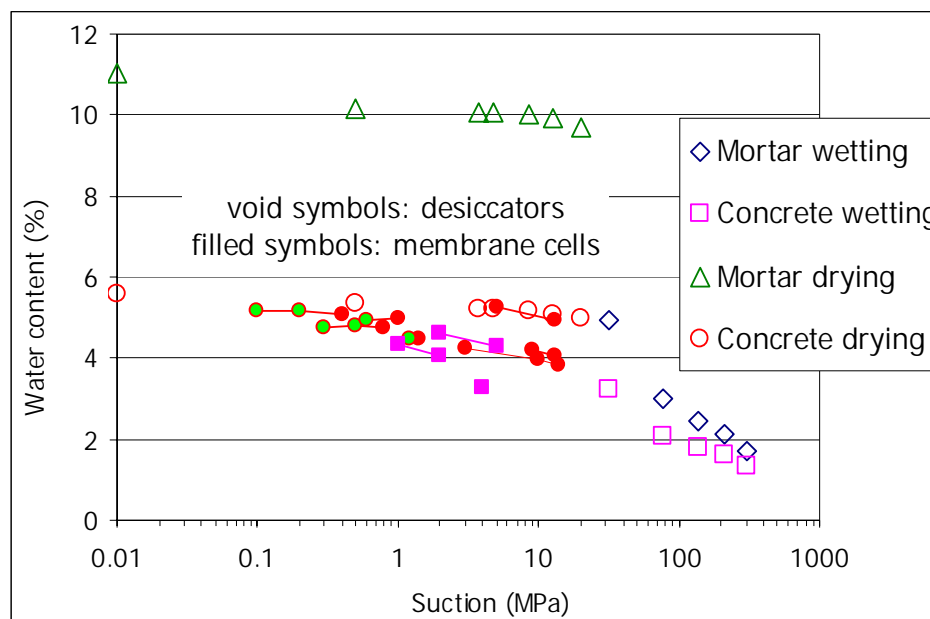
Figure 3: Preliminary values of permeability to gas measured in concrete samples under low pressure

Water retention curves

The water retention curves of specimens of concrete and of the mortar used to prepare it have been determined with two different methods: axis translation technique and control of relative humidity. In the first method matric suction is imposed to the sample by increasing the air pressure in the membrane cell in which the sample is placed (thus in the concrete pores) while water pressure is kept atmospheric. In the second one, the total suction of the atmosphere in which the sample is placed (a desiccator) is controlled by using sulphuric acid solutions of different concentrations. In both cases the samples are kept under a given suction until stabilisation of their water content, which is checked by drying at 110°C. All the tests have been performed at 20°C and the stabilisation times for each suction have been very long (several months), despite the small size of the specimens (diameter 4.3-4.5 cm, height 1.1-1.4 cm). The results obtained are plotted in Figure 4.

Despite the fact that with the membrane cell method the osmotic suction is not controlled and only matric suction is applied, the results obtained with both techniques are quite coherent, which would point to a minor contribution of osmotic suction to the water retention capacity of concrete. As expected, the water retention capacity of the mortar, whose porosity is higher and in which no inert components are present, is higher than that of concrete.

Figure 4: Preliminary water retention curves obtained in concrete and mortar (matric suction in membrane cells and total suction in desiccators)



Conclusions

Some hydraulic properties of the concrete used to manufacture the disposal cells of an intermediate-level radioactive waste disposal facility have been tested in the laboratory, as well as its thermal conductivity. Reaching hydraulic equilibrium takes long periods of time and the behaviour of concrete concerning permeability and water retention capacity is highly hysteretic, for which reason these properties are affected by the hydraulic history of the material, which suggests that important changes in porosity and microstructure are caused by hydraulic interaction. Distributed microcracking produced by shrinkage of the gel on partial dehydration could be one of the reasons for the changes in dried concrete. This drying shrinkage is not fully reversible on wetting (Hall & Hoff 2002).

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22 -INTERACTION OF LOW PH CEMENTITIOUS CONCRETES WITH GROUNDWATERS

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Introduction

Some engineering construction concepts for high level radioactive waste underground repositories consider the use of a bentonite barrier in contact with cementitious materials with a pore fluid pH value ≤ 11 (based on low-pH cements) to maintain the bentonite stability. The research on low-pH cementitious materials is mainly addressed from two different approaches: 1) Calcium Silicate Cements (OPC, Ordinary Portland Cement based), 2) Calcium Aluminates Cements (CAC based). In both approaches mineral admixtures as Silica Fume (SF) are added with the based cement. To decrease the pore fluid pH of OPC based cementitious materials, the portlandite content has to be reduced or even eliminated using mineral additions with high silica content (Saeki 2005), due to it is the main responsible of their long term high alkalinity. The blends follow the pozzolanic reaction that consumes portlandite to form Calcium Silica Gel Hydrates (CSH). CAC based cements have themselves a lower pore fluid pH value, but the challenge is to control their most widely identified degradation process, the so called conversion process. An interesting way to reduce the Calcium Aluminate Hydrates conversion is to replace some of the CAC by mineral admixtures with high silica content (Majumdar 1992; Hidalgo 2008), increasing the microstructure stability of the mixes and even contributing to decrease the pore fluid pH value (García Calvo 2009). So it is obvious that the use of both types of cements (OPC based or CAC based) implies the use of high mineral additions contents in the binder that should significantly modify most of the concrete "standard" properties. Once these properties have been addressed (García Calvo 2008) and taking into account the long life expected in this type of repositories, parameters related to the durability of the low-pH concretes must be analyzed. This work shows some recent studies that deal with the evaluation of the resistance of low-pH concretes to long term groundwater aggression. The research has been carried out within the frame of the ESDRED EC project (FI6W-CT-2004-508851) and the Spanish waste national management agency "ENRESA".

Experimental

Due to the difficulties for long timescales involved in laboratory experiments using groundwaters, accelerated tests have to be used to qualify the different concretes for deep repositories. The resistance against ground water aggression has been evaluated in three types of low-pH concretes: a) basic concrete based on the low-pH cement formulation 70%CAC+30%SF; b) basic concrete based on the low-pH cement formulation 60%CAC+40%SF; c) concrete cores extracted from a real shotcreted low-pH plug fabricated in Äspö facilities using the low pH cement formulation 60%OPC+40%SF.

The accelerated leaching test used is based on a percolation method. Cylindrical concrete samples were placed between two cylinders of methacrylate containing holes for water inlet and outlet. A water head of 0.5 bars pressure was maintained to pass water from the upper surface of the concrete. At the lower part, the leachate was collected for analysis. The groundwater used for leaching tests was taken from the site of Äspö (Sweden) in order to simulate real conditions.

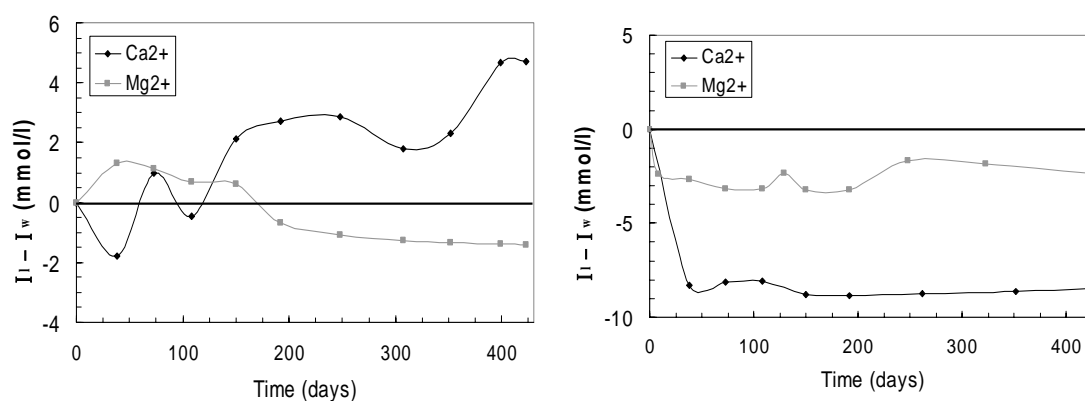
This groundwater contains as main relevant ions Cl^- and Mg^{2+} (Cl^- : 2500ppm; Mg^{2+} :80ppm). Variables measured continuously in every case were: effluent flux (to determine the hydraulic conductivity), chemical composition and pH. At the end of experiments (14 months in basic concretes and 2 years in cores from the plug) the modifications in the solid phases were evaluated by BSEM with EDX analyses, phenolphthaleine test and Mercury Intrusion Porosimetry.

Results

Characterization of the leaching solution evolution

The pH values measured in the leachates were never above 11 in the studied concretes (except in the first 50 days for that with CAC+SF), being lower than 9 in the concretes based on OPC+SF during all the test period. Figure 1 shows the Ca^{2+} and Mg^{2+} contents evolution in the leachates of the two basic concretes evaluated.

Figure 1: Evolution of Ca^{2+} and Mg^{2+} leachate contents (left: concrete based on OPC+SF; right: concrete based on CAC+SF). I_l = ion content in leachate; I_w = ion content in the groundwater used



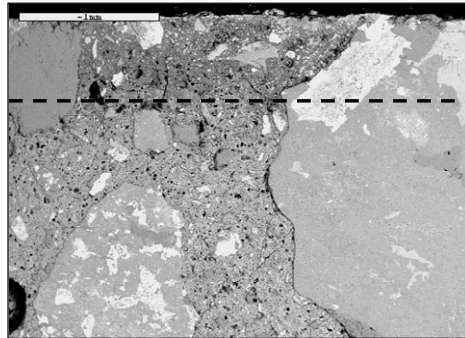
Changes in the chemical composition of the leachates in concrete based on CAC+SF show lower Ca^{2+} , Mg^{2+} and Cl^- contents with respect to those present in the Äspö water, indicating an incorporation of these ions in the Calcium Silico-Aluminate Hydrates, CASH, a possible secondary hydration and/or a calcite precipitation. In the OPC+SF concretes, the Ca^{2+} content decreases at the beginning of the leaching test but increases with time, whereas Mg^{2+} shows exactly the opposite behaviour. This can be related with an initial secondary hydration followed by decalcification of the CSH phases compensated by the incorporation of magnesium. The chloride content evolution of the 2 concretes leachates shows an important decrease at the beginning of the test, increasing slowly with time up to the characteristic values of the groundwater, indicating an initial incorporation of Cl^- ions in the cement matrixes, being this phenomenon more marked in the concrete based on CAC. With regard to the hydraulic conductivity values, the three concretes fulfil with the requirements demanded because they are similar to that of the surrounding rock expected in a granitic underground repository (which is in the order of $1 \cdot 10^{-10}$ m/s.). The hydraulic conductivity remains almost stable in the concretes based on OPC+SF during all the test period and decreases slowly with time in that based on OPC+FA.

Evaluation of the modifications generated in the solid phases.

In general, results from leaching tests show that the low pH concretes have good resistance against groundwater interaction. After the test period, in the concretes based on OPC+SF a small altered front from the surface ($<700\mu\text{m}$) can be observed, as that shown in the microscopy image of figure 2. In this altered front, there are not any significant modifications in the porosity of the

concrete, but a decalcification of the CSH gels followed by the incorporation of magnesium ions from groundwater into them (even forming Magnesium Silicate Hydrate, MSH phases) and into the anhydrous phases (as “magnesia nodules”) are observed. This is graphed in Figure 3 that shows the XRay Diffractometry (EDX) microanalyses profiles obtained in the pastes of the two OPC+SF low-pH concretes, presenting the modifications occurred with the depth of the samples in the C/S ratios of the CSH gels and in the Mg²⁺ concentration. The incorporation of Cl⁻ ions from groundwater into the CSH gels structure is also detected.

Figure 2: Altered front observed in OPC+SF concrete. BSEM image (x35).



In the case of the low-pH concrete based on CAC+SF, the results also indicate a good resistance against groundwater interaction. After the leaching test period (14 months), this concrete has a similar aspect and similar CASH paste phases than those observed in the concrete before testing maintained in a curing chamber at 100%RH. It is also observed the incorporation of chloride ions in the CASH matrixes as well as a calcite precipitation on the surface (see figure 4) that could be playing a protective role against water effects. However, instead of any altered zone is clearly observed (as in the case of the OPC+SF concretes), an increase in the total porosity is detected in the upper zone.

Figure 3: EDX profiles in low-pH concretes based on OPC+SF after leaching test. Concrete-1: Basic concrete. Concrete-2: shotcreted concrete.

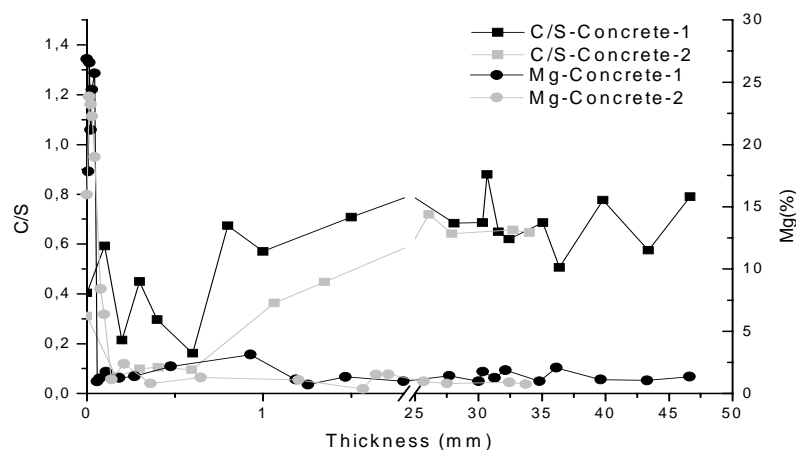
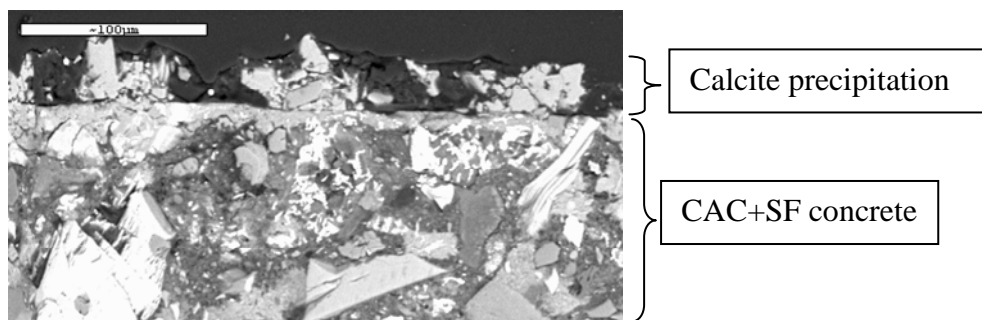


Figure 4: Calcite precipitation in the surface of CAC+SF sample. BSEM image (x350).



Conclusions

It seems that the low-pH concretes evaluated have good resistance against groundwater interaction, although an altered front can be observed from the surface in all the tested samples. In this altered front, in concretes based on OPC+SF the incorporation of Mg^{2+} ions from ground water into the CSH gels (even forming MSH phases) and into the anhydrous phases (as “magnesia nodules”) are suggested. The retention of Cl^- in hydrated cement phases has been also detected in the three concretes studied.

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