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R&D on LOW-pH CEMENT
FOR A GEOLOGICAL REPOSITORY

Workshop June 15-16, 2005 in Madrid

ESDRED

PRESENTATIONS AND DISCUSSIONS

PAPERS

PROGRAMME

PARTICIPANTS

Editor: Göran Bäckblom, Conrox AB

conrox

Preface

As agreed at the previous workshop arranged by SKB in Stockholm in October 15-16, 2003, the 2nd workshop on low-pH issues was arranged during 2005.

The 2nd workshop was hosted by Enresa in Spain in co-operation with SKB, Sweden and the EU Integrated Project ESDRED. The ESDRED project is part of the European Union Sixth Euratom Framework Programme for Nuclear Research and Training and partially funded through this programme.

The objectives of this 2nd workshop were to:

- Share the experience and progress of research and development since the 1st workshop;
- Learn and discuss how performance assessors treat the safety case regarding cement issues;
- Provide information regarding the R&D-plans in progress;
- Search for possible future collaborative efforts.

Close to 30 participants from 8 countries joined the workshop. Photographs of presenters in the back of the report is by Stig Pettersson, SKB.

Täby, Sweden in August 2005

Göran Bäckblom
Editor

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1 Presentations and discussions

This Chapter is a short summary of the presentations and discussions during the workshop, with emphasis on the discussions.

1.1 Welcome speech and practical matters

Maria Cruz Alonso welcomed the participants to the institute IETcc. The chairman Fernando Huertas welcomed the participants to the workshop. The participants introduced themselves.

1.2 FINLAND – Safety case aspects

Paper: LONG-TERM SAFETY ASPECTS OF THE USE OF CEMENT IN A REPOSITORY FOR SPENT FUEL.

Presentation file: SNELLMAN_050615.ppt

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Margit Snellman informed of the sudden death of her co-author Timo Vieno.

The safety concept and definition of the safety case was presented. For Posiva's spent fuel repository (5800 tU spent fuel) the total amount of cement remaining in the host rock after closure is estimated to 10-23kton depending on the method used to support the tunnels, with 5kton for grouting purposes. With respect to the harmful components of cement it has been recognised that even pure cement contain organics , such as amines and derivates as grinding aid in cement manufacturing. The range of pH-plume in crystalline rock is associated with large uncertainties, estimations range from 10-100m in the flow direction. Advance of a pH-plume in rock is in addition to flow conditions influenced by matrix diffusion, and widening and/or sealing of fractures. During the open phase of the underground facility calcite precipitation and sulphide dissolution processes will neutralise a significant part of the high-pH waters emerging on the tunnel walls.

Recognised harmful effects due to cement are apart from cementation by secondary phases the dissolution of montmorillonite, which will lead to reduced buffer function. It was noted that the dissolution rate for smectites strongly increase for pH > 11. Modelling is still not very precise: dependent on model there is small montmorillonite dissolution in one million years or complete removal of the buffer up to 60cm when in contact with cement in 1000 years. An open issue is the redox stability of spent fuel pH > 12.

Several research tasks were suggested: Compared to the situation at the 1st workshop the effort to get a grip on super-plasticizers (SP) was underestimated as it in reality is difficult to receive information on the constituents of the SP from the manufacturers. The SPs need to be studied case-by case with respect to release of SPs from cement, their composition, degradation and complexation properties and effect on sorption of radionuclides.

Fernando Huertas questioned the importance: How critical is 5kton of cement in a 100 000 years – perspective in a large rock volume - are we making ghosts? Margit Snellman answered that the hydraulic conditions are investigated; the grouted sections are the most flowing sections that are avoided for deposition. First mass transport calculations have already been done when the effect of disturbances due to construction of ONKALO was evaluated. Additional mass balance modelling in combination with more sophisticated modelling on the net interaction in the planned repository need also to be done; the experience and new data gained from the investigations and monitoring in ONKALO will be used.

Göran Bäckblom asked about the monitoring programme and the participants were informed that grouted borehole sections were to be packed-off and monitored with probes online. In addition sampling is to be conducted where total and minor constituents, even SP was to be analysed. Tapani Lyytinen informed that different types of cement will be monitored.

Wolf Seidler asked about the function of ONKALO and Johanna Hansen informed of that ONKALO is a test facility that is planned to become an integral part of the final repository.

Fernando Huertas stressed engineering so some buffer degradation can be offset by higher density. Stig Pettersson thought that the influence on spent fuel properties also is important.

1.3 SWEDEN – Bentonite buffer and pH

Paper: LABORATORY EXPERIMENTS WITH COMPACTED BENTONITE IN CONTACT WITH HIGHLY ALKALINE SOLUTIONS

Presentation file: KARNLAND_050615.ppt

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Ola Karnland presented the background and objectives for the study. The issue of bentonite swelling pressure was thoroughly treated. Answer: Full reversibility was noted when testing with Cl^- - ions but the changes due to exposure to OH^- ions were permanent. The lower swelling pressure due to salinity in the water is important for the backfill, not for the buffer due to the high density of the buffer. The long term effects of hydroxide are important for all bentonite components in the repository.

His conclusions were:

- Hydroxide may pass through bentonite at high pH gradients
- Bentonite strongly buffer high pH solutions
- Cristobalite (and quartz) are dissolved
- Montmorillonite is incongruently dissolved
- Swelling pressure reduction at high pH - mass balance with chemical analyses
- No swelling pressure reduction with pH 13 and 12.4 solutions in the short term laboratory tests.
- Possible "buffering effect" by ion equilibrium clay-solution at high clay density

A high-pH plume may reach the canister and the montmorillonite of the buffer may change. The montmorillonite is not thermodynamically stable at high pH, the alteration reactions are relatively fast, and a relatively small amount of cement is needed to alter montmorillonite. Therefore, an overarching result from this study is that the processes due to exposure to high pH cannot be removed from the agenda based on thermodynamic, kinetic or stoekiometrik arguments alone. Geochemical modelling is therefore needed in order to find the proper limits.

Ola Karnland suggested additional work:

- Modelling, including kinetics and transport
- Experiments
  - Neoformation of minerals
  - Silica precipitation from high silica concentration

He also warned for a common modelling aspect: Neoformed minerals with lower density than the original montmorillonite mineral leads to lower porosity in the clay, which is often claimed to reduce permeability. However, this effect is totally overshadowed by the loss of montmorillonite, which radically reduces the sealing properties.

Bernhard Schwyn questioned testing with NaOH when not much of NaOH is available. Ola Karnland argued that NaOH represent the initial limited scenario, but also serves as accelerating conditions for the subsequent period governed by Portlandite in standard

OPC. In the long term perspective also these conditions are expected to result in significant mineralogical alteration. Ola Karnland also presented the background to why batch experiments and tests on compacted bentonite show different release rates for silica; it may be explained by ion-equilibrium established between the hydroxide ions and the montmorillonite counter-ions in the pore fluid of compacted bentonite.

The issue of backfill and swelling pressure was discussed by Johanna Hansen, Margit Snellman and Fernando Huertas. What density should be used for the backfill to be safe from the pH-plume effect?

Russell Alexander asked about the pore structure. Changes due to the bentonite change? Ola Karnland informed that there were no indications of change in the internal pore structure as a result of exposure to high pH solutions, except for what can be explained by the density drop. Philip Rendell asked what concentration level is safe: 0.1 M or a boundary level as 0.3 M? According to OK, a hydroxide concentration of 0.001 M (pH 11) is the tentative SKB limit in order to avoid significant reduction of sealing properties. Xavier Bourbon asked about Potassium. Ola Karnland informed that only a few experiments were made in this study with potassium hydroxide, since the solubility of silica is expected to be similar compared with sodium hydroxide. However, the role of Potassium has to be addressed if also neoformation of subsequent minerals is to be taken in account. This was not addressed in the present study.

Russell Alexander asked about the changes in pore structure due to the change in bentonite. Ola Karnland informed that there were no indications of change in the internal pore structure as a result of exposure to high pH solutions, except for what can be explained by the density drop. Philip Rendell asked what concentration level is safe: 0.1 M or a boundary level as 0.3 M? According to Ola Karnland a hydroxide concentration of 0.001 M (pH 11) is the tentative SKB limit in order to avoid significant reduction of sealing properties. Xavier Bourbon asked about K. Ola Karnland informed that only a few experiments were made in this study with potassium hydroxide, since the solubility of silica in KOH-solution is expected to be similar compared with sodium hydroxide. However, the role of potassium has to be addressed if also neoformation of subsequent minerals is to be taken in account. This was not addressed in the present study.

1.4 SWITZERLAND – Opalinus clay and pH

Paper: USE OF CEMENT IN OPALINUS CLAY AND ITS CONSEQUENCES

Presentation file:SCHWYN_050615.ppt

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Bernhard Schwyn presented the design of the proposed repository in Opalinus Clay where transport would be diffusion dominated. Depending on the assumption how much of the buffering capacity is consumed the rock might be affected 0.5m-17m around the disposal drifts. His conclusions were:

- An alkaline plume can only spread in the range of centimetres to a few metres into the Opalinus Clay
- Due to inhomogeneous porosity distribution the system will most likely seal, slowing further down radionuclide transport
- A alkaline plume may even have beneficial effects on the long term safety; in any case such effects are negligible in the performance assessment
- The use of ordinary portland cement is suggested to be safe for Intermediate Level Waste tunnels and construction elements a few metres away from the Spent Fuel/High Level Waste tunnels
- The results are not necessarily applicable to the use of cement for rock support in the Spent Fuel/High Level Waste tunnels since bentonite may have a different reactivity and is only present in small amounts

Future work suggested is:

- A more detailed assessment for the option of ordinary cement use
- Use of low-pH cement. This option does not make a safety assessment unnecessary (e.g. admixtures!)
- Use of alternative materials like organic polymers

One idea brought forward was to use ordinary portland cement and add clay as a aggregate as a “scavenger” for high-pH fluids.

Ann Emmelin asked about the Opalinus Clay. Answer. The clay was described as hard and with a self-healing capacity. The word Opalinus is connected to the content of fossiles.

Göran Bäckblom complimented on the slide showing concrete and OPA evolution from 50 years to 1 million of years; he also asked about possible changes in the Swiss building code where low-pH concrete would be used to minimise NO_x release and Bernhard Schwyn also had some information that he will follow up. Margit Snellman asked if tests on organics were planned, but only desk studies are foreseen now. Ola Karnland asked what effects are outside the 10cm influence zone, but not much, according to the model.

We discussed technology and Göran Bäckblom asked about the usage of membranes instead of shotcrete and Bernhard Schwyn confirmed that this technology is more and more common – will shotcreting be obsolete technology in 20 years time?[1]

1.5 SPAIN – Methods for testing pH

Paper: TESTING METHODOLOGY FOR pH DETERMINATION OF CEMENTITIOUS MATERIALS. APPLICATION TO LOW pH BINDERS FOR USE IN HLNWR.

Presentation file:ALONSO 050615.ppt

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Maria Cruz Alonso presented the tests on porewater pH – the highest expected pH compared to “apparent pH” as measured at leaching tests. She compared methodology for pore pressing and slurry methods to decide pH. The former method can be viewed as “reference” and the latter as the proposed “routine method”. The experimental study performed has allowed the definition of a protocole test method for determination of accurate and reliable pH of pore solutions of low pH cementitious materials. It has also been found that mineral additions were effective to lower pore pH for OPC, but not for CAC (Calcium Aluminate Cement) samples.

Conclusions:

- The pore pressing test is the most accurate method to determine the pH of the pore aqueous phase. The preconditioning of the samples does not significantly affect the final pH value of the pore fluid.
- The pH is significantly affected by the curing time. The accurate determination of low pH cementitious materials should be given at curing ages of 90 days.

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[1] Wolf Seidler after the conference distributed an e-mail to all participants to share information regarding the Membrane and Shotcreting technology matter. He clarified 2 points: *“First that there is no doubt, that spray on membranes do indeed provide significant rock support even when applied in very thin layers i.e. less than 5mm and that suppliers of these products claim that 2 mm of membrane is equivalent to 50 -70 mm of shotcrete. Secondly that spray on membrane rock support has not replaced standard shotcrete in North American mining applications and that it probably never will. At best the spray on membrane method has probably captured something less than 5% of the mining market otherwise covered by shotcrete. Nevertheless it does have a very specific niche application and many companies are interested in testing the available products. One of the maintain attractions for people doing development work (drifting and tunnelling) is that it is quicker to apply hence making it easier to maintain repeatable cycle times. Some suppliers claim that their spray on product can cover up to 185 m^2/hour."*

- The water/solid ratio used of the leachant influences the pH value. A decrease of pH is measured with the increase of dilution of the leachant, more relevant for CAC based cements than in OPC with mineral additions.
- A slurry 1/ 1 solid/ liquid ratio is recommended.

Céline Cau Dit Coumes asked about how fly ash and silica fume influenced pH. Answer: Fly ash and silica fume produce similar results, but reactions are quicker with silica fume. Too much of silica fume is not good as the necessary technical properties are lost. Céline Cau Dit Coumes also asked if 3 min of stirring is sufficient. Answer: Stirring time was supposed to be sufficient and the risk for carbonation is also increasing with longer stirring time.

Göran Bäckblom asked if IETcc planned to qualify the test method as a standard; there are no such plans answered Carmen Andrade. IETcc is not operated according to a formal quality system.

1.6 FRANCE – Formulation and characterization of cement

Paper: FORMULATING A LOW-ALKALINITY, HIGH-RESISTANCE AND LOW-HEAT CONCRETE FOR RADIOACTIVE WASTE REPOSITORIES

Presentation file:BOURBON 050615.ppt

Presentation file: CAU DIT COUMES 050615.ppt

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Xavier Bourbon provided the context before Céline Cau Dit Coumes explained the experimental set-up and results. She noted for example that pore solutions analysed by XRD all showed Portlandite. She also confirmed higher viscosity with increased content of silica fume. The fraction of pores > 20nm increased with increased volume of silica fume. Pro et con with silica fume and fly ash was presented.

Future work would be needed for

Formulation studies

- Optimisation of the concrete recipes to reduce shrinkage

Investigation of low-pH cement chemistry

- Characterization of the solid and liquid phases of fully hydrated cement suspensions, and comparison with thermodynamic predictions based on the dissolution equilibria of cement phases
- Extraction and analysis of the pore solution of cement pastes at different stages of hydration
- Determination of the location of alkalis in the solid phase

Durability studies

- Investigation of the leaching behaviour of the most promising cement pastes
- Modelling of the results by taking into account both chemistry and transport phenomena

Carmen Andrade thought it necessary to look on microcracks to understand shrinkage and to use fibres for high performance. Answer: Studies on microstructure are in progress.

Céline Cau Dit Coumes also informed that commercially available low-alkaline cement was used. To explain the low concentrations of alkaline ions in interstitial waters, sorption on CSH is not enough. Using Glasser's data (sorption of alkali on CSH phases) and the associated sorption model, we cannot explain why so low concentrations are measured. Sodium and Potassium ions are probably sorbed on silica too. As silica has high sorption property with regards to alkaline ions, this could be the major process to consider. This has to be verified. Further investigations are planned.

Johanna Hansen asked why microcracking occurs; this is caused by the shrinkage, not only due to chemical reasons. The shrinkage is strongly dependent on the recipe. Tapani Lyytinen also though that w/c is important as higher quotient increased shrinkage. Luis Fernandez-Luco also thinks amount of paste to be important. Fernando Huertas thought that shrinkage is relevant to thick construction elements, not to thin rock support by shotcrete.

Maria Cruz Alonso asked about the relation strength and shrinkage, but this has not been tested yes; Maria Cruz Alonso also thought that curing age for tests should be standardized, but Céline Cau Dit Coumes said the Portlandite depletion is dependent on cement composition. Using fly ash the depletion is finished after 12 months.

1.7 JAPAN – Properties of cement tested by CRIEPI and NUMO

Paper: Properties of Low-pH cementitious materials developed and tested by CRIEPI and NUMO

Presentation file: IMOTO_050615.ppt

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Harutake Imoto presented results of testing different cements - a Japanese LAC cement and an Ukranian SAC cement.

- The setting time of LAC and SAC mortars was earlier than OPC. So, early setting time must be controlled by adding a retarder.
- The strength development of SAC depends on the concentration of its mixing solution.
- Hardened LAC mortar, which cured enough, showed better dimensional stability than SAC and OPC mortar.
- LAC has lower permeability than other cements which were investigated in this study.

Göran Bäckblom asked about the difference in hydraulic conductivity – was it due to different particle size distributions? Harutake Imoto explained that the pore size distribution affects the permeability, but from the results, there are no clear relationship between pore size distribution and porosity, and this was unexpected finding. Although, he thinks there might be possibility that the permeability could be evaluated by total pore volume from the engineering viewpoint.

Céline Cau Dit Coumes asked the reasons for shrinkage at high temperatures. She also noted that cement phases are not stable at temperatures 80-100°C. Answer: The project only had a few months for the experiments, that is why we performed the drying shrikage tast at high temperature. The second reason is that the temparature of the repository might become high due to the waste content for HLW disposal in Japan.

Johanna Hansen asked about setting tests. Answer: European standards are used. Carmen Andrade thought it would be better to activate with lime like the Romans did than to use alkalis. Harutake Imoto was not aware of the Roman cement, but that meta-sodium-silicate was proposed.

1.8 FINLAND – Leaching experiments and modelling

Paper: LOW-pH GROUTING CEMENTS - RESULTS OF LEACHING EXPERIMENTS AND MODELLING

Presentation file:VUORINEN_050615.ppt

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Ulla Vuorinen presented test methodology, results and modelling exercises. (pH < 11 is equivalent to 1mmol/L of OH^-). A few promising low-pH mixes fulfilling technical requirements set on the materials were selected for leaching studies. It was concluded that the alkali content did not directly influence the measured pH and that the equilibrium pH of the pore solution mostly depends on the silica content of the binding whatever the added pozzolan is. It was also suggested that minimum content of SiO_2 should be above ~ 50 w% of total binder material and that the Ca/Si mole ratio should be around or below 0.80.

The results measured at VTT and at IETcc were different and Maria Cruz Alonso thought that the results cannot be compared as different systems were measured (pore water vs. leaching). IETcc measured pore water to design the paste. Ola Karnland commented that high silica is good for stability of the buffer if it does not precipitate; then the properties of the buffer may change.

1.9 FINLAND – Lab and field tests

Paper: LOW-pH GROUTING CEMENT TESTING AT THE LABORATORY AND IN THE FIELD

Presentation file: HANSEN_050615.ppt

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Johanna Hansen presented laboratoty results and field tests at ONKALO. She concluded that low pH grouting cement exist and is technically feasible for grouting ”large fractures” > 100µm in hydraulic aperture.

Wolf Seidler asked about grout packers. Answer: They are installed close to the collar. Fernando Huertas questioned tests at low depths (20m) as the higher hydraulic head at deeper levels might influence the results. Answer: Tests will also be conducted at deeper levels in the rock as ONKALO is a test facility.

Göran Bäckblom asked about ”commercial availability” and Tapani Lyytinen explained that materials are selected that is thought to be commercially available for 50 years.

1.10 SWEDEN – Sealing of deep boreholes

Paper: SELECTIVE STABILISATION OF DEEP CORE DRILLED BOREHOLES USING LOW-pH CEMENT

Presentation file: HUGO-PERSSON_050615.ppt

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Torbjörn Hugo-Persson presented techniques for and results from borehole grouting of exploration boreholes.

Russell Alexander did not understand why the holes were grouted; Torbjorn Hugo-Persson explained that the boreholes are for multiple purposes, not only for chemical and hydraulic tests.

The grinder manufactured to ream the borehole could also be used to ream investigation holes to avoid securing packers, thought Tapani Lyytinen.

1.11 Summary of the first day June 15th

Presentation file:BACKBLOM_050616.ppt

In the morning June 16th, Göran Bäckblom conveyed some general impressions:

- We are more experienced compared to the first workshop
- We are involved in product development
    - Implementor-RTD is one tool
    - Let the market do their job as well – do market development to promote low-pH functionality that serves the market (like low release of NOx)
- We are moving theory into practice
- Co-operation seems to be smooth and efficient where methods, products and results are shared between the participants

Significant progress has been achieved in the last 18 months.

We discussed the main conclusions from the previous workshop and most of the conclusions are still valid. However it would be difficult to avoid using super-plasticizers and additives in reality.

The previous statement at the 1st workshop *"Pozzolanas also enhance alkali (Na, K) sorption to the C-S-H phases but the extent of the reactions is not known nor the long-term behaviour of the bound Na and K"* was commented by Céline Cau Dit Coumes as follows: Experiments carried out by different groups in France and Finland show that the Na^+ and K^+ concentrations in the pore solutions or in the leach water are very low (around 1 mmol/L). Preliminary modelling assuming sorption of the alkalis on the low C/S CSH cannot account for such low contents in the solution. There is a need to go further on that point and to test the reversibility of the Na^+ and K^+ "buffering".

The participants were given the opportunity to express impressions, share comments and ideas:

Philip Rendell informed that due to the shift in Nirex responsibility to include HLW/spent fuel in the programme, there is much more interest for the cement issues. He stressed the need of coming to consensus on methodology for pH-measurements; the idea forwarded to use scavengers was interesting.

Bernhard Schwyn stated that Opalinus clay is the main Nagra alternative with granite as an option. In this context, low-pH is not top-priority, but he anyhow thought it good to participate in the workshop. Xavier Bourbon also confirmed clay as the main Andra alternative where considerably amount of concrete will be used. Neither Nagra nor Andra are particularly interested in rock grouting.

Fernando Huertas expressed particular interest in shotcreting applications; Enresa has both clay and granitic options and the granites in Spain are quite dry, so grouting is not high priority. He also expressed a concern that we did not have figures enough to quantify the relevance of the work: How cautious do we need to be? Are we to "academic"? Philip Rendell reminded of the 1st workshop where the licensing was a rationale for the Rsearch and Technological Development (RTD). He thinks it is important to involve the regulators in the work somehow.

Johanna Hansen thought we need a general approach to introduce "new materials" in the repository system and to analyse the long-term effects. From grouting point of view, the durability of the materials is of concern. Fernando Huertas reminded of an SKB visit and discussions on the EBS and rock. Do we give less credit for the barrier function of the buffer? Margit Snellman reminded of the work at the 1st workshop where first results on mass transport modelling were presented..

Ola Karnland reiterated the reality: high-pH plume can impair the barrier function, but Fernando Huertas also thought we need to take into account how the bentonite is saturated as it would be unlikely that a single fracture can transport very much – numbers now are missing. We are concerned of organics but we also need to account for the human organics when operating a facility for several decades. Margit Snellman commented that this is the case for ONKALO and the repository at Olkiluoto, all foreign materials need to be taken into account and minimised.

Stig Pettersson revisited how the low-pH issue developed as an issue and how this issue would have been handled much earlier in the programme with better communication between engineering and safety assessment. He however appreciated the fast advancements to develop low-pH paste, mortar and concrete. The programme in France is aimed for cast concrete, in Spain for shotcrete and in Sweden/Finland/Japan on grouting. Issues to deal with is rock bolting – shrinkage and selection of bolt material, shotcrete fibres and also to change culture to facilitate communication between engineering and safety assessment. A new issue is also the effects o low pH on backfill properties as noted by Ola Karnland and Margit Snellman.

Göran Bäckblom expressed strong concern that many implementers by some reason understate the staff needed for the safety assessment units; the safety assessors have interest to cooperate but no time to interact with engineering and provide guidance during optimisation; the workshop participants classified themselves. ONE participant clearly classified himself as safety assessor, 17 as engineers and 9 as chemists. Göran Bäckblom thought that many implementers should re-think staffing and ensure that core competence for safety assessment is readily available for close co-operation with engineering.

1.12 SWITZERLAND - Long-term cement studies at GTS

Paper: -

Presentation file: ALEXANDER_050616.ppt

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Russell Alexander shared an overview of previous work on the high-pH plume and also invited the participants to join a new experimental/modelling exercise - Long-term Cement Studies to:

- Integrate basic information for high pH-modelling such as TDB, kinetic and sorption database
- Test codes by using existing HPF-results (laboratory experiments, in situ tests and overcoring results)
- Model existing low-pH lab data (JNC-Obayashi-Nagra)
- Further development reactive transport modelling (eg Chalmers, US-DOE/LLNL, PSI, CSIC, Univ. Berne)
- Integrate natural analogue data (Jordan, Roman cements)

- Incorporate the capability of thermodynamic treatment of colloid formation, stability and dissolution (e.g in CRUNCH)

He also confirmed previous discussions: Depth of the facility is really important – a pressure at 45 bars poses technical challenges.

Maria Cruz Alonso asked for what purposes the low-pH cement were to be used as each particular application needs its particular recipe. Answer: JNC is interested in concrete for structural support (underground lab at Horonobe) and Oyabashi for backfill (repository at Rokkashomura. Concerning cement paste there are many sources and Russell Alexander informed of the test programme at University of Sheffield. Bernhard Schwyn expressed the need to involve experts outside the waste community as well.

1.13 EC – Overview of the ESDRED project

Paper: ESDRED & TECHNOLOGY DEVELOPMENT

Presentation file: SEIDLER_050616.ppt

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Wolf Seidler presented the ESDRED project and recent achievements. An interesting detail was that a 65 000 kton press (double weight of the Eiffel Tower) will be used for buffer ring fabrication.

1.14 SPAIN – Shotcrete: engineering and chemical aspects

Paper: POTENTIAL APPLICATIONS OF SHOTCRETE TECHNIQUES IN HLW REPOSITORIES. ENGINEERING ASPECTS AND CHEMICAL IMPLICATIONS

Presentation file: FUENTES-CANTILLANA_050616.ppt

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José Fuentes- Cantillana presented ongoing work to prepare a low-pH shotcrete plug. He stressed the importance of the aggregate grading and the need to use super-plasticizers and additives. Field tests for the FEBEX experiment using OPC showed that layers up to 67cm were sprayed, but that due to thermal cracking 30cm layers were selected.

- Shotcrete has many practical and engineering benefits for rock support and plug construction in HLW repositories
- Problems with alkalinity are similar to conventional concrete
- ESDRED project is investigating a low pH formulation
- Lack of knowledge of long term effects of additives

Louis Londe asked where the cracks formed. Answer: They formed at the centre where temperature was highest. Temperature was measured during curing and the highest temperature measured was 52°C after 22h of curing and measured 50cm from the drift face.

Margit Snellman asked about the selection of the super-plasticizer polycarboxylate. Answer: This is not to be viewed as a recommendation.

1.15 SPAIN – Shotcrete development

Paper: SHOTCRETE DEVELOPMENT FOR LOW-pH CEMENTS

Presentation file: FERNANDEZ-LUCO 050616.ppt

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Luis Fernandez-Luco presented the ongoing preparations to construct a low-pH plug at Äspö Hard Rock Laboratory. The organic content of the hardened concrete would be around 2kg per m^3. Tests of mortar would be good tests for the properties of the final concrete product. He concluded:

- Designed low-pH cement formulations are suitable to produce a low-pH concrete, which can be pumped and shotcreted.
- Slump loss is negligible and the mixes are robust (i.e. minor changes in mixture proportions do not significantly alter the main properties)
- It is possible to fulfil the functional requirements related to mechanical properties
- Further test on cores will give a more comprehensive figure on shotcrete properties.

One surprise is the 50% loss of shotcrete strength compared to base-concrete to be shotcreted.

Johanna Hansen thought it odd that the base-concrete strength increased so slowly with time. Answers: Final strength and water cement ratio is factors to take into account. 40% silica fume was used. Tapani Lyytinen did not understand why aggregates were given and cannot be changed as selection of aggregate is critical for the technical feasibility of shotcreting.

1.16 SWEDEN – Sealing of small fractures

Paper: MATERIALS FOR SEALING OF SMALL FRACTURES

Presentation file: BODEN_050616.ppt

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Anders Bodén gave an overview of the SKB-Posiva-NUMO project to find alternative materials for grouting of narrow fractures (hydraulic aperture <100µm). He concluded with respect to Silica sol:

- Seems suitable to seal very small fractures (<50µm).
- No chemicals are foreseen released in concentrations that would be harmful to the environment.
- The long-term stability of silica sol has not yet been clearly demonstrated.
- Investigations presented gives a better understanding of gel behaviour, but need to be supplemented with other types of long-term stability tests, e.g.
    - leaching tests
    - dry-out/wetting tests
    - behaviour under different climatic conditions

With respect to Periclase – Magnesium oxide he concluded that no further studies are planned because it appears difficult to control setting time and that Periclase so far only has used as a temporary water blocker.

Carmen Andrade questioned the use of sodium chloride for accelerator; Margit Snellman explained that the anticipated concentration of the accelerator being leached from the silica sol is well below the natural background level. Carmen Andrade also asked why low-pH cement was not used for sealing the fine fractures; Ann Emmelin explained that cement particles clog and cannot be used for very fine fractures as no penetrability is achieved.

1.17 SWEDEN – Sealing of small fractures – field testing

Paper: SILICA SOL FOR SEALING OF FINER ROCK FRACTURES – FIELD TESTING

Presentation file: EMMELIN_050616.ppt

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Ann Emmelin presented results from field testing at Äspö Hard Rock Laboratory and the road tunnel Törnskog. The experience using silica sol for grouting fine fractures is very promising and she concluded:

- Ordinary grouting equipment works fine
- Material is easy to mix. Can be done in agitator
- Careful dosage is vital
- Materials should have same temperature as the rock
- Workers adapted easily to new routines.
- Grouting time and cycle time same or shorter compared to cement
- Good sealing results!
    - Before grouting k= $1.2 \cdot 10^{-8}$ m/s
    - After grouting k= $1.2 \cdot 10^{-10}$ m/s

Johanna Hansen asked about what fan length was used. Answer: The length used was as for a standard grouting fan that very often is grouting 20m fans for three round of excavation and one overlapping round.

1.18 Final discussion, collaborations and future actions

Wolf Seidler expressed concern that the wheel was re-invented. Several participants are knowledgeable of present international state-of-the-art and confirmed independently that usage of low-pH issues needed specific genuinely new development work for technology that is not available elsewhere.

Bernhard Schwyn thought we should try to connect to industry and competence outside the waste community as well. Philip Rendell thought it be necessary to connect to regulators as well.

Margit Snellman brought forward the need to prepare “reference solutions” and compare different pH measurement tests and strive for standardisation. There is need both for pore water measurements as well as for leaching as the latter results are used for mass transfer modelling.

The following actions were decided:

- Maria Cruz Alonso will act as facilitator and arrange so that Céline Cau Dit Coumes, Margit Snellman and herself meet to prepare plans and actions in detail. The workshop participants will be kept posted of the progress.
- The invitation for a 3rd workshop arranged by ESDRED/ANDRA in Paris during Q3 2007 was acknowledged and gladly accepted.

Wolf Seidler was impressed by the workshop and that no translators were needed; with one exception all participants used a second language.

The chairman Fernando Huertas conveyed appreciation to IETcc for the use of the premises, the active participation of the delegates and closed the workshop before the IETcc laboratory facilities were toured.

2 Long-term safety aspects of the use of cement in a repository for spent fuel

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2.1 Introduction

Posiva aims to present the Safety Case supporting the construction license application of the spent fuel repository at Olkiluoto by 2012 /Posiva 2003/. The KBS-3 type repository is planned to be constructed at a depth between 400 and 600 metres in crystalline bedrock. Construction of the underground rock characterisation facility ONKALO was started in 2004.

In the KBS-3 concept safety rests first and foremost on the long-term isolation and containment of radionuclides within the copper-iron canisters. The repository design aims at preventing any releases of radionuclides from the repository into biosphere as well as into the geosphere, for 100 000 years at least. Long-term containment within the canisters in turn depends primarily on

- the probability of initial defects being kept at an acceptably low level, i.e. on the proven technical quality of (at least this aspect of) the Engineered Barrier System (EBS), and on
- favourable near-field conditions for the canisters that promote their longevity.

The technical quality of the EBS is favoured by the use of components with well-known material properties and by the development of appropriate acceptance specifications and design criteria. Favourable and predictable bedrock and groundwater conditions are a prerequisite for favourable near-field conditions. Besides providing a protective environment for the canisters, the siting and design of the disposal system ensure that any radionuclides released from an initially defective or subsequently breached canister undergo retention, retardation and dilution by other barriers, in accordance with the multi-barrier principle.

The aim at long-term and complete containment of radioactive substances within the copper-iron canisters emphasises the need to evaluate the evolution of the disposal system and the integrity and performance of the EBS, in the first place those of the canisters and the bentonite buffer surrounding the canisters in the deposition holes.

A plume of high pH originating from cement may affect transport processes in the geosphere and the performance of the EBS. The main concerns are related to the alteration of bentonite, stability of fuel matrix, and validity of perfomance assessment databases in high pH environments. The potential disturbances due to superplasticizers and other organic admixtures of cement are not known. In the long term degrading concrete structures, such as injection borehols, liners and floors, may become preferential flow and transport pathways.

2.2 Safety case

Safety case is a synthesis of evidence, analyses and arguments that quantify and substantiate the safety, and the level of expert confidence in the safety, of a geological disposal facility for radioactive waste /NEA 2004/. A safety case includes a quantitative safety assessment, which involves the process of systematically analysing the ability of the disposal facility to provide the safety functions and to meet technical requirements and evaluating the potential radiological hazards and compliance with the safety requirements. The safety case broadens the scope of the safety assessment to include the collation of a broad range of evidence and arguments that complement and support the reliability of the results of the quantitative analyses.

Stated in another way, a safety case includes all what the applicant presents to the authorities and other stakeholders in support of an application to site, construct, operate or close a disposal facility. The safety case is a key input to decision making at several steps in the repository planning and implementation process, and it will become more comprehensive and rigorous as the programme progresses. Posiva’s safety case supporting the construction license application of the disposal facility at Olkiluoto will include demonstrations of canister manufacturing, repository technologies and constructability /Posiva 2003/.

Deposition tunnels will be backfilled and plugged soon after the emplacement of the canisters and buffer in the deposition holes. The gradual construction and operation of the repository will, however, continue over several decades. To emphasise the important role of the thermal, hydraulic, mechanical, chemical, (micro)biological as well as gas and radiation related (THMCBGR) processes (e.g. resaturation, swelling of the buffer, thermal pulse) taking place during the operation phase, when parts of the repository cavities are under construction or in operation, we use the term *post-emplacement* (instead of post-closure) assessment, indicating that the starting date (year T0) of the safety case is when the first canisters are emplaced in the repository.

Posiva’s Safety Case aiming at the construction licence by 2012 will be organised in a portfolio including approximately ten main reports (based on supporting technical reports), which will be periodically updated. The nature of the reports and the most important links between them are illustrated in Figure 2-1. /Vieno & Ikonen, 2005/.

The **Site report** /Posiva 2005/ describing the present state and past evolution of the Olkiluoto site, as well as the disturbances caused by the construction of ONKALO and the first stage of the repository (until emplacement of the first canisters in the repository), forms the geoscientific basis of the Safety Case.

The **Process report** containing descriptions and analyses of features, events and processes potentially affecting the disposal system, and the report on the **Evolution of site and repository** form the scientific basis of the Safety Case. The report on the Evolution of the site and repository is expected to provide:

- qualitative description of the evolution of the disposal system from the emplacement of the first canisters in the repository over the various transient phases into the far future;
- quantitative analyses on mass and energy balances and flows within and around the repository, including
- analyses of flow and transport of groundwater and solutes.

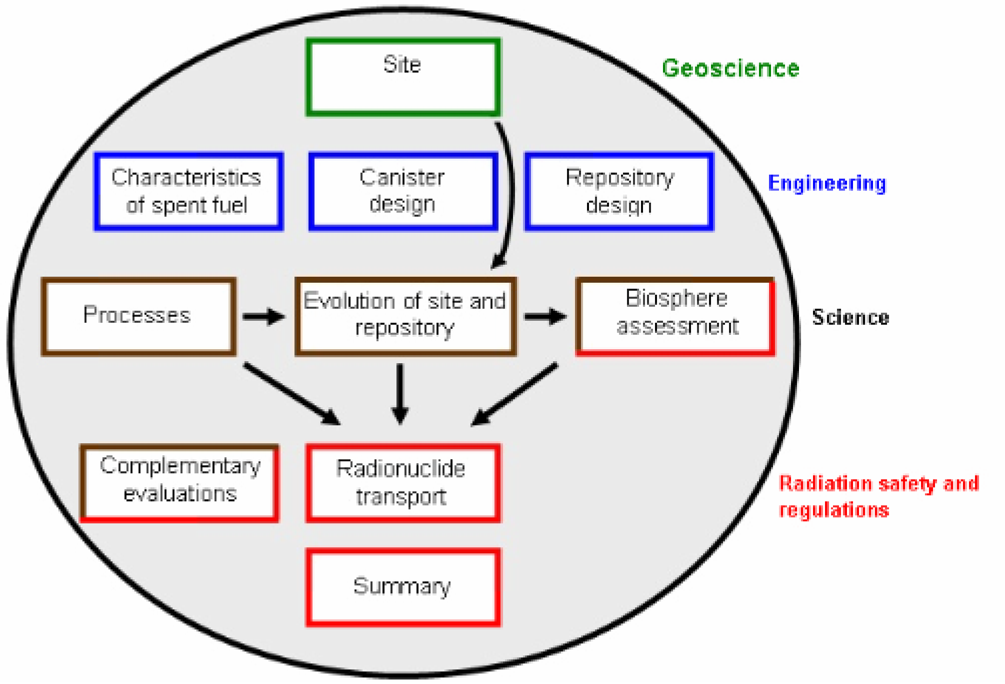

Figure 2-1. Main reports of the Safety Case /Vieno & Ikonen 2005/. The nature of the reports is indicated by the colours of the boxes and the arrows show the most important transfers of knowledge and data.

Important inputs to the Evolution report will come from the Site report, providing information, data and modelling results on the past evolution, present state as well as on the disturbances caused by the pre-emplacement (i.e. pre-2020) construction of ONKALO and the repository. The items to be discussed in the **Complementary**

evaluations report include e.g., natural analogues of the disposal system and observations from the ONKALO monitoring programme and their implications.

2.3 Use of cement

Planned use of concrete or cement in repositories for HLW is generally for limitation of water ingress, stabilization of walls, pavement of floors during operation, and in plugs for prevention of backfill intrusion or for sealing of tunnels.

Concrete and cement is used in ONKALO, e.g. for grouting to limit the groundwater flow, as shotcrete and as casting material for rock bolts to reinforce the excavations, which is necessary for operational safety and also limits mechanical disturbances. Sealing of rock by means of grouting is a key method in restricting the leakage of groundwater into ONKALO and the repository at Olkiluoto. The inflow rate of groundwater should be: “as low as reasonably achievable” to limit hydrogeological and hydrogeochemical disturbances (intrusion of superficial waters, upconing of deep saline groundwater). On the other hand, the sealing materials to be used must not cause any harmful changes to the rock and barrier materials in the repository. The amount of cement and additives used should be minimized and the number of grouting holes should be mimimized.

For Posiva´s repository (hosting about 5800 tU of spent fuel), the total amount of cement remaining in the host rock after the closure of the repository is estimated to be 10 000 – 23 000 tons, depending on the methods used to support tunnels /Hjerpe 2003/. The amount of grouting cement is estimated to be approximately 5 000 tons. These estimates include the cement used in ONKALO.

2.4 Harmful components of cement

There is an agreement on the evolution of the key chemical parameters that takes place at the interface of any piece of concrete (cement) once it has got in contact with groundwater, which is summarised in Figure 2-2 and Figure 2-3. The initial high Na and K concentrations are a consequence of the non-restricted solubility of NaOH and KOH present in freshly hydrated cement. The following increasing/high Ca concentration is a result of $Ca(OH)_2$ solubility. The peak in SiO_2 reflects SiO_2 release from CSH phases.

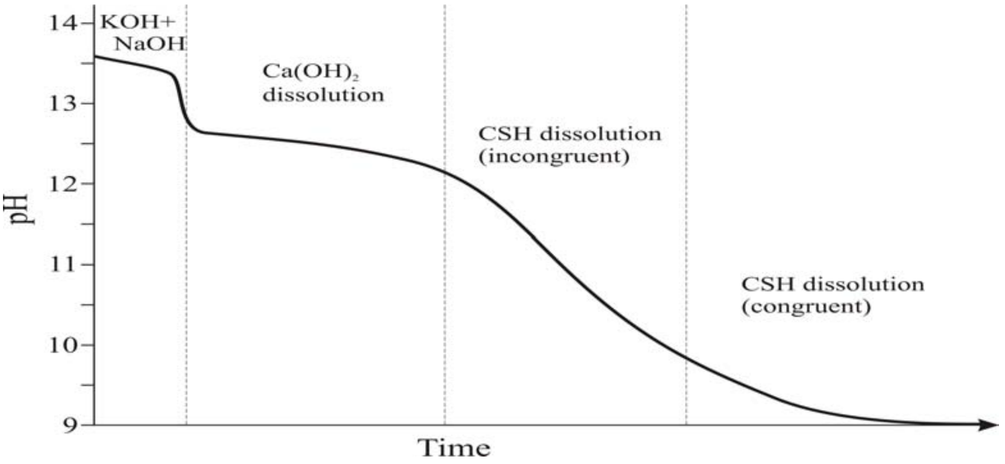

***Figure 2-2**. Schematic illustration on pH evolution in cement equilibrated porewater as a function of time.*

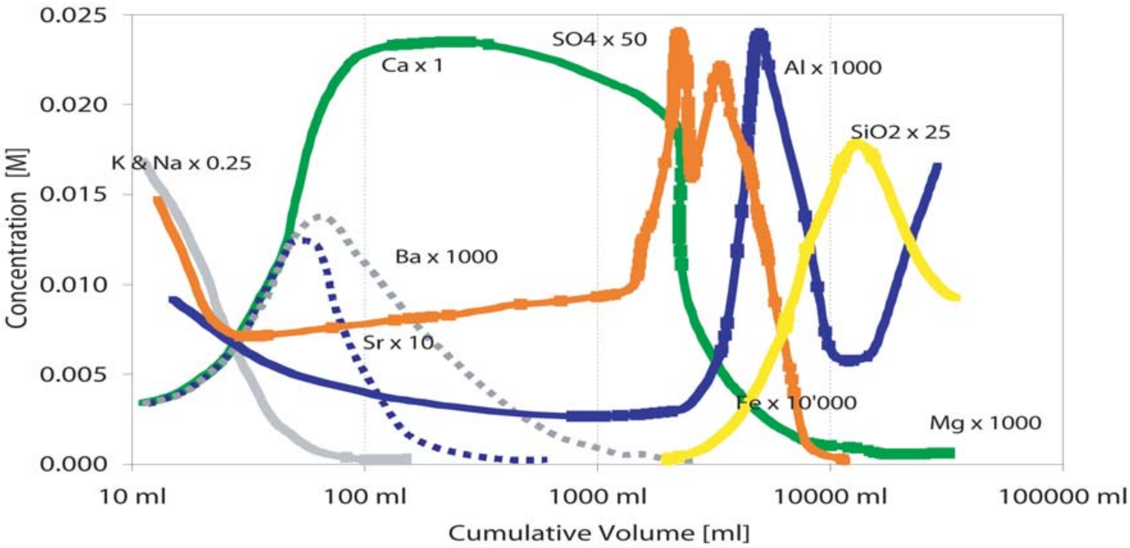

***Figure 2-3.** Schematic representation of ion release from degrading cement (10 ml of cumulative volume correspond to 1 sample pore volume) /Berner in Metcalfe & Walker, 2004/. The apparent double peak in the sulphate concentration represents an experimental failure*

The alkali and alkali earth species in cement are the main substances of concern as they may impair the key functions of the bentonite buffer. Other components of cements or concretes, which might be harmful with respect to the EBS and spent fuel include e.g.:

- Organics added to cement during the manufacturing, e.g. to reduce drying time, and protect against freezing and thawing. A mix of different amines, e.g., triethylene-tetramine, diethanolamine and their hydroxyl derivates, about 60-200 ppm is added in the cement grinding during the manufacturing of cements by

Cementa in Sweden. Ultrafine 16 (Cementa) contains about 0.005-0.01% grinding aid /Sievänen et al. 2005/

- Organic additives added during the mixing of the grout, e.g. superplasticizers, mostly sulphonated organic polymers based on melamine, naphtalene, carobxylate or acrylate, often mixed with various inorganic compounds, such as nitrates. The additives are typically added in 1-3 weight-% of dry materials in the grout.
- Phosphor or nitrogen compounds, these may be present in silica fume or gypsum added to the cements, e.g. gypsum may contain 0.02% NH_3 /Sievänen et al. 2005/.
- Sulphides present in pozzolans added to cements or concretes, such as blast furnace slag, e.g. Finnish slag may contain up to 1.1-1.5 % of sulphides /Sievänen et al. 2005/.
- Sulphates leaching from cement may also be potential sources of sulphides due to reduction by sulphate reducing bacteria present in the bedrock.

These compounds may either act as complex formers (organics, phosphor compounds) or may enhance the corrosion of the copper canister (sulphides, nitrogen compounds).

2.5 Extent and effect of an alkaline plume in rock

Questions of concern for the near-field rock are due to the extent of and effect of the alkaline plume. In the case of fractured rock the advance of the plume through the fractures is associated with uncertainties being conditioned by the flow conditions, the effectiveness of matrix diffusion (sealed by the same plume), and the effectiveness of fracture sealing or widening. The estimations made are of tens of metres, to a maximum of about 100m in the flow direction. In these circumstances uncertainties are also related to the extent of rock-matrix diffusion and the location of reaction products /ECOCLAY II 2005/.

The consequences in a fractured rock include possible reduction of mechanical strength facilitating strain, alkaline weathering and porosity reduction (sealing of fractures). Reactions with matrix minerals, precipitation and dissolution reactions and formation of CSH, alumina and zeolites are occurring /ECOCLAY II 2005/. For example, the Hyperalkaline Plume in Fractured Rocks (HPF) study at the Grimsel rock laboratory demonstrated a strong decrease in transmissivity already over a two-year experimental time due to changes in flow field caused by high-pH alteration products formed /Mäder et al. 2003/.

During the time-span of the open tunnel phase of a repository, e.g. about 100 years at Olkiluoto, it can be expected that calcite precipitation, of released calcium with CO_2 present in the tunnel air, on the tunnel walls and sulphide dissolution as long as O_2 is present in the tunnel air are active processes. A significant part of the high pH-waters emerging on the tunnel walls will likely be neutralised with these mechanisms /Luukkonen, 2004/.

The extent of the alkaline plume in rock can be estimated based on mass balance and mass transport analyses, as has been done by /Vieno et al. 2003a,b/. For the fractured rock at Olkiluoto the key factors controlling the extent of the alkaline plume are due to local groundwater flow and transport conditions, which have a major influence on the release and transport of cement and subsequently on the magnitude of the high pH plume in the bedrock.

1. Sub-horizontal fracture zones divide the flow pattern into layered zones. It is unlikely that a significant amount of cement above or from major sub-horizontal zones would be transported into the sparsely fractured rock below the zones.

2. The water leaving a grouted rock spot will not have the pH and other property of cement pore water, but is diluted by the groundwater flowing around/through the grouted area. This source term dilution is enhanced by the fact that grouting is carried out at fracture zones and other locations where flow rates are highest.

3. Further buffering and dilution take place during transport in the geosphere. Rock-groundwater systems have two buffering mechanisms, which may neutralise a high pH-plume. Silicate minerals and carbon acid are able to consume OH- ions in alkali hydroxide fluids released from cement. High-pH water – mineral interactions in rock follow complicated neutralisation processes that are likely mostly governed by silicate dissolution reactions as based on theoretical evaluation and experiments with crushed rock in contact with alkaline solutions /Luukkonen, 2004, Vuorinen et al. 2003/. The results emphasise the significance between the reactive surface areas and the time available for reactions and the flow-rate of high-pH water.

4. In open fractures with a limited buffering capacity and a small WL/Q (half of the "flow wetted" surface divided by the flow rate), the leachate may, however, be transported over long distances.

5. Transfer of OH^- -ions from water-conducting fractures intersecting a deposition hole is limited by the boundary layer (film) resistance between the flowing groundwater and the stagnant pore water in the buffer. The fraction of OH^- ions entering the buffer decreases with an increasing flow rate of groundwater along the fractures.

6. Also in the assessment of the effects of OH^- ions entering the bentonite buffer from rock fractures, one must take into account that the attack is localised. Diffusion processes and reactions between the intruding solution and the clay govern the shape and volume of the affected bentonite.

The overall conclusion from the “simple” mass transport analyses performed is that it is fairly unlikely that cement transported from ONKALO would significantly impair the key functions of the EBS in the repository.

2.6 Effect of alkaline solutions on bentonite

In order to assess potential impact of the chemical alteration of the bentonite on its barrier performance, the following key questions have to be answered:

- How will the bentonite clay be altered by reactions with the alkaline pore fluid?
- How much bentonite will be altered in the PA relevant time scale?
- Will the chemical alteration of bentonite lead to any significant advert effect on its barrier performance?

Based on the research during the last year bentonite when exposed to a highly alkaline solution will undergo chemical and physical changes /e.g., ECOCLAY II 2005, Karnland et al 2005 a,b, Metcalfe & Walker, 2004, Savage et al., 2005/ including dissolution and precipitation reactions, formation of new minerals, and cementation and fracturing effects (Figure 2-4).

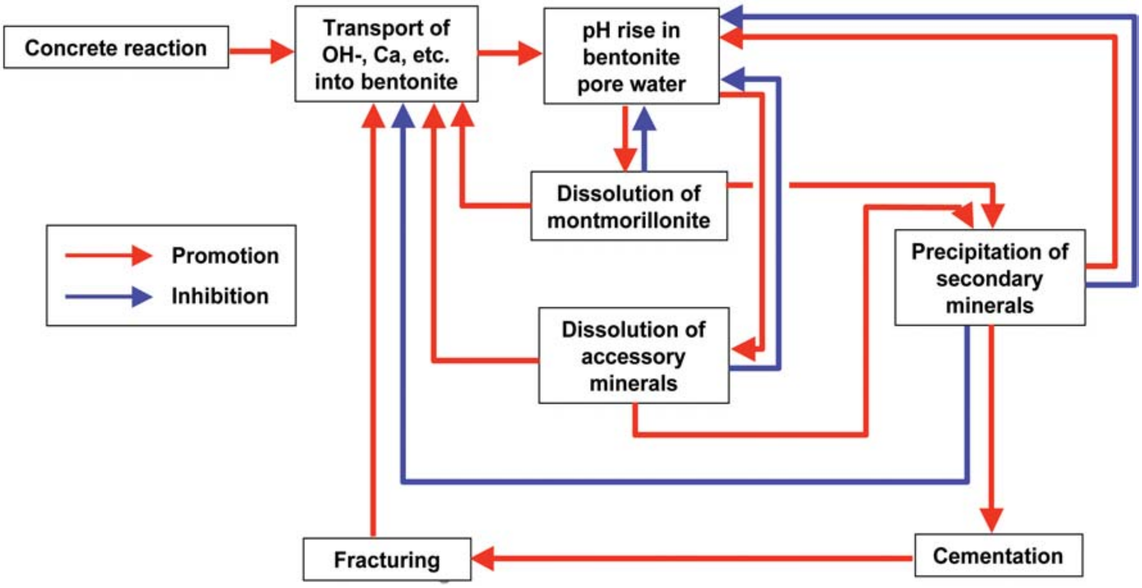

Figure 2-4. *Cement/Bentonite interaction as a coupled non-linear dynamical system /Takase in Metcalfe & Walker, 2004/.*

The degree of bentonite alteration is sensitive to a number of factors, such as rate and mechanism of montmorillonite dissolution, the variation of bentonite transport properties with time, the composition of cement pore fluid, and the crystallinity and types of secondary minerals.

Solids forming from the interaction of cement pore fluids with bentonite depend upon temperature, the composition of the bentonite (nature of the montmorillonite itself and content of accessory minerals), the composition of migrating cement pore fluids, the composition of ambient groundwater, and the fluid/solid ratio (more likely expressed as the compaction density of the bentonite). Ionic equilibrium effects between external hydroxide solution and the montomorillonite pore fluid may also influence the chemical reactions /Karnland et al. 2005a/. The rise of temperature and the increase of time, solution pH and the solution-to-solid ratio tend to favour the reaction progress. In addition, the nature of reaction products is strongly affected by the cation content of the reactant fluid /Savage et al. 2005, Lehikoinen in Metcalfe & Walker, 2004/.

It seems that mineral transformation in compacted systems under diffusion control is a powerful chemical buffer against a high-pH solution. Furthermore, it is conceivable that the propagation of the high-pH front will slow down to some extent[2] due to the fact that the solid reaction products, in their part, buffer the ingress of the aggressive plume /Lehikoinen in Metcalfe &Walker 2004/. Though, it is obvious that OH- solutions migrate through highly compacted bentonite if the pH-gradient is sufficiently high /Karnland et al. 2005a/.

Calcium/Magnesium (aluminium) silicate hydrates (C(A)SH), zeolites, hydroxides, carbonates, polymorphs of silica, and some sheet silicates (all of varying degrees of crystallinity) are potential products of cement-bentonite interaction. Evidence from natural systems and laboratory studies suggests that these phases may precipitate on timescales of interest to the safety assessment of radioactive waste disposal. The effect of cement can be presented as a “moving front” of alteration of the bentonite, driven by the rate of migration of cement pore fluids, with zeolites of variable Si/Al ratio preceding predominantly C(A)SH solids of variable Ca/Si ratio. Over time, K-Na-Ca solids will be replaced by more calcic varieties /Savage, 2005/.

2.6.1 Dissolution rate vs. pH conditions

According to /Sellin et al. 2003/ the dissolution rate for a number of aluminium silicates, e.g. quartz, kaolinite, increases by a factor of 10 if pH is increased from 11 to 13, and laboratory experiments referred to implied that bentonite is much more stable at pH 11 as compared to pH 13. Kinetics of montmorillonite dissolution can be regarded as a direct constraint on the amount of dissolution, and enhanced dissolution rate under higher pH has been observed /Metcalfe & Walker 2004/. The recent studies by Huertas et al. /in ECOCLAY II 2005/ confirm these observations as it was found that for smectite dissolution the pH value 11 is a critical value, above this the smectite dissolution rate increases significantly. This effect will be strengthened at higher temperature.

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[2] Assuming that the hydraulic properties do not increase drastically upon mineral alterations.

2.6.2 Consequences of the alteration of bentonite

Apart from general cementation by secondary phases the most important effect is dissolution of montmorillonite, which will lead to reduced buffer functions. The reaction between the hydroxyl groups in the cement leachate and bentonite gives a significant release of silicon. Initially silicon in solution is controlled by the dissolution of silica polymorphs (cristobalite and quartz) followed by the dissolution of montmorillonite /Karnland et al.2005a/. Dissolution of accessory minerals may lead to reduced buffer functions if the dissolution products are transported away and/or if the secondary products have higher densities than the original minerals. On the other hand, the porosity will decrease if neo-formed minerals have lower density than the original minerals. It is necessary to consider the possibility that alteration may lead to the formation of regions with high porosity next to regions with low porosity and cause mechanical instabilities.

The consequences of the above reactions include decrease of swelling pressure due to mass loss and decrease in density (Figure 2-5), increase of hydraulic conductivity, decrease of permeability (small effect), increase in cation exchange capacity and increase of fissuring due to cementing processes (CSH-gel). If cement-bentonite alteration results in porosity reduction that causes a permeability decrease there could be an adverse effect since the potential for gas pressures to raise, leading to eventual cracking of the barrier, might be enhanced.

For compacted bentonite a permanent decrease in swelling pressure and increase in hydraulic conductivity has been found for alkaline solutions with $pH > 13$ (>0.1 M NaOH), whereas typically no or small decrease in swelling pressure has been recorded for compacted bentonite in contact with a hyperalkaline fluid with $pH <13$ /for details see Karnland et al. 2005a,b/. The permanent decrease in the swelling pressure is caused by the dissolution of the bentonite minerals, which changes the sample mass.

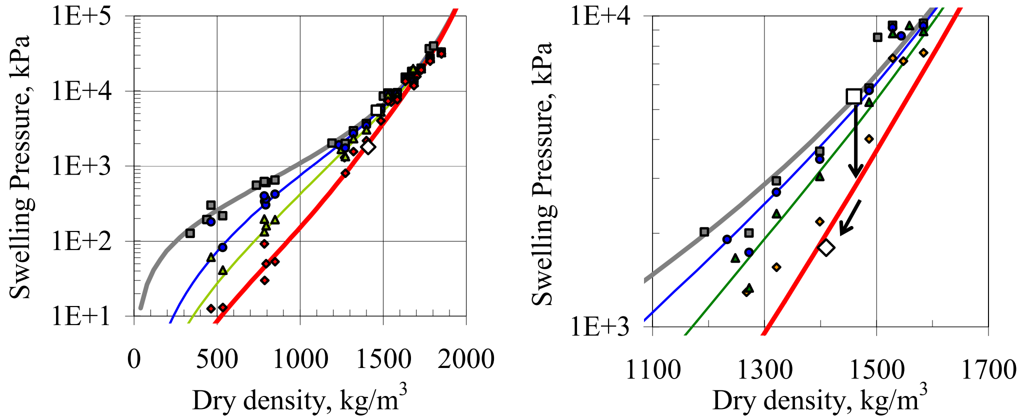

Figure 2-5*. Left: Measured (dots) and calculated (lines) values of swelling pressure versus density in pure montmorillonite exposed to NaCl solutions Right: Close up showing initial (□) and final (◊) pressure versus density in MX-Na contacted with 1.0 M NaCl/NaOH. Upper bold line and squares represent de-ionized water conditions, and lowermost line and diamonds represent conditions in 1M NaCl solution /for details see Karnland et al. 2005, this report/*

2.7 Effect on other components

The copper canister is more strongly passivated the higher the porewater pH is and less likely to undergo localised attack. However, if the porewater salinity increases prior to the increase in the pH (above 9) there could be a period of active canister corrosion before passivation occurs /King 2002/.

The dissolution of spent fuel cladding may increase and solubilities of radionuclides will be affected. The redox stability of spent fuel is questionable if it comes in contact with a high pH solution, at pH above 11 the uranium dioxide matrix may get instable and “dissolve fast” /Sellin et al. 2003/.

The influence on radionuclide transport at pH values above groundwater pH can be both positive and negative. Transport calculations must be done /Sellin et al. 2003/. Solubility and sorption databases specific to the KBS-3 concept and crystalline rock at high pH conditions (pH > 10-11) are scarce.

For colloid transport especially effect on additives and precipitations due to pH transitions need to be evaluated, silica colloids may be formed at the plume front.

2.8 Future efforts needed

In addition to “simple” mass balance and mass transport modelling of the effect of cement in a repository a more sophisticated modelling is though needed in order to have the net effects of individual interactions in the overall performance of a repository. The evolution of the system components is a sum of THMCBGR interactions which will vary at different time steps, and also part of the components are not yet well understood, e.g. the composition and effects of the organic additives. To build a robust safety case a full overview of all relevant processes is needed /Alexander et al. 2005, Metcalfe & Walker 2004, Vieno et al. 2003/.

Uncertainties in the transport analyses could be reduced by further experiments and modelling studies on transport and effects of cement in fractured rock, such as the Long-Term Cement Studies (LTC) project, which is a continuation of the Hyperalkaline Plume in Fractured Rock (HPF) project in the Grimsel Rock laboratory in Switzerland. Long-term monitoring of the leaching and spread of the cement in ONKALO, both ordinary Portland cement used and low-pH cement tested, and experiences gained from grouting in ONKALO will likely give valuable input to the evaluation of the further use of cement in fractured rock at Olkiluoto.

As it is obvious that high pH is detrimental for the EBS and spent fuel, the amount of cement to be used should be minimised and further testing of low-pH cement materials (pH $\leq$ 11) must be done in relevant repository conditions. As there is and will not be any long-term experience of the materials at the time when they are foreseen to be taken into use, theoretical evaluation of the long-term behaviour of the low-pH grouts is needed; such as phases formed, kinetics of reactions, degradation rates etc.

Many of the organic additives used in cement and concrete structures have a potential for forming strong complexes with radionuclides. The additives are commercial products of fairly ill defined composition and mostly contain also components other than those indicated in the safety sheets. It follows that the product and specific effects of the product to be used must be evaluated as case-by-case study. The composition of the organic additives, their release and degradation properties including also the potential effects of microbes on the degradation of the additives as well as their complexation properties and effect on sorption will be studied in a starting SKB-NUMO-Posiva project.

In case of bentonite the relatively fast diffusion of hydroxide ions through bentonite with apparently little chemical buffering clearly needs more effort, in particular, the propagation of OH^- in relation to the "buffering rate" of compacted bentonite.

So far, predictive model calculations on the long-term evolution of the bentonite buffer in contact with high-pH solutions have been fairly speculative, the model results ranging from a small amount of montmorillonite dissolution in one million years to total removal of primary bentonite minerals up to 60 cm from the contact with cement in about 1 000 years /Vieno et al. 2003/. Unfortunately, the mass flow rates of OH^- ions and other solutes entering the bentonite from concrete were not recorded in any of these simulations. A common problem with all the model calculations with complex mineral assemblages is poor knowledge of possible reaction products and of mineral dissolution and growth kinetics, which are thus subject to considerable uncertainty. It is also important to consider the range of secondary minerals that may form and the temporal sequences in which they form /Lehikoinen in Metcalfe & Walker 2004/.

Effects of cement on backfill materials need to be considered, too.

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

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3 Laboratory experiments with compacted bentonite in contact with highly alkaline solutions

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3.1 Introduction

In a future repository for spent fuel, it will be most practical to use concrete for various constructions, and cement for sealing of fractures. In the Finnish ONKALO underground facility, the estimated quantity of cement is $3 \cdot 10^6$ kg /Vieno et al. 2003/, and in the planned Swedish KBS3 repository /SKB, 1999/ the corresponding figure is around $9 \cdot 10^5$ kg /PLAN 2003/. However, the release of alkali metals from fresh cement will increase the activity of cation/proton ratio significantly compared to ground water conditions. The pore fluids of fresh cement range in pH from 13 to 14, and in matured cement portlandite ($Ca(OH)_2$) supports pH at c. 12.4. These highly alkaline conditions may affect other repository components in a KBS3 repository, such as the fracture minerals, the bentonite buffer, the canister and the spent fuel in case of a canister failure. The resulting reactions in the bentonite buffer are of special interest, since the buffer completely surrounds the canisters and thereby may protect them by chemical buffering. The interaction between high pH solutions and bentonite involves both ion-exchange on montmorillonite surfaces, and dissolution of accessory minerals and of the montmorillonite (Figure 3-1). These reactions may lead to significant negative changes in the favourable physical properties of the buffer, e.g. increase of hydraulic conductivity and decrease of swelling pressure.

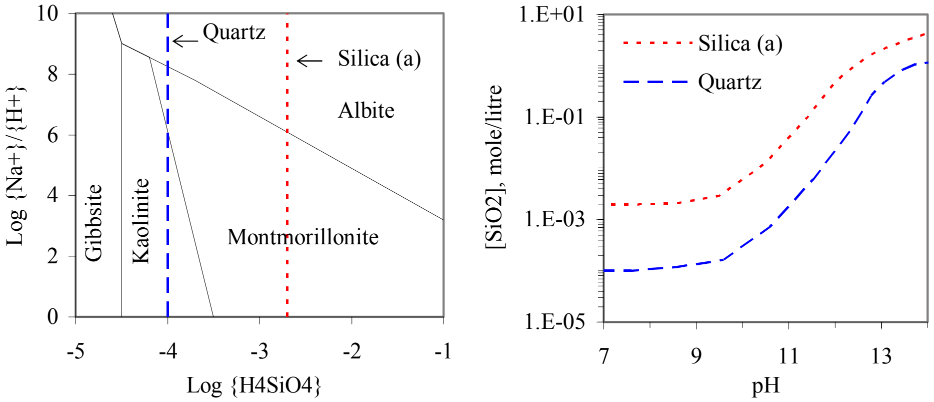

Figure 3-1. *Left: Stability relations of some phases in the system Na2O-Al2O3-SiO2-H2O at 25 oC and 1 atm, as function of {Na+/H+} and {H4SiO4} (simplified after Helgeson et al. 1969). Right: Solubility of silica versus pH in NaOH solutions. Hatched line indicates quartz saturation and dotted line indicates amorphous silica saturation. Calculations with PHREEQC v. 2.8 /Parkhurst & Appelo 1999/.*

Most studies on the interactions between bentonite and cement pore-water have been performed either as batch experiments with a high solution/solid ratio /e.g. Bauer & Berger 1998; Bauer & Velde 1999; Cama et al. 2000/, as flow-through experiments /Cama et al. 2000/ or as modelling studies /e.g. Jefferies et al. 1988; Savage et al. 2002/. In contrast, our study focuses on the interaction between hyperalkaline solutions and highly compacted bentonite in order to simulate e.g. ion-equilibria and transport restrictions prevalent in a KBS3-type bentonite buffer, which may affect migration rates, as well as reactions and reaction rates. The major questions addressed were:

- at what rate will a high molar hydroxide solution migrate through bentonite which has been compacted to the density of a KBS3-type buffer (2000 kg/m^3 at full water saturation)?
- at what rate will the reactions between the bentonite minerals and hydroxide solutions proceed?
- how will vital physico-chemical properties, of the bentonite change due to the interaction with highly alkaline solutions?

3.2 Experimental

3.2.1 Experimental design

To simulate the interactions of cement pore water with a bentonite buffer, pressure cells with permeable filters were loaded with highly compacted discs of bentonite. A hydroxide solution was circulated on one side of the cell and an isotonic chloride solution on the other, using the equipment and experimental design shown in Figure 3-2.

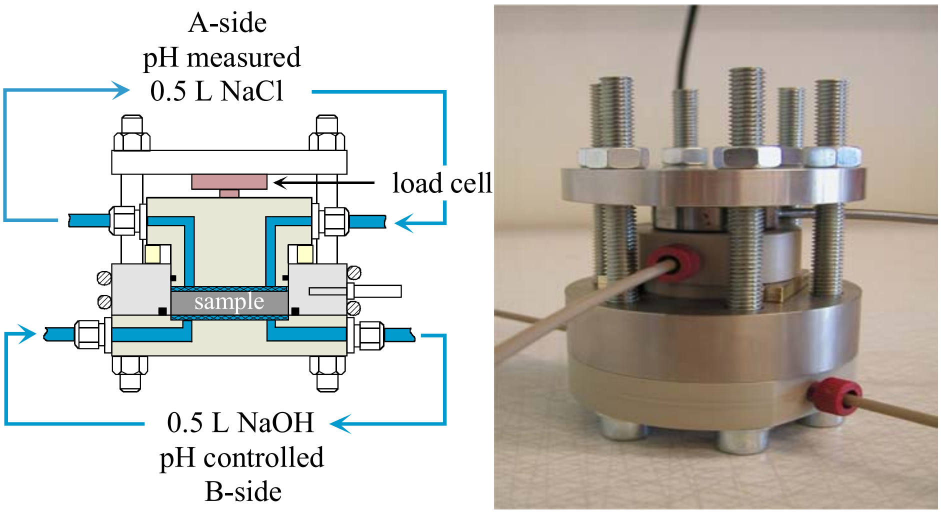

Figure 3-2*. Schematic drawing and photo of the pressure cell used for all tests.*

Swelling pressure and solution pH were monitored during the tests, which lasted for a minimum of 45 days. With the experimental arrangements used, the access to air was limited and the system performed virtually as a closed system. To allow discrimination of reactions with the accessory minerals on one hand, and montmorillonite on the other, both bulk bentonite and purified montmorillonite were used as test materials. In the most unfavourable scenario from a safety assessment perspective, the rate of hydroxide transport through the bentonite buffer and the rate of mineral dissolution are high. To keep test conditions conservative in this respect, the solution volumes were kept large enough (0.5L in each loop) to maintain solutions undersaturated with respect to silica.

3.3 Materials and methods

The bulk material from one batch of commercial Wyoming bentonite (MX-80, 2001-01-19 from American Colloid Co.) was used for the tests together with the <2 µm fraction separated by sedimentation in de-ionized water. The <2 µm fraction was converted to homo-ionic Na- and Ca-montmorillonite (referred to as MX-Na and MX-Ca in the following text) by addition of analytical grade NaCl and $CaCl_2$ to the clay suspensions. To remove excess electrolytes, the suspensions were transferred to dialysis membranes (Spectrapore 3, 3500 MWCO) placed in plastic tanks with de-ionized water. The <2 µm fraction consists of almost pure montmorillonite (96%). The montmorillonite content of MX-80 is around 85 %, which is consistent with the value calculated by use of the CEC-values (85% montmorillonite), assuming that no other minerals than montmorillonite contribute to CEC. The accessory minerals were feldspars (~6%), quartz (~5%), cristobalite (~3%), muscovite (~1%) and small amounts i.a. calcite and gypsum.

Twelve separate tests with four hydroxide solutions were carried out. The details of each test are summarized in Table 3-1. A density of 2000 kg/m^3 at full water saturation is proposed for the KBS3 bentonite buffer and was aimed at in all tests. Slightly over-compacted discs (Ø 35 mm, thickness 5 mm) of air dry test material were placed in cylindrical sample holders of titanium and PEEK (a plastic material). The samples were saturated with de-ionized water, which was slowly circulated behind the filters of the sample holder by means of a peristaltic pump. At pressure equilibrium the water was replaced on both sides by the pre-defined chloride solution (0.5L), and when new pressure equilibrium had established, the chloride solution on the bottom side (B = high pH side) was changed to 0.5L isotonic hydroxide solution. In some of the tests the same solution was circulated on both sides and then replaced on both sides.

Table 3-1.Clay samples, test solutions and initial pH, calculated with PHREEQ.

Clay	Solution A =low pH side	Solution B	Initial pH solution B
MX-80	0.1M NaCl	0.1M NaOH	12.9
MX-80	0.3M NaCl	0.3M NaOH	13.3
MX-80	1.0M NaCl	1.0M NaOH	13.7
MX-Na	0.1M NaCl	0.1M NaOH	12.9
MX-Na	0.3M NaCl	0.3M NaOH	13.3
MX-Na	1.0M NaCl	1.0M NaOH	13.7
MX-80	0.1M NaCl	0.1M NaCl	~7
MX-80	1.0M NaCl	1.0M NaCl	~7
MX-80	0.02M CaCl2	0.02M Ca(OH)2	12.4
MX-80	0.02M CaCl2	0.02M Ca(OH)2	12.4
MX-Ca	0.02M CaCl2	0.02M Ca(OH)2	12.4
MX-Ca	0.02M CaCl2	0.02M Ca(OH)2	12.4

All tests were conducted at room temperature. The axial force, F, was recorded automatically every half an hour, and the swelling pressure, Ps, was calculated according to Ps = F/A, where A is the piston/bentonite contact area. pH was measured daily by a Metrohm 691 pH meter equipped with a T-glass electrode in the low pH solutions (chloride), and weekly in the high pH solutions (hydroxide). After a 45-day solution-solid contact period the solutions were analysed for dissolved solids by use of ICP/AES and ion chromatography (IC). The bentonite discs were split as shown in Figure 3-3.

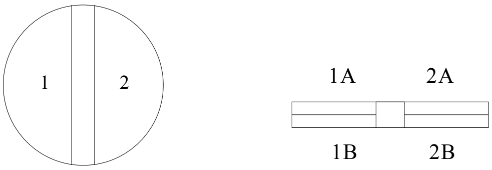

***Figure 3-3**. Partition of the bentonite test disc in a low pH (A) and a high pH side (B) for subsequent analysis.*

The central part was used for SEM analyses. Part 1 and 2 were split in the axial direction into a low pH (A) and a high pH (B) side, and each part was analysed for their chemical and mineralogical compositions by use of powder XRD, ICP/AES and the cation exchange capacity was determined.

3.4 Results

3.4.1 Swelling pressure

The typical pressure response in a sample of Mx-80 contacted successively with de-ionized water, 1M NaCl, NaOH, NaCl, and finally de-ionized water is illustrated in Figure 3-4 (left). Figure 3-4 (right) illustrates the effect of each of these solutions on four individual Mx-80 samples. The swelling pressure decreased significantly when 1.0M solutions of either NaCl or NaOH were introduced in the system. Whereas the contact with chloride solutions resulted in a fast drop to a new stable pressure, the contact with hydroxide solutions led to a continuous decrease of the pressure. The swelling pressure stabilized when NaCl was re-introduced and increased again when water replaced NaCl in the system.

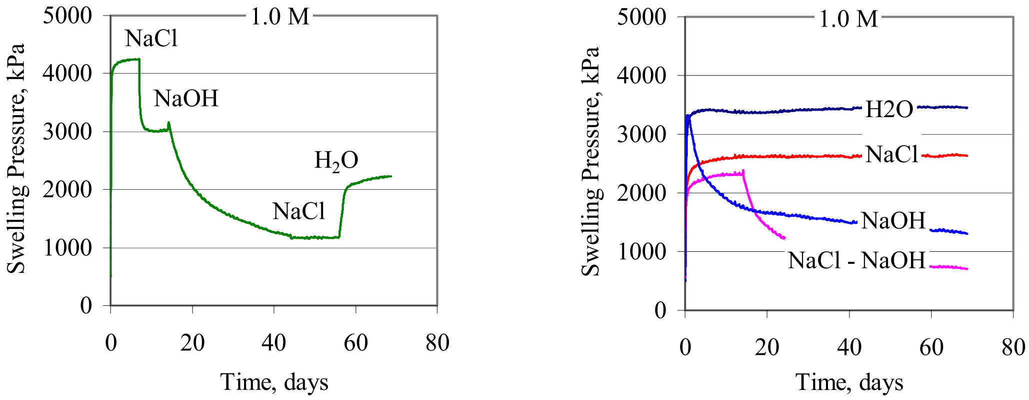

Figure 3-4. *Left: Swelling pressure response in MX-80 successively saturated with de-ionized water, 1.0 M NaCl, 1.0M NaOH, 1.0 M NaCl, and, finally, de-ionized water. Right: Swelling pressure response in four individual MX-80 samples saturated with de-ionized water, 1.0M NaCl, 1.0M NaOH and 1.0 M NaCl, which was replaced by 1.0 M NaOH solution after 15 days.*

A significant and continuous reduction in the swelling pressure was observed in the tests with 1.0M and 0.3M NaCl/NaOH solutions (Figure 3-5), while no change was noticeable in any of tests with 0.1M NaCl/NaOH solutions or with 0.02M $CaCl_2$ /$Ca(OH)_2$ solutions.

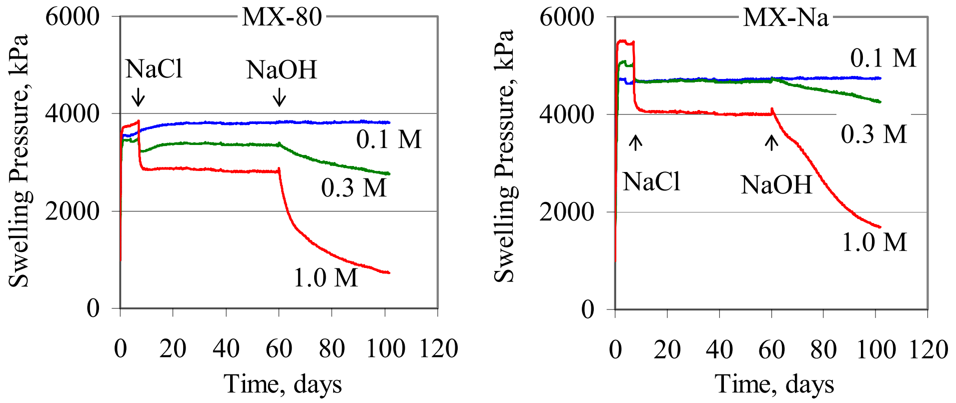

Figure 3-5. *Swelling pressure response in MX-80 (left) and MX-Na samples (right) on saturation with 0.1M, 0.3M and 1.0M NaCl/NaOH, respectively. All samples were initially saturated with de-ionized water, chloride solutions were introduced in the systems after 5 days, and finally, hydroxide solutions after 60 days.*

3.4.2 pH

During a 45-day solution-solid contact period, pH of the chloride solution increased significantly in the tests with 1.0 M and 0.3 M NaCl/NaOH solutions and MX-80 and MX-Na, respectively. As illustrated by the plots of pH (Figure 3-6) the OH-breakthrough occurred quicker and the increase in pH was significantly larger in the solutions contacted with MX-80 than in those contacted with MX-Na. However, in the test with MX-80 and 1.0 M solutions, an apparent steady state was reached after c. 35 days and pH remained constant at c.12.6 during the last part of test period, although the swelling pressure continued to fall from 829 to 722 kPa, indicating that dissolved solids still migrated through the filters of the test cell. The pH of the isotonic chloride solution was more or less unchanged still after 110 days of solution-solid contact in the tests with 0.1M NaOH and saturated $Ca(OH)_2$ solutions.

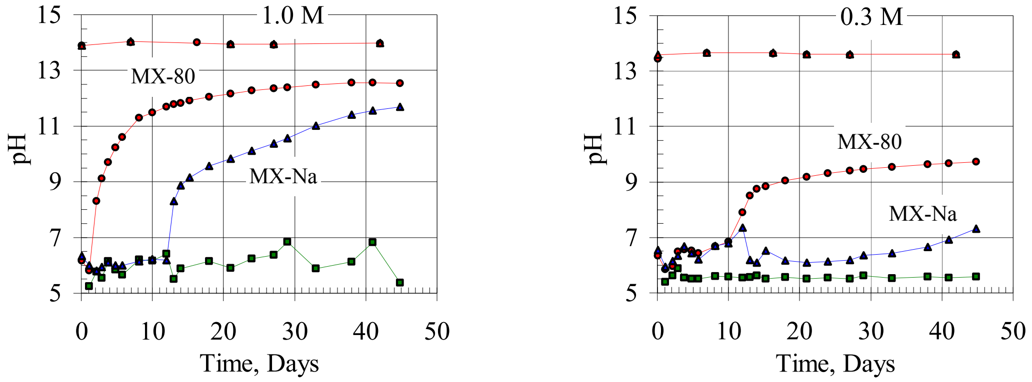

Figure 3-6. *pH evolution in the NaCl solutions (A-side) in tests with MX-80 and MX-Na exposed to 1.0M solutions (left), and 0.3M NaCl/NaOH solutions (right). Uppermost line indicates pH in the NaOH solutions (B-sides), and lowermost line pH in a NaCl reference solution.*

3.4.3 Solution compositions and bentonite mineralogy

The SiO_2/Al_2O_3 ratio of the bentonite samples contacted with NaCl/NaOH solutions (Figure *3-7)* decreased, with a gradient in the ratio from the NaCl to the NaOH side.

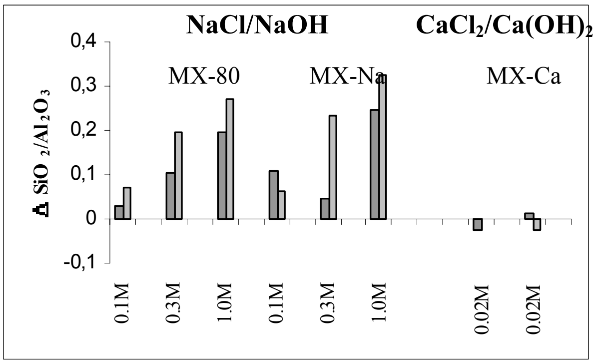

Figure 3-7. *Change in the SiO_2/Al_2O_3 ratio in bentonite samples MX-80 and MX-Na after contact with 0.1M, 0.3M and 1.0M NaOH/NaCl and in MX-Ca after contact with 0.02M $CaCl_2/Ca(OH)_2$ solutions for 40 days. Dark grey = chloride side, light grey = hydroxide side.*

The XRD analyses suggest that cristoballite, and also quartz to some extent, are the major sources of dissolved silica. Dissolution pits and other chemical etch microtextures produced by the reaction with the hydroxide solutions were seen on quartz grains in the scanning electron microscope. No neoformed phases were observed in the investigation by SEM or by XRD, and the d-values and the expandability of the smectite were essentially unchanged after the reaction with alkaline solutions.

The Cation Exchange Capacity (CEC) of samples contacted with the $CaCl_2/Ca(OH)_2$ solutions was more or less unchanged, whereas the CEC of samples from the test with 0.3 and 1.0M NaCl/NaOH solutions had increased. Diminishing dilution by quartz and cristobalite due to dissolution explains some of the increase, but can not explain the entire increase from 0.86 to >1.00 eq[3]/kg in the Na-MX samples. The structural formula of the smectite in each of the MX-Na test samples was calculated according to Newman & Brown,1987 by combining the CEC and the chemical data (Table 3-2).

Table 3-2. Structural formulas of MX-Na after a 40-days contact period with NaCl/NaOH solutions. The calculations are based on the chemical compositions and CEC-values.

Sample	Structural formula of MX-Na smectite		Excess SiO_2 %
MX-Na ref	$(Si_{7.82}\ Al_{0.18})\ (Al_{3.13}\ Fe^{3+}_{0.38}\ Mg_{0.47}Ti_{0.01})O_{20}(OH)_4$	$Na_{0.59}\ Mg_{0.02}\ Ca_{0.01}$	--
0.1M NaCl	$(Si_{7.82}\ Al_{0.18})\ (Al_{3.14}\ Fe^{3+}_{0.38}\ Mg_{0.47}Ti_{0.01})\ O_{20}\ (OH)_4$	$Na_{0.63}$	1,1
0.1M NaOH	$(Si_{7.83}\ Al_{0.17})\ (Al_{3.09}\ Fe^{3+}_{0.38}\ Mg_{0.51}Ti_{0.01})\ O_{20}\ (OH)_4$	$Na_{0.67}$	1,2
0.3M NaCl	$(Si_{7.78}\ Al_{0.22})\ (Al_{3.10}\ Fe^{3+}_{0.39}\ Mg_{0.49}Ti_{0.02})\ O_{20}\ (OH)_4$	$Na_{0.70}$	2,9
0.3M NaOH	$(Si_{7.73}\ Al_{0.27})\ (Al_{3.10}\ Fe^{3+}_{0.39}\ Mg_{0.49}Ti_{0.01})\ O_{20}\ (OH)_4$	$Na_{0.74}$	0
1.0M NaCl	$(Si_{7.71}\ Al_{0.29})\ (Al_{3.09}\ Fe^{3+}_{0.41}\ Mg_{0.49}Ti_{0.02})\ O_{20}\ (OH)_4$	$Na_{0.77}$	0
1.0M NaOH	$(Si_{7.65}\ Al_{0.35})\ (Al_{3.10}\ Fe^{3+}_{0.40}\ Mg_{0.49}Ti_{0.02})\ O_{20}\ (OH)_4$	$Na_{0.80}$	0

Increasing concentrations of the NaCl/NaOH contact solutions are paralleled by increasing tetrahedral layer charge of the smectite. Artifacts may certainly be introduced in this manipulation of the chemical data, but the trend could be verified by an X-ray diffraction test for non-expandability /Greene-Kelly 1953, 1955/, which is used to differentiate between montmorillonite (octahedral charge>tetrahedral charge) and beidellite (octahedral charge<tetrahedral charge).

3.5 Discussion

It is obvious that hydroxide solutions migrate through highly compacted bentonite if the pH gradient is sufficiently high. For the given concentrations 0.3 and 1.0 M, the evaluated effective hydroxide diffusivity coefficients in MX-80 was around $2 \cdot 10^{-13}$ m^2/s and $4 \cdot 10^{-11}$ m^2/s, respectively. The effective diffusivity in MX-Na exposed to 1.0 M NaCl/NaOH solutions was less than one third of that in the MX-80 sample.

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[3] Eq: Equivalents, mole·valence

When a NaCl solution replaces water in the bentonite, the swelling pressure drops more or less instantaneously to a new equilibrium level due to the osmotic effects of the salt (Figure 3-4) No immediate response can be seen when NaCl is replaced by NaOH, or the reverse, which suggests that the osmotic effects of these two solutions are similar. When contacted with NaOH solution, the swelling pressure of the bentonite decreases continuously but at a diminishing rate. When the NaOH solution is displaced by a NaCl solution, the swelling pressure stabilizes almost immediately, suggesting that the preceding trend was due to fast reactions between the NaOH solution and the bentonite, and not just a slow equilibration. The swelling pressure increases again when de-ionzed water is re-introduced in the system. The increase is more or less equal to the decrease at the first contact with the NaCl solution, and, accordingly, the final swelling pressure is considerably lower than the pressure at start. This pattern shows that the contact with NaOH results in a permanent reduction in the swelling pressure, whereas the effect of NaCl is reversible. With support of the mineralogical analyses, we interpret the initial part of the response to the NaOH solution (high rate of pressure decrease) as an effect of cristobalite dissolution, while the subsequent part of the response pattern is due mainly to dissolution of montmorillonite and quartz, when cristobalite has been consumed.

The reaction between montmorillonite and 0.1 M NaOH solutions was minimal, which contrasts the results of batch experiments, where the silica release from montmorillonite seems to vary little as a function of the hydroxide concentration /eg. Bauer & Berger 1998; Bauer & Velde 1999/. Based on batch experiments with two types of bentonites and KOH solutions ranging from 0.1 to 4.0 M, Bauer & Berger (1998) estimated the silica dissolution rate at $1.2\cdot 10^{-8}$ [g/(g of clay·s)$^{-1}$] for 1.0 M KOH and $0.9\cdot10^{-8}$ [g/(g of clay·s)$^{-1}$] for 0.1 M KOH. According to our data on montmorillonite dissolution, which are based on the structural formulas of the smectite before and after the reaction with NaOH, around 40 mg Si was released during a 40-days contact period with 1.0M NaOH. A rough estimate of the silica dissolution rate would then be $1.6\cdot10^{-9}$ [g/(g of clay·s)$^{-1}$] for the 1.0 M NaOH solution. The rate for 0.3 M NaOH solution, calculated in the same way, is $0.5\cdot10^{-9}$ [g/(g of clay·s)$^{-1}$]. Thus, with the specific test geometry and bentonite composition/density we used, the Si release rates are considerably lower than those reported for batch experiments by e.g. Bauer & Berger (1998). Moreover, the rate of Si release is not a straight-forward measure of the montmorillonite dissolution rate, since dissolution proceeds incongruently through an initial step of "beidellitization", and not congruently, as generally reported in studies based on batch experiments /e.g. Bauer & Berger 1998; Bauer & Velde 1999; Cama et al. 2000/.

These discrepancies between batch experiments and experiments with compacted bentonite may be explained by ion-equilibrium established between the hydroxide ions and the montmorillonite counter-ions in the pore fluid of compacted bentonite. This kind of equilibrium has been demonstrated experimentally for sodium chloride solutions /Karnland et al. 2002/, but the similarities in the osmotic response of hydroxide and chloride solutions suggests that the same equilibrium may establish also with NaOH as external solution. If so, the OH concentration of the clay pore water will be lower than that of the external solution and, theoretically, this effect will increase with increasing clay density and decreasing concentration of the external solutions. For an external solution of 1.0M NaOH in contact with compacted bentonite, the theoretical hydroxide activity of the pore solution corresponds to a pH below 13.3, the corresponding pH for

0.1 M NaOH is below 11.5, and the pH for 0.02M $Ca(OH)_2$ is below 10. One of the expected effects of the equilibrium is thereby a lower dissolution rate of the silica minerals.

Figure 3-8 shows a schematic drawing of the expected conditions in a sample contacted to 1.0M solutions. Ion equilibrium between the clay counter-ions and the external solution (1.0 M NaOH solution, pH 13.8), results in a hydroxide ion activity of around 0.2 M, corresponding to a pH of 13.3 in the bentonite pore water. Equilibrium condition, calculated by use of PHREEQC for this solution and an excess of montmorillonite and quartz, is pH 11.8. Finally, ion equilibrium between the reacted pore water and an external solution gives a pH of 13.2. This calculated pH is higher than the measured pH (12.6), and the reaction between the hydroxide solution and the clay minerals was consequently fast enough to be completed before the hydroxide reached the chloride solution. On the other hand, the calculated silica concentration is two orders of magnitude higher than that measured for the test with MX-80 and 1.0M solutions (1.3 mM in the NaCl solution). Dissolving silica will consequently continue to diffuse into the surrounding solutions, continuously changing the swelling pressure and consuming hydroxide.

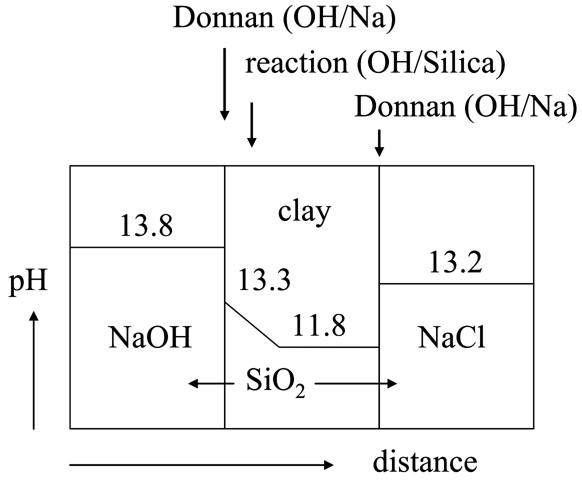

Figure 3-8 *Schematic drawing showing the hypothetic pH evolution in the bentonite pore fluid at equilibrium between the pore fluid and the contact 1.0M solutions on each side of the bentonite (NaOH and NaCl, respectively).*

3.6 Conclusions

At a sufficiently high pH gradient, hydroxide solutions migrate through highly compacted bentonite, but the effective transport is strongly affected by the reactions between the hydroxide solution and the bentonite minerals, and therefore not well described by diffusion parameters only.

Due to the interaction between bentonite and hydroxide solutions of high concentration (0.3 and 1.0 M NaOH solutions in our tests) the swelling pressure will be significantly reduced. The pressure reduction seems to be due to an instant osmotic effect, and a continuous dissolution of silica minerals leading to a mass loss, and consequently, a lowering of the bentonite density. The rate of decrease in swelling pressure due to dissolution was retarded after a relatively short time, and the subsequent decrease rate was more or less constant. We interpret the initial part of this response pattern as an effect of cristobalite dissolution, and the latter part as an effect of dissolution of montmorillonite and quartz, when cristobalite has been consumed.

A significant increase in CEC was observed in samples exposed to 0.3 and 1.0 M NaOH solutions. The structural formulas of the smectite, as well as its expansion behaviour after neutralization of the octahedral layer charge by Li-saturation and heating, indicate that the loss of silica was paralleled by an increase in the tetrahedral layer charge. Thus, the dissolution of montmorillonite proceeds incongruently through an initial step of beidellitization. Experiments of short duration, like ours, can only provide trends in the alteration of the buffer minerals and a moderate increase of the charge of the smectite may be a minor problem with respect to the buffer functions of the bentonite. However, the physical properties of the clay will change dramatically if this reaction proceeds until a high charge mineral, i.e. illite, is formed, or the mineral structure is destroyed. With the specific geometry and bentonite composition/density we used for our tests, the rate of silica release from montmorillonite was calculated to $1.6 \cdot 10^{-9}$ [g/(g of clay·s)$^{-1}$] for the 1.0 M NaOH solutions conditions and $5 \cdot 10^{-10}$ [g/(g of clay·s)$^{-1}$] for the 0.3 M conditions. However, the rate of Si release is not a straight-forward measure of the montmorillonite dissolution rate due to the non-stoichiometric dissolution.

No effect on swelling pressure was observed in the samples exposed to 0.1 M NaOH (pH 12.9) or saturated $Ca(OH)_2$ solutions (pH 12.4) and no mineralogical/chemical changes was detected in any of our tests with saturated $Ca(OH)_2$ solution.

Ion-equilibrium between sodium chloride solutions and the montmorillonite counter-ions in the pore fluid of compacted bentonite has been demonstrated experimentally in previous studies. The similarities in the osmotic response of hydroxide and chloride solutions suggest that equilibrium of the same nature may establish also with NaOH as external solution. If so, the OH concentration of the pore fluid will be lower than that of the external solution and, theoretically, this effect increases with bentonite density and with decreasing pH of the external solution. The chemical reactions between the hydroxide and the clay will therefore be less intense, more localized, and the resulting pH will be lower. These combined effects may explain the large difference in the mineral alteration rates, and possibly also the different reaction paths, between batch experiments and this study on highly compacted bentonite. Further, ion equilibrium conditions may explain the minimal chemical/mineralogical changes and low hydroxide migration rates observed in tests with bentonite exposed to 0.1 M NaOH and saturated $Ca(OH)_2$ solutions.

Acknowledgments

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4 Use of cement in opalinus clay and its consequences

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Abstract

The interaction of the concrete in an emplacement tunnel for long-lived intermediate level waste with the surrounding Opalinus Clay was assessed using mass balance constraints, and results from experiments and reactive transport modelling. It is shown that an alkaline plume cannot spread farther than a few metres into the Opalinus Clay. Dissolution and precipitation of minerals in connection with transport lead to an inhomogeneous porosity distribution and porosity clogging which additionally slows down the spreading. The results suggest that concrete containing ordinary cement can likely be used not only for cementitious waste tunnels, but also for the construction of the access tunnel, for seal securing plugs and for infrastructure (floors, etc.). An open question is whether and how the alteration of the Opalinus Clay influences its self-sealing properties in the excavation disturbed zone around the tunnels. The above conclusion may not necessarily be applicable to cement used in the emplacement tunnels for spent fuel and vitrified high level waste. Due to the relatively small amount of the bentonite buffer and its observed lower reactivity the results for Opalinus Clay cannot be directly applied, and further investigations may have to be carried out. An alternative material like organic resins or low-pH cement may be used for rock support purposes. It is suggested that addition of clay material to the shotcrete (aggregates) could suppress the emanation of a hyperalkaline plume from the cement.

4.1 Introduction

Cementitious material will be used for the construction of repositories for radioactive waste. Repositories for low and intermediate level waste and long-lived intermediate level waste (ILW) are mainly built from concrete which is part of the engineered barrier system. Repositories for spent fuel (SF) and high level waste (HLW) use cementitious material usually only as an auxiliary material. The material used has to be compatible with the waste, the engineered barrier and the host rock. The use of cementitious materials results in alkaline porewater which can interact with the surroundings. This paper focuses on the interaction of cement with Opalinus Clay, a potential host rock for a repository for radioactive waste in Switzerland.

4.2 The use of cement

Nagra has recently proposed a repository for SF, HLW and ILW in Opalinus Clay (Nagra, 2002; Figure 4-1). A sufficient spatial separation avoids a cross influence between SF and HLW on one hand and ILW on the other hand.

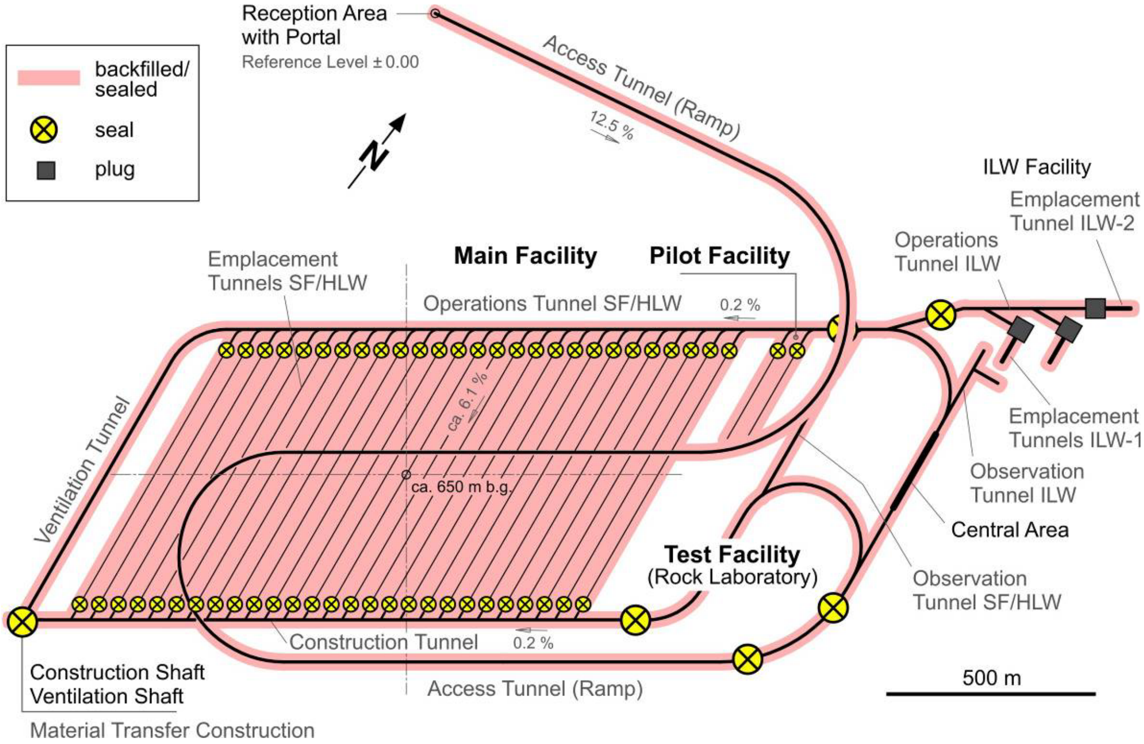

Figure 4-1. Plan view of the repository for SF / HLW / ILW in Opalinus Clay after closure of the facility

4.2.1 Long-lived intermediate level waste

Most of the long-lived intermediate level waste (ILW) is or will be conditioned in a cementitious matrix. Canisters containing such waste will be placed in tunnels made of concrete which will finally be backfilled with a cementitious mortar (Figure 4-2). Cement as the predominant material is part of the engineered barrier system providing favourable chemical conditions. Many radionuclides have low solubilities in the alkaline environment and sorb strongly to the cement minerals /Wersin & Schwyn, 2004/.

4.2.2 Spent fuel and high level waste

Spent fuel (SF) and vitrified high level waste (HLW), emplaced in massive steel canisters, will be put in horizontal tunnels (Figure 4-3). Compacted bentonite will be used as a buffer. In contrast to an ILW repository, cementitious material will not have a safety function within the engineered barrier system; the use of small amounts of such material, however, may be unavoidable. Concrete will be used for the construction of the access tunnel (ramp) and for the securing plug of the tunnel seals (see Figure 4-1). In the emplacement tunnels for the waste canisters the use of cement is not foreseen, but might be necessary for rock support in addition to the planned rock bolts.

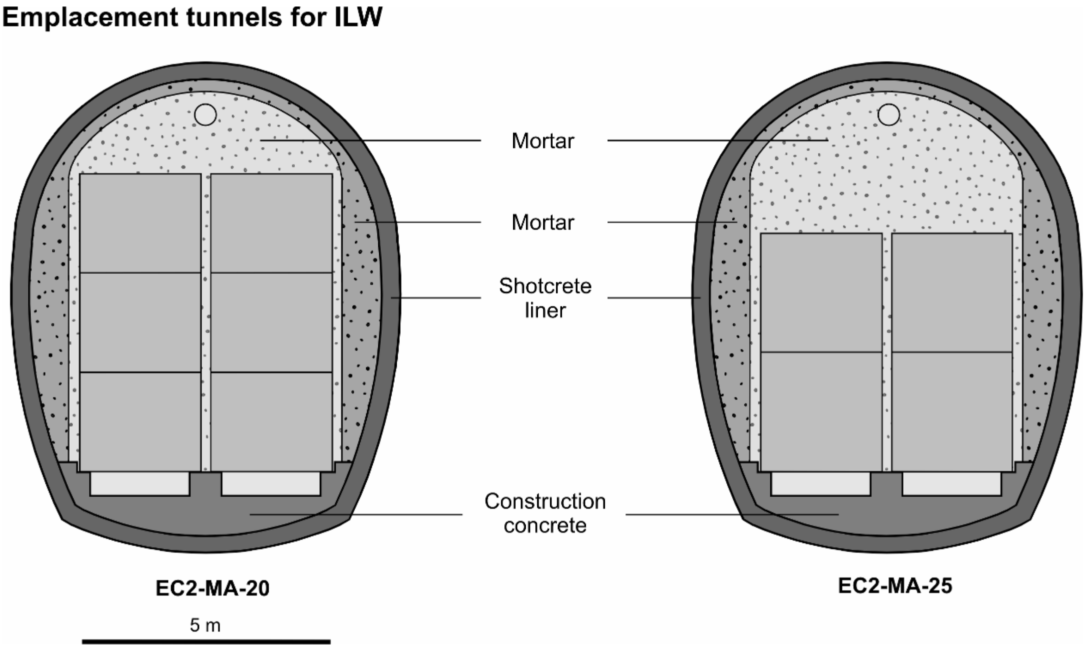

Figure 4-2: *Cross-section of the ILW emplacement tunnels after completion of waste emplacement, with two different types of waste emplacement containers*

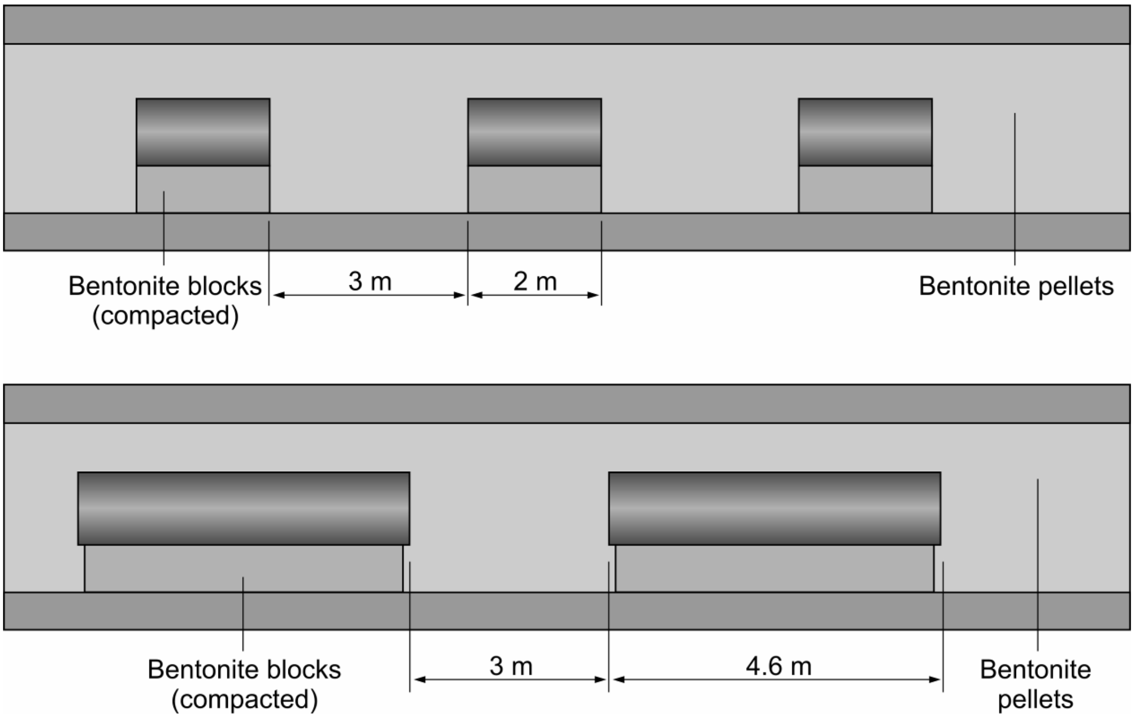

Figure 4-3: Longitudinal section through the disposal tunnels for canisters of HLW (top) and SF (bottom) at completion of canister and buffer emplacement

4.3 Cement interaction with the barrier system

Cement is thermodynamically not stable in contact with host rock porewater and will therefore slowly degrade. The degradation can be divided into three stages /e.g. Berner, 1990/. During the first stage the porewater is dominated by alkali hydroxides present in the cement resulting in a pH of 13 or higher. During the second stage the porewater is buffered by the dissolving portlandite leading to a pH of about 12.5. Within stage 3, when all portlandite is dissolved, the remaining C(-A)-S-H phases are degrading, their Ca/Si ratio is decreasing and the pH is dropping below 11.

The alkaline porewater emanated by the degrading cement will interact with the surrounding engineered barriers and the host rock. Interactions depend on the porewater composition which varies as a function of the degradation stage.

4.3.1 The ILW case

As mentioned above, the backfilled ILW tunnels will be dominated by ordinary cementitious material which is designed to be part of the barrier system (chemical retention of radionuclides, limited solubilities). The interaction of the emanated alkaline porewater with the surrounding host rock has to be assessed since such an interaction could be detrimental to the barrier performance of the host rock. Within Project Opalinus Clay, the effects of an alkaline plume on the claystone was assessed as discussed below (Chapter 4.4).

4.3.2 The SF / HLW case

Close to the waste containers ordinary Portland cement should only be used with caution because the hyperalkaline porewater could interact with the bentonite jeopardizing its barrier functions, mainly its swelling capacity but also its property to restrict porewater and radionuclide migration. Alkaline porewater should also be kept away from the HLW and SF matrix (after canister breaching) because the glass would dissolve rapidly at high pH, and the influence on UO_2 dissolution may also be detrimental. The use of ordinary Portland cement for rock support in the emplacement tunnels may therefore not be advisable. For the interaction with the host rock we refer to the ILW case and the corresponding assessment within Project Opalinus Clay (Chapter 4.4).

The use of ordinary Portland cement in the access tunnel and for the securing plugs of the seals, sufficiently apart from the emplacement canisters (see Figure 4-1), appears to be safe since the reach of an alkaline plume is very limited as shown below.

4.4 The assessment of the effect of alkaline fluids on Opalinus Clay

The assessment presented here was carried out for a cementitious ILW repository located in Opalinus Clay /Mäder, 2003/. The investigations carried out up to now demonstrate that transport in Opalinus Clay is diffusion dominated and advection only contributes over longer distances (>10m). Even in fracture zones no significant transmissivities are observed at the depth of the repository, a fact that can be explained by the efficient self-sealing capacity of Opalinus Clay /Gautschi, 2001/. Thus, advective transport and spreading of an alkaline plume along an open facture can be ruled out.

To assess the potential effect of an alkaline plume two approaches were chosen: On one hand mass balance constraints were evaluated to bound the maximum possible spreading around a repository /Mäder, 2003/. On the other hand 1-D reactive transport was modelled to quantify such a spreading or, at least, to understand its relevant features /Traber & Mäder, 2005/.

4.4.1 Mass balance constraints

A limiting case for the spreading of a pH plume in a diffusion-dominated system involves the assumption that all of the cement in the near field will degrade and that the hydroxide released will diffuse into the Opalinus Clay and react with its components. Assuming that the total buffer capacity of Opalinus Clay is used, the latter would consume the leachate of four volumes of degraded near field per volume clay. Using such a mass balance basis, a high pH plume would reach about 0.5 metres into the host rock; if only 10 % of the total buffering capacity of the Opalinus Clay components is used the plume spreading would be about 4 metres /Mäder 2003/.

4.4.2 Reactive transport modelling

The diffusive interaction of a domain of 1.5 metres of concrete adjacent to a domain of 8.5 metres Opalinus Clay was investigated in a 1-D model using the reactive transport numerical code CRUNCH /Steefel & Yabusaki, 1996/. The model included the reaction of the concrete with the porewater diffusing in from the clay (cement degradation) as well as the reaction of the resulting cement porewater with the concrete aggregates and the adjacent Opalinus Clay /Traber & Mäder, 2005/.

The geochemical reaction model in the clay was based on core infiltration experiments, on a field experiment carried out at Mont Terri, and on their modelling /Adler 2001, Adler et al. 2001, 2005/. Cement and Opalinus Clay porewater compositions were calculated assuming equilibrium with the present minerals. For the dissolution of minerals the corresponding kinetics were considered. Which secondary minerals may form under the given chemical conditions is still under debate. The set included in the model may therefore only be an example but is certainly representative since it was based on observations in the above mentioned experiments.

Figure 4-4 shows the results of one example of several modelled scenarios. It starts with young cement with a porewater pH of about 13.5. After one million years the pH plume has spread less than 0.5 metres into the Opalinus Clay. For details concerning the evolution of the mineral composition in the concrete and Opalinus Clay as a function of the distance to the interface, we refer to Traber & Mäder (2005). In the present paper the modelling results are summarised.

In the concrete, portlandite is consumed, the C to S ratio of the C-S-H phases decreases with time and these are finally replaced by zeolites. The quartz of the aggregates is consumed at a slow rate because of the small specific surface.

In the Opalinus Clay, dolomite and kaolinite are consumed and mainly illite is formed (Figure 4-4). Close to the interface C-S-H phases are temporarily formed which are later replaced by zeolites (data not shown).

No porosity feedback on transport was considered in the scenario shown here. At the surface to the concrete the porosity of the Opalinus Clay has dropped to zero while it is increased in the outer part of the concrete (Figure 4-4).

Porosity plugging is predicted for all modelled scenarios typically after 10 to several 100 years and is inherent for this concrete/ clay system. Obviously, the coupling of dissolving and precipitating minerals to transport leads to an inhomogeneous spatial porosity distribution; a porosity increase at one location is connected with a porosity decrease or plugging at another one.

In summary, including arguments not discussed in this paper, an alkaline plume in a diffusion dominated claystone may even improve the barrier effect of the latter. In any case, it is usually negligible in performance assessment due to the small amount of affected Opalinus Clay.

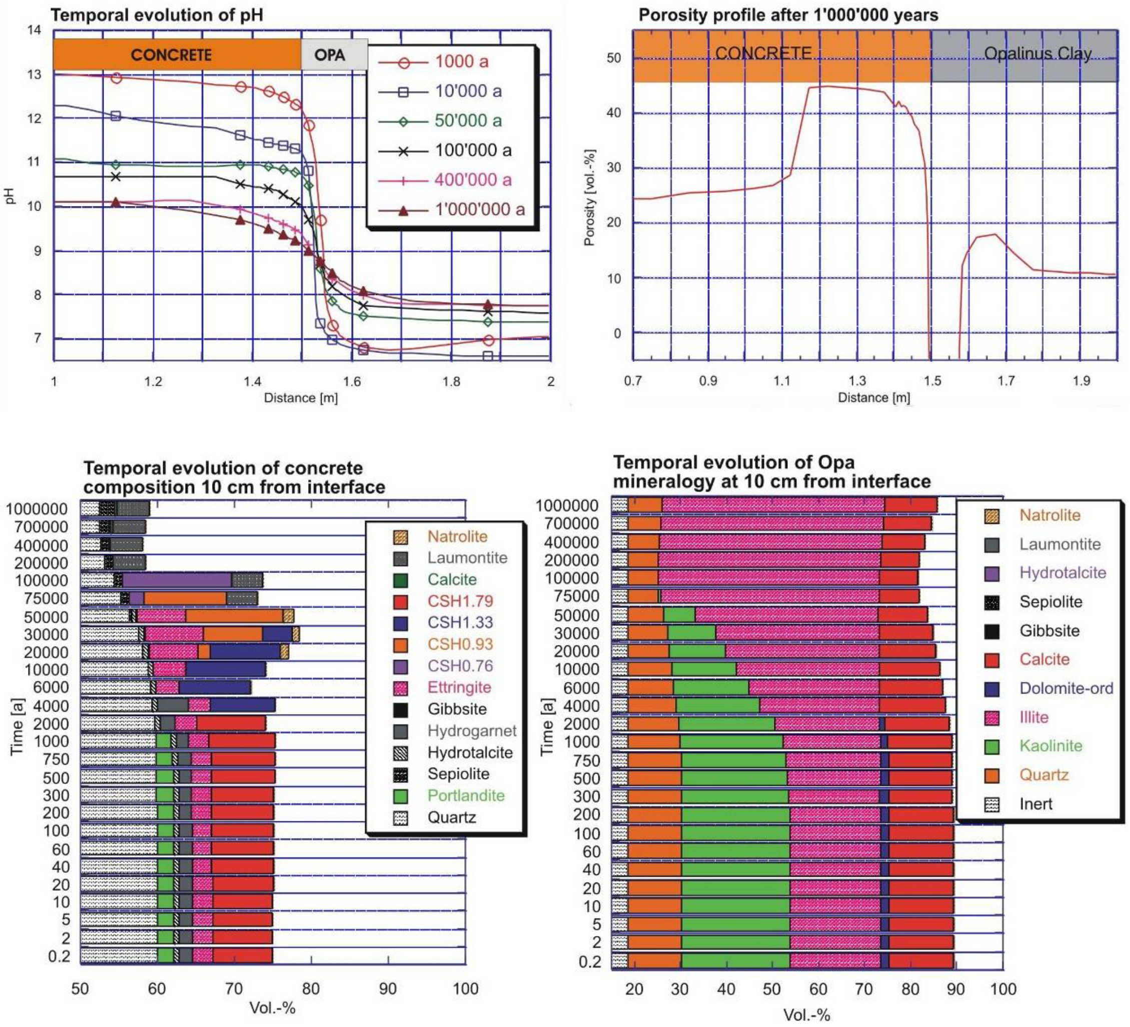

Figure 4-4: *Modelling results of diffusive cement – Opalinus Clay interaction.*

4.5 Discussion and conclusions

Our experience about the effects of cement used in a repository located in Opalinus Clay is based on the assessment of the interaction between ordinary Portland cement, as used for the ILW tunnels, and Opalinus Clay. Because a very limited spreading of alkaline fluids in the host rock is predicted, the conclusions are also applicable to the use of Portland cement for the construction of securing plug for the foreseen seals and the access tunnel (see Figure 4-1). Both are sufficiently separated from the emplacement tunnels for spent fuel and vitrified high level waste.

According to the current knowledge, there is no doubt that for the above mentioned applications ordinary cement will not jeopardise the barrier functions in a repository for radioactive waste. In diffusion dominated system, in which the existence of transmissive fractures can be ruled out, an alkaline plume can only spread in the range of centimetres to a few metres within long time scales. Due to the relatively high reactivity of the minerals in Opalinus Clay an alkaline plume can never spread much farther because of the limited amount of cement available. An open question is whether and how the alteration of the Opalinus Clay influences its self-sealing properties in the excavation disturbed zone around the tunnels.

The dissolution and precipitation of minerals, together with porewater transport, leads to an inhomogeneous porosity distribution. The denser regions will dominate and further slow down transport rates. The degree of resulting porosity inhomogeneity depends on the overall volume balance of dissolving and precipitating minerals and may therefore depend on the cement composition: With ordinary cement containing portlandite a system may show a higher tendency to seal than a system with low pH cement containing no portlandite.

A higher tendency to seal is an advantage in diffusion dominated host rock but may be detrimental to performance in a fractured system if the matrix is affected, impairing diffusion of radionuclides into the matrix. The choice of low pH cement may be indicated for a fractured system; based on the current knowledge, however, ordinary cement is preferred for ILW and access tunnels as well as for construction elements (e.g. floors) which are separated from the SF and HLW emplacement tunnels.

If cement has to be used for rock support in the SF and HLW emplacement tunnels located in Opalinus Clay, further investigations will be needed. According to the above findings the interaction with the host rock is not of concern. The same has not been shown yet for the bentonite buffer. Although there is evidence that bentonite is less reactive /ECOCLAY II, 2005/, the effect of an alkaline plume may be similar to the effect on the clay host rock. The consequences, however, are different: Half a metre of an affected clay host rock is negligible; half a metre of an impaired bentonite barrier, however, is decisive for its performance if important properties like plasticity and swelling capacity are affected.

As next steps the following possibilities are recommended:

- The consequences on the engineered barrier system are assessed in more detail for the option of ordinary cement use.
- Low pH cement is used. Nevertheless, the consequences for the long-term safety have to be assessed. The weight may, however be shifted from the cement components to the admixtures to be added to get a workable shotcrete.
- Alternative materials like organic polymers are considered.

Finally, it is suggested to test whether low pH shotcrete could be replaced by ordinary shotcrete containing claystone as part of the aggregates. Müller & Plötze (2005) showed that kaolinite added to the cement reacted with portlandite within months. It may well be that such a concrete does not emanate highly alkaline water since the latter will react with the clay aggregate before it leaves the concrete.

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5 Testing methodology for pH determination of cementitious materials. application to low pH binders for use in HLNWR.

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5.1 Introduction

Cementitious materials are considered relevant components in several European concepts for the construction of underground repositories of high level nuclear waste (HLNWR).

Cementitious materials made of Ordinary Portland Cement (OPC) when they are in contact with water leach alkaline ions from the pore solution towards the other materials in the repository, as the bentonite. Besides, the groundwater flowing from the host rock interacts with the solid cement paste phases that contain calcium (CH, CSH and ettringite) producing a progressive neutralisation of its alkaline nature.

The pH of OPC cement paste pore solution is initially greater than 13, as a result of the dissolution of sodium and potassium hydroxides (this hyper-alkaline process is a short-term stage). Later, the pH of the cement paste is expected to decrease to around 12.5, and the pH of the pores is controlled by the dissolution of the calcium compounds from the solid phases of hydrated cement. The alkaline plume may affect transport processes in the geosphere as well as the performance of the Engineered Barrier System (EBS) of the repository. This impact could be minimized by different methods: 1) Reducing the use of Portland cement, 2) Removing concrete structures before sealing the repository and 3) Using low-pH cementitious materials.

Several experimental and modelling studies have shown that compacted bentonite is not stable in contact with OPC pore waters. They have also shown that pore waters of simulated cement pastes with $\text{pH} \approx 11$ are less reactive towards compacted bentonite. For this reason the developing of low pH cements is a relevant concern in the stability of HLNWR.

The developing of low pH cementitious materials needs for an accurate measurement of the pH of the pore water in order to be able to qualify low pH cements. The most reliable method to measure the pH of the aqueous phase in a hardened cementitious material is the extraction of the pore aqueous phase. However, this method, ”*Pore Pressing Method*”(considered as the reference in this study), requires the use of a special equipment and a relatively high amount of cementitious material, as well as long time consuming. Furthermore, there are not already developed specific standards or protocols that take into account all the parameters involved.

The Pore Pressing Method has been referred in the literature for the extraction of the aqueous phase of the pores of cementitious materials and the further analytical determination of the electrolyte composition, Longuet et al. (1973), Barneyback et al. (1980), Diamond (1981), Page et al (1983), Byfors et al (1986), Duchesne et al (1993). It is believed that the compositions of the pore solutions obtained are representative of that of the bulk of the pore solution within the paste or mortar from which the solutions have been obtained, Barneyback et al. (1980). The method used to determine the pH may affect the value depending on if a direct measurement of the pH with an electrode or titration of OH^- ions is followed, Diamond (1981), Byfors et al. (1986). The reason is that the in the first case the activity of the electrolyte is considered while in the second the OH^- concentration is measured, Hidalgo et al (2001).

Several leaching procedures have been tried in order to develop a suitable method that allows an accurate determination of the OH^- content and pH in the pore solution of cementitiuos materials without the need to employ the pore pressing technique /Castellote, 2001, Cau Dit Coumes et al., 2003, Räsänen, 2003; Lianfang, 2004/ for use in laboratory and in-situ, (Sagüés, 1997), Hoffard et al.. Although no agreement has been found with the methodology or in same cases have not been calibrated with the pore pressing.

This paper deals with the developing of a rapid and simple method that allows obtaining reliable values of pore pH in cementitious materials. A simplified pH measurement method has been selected and calibrated with the *Pore Pressing Method*. Differences between both methodologies are analyzed.

5.2 Experimental procedure

5.2.1 Materials

Blended cement mixes were prepared, based on two types of cements, Calcium Aluminate Cement (CAC) and Ordinary Portland Cement (OPC) with low alkaline content, and adding different percentages of mineral additions as Silica Fume and Fly Ash, preparing binary and ternary mixes, (binders). The chemical compositions of the cements and the mineral additions are given in Table 5-1.

Cement pastes of the binders were fabricated using a water/binder ratio of 0.5. They were cured in 98% humidity and 21±2ºC temperature. Curing times considered were in most cases 7, 30 and 90 days.

Table 5-1. Chemical Composition (in %) of the cements (OPC and CAC), silica fume and fly ash.

	SiO_2	Al_2O_3	Fe_2O_3	CaO(total)	MgO	SO_3	Na	K	CaO(free)	L of I	I R
OPC	18,00	4,85	5,26	62,36	1,84	3,28	0,02	0,13	1,92	4,34	1,13
CAC	2,60	45,29	14,66	36,90	0,71	0,00	0,02	0,02	0,11	0,43	2,31
Fly Ash	55,63	27,92	5,51	4,63	2,30	0,00	0,09	0,53	0,15	2,24	0,53
Silica fume	91,80	0,59	3,74	1,30	0,92	0,00	0,02	0,06	0,01	0,09	0,06

5.2.2 pH Measurement Methods

Two different pH measurement methods were used:

- M1- Direct measurement of pH in pore cement paste fluid extracted by the *Pore Pressing* technique
- M2- Direct pH measurement in powdered cement paste-water slurries using different solid/liquid ratios.

Pore Cement Fluid pH (M-1)

The pore pressing method involves a cement paste pore cement paste fluid extraction as well as a pH measurement in the aqueous phase. This technique is considered within this study as the reference, so the pHs measured by this method are named the *real pH* values.

To determinate the pH of the cement paste pore fluid, approximately 125g of paste samples were divided in some pieces of a diameter size < 0.5cm.

Due to the difficulties in some cases to extract sufficient amount of liquid phase to perform the pH measurements, it is necessary to add some extra deionised water to the samples. Then, after each specific curing time, a sample was taken and pre-conditioned in different ways:

- *Procedure 1 (P1)*: 24 hours before the aqueous phase expression, deionised water was sprayed to the sample until it seemed to be saturated.
- *Procedure 2 (P2)*: just before the aqueous phase expression, deionised water was sprayed to the sample until it seemed to be saturated.
- *Procedure 3 (P3)*: just before the aqueous phase expression, a fixed amount of water (15% by weight of cement paste) was sprayed to the sample.

- *Procedure 4 (P4)*: the sample was expressed without any extra addition of deionised water.

As soon as possible, after the sample pre-conditioning, specimens were placed in the cylinder of the pore pressing device. Pressure was increased in steps of approximately 10-20MPa, until a maximum load pressure of 483MPa (70 Psi) was achieved, and then maintained for ten minutes to completely express the pore solution. The pore solution was collected in a syringe, and stored in plastic containers until analysing. **Figure 5-1** shows the experimental device. After that, the pore fluid pH was directly measured with a glass combined electrode (Metrohm 6.0235.100).

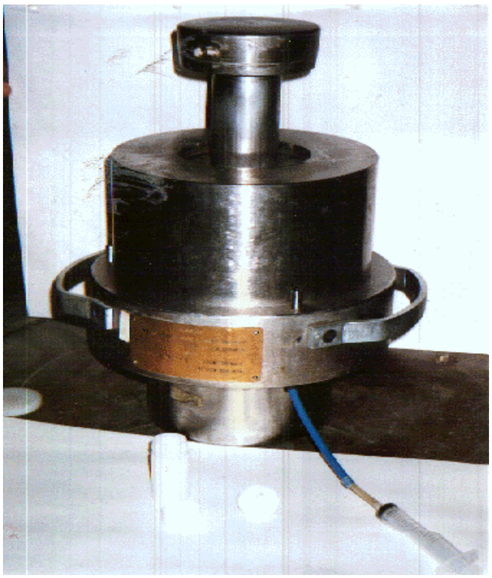

Figure 5-1. *Pore Pressing Device.*

Slurry pH Method (M-2)

In this work, slurries were prepared with different Solid/Liquid ratios (S/L) (water/cement paste in this case) in order to determine the optimal S/L ratio which gives results that can be comparable with the pore pressing pH values. The S/L ratios considered are: 1/1, 1/5 and 1/9 in order to select the most appropriated one.

Then, a piece of the cement paste is finely grounded to a particle size < 75µm. Different portions of this powder were weighed (10g for 1/1, 2.4g for 1/5 and 1.3g for 1/9) and put in a small glass, and addition of the corresponding amounts of deionised water, so slurry mixtures with a determined S/L ratio were obtained. The slurries were continuously stirred during approximately three minutes. The pH measurement was performed with a glass combined electrode (Metrohm 6.0235.100). The stirring of the slurry was maintained during the measurement.

The methodology for pH determination in the slurries was varied in two ways:

1. Using de-ionized water
2. Using boiled de-ionized water in order to eliminate the dissolved CO_2 in the water. After cooling the slurry was prepared and the pH measured in isolated atmosphere using N_2.

Two identical cement paste samples were tested in all cases, and the pH was measured in every slurry. The pH values presented in this work are the average of the measurements performed for each sample.

5.3 Results and Discussions

5.3.1 Pore Cement Paste Fluid pH (M1)

Influence of cement paste conditioning

Figure 5-2 shows the pH values obtained for one CAC and one OPC samples after expression of liquid phase using the four procedures of samples pre-conditioning.

pH values obtained from samples without any addition of water before expression, are considered in principle as *the real* ones. However, not always is possible to extract enough amount of liquid phase to perform the pH measurements; in fact, in the case of CAC samples, it was only possible to extract pore aqueous phase without addition of extra water at 7 days of curing time.

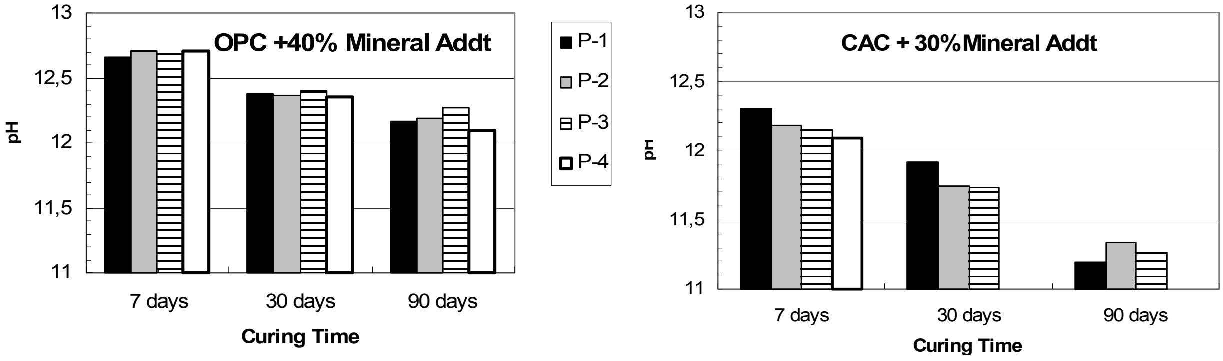

Figure 5-2. Comparison between pH obtained by the four different pre-conditioning Procedures of the Pore Pressing Method.

The differences between the pH values obtained with the four methods are not higher than 0.1 in the OPC samples, and 0.2 in the CAC ones. Taking into account that the measurement precision of the electrode is ± 0.05, it can be considered that these pH values are reliable whatever the procedure used. So it was possible to conclude that, although the P4 is the procedure preferred, when the addition of extra water is necessary, the obtained pH value will not differ significantly from pH of P4. The values from all procedures employed may be considered as real pHs.

The changes in the pH are significantly influenced by the maturity of the cement paste. Variations of more than 1 unit of pH are measured from 1 week and 3 months, either using OPC or CAC based binders. The reason is attributed to the hydration evolution with the curing inducing changes in the composition of the aqueous phase, being most relevant as higher is the mineral addition employed. So long curing times are more accurate for determination of the pH within the pores. 90 days are recommended from present results.

Table 5-2 presents the pH values for every sample and every procedure used, the mean pH and the standard deviation (SD). It can be observed that the SD is very small, so although the addition of extra water may cause certain dissolution of solid phases it does only result in small difference in the pH value.

Table 5-2. Direct pH values obtained in Pore Cement Fluid (M1)

	Curing time (days)	**pH P1**	**pH P 2**	**pH P 3**	**pH P4**	**Mean pH**
OPC Samples	7	12.66	12.71	12.68	12.71	12.69±0.02
	30	12.38	12.36	12.4	12.35	12.37±0.02
	90	12.16	12.19	12.27	12.09	12.18±0.07
CAC samples	7	12.31	12.18	12.15	12.09	12.18±0.09
	30	11.92	11.75	11.73		11.8±0.10
	90	11.19	11.34	11.27		11.27±0.08

Influence of percentage in mineral addition

The pH of the pore aqueous phase expressed from cement paste of different samples containing variable portions of mineral additions was measured using the Pore Pressing Method (P3). Five cement pastes were based on OPC and seven on CAC. The obtained results are given in Figure 5-3. The measurements were performed after 90 days of curing.

The results show that the amount of mineral additions in the cement pastes based on OPC had a greater influence in their pore pH value. In fact, with high percentages of mineral additions (>60%), values of pH bellow 11 could be achieved (at 90 days of cutting time). On the other hand, the mineral additions show the same effect in the pastes based on CAC. Altough, a slighter decrease in the pH can be appreciate in these last cements in comparison with OPC based pastes containing similar proportions of mineral addition. By these reasons, it can be concluded that the minerals additions play an important role in the diminution of the pH value of pastes based on OPC, but they do not behave the same with CAC pastes.

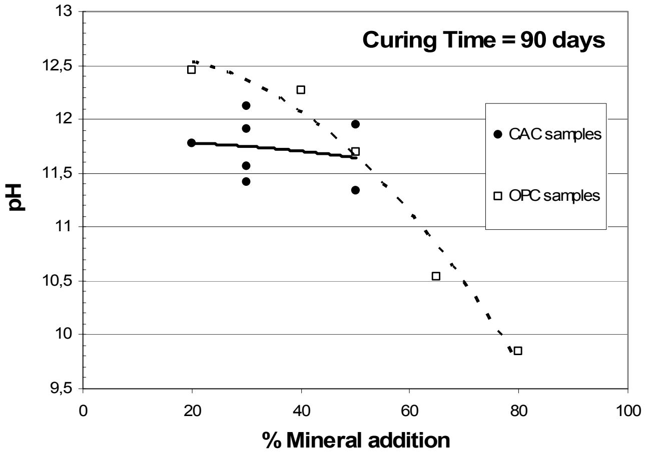

Figure 5-3. *Influence of the percentage in mineral additions in the pH value of cement pastes.*

5.3.2 Slurry pH determination (M2)

Reproducibility of pH measurements

Whatever the pH method used, good reproducibility of the measurement is essential. By this reason, in this study the measurement of the pH with the M2 at different curing times was analyzed in two different samples having the same binder composition. As can be observed in Figure 5-4 , the results are almost the same in all cases, so the mean pH value of both measurements can be used. Figure 5-4 shows pH values measured using deionised water and a solid/liquid ratio of 1/1. The reproducibility was as good as this one using decarbonated water and measuring in N_2 atmosphere, and using different solid/liquid ratios.

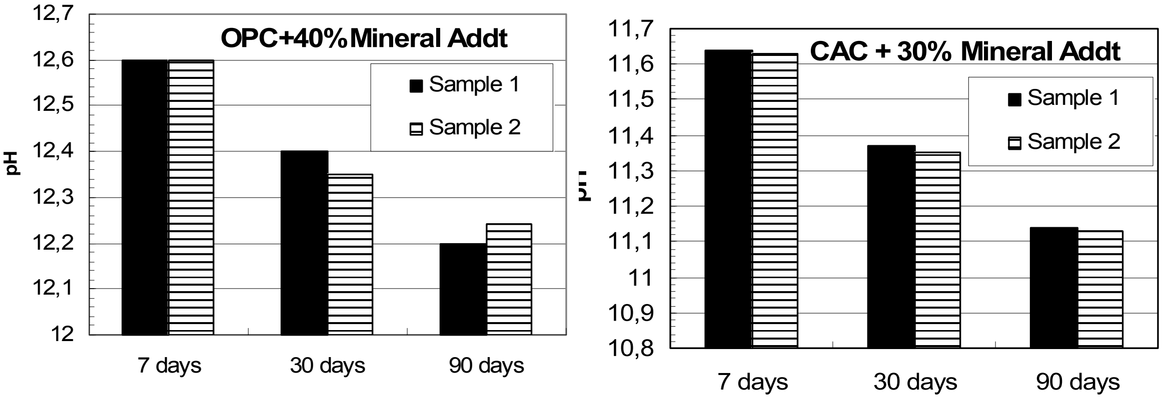

Figure 5-4 *pHs and dispersions in the measurements using Slurry pH Method (1/1).*

pH Measurement with decarbonated water and N_2 atmosphere

Due to the great percentage of minerals additions present in the cement pastes analyzed to decrease the pH of the aqueous phase within the pores, in addition to the made analysis with deionised water, the M-2 was modified to analyze the possible influence in the pH of the dissolved CO_2 in the water, that would cause also a decrease of the pH. The pH was measured in atmosphere of nitrogen and using decarbonated water (free CO_2 deionised water). As noted in Figure 5-5, the results indicate that there are no significant differences between these values and those obtained using deionised water and without measure in N_2 atmosphere. In fact, the differences between both values is never higher than 0.1. However, although not always higher values of pH are measured in nitrogen atmosphere and using free CO_2 deionised water, this last method is more advisable.

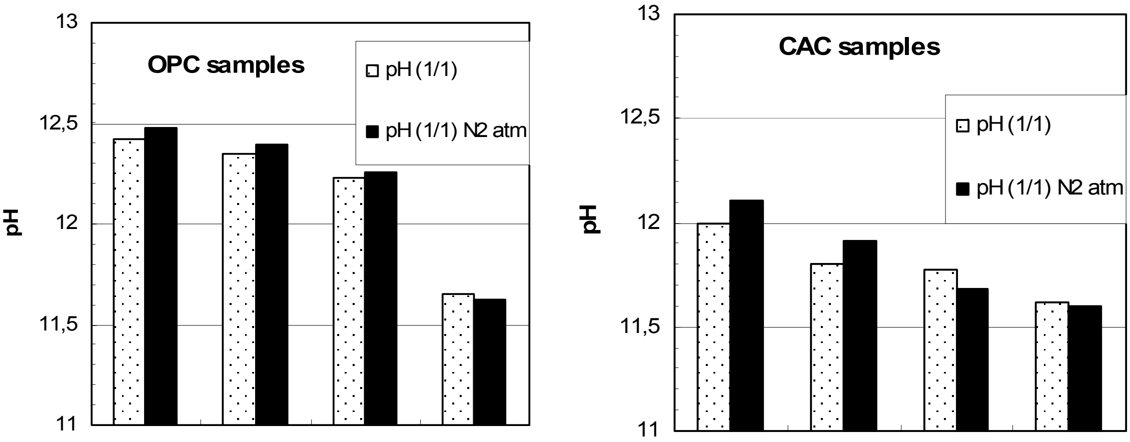

Figure 5-5. Comparison between "slurry pH" measured with deionised water and the measured ones in atmosphere of nitrogen and using deionised CO2 free water.

Influence of Solid/Liquid Ratio on pH values

The use of slurry methods or leaching methods to determine the pH of cementitious materials implies additional the dissolution of solid phases and dilution processes that may affect the final pH determination. In order to analyze the influence of the solid/liquid ratio in the slurry pH value, the three S/L ratios were considered: 1/1, 1/5 and 1/9. The results are given in Figure 5-6, where it can be observed that the greater the amount of water used the lower the measured pH value. This phenomenon occurred in all analyzed cement pastes and was more marked in the pastes based on CAC.

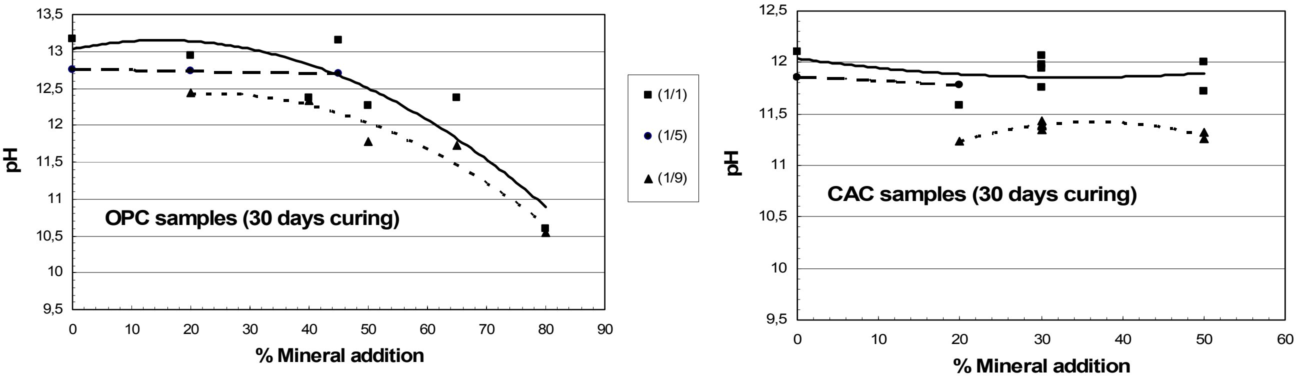

***Figure 5-6.** Influence of the Solid/Liquid Ratio in the pH values of the cement pastes.*

These results suggest that an important dilution effect exists when the percentage of water used was much greater than the solid one. Of course, with a solid/liquid ratio of 1/1 also a dilution effect takes place and the obtained pH may be different than that measured with the Pore Pressing method (P4), considered as the reference. However the differences on pH between the three S/L methods is not constant and may vary with the type of binder used, from 1 to 0.5 decrease in 1/1 to 1/9 dilution in OPC based pastes and more than 1 pH unit for CAC based cement pastes.

Influence of curing age on pH values

As commented before the curing age influences in the pH of the pores by decreasing with time noticed with M1 method.

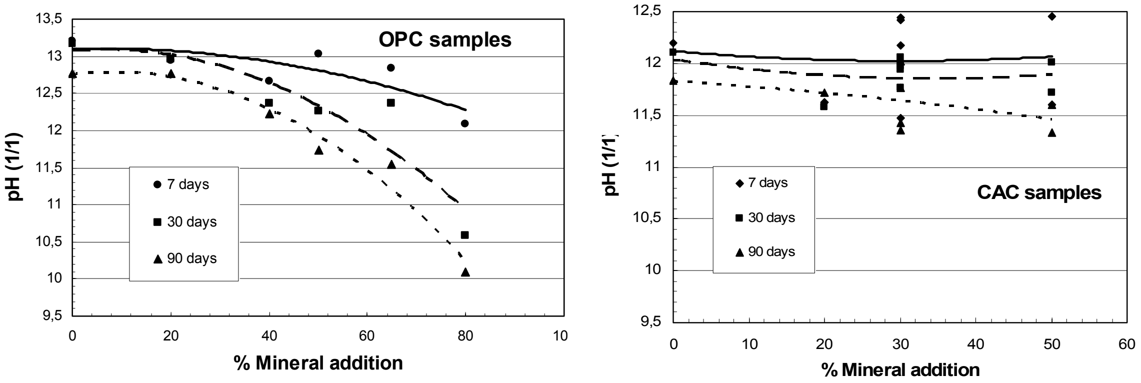

***Figure 5-7**. Influence of the Curing Age on pH values.*

The results with M2, showed in the Figure 5-7, demonstrate that in all the cement pastes studied, the pH varies with the curing age. In general, the greater the curing ages the lower the pH value. It can be stressed that also detected with M2 method, the influence on pH was higher in the pastes based on OPC, so the hydration of the OPC cement pastes must be slower than the hydration of the cement pastes based on CAC. pH decreases of 1 to 2 units from 7 to 90 days are measured depending on the percentage in mineral addition while this is reduced to 1 unit for CAC pastes. With these results, it can be concluded that to more accurately measure the pH of a cement paste is better used large curing ages, 90 days recommended.

5.3.3 Calibration of slurry pH (M2) with pore pressing pH (M1)

To calibrate the Slurry Methods proposed in this study, the measurements of pH obtained with the M2 were compared with those obtained with the Pore Pressing Method (P4). The values were calibrated using two types of binders, one based in OPC and the other based on CAC. Both cement mixes have a high percentage of mineral additions. The results are given in Figure 5-8. Due to with the P4 of M1 no pore fluid was extracted with the CAC pastes at 30 and 90 days of curing time, in this cement paste the methods could only be used for comparison results of pH at 7 days.

The results show that in OPC samples, the Slurry pH (with a solid/liquid ratio of 1/1) is more similar to the Pore Pressing pH (<0.1), so the obtained results are more reliable. In fact, at 30 and 90 days of curing time both values were almost the same. In the analyzed CAC samples the results show differences of more than 0.5 even with the M2 1/1. Always the M2 1/9 gives lower values of pH respect to M1, below 0.3 to 0.7.

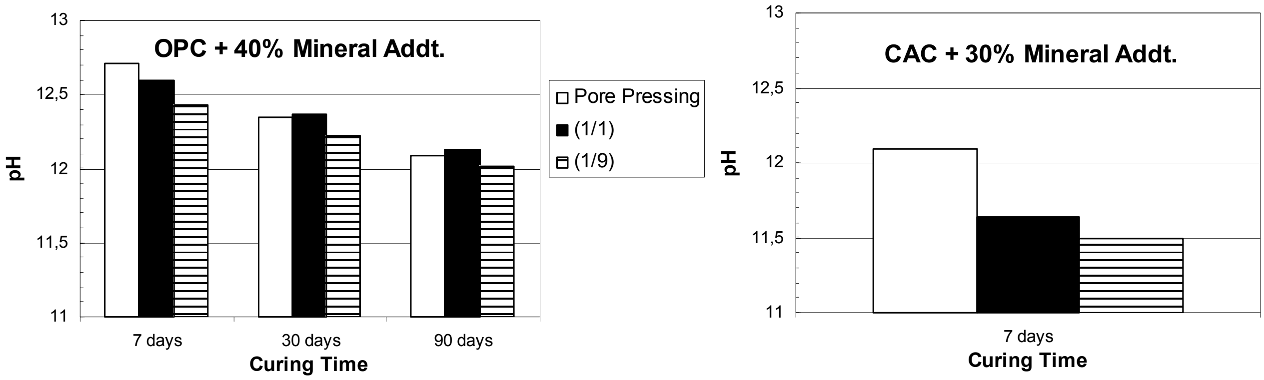

***Figure 5-8**. Calibration of the Slurry Method with the Pore Pressing Method (P4).*

5.3.4 Simple testing methodology for pH determination of low pH binders

Although the most accurate method to measure the pH of the pore aqueous phase is the pore pressing, its complexity made impractical the technique for the qualification of binders with regard to the pH value, particularly if the technique needs to be used as a routine and wide number of pH determinations are needed, as in the case of low pH developing of binders suitable for using in HLNWR. However once the binder has been designed is recommended to calibrate the pH of the cement mix by the pore pressing method, (M1) in present work.

Furthermore, a more simple but reliable method based on a slurry methodology may be used. The following protocol of testing is recommended:

- The Curing Age of the pastes must be large enough in order to guarantee stability of the pore aqueous phase. 90 days is a good one. The reason is that the use of high contents in mineral additions needs for longer times of hydration.
- The cement pastes have to be saturated, so the curing must be performed in a 100% of HR chamber. The temperature is also important. The pastes of this study were cured at 21 ± 2ºC.
- The sample has to be powdered to a size of approximately 75 µm and quickly prepared the slurry.
- The optimal solid/liquid ratio recommended to prepare the slurry for the measurement of the pH is 1/1.
- Although it has been demonstrate that the CO_2 in the water did not affect significantly the pH value, it is better to used free CO_2 deionised water to prepare the slurry. In addition, during the measurement of the pH a N_2 atmosphere is better. This is very important for pH values bellow 11.5.
- A stirring period of the slurry of 3 min will be used and at the end the pH has to be measured without stopping the stirring. An electrode stable in alkaline region should be used.

5.4 Conclusions

The experimental study performed has allowed the definition of a protocole test method for determination of accurate and reliable pH of pore solutions of low pH cementitious materials.

It has also been found that:

- The pore pressing test is the most accurate method to determine the pH of the pore aqueous phase. The preconditioning of the samples does not significantly affect the final pH value of the pore fluid.
- The pH is significantly affected by the curing time. The accurate determination of low pH cementitious materials should be given at curing ages of 90 days.

- The water/solid ratio used of the leachant influences in the pH value. A decrease of pH is measured with the increase of dilution of the leachant, more relevant for CAC based cements than in OPC with mineral additions.
- A slurry 1/ 1 solid/ liquid ratio is recommended.

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6 Formulating a low-alkalinity, high-resistance and low-heat concrete for radioactive waste repositories

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A pluri-annual research program has been launched in January 2003 by CEA, EDF and ANDRA in order to formulate and characterize low-alkalinity and low-heat cements which would be compatible with an underground waste repository environment. Several systems comprising ordinary Portland cement (CEM I), a fast-reacting pozzolan (silica fume (SF) or metakaolin (MK)) and in some cases a slow-reacting product (fly ash (FA) or blastfurnace slag) have been investigated. Promising results have been obtained with some binary mixtures of CEM I and SF, and with some ternary blends of CEM I, SF and FA or slag: pH of water in equilibrium with the fully hydrated cements is below 11. Dependence of the properties of standard mortars on the high contents of FA and SF in the low-pH cement blends has been examined. Combining SF and FA seems attractive since SF compensates for the low reactivity of FA, while FA allows to reduce water demand, heat release, and dimensional variations of the mortars. Finally, low-heat (<20°C under semi-adiabatic conditions), high strength (>70 MPa) concretes have been prepared from two low-pH cements: a binary blend made from 60% of CEM I and 40% of SF, and a ternary blend including 37.5% CEM I, 32.5% SF and 30% FA.

6.1 Introduction

In the French underground waste disposal concept (drilled in an indurated deep clayey formation), concrete may find different applications such as structure manufacturing, backfilling, supporting, coating or containerizing material. In this context, it has been pointed out that the clay properties may be modified due to the high pH conditions set by the cement interstitial pore water. What's more, a high temperature rise caused by cement hydration in massive concrete could induce micro-cracking of the material, with negative consequences on its long term durability.

Investigations have thus been carried out to formulate and characterize low-alkalinity and low-heat cements which would show an improved compatibility with the repository environment, and which could be used to elaborate high-resistance concrete. Emphasis has been placed on the design of blends of calcium silicate cements and pozzolans. Indeed, adding pozzolanic materials to Portland cement (OPC) has been shown to be advantageous in at least three respects:

- portlandite formed by the hydration of OPC is converted into calcium silicate hydrate by pozzolanic reaction /Taylor, 1997/,
- OPC is diluted,
- Ca/Si ratio of the calcium silicate hydrates is lowered, which enhances their sorption capacity of alkalis and reduces their equilibrium pH /Strinach, Glasser, 1997/.

This article presents the first three steps of the experimental program currently under way

- use of experimental designs to select cement formulas leading to pore solution pH below 11,
- characterization of mortars using the most promising cement blends,
- formulation of low-alkalinity, high-resistance and low-heat concrete.

6.2 Experimental

6.2.1 Components of the blends

Table 6-1 shows the properties of the components used to formulate low-pH cement blends. Three pozzolans were investigated : silica fume (SF), which was used in a densified form for easier handling, commercial metakaolin (MK), and low CaO fly ash (FA). They were characterized by their pozzolanic index, which represents the amount of portlandite reacting with one gram of pozzolan. SF and MK were much more reactive than FA in the short term, which was due for a part to their high specific area. The OPC cement and blast furnace slag were selected for their low alkaline content.

Table 6-1. Characteristics of the components of the cement blends.

		Silica Fume	**Fly ash**	**Metakaolin**	**Blast furnace slag**	**OPC**
Chemical composition (weight %)	SiO_2	95.00	50.80	54.4	36.20	22.84
	Al_2O_3	0.60	25.40	38.4	11.10	2.70
	CaO	0.40	5.50	0.1	42.30	67.41
	Fe_2O_3	<0.05	7.10	1.27	0.97	1.84
	MgO	0.30	1.80	<0.20	7.60	0.81
	MnO	n.d.	0.06	n.m.	0.15	n.d.
	P_2O_5	n.d.	1.07	n.m.	<0.05	n.d.
	TiO_2	n.d.	1.25	1.60	0.51	n.d.
	K_2O	0.29	1.40	0.62	0.34	0.23
	Na_2O	<0.20	0.50	<0.20	<0.20	0.14
	$Na_2O + K_2O$	0.29<<0.49	1.45	0.62<<0.82	0.34<<0.50	0.37
	SO_3	<0.20	0.50	<0.20	-	2.23
	Sulfur	<0.10	-	-	0.90	<0.01
	Fire loss at 1000°C	4.20	3.80	1.9	<0.10	1.72
Granulometry (µm)		-	d_{10} = 3.3 d_{50} = 21.5 d_{90}= 156.3	d_{10} = 1.2 d_{50} = 5.9 d_{90}= 52.3	d_{10} = 3.4 d_{50} = 19.8 d_{90}= 51.9	d_{10} = 2.6 d_{50} = 18.5 d_{90}= 50.3
Specific area (m^2/g)		25 (BET)	2.6 (BET)	19 (BET)	3.4 (BET)	0.34 (Blaine)
Pozzolanic index (g/g – 42 d)		0.76	0.17	0.96	-	-

Densified silica fume (Chryso Silica); Metakaolin AGS (Pieri); class F Fly Ash (Calcia); Blastfurnace slag (Calcia – Ranville); OPC: CEM I 52.5 PM ES CP2 (Lafarge Le Teil)

6.2.2 Formula selection

In a first approach, cement formulas were selected according to the following criterion: pH of water in equilibrium with hydrated cement should be below 11. Given the very long time required to get complete hydration of cement in standard curing conditions, a special procedure was developed. Experiments were carried out under nitrogen atmosphere on cement suspensions (water/cement ratio of 9) under mild milling conditions. Hydrates formed at the surface of the cement grains were eroded, and anhydrous cement was thus maintained in direct contact with water. The suspension pH was monitored until stabilization. The solid and liquid phases were then analyzed using XRD, TGA and ionic chromatography.

6.2.3 Elaboration of mortars

Standard mortars were prepared from cement, water and siliceous sand (0/2). The water/cement and sand/cement ratios were fixed respectively to 0.5 and 3. Mixing was performed with a standard mortar mixer (European standard EN 196-1) according to the following sequence: (1) introduction of water, (2) addition of the premixed pulverulents while maintaining slow stirring, (3) adjustment of the gout workability with a superplasticizer made of polycarboxylic ether (Chryso Fluid Optima 175), and (4) mixing at high speed for 3 min.

Elaborated materials were characterized by measuring various parameters according to standard procedures : bleeding (French standard NF P 18-359), Vicat setting (EN 196-3) heat of hydration (NF P 15-436), compressive strength (EN 196-1) and swelling or shrinkage (NF P 15-433) of prismatic samples (4x4x16cm) cured for 1 year at 20°C under water, air or in an air-tight bag. Porosity was characterized using Hg porosimetry (Micromeritics Autopore III – investigated pressures ranging from 0.8 to 5300000 psia). Crystallized phases of the hardened mortars were identified using XRD (Siemens D8 – Copper anode $\lambda_{K\alpha1}$ = 1.54056 Å), and the portlandite content was estimated using TGA (TA-SDT 2960).

6.2.4 Elaboration of concrete

Concrete samples included crushed non alkali-reactive calcareous aggregates (Table 6-2). They were prepared with a 50L mixer according to the following procedure : *(1)* mixing of the aggregates for 30 s, *(2)* addition of cement and mixing for 1 min, *(3)* addition of water and superplasticizer (Chrysofluid Optima 175) and mixing for 2 min, *(4)* measurement of the concrete workability with the Abrams cone (French standard NF P 18-541), *(5)* possible adjustment of the water and superplasticizer contents in case of insufficient slump.

Table 6-2. Properties of the concrete aggregates.Properties of the concrete aggregates.

Mineralogy	Density	Granulometry (mm)	Coefficient of water absorption	Los Angeles Coefficient	Micro-Deval Coefficient
Urgonian limestone	2.7	0/4 4/15	1%	24	15

Compressive strength was measured on cylindrical 11·22 cm samples after 28 days of curing under water at 20°C, as well as on 7·7·28 cm prismatic samples after 90 days of curing at 20°C under water, in air-tight bag, or in air (50% relative humidity). Dimensional variations of the 7·7·28 cm samples were also recorded during their whole period of curing (French standard NF P 18-427).

6.3 Results and discussion

6.3.1 Formula selection

Binary blends

Binary blends consisting of OPC (40 to 70%) and SF or MK (30 to 60%) were first investigated (Figure 6-1).

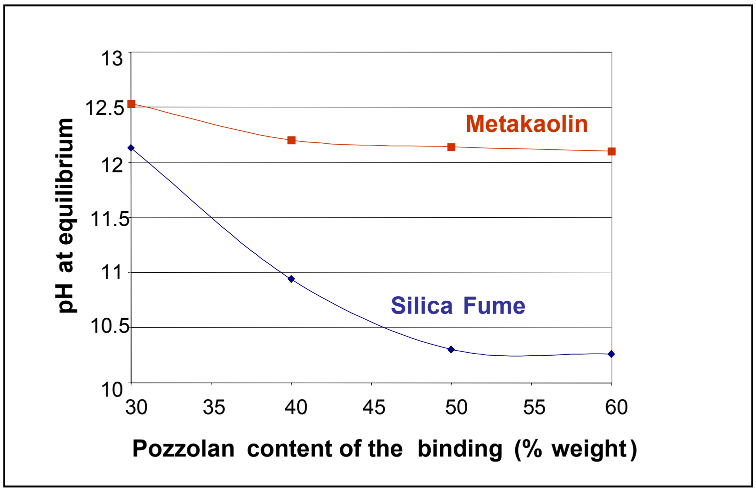


Figure 6-1. *Equilibrium pH of binary blends consisting of OPC and SF or MK.*

pH decreased when the amount of SF increased. A leveling-off was however observed for SF contents above 50%. pH below 11 could be obtained with blends containing at least 40 % of SF. As for MK, the results were quite disappointing since the equilibrium pH remained above 12 whatever the replacement level of OPC.

Ternary blends

The combination of a fast reacting pozzolan such as SF or MK and of a slow reacting compound such as fly ash or slag could result in a number of synergistic effects (Mehta, Gjorv, 1982, Thomas et al, 1999, Lam et al, 1998). Potentialities of ternary blends were thus studied using experimental designs.

The factors were the proportions of OPC (X_1), SF or MK (X_2), and FA or Slag (X_3) in the blend. They checked eq. (1), which was characteristic of a three-component mixture problem.

$$X_1 + X_2 + X_3 = 1 \qquad (1)$$

The factors were constrained between a lower limit a_i and an upper limit b_i ($0 < a_i < X_i < b_i < 1$), as shown in Figure 6-2. The resulting region of interest was a simplex.

OPC proportion	X_1	20 - 55%
SF or MK proportion	X_2	15 - 50%
FA or slag proportion	X_3	30 - 65 %

N° Exp	X_1	X_2	X_3
1	0.5500	0.1500	0.3000
2	0.2000	0.5000	0.3000
3	0.2000	0.1500	0.6500
4	0.3750	0.3250	0.3000
5	0.3750	0.1500	0.4750
6	0.2000	0.3250	0.4750
7	0.3167	0.2667	0.4167
8	0.4333	0.2083	0.3583
9	0.2583	0.3833	0.3583
10	0.2583	0.2083	0.5333

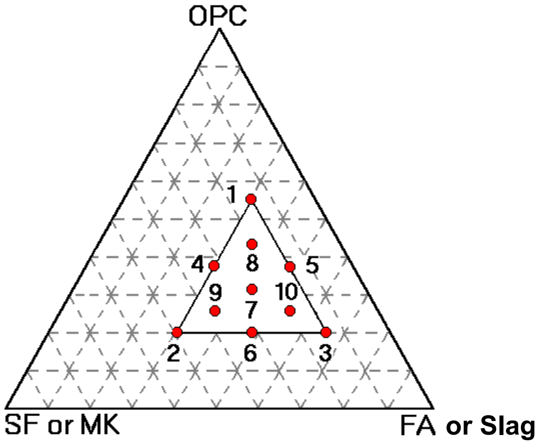


***Figure 6-2**. Experimental domain and selected design.*

Response surface methodology is based on the hypothesis that the responses (i.e. pH of the suspensions) can be approximated, within the range of the data, by a low order polynomial model. The postulated model was thus a special cubic polynomial in the canonical form.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1x_2 + \beta_{13} x_1x_3 + \beta_{23} x_2x_3 + \beta_{123} x_1x_2x_3 + \varepsilon \qquad (2)$$

where y = response, and ε = error

The positioning of experimental points within the experimental domain is of great importance to obtain a good precision on the estimates of the model parameters and, in a second step, on model-predicted response values. The well-known simplex-lattice design introduced by Scheffé, 1958, was used in order to estimate the seven parameters of the model defined by eq. (2). It included the 3 vertices of the simplex, the 4 edge centroids, and the overall centroid. Three validation points corresponding to mixtures homogeneously distributed in the investigated domain were added, for a total of 10 runs (Figure 6-2). Experimental data are summarized in Table 6-3. Two replicates of the overall centroid provided a measure of the experimental error.

Table 6-3. Measured responses

		OPC / SF / FA blends			**OPC / MK / FA blends**			**OPC / SF / Slag blends**		
pH at		**17 d**	**29 d**	**73 d**	**29 d**	**40 d**	**59 d**	**17 d**	**40 d**	**112 d**
Run n°	1	12.34	12.18	12.14	12.36	12.40	12.44	12.70	12.25	12.26
	2	11.27	11.14	10.99	11.70	11.63	11.59	10.88	10.24	10.14
	3	11.99	11.67	11.51	11.83	11.84	11.78	12.24	11.95	11.70

		OPC / SF / FA blends			**OPC / MK / FA blends**			**OPC / SF / Slag blends**		
pH at		**17 d**	**29 d**	**73 d**	**29 d**	**40 d**	**59 d**	**17 d**	**40 d**	**112 d**
	4	11.33	11.10	10.98	11.85	11.96	11.96	11.88	11.18	10.72
	5	12.04	1157	11.35	12.07	11.97	11.95	12.41	12.18	11.96
	6	11.29	11.13	11.00	11.76	11.73	11.69	11.66	10.81	10.47
	7	11.53	11.25	11.04	11.92	11.96	11.92	12.01	11.45	11.15
		11.45	11.18	10.98	11.93	11.94	11.90	12.03	11.50	11.12
		11.43	11.16	10.99	12.05	12.08	11.95	12.03	11.51	11/17
	8	11.94	11.58	11.31	12.20	12.14	12.05	12.35	12.03	11.87
	9	11.15	10.99	10.87	11.74	11.80	11.76	11.41	10.66	10.37
	10	11.79	11.47	11.25	11.94	11.94	11.94	12.16	11.84	11.48

For each response, the model coefficients were estimated by standard least squares regression techniques (Table 6-4). Possible model deficiencies were looked for by using analysis of variance.

Table 6-4. Estimated model coefficients

		OPC / SF / FA blends			OPC / MK / FA blends			OPC / SF / Slag blends		
pH at		17 d	29 d	73 d	29 d	40 d	59 d	17 d	40 d	112 d
Model coefficients	b_1	15.882	19.017	19.685	16.132	17.505	16.634	14.690	15.351	19.547
	b_2	16.047	16.854	15.504	15.336	15.209	13.424	8.012	14.521	20.415
	b_3	13.645	14.446	14.346	12.795	13.967	13.187	12.905	14.694	15.861
	b_{12}	-20.295	-30.775	-26.836	-24.199	-26.448	-16.693	-1.861	-25.536	-53.538
	b_{13}	-5.731	-17.235	-19.146	-9.591	-17.005	-12.668	-4.257	-8.766	-19.392
	b_{23}	-14.370	-17.117	-12.774	-12.604	-16.368	-9.769	0.207	-25.023	-40.000
	b_{123}	16.064	41.301	24.849	61.182	-81.662	49.640	15.785	76.964	125.579

The models provided a good correlation of the experimental data for all the investigated responses and were thus regarded as acceptable prediction tools. From the response contour plots (Figure 6-3), it can be seen that, after 17 days of hydration, pH of the suspensions made from OPC/SF/FA or OPC/SF/Slag blends mainly depended on the SF content : the higher the SF fraction, the lower the pH. Then, a curvature of the plots was noticeable, which indicated that FA or slag had also begun to react. When equilibrium was reached (at 73 d or 112 d), all blends checking eq. (3) or (4) led to pH below 11.

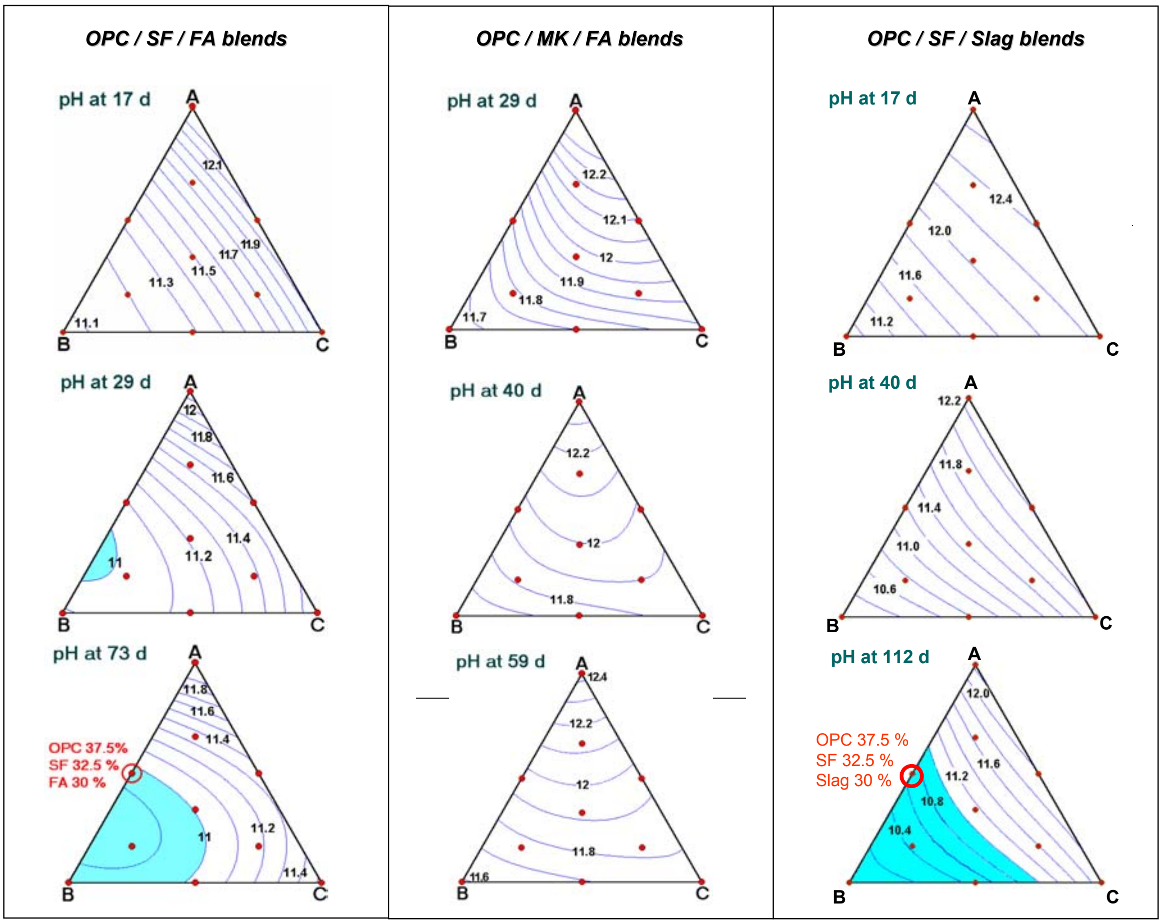


Figure 6-3. *Evolution of pH contour plots for OPC / SF / FA, OPC / MK / FA and OPC / SF / Slag blends.*

OPC / SF / FA blends

$$19.685\ x_1 + 15.504\ x_2 + 14.346\ x_3 - 26.836\ x_1x_2 - 19.146\ x_1x_3 - 12.774\ x_2x_3 + 24.849\ x_1x_2x_3 \leq 11 \qquad (3)$$

OPC / SF / Slag blends

$$19.547\ x_1 + 20.415\ x_2 + 15.861\ x_3 - 53.538\ x_1x_2 - 19.392\ x_1x_3 - 40.000\ x_2x_3 + 125.579\ x_1x_2x_3 \leq 11 \qquad (4)$$

OPC / MK / FA blends did not allow to meet the requirement of an equilibrium pH below 11 : this latter always remained above 11.5. The binders comprising 37.5% OPC, 32.5% SF and 30% FA or Slag were selected for further experiment. Indeed, among all blends leading to pH below 11, they had *(i)* limited SF content, which should reduce water demand, plastic shrinkage and material cost, as well as *(ii)* a significant OPC content, which should provide high mechanical strength.

A: OPC 55% - SF or MK 15% - FA or Slag 30%   B: OPC 20% - SF or MK 50% - FA or Slag 30%

C: OPC 20% - SF or MK 15% - FA or Slag 65%

Equilibrium pH was shown to depend on the silica content of the binder whatever its origin (Figure 6-4). pH below 11 were obtained for silica contents higher than 55%, which was only checked by some of the OPC/SF, OPC/SF/FA, and OPC/SF/Slag blends.

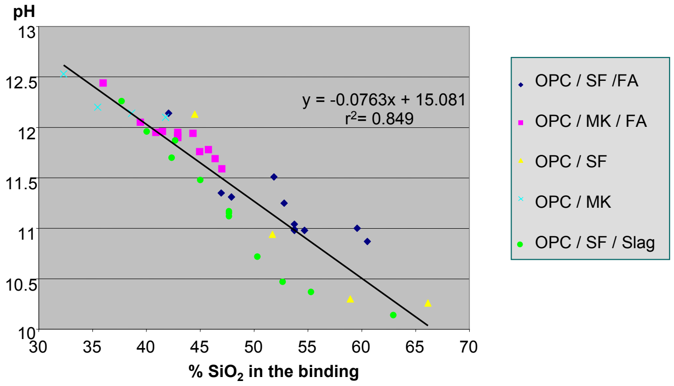
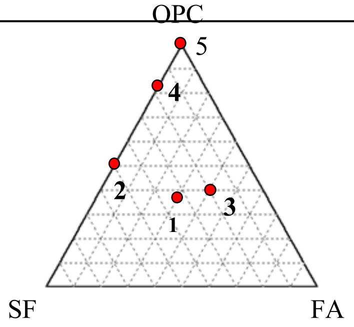


***Figure 6-4**. Correlation between equilibrium pH and silica content in the cement blends.*

6.3.2 Characterization of mortars

Mortars were elaborated using the selected ternary blends. Their properties were compared to a probe made from OPC only, and to low pH materials described in the literature (Gray, Shenton, 1998, Iriya et al, 1999, Lagerblad, 2003), Figure 6-5, Table 6-5. Results about slag blend will be published later since the experiments are still going on.



Blend compositions :

1: OPC 37.5% - SF 32.5% - FA 30%
Selected from previous study
2: OPC 50% - SF 50%
Canadian blend developed by AECL
3: OPC 40% - SF 20% - FA 40%
Japanese HFSC blend
4: OPC 83.3% - SF 16.7%
Swedish blend developed by SKB
5: OPC 100 %

Mortars : W/C = 0.5 , Sand /Cement = 3

***Figure 6-5**. Investigated blend compositions.*

Table 6-5. Properties of elaborated mortars

	Blend 1	**Blend 2**	**Blend 3**	**Blend 4**	**Blend 5 (probe)**
Blend composition	CEM I 37.5% SF 32.5% FA 30 %	CEM I 50 % SF 50 %	CEM I 40 % SF 20 % FA 40 %	CEM I 83.3 % SF 16.7 %	CEM I 100 %
Plasticizer content to get a workability comparable to that of the probe (/ weight of cement)	1.1 %	2.6 %	0.5 %	0.3 %	0 %
Bleeding at 24 h	Nul	nul	Nul	nul	Nul
Vicat setting	beginning : 6 h end : 7 h	beginning : 4 h end : 5 h	beginning : 7 h end : 8 h	beginning : 3 h end : 5 h	beginning : 3 h end : 5 h
Temperature rise (°C) (Langavant calorimetry)	13.1	20.0	14.7	23.0	23.4
Total porosity (1 year of curing under water)	20.0 %	14.3 %	22.0 %	21.4 %	14.1 %
Porosity below 20 nm (% of total porosity)	67.6 %	75.5 %	57.9 %	33.1 %	38.9 %
Dimensional variations after one year of curing (µm/m)	Air : -1042 Bag : -474 Water : +324	Air : -1171 Bag : -591 Water : +349	Air : -923 Bag : -437 Water : +293	Air : -824 Bag : -337 Water : +225	Air : -660 Bag : -323 Water : +199
Compressive strength after one year of curing (MPa)	Air : 28.3 Bag : 46.7 Water : 60.3	Air : 61.3 Bag : 91.8 Water : 89.0	Air : 21.1 Bag : 44.3 Water : 51.7	Air : 32.2 Bag : 51.5 Water : 55.2	Air : 39.8 Bag : 62.6 Water : 65.4
Portlandite content after one year of curing in air-tight bag	Undetectable by TDA	Undetectable by TDA	Traces	1.78 %	5.50 %
pH of suspension prepared from crushed mortar after one year of curing in air-tight bag (Liquid/Solid = 9 mL/g)	11.3	11.3	11.5	12.5	12.6

Rising the silica fume content in the cement blends had several positive effects.

- It induced rapid hardening and high compressive strength.
- The porosity was refined (although the total porosity remained higher than that of the probe), which was interesting with a view to durability aspects. The fraction of pores with a diameter below 20 nm (related to the C-S-H gel)

increased almost linearly with the silica fume content, as shown in Figure 6-6.

- Portlandite formed by CEM I hydration was rapidly depleted. It was not detectable anymore by TGA after 90 days in mortar 2, and 6 months in mortar 1.

However, it also resulted in:

- a bad workability of the grout, which was counteracted by adding increasing amounts of plasticizer,
- an increase in the dimensional variations of 4·4·16 cm specimens cured under water, in air or in air-tight bag (Figure 6-7).

The shrinkage increase with the silica fume content is a consequence of the refinement of the porosity. Empty porosity is created within the capillary pore system of the mortars microstructure due to water depletion by cement hydration and by desiccation. Largest pores empty first, followed by pores of decreasing diameter. The water / air menisci created in the partly empty pores induce shrinkage, the magnitude of which depends on the diameter of the pores being emptied: the lower the pore diameter, the higher the stress.

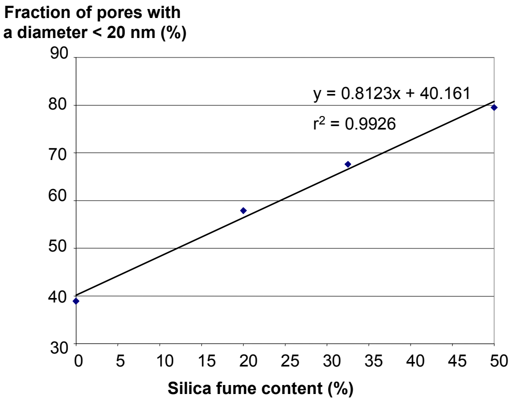


Figure 6-6. Influence of silica fume content on the pore fraction with diameter below 20 nm.

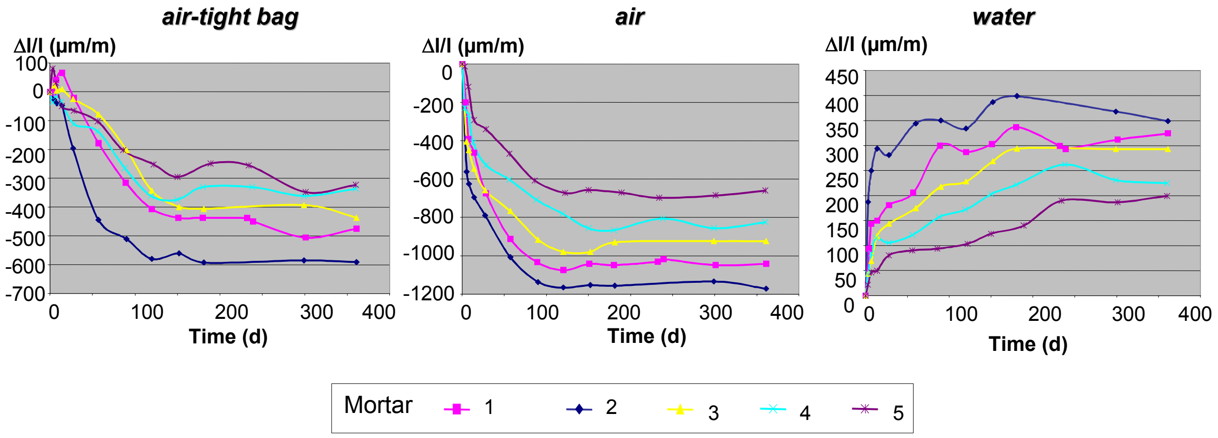


Figure 6-7*. Shrinkage or swelling of 4·4·16 cm specimens cured in air-tight bag, in air or under water.*

Introducing fly ash to the cement blends allowed to decrease the viscosity of the grout, to limit the heat release and to reduce the dimensional instability. However, hardening was slowed down, as well as portlandite consumption. Blend 1 comprising 37.5% OPC, 32.5% SF and 30% FA could constitute a good compromise between SF-rich (blend 2) and FA-rich (blend 3) formulas:

- silica fume compensated for low early strength of fly ash materials and allowed a total depletion of portlandite after 6 months,
- fly ash reduced increased water demand of silica fume, limited heat release and reduced dimensional instability.

6.3.3 Concrete mixture-proportioning

The next stage of the project was to design concrete from two low-pH binders : binary blend #2’ made from 60% CEM I and 40% silica fume (the minimum silica fume content to get a pH below 11 under the experimental conditions of section 6.3.1), and ternary blend #1 comprising 37.5% CEM I, 32.5% silica fume and 30% fly ash. The desired properties were as follows :

- the concrete should be workable, with a slump within the range 100-150 mm,
- the temperature rise under semi-adiabatic conditions should be below 20°C,
- the compressive strength after 90 days of curing under water should exceed 70 MPa.

Mixture-proportioning was performed using the conventional Dreux’s method, /Dreux, Festa, 1998/. After the production of trials batch, minor adjustments on the plasticizer and water contents were carried out to obtain the required rheological properties, producing the actual recipes given in Table 6-6.

Table 6-6. Concrete recipes - properties of resulting materials.

Blend composition	Reference	1	2’	5
	% CEM I	37.5	60	100
	% SF	32.5	40	0
	% FA	30	0	
Concrete recipe	Cement	400 kg/m^3		
	Sand 0-4	710 kg/m^3		
	Aggregates 4-15	1158 kg/m^3		
	Water	160 kg/m^3	160 kg/m^3	132 kg/m^3
	Superplasticizer	4 kg/m^3	6 kg/m^3	3 kg/m^3
Concrete properties	Slump (mm)	100	140	145
	Temperature rise (°C)	14.2	20.6	23.3
	Compressive strength (MPa)	28 d – water : 55.0 90 d – water : 69.0 ± 3.7 90 d – bag : 66.6 ± 0.7 90 d – air : 48.1 ± 0.9	28 d – water : 77.0 90 d – water : 82.0 ± 2.0 90 d – bag : 78.4 ± 3.0 90 d – air : 67.5 ± 0.9	28 d – water : 76.0 90 d – water : 80.0 ± 2.9 90 d - bag– 70.4 ± 1.2 90 d – air : 59.1 ± 1.1
	Dimensional variations (µm/m)	28 d – water : 110 90 d - water : 130 28 d – bag : 158 90 d – bag : 265 28 d – air : 265 90 d – air : 350	28 d – water : 75 90 d - water : 97 28 d – bag : 130 90 d – bag : 243 28 d – air : 260 90 d – air : 352	-

Temperature rise was measured on equivalent mortars in Langavant calorimeters. Compressive strength at 90 d was measured on 7·7·28 cm samples. The results were corrected so as to obtain estimates of the strength of 11·22 cm samples.

The mix compositions proved to be satisfactory. It was possible, by simple means, to prepare workable concrete despite the very high amounts of pozzolans in the blends. Concrete made with blend #2’ matched all the requirements. As for concrete made with blend #1, its low heat output should allow to increase the cement content of the recipe, which in turn should improve the mechanical strength of the samples.

6.4 Future prospects

Future work will include formulation, low-pH cement chemistry and durability studies.

- *Formulation.* Emphasis will be placed on concrete mixture-proportioning with ternary blends: optimization on the concrete recipe with the CEM I / SF / FA blend, and design of a concrete including CEM I, SF and slag.
- *Investigation of the low-pH cement chemistry*. Two types of studies have already been undertaken and will be completed :
    - characterization of the solid and liquid phases of fully hydrated cement suspensions, and comparison of the results with thermodynamic predictions based on the dissolution equilibria of the cement phases;
    - extraction and analysis of the pore solution of hydrating cement pastes.

- *Durability studies*. Leaching of cement pastes in pure water will be performed at 20°C and 80°C in order to determine the kinetics of degradation of the materials and to identify the mineralogical changes involved in the process.

6.5 References

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7 Properties of low-pH cementitious materials developed and tested by CRIEPI and NUMO

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7.1 Introduction

In Japan, high level radioactive waste (HLW) will be geological disposed in deep repository. Cementitious material will be used for supporting member, plug, also grout and rock bolts. It is important for long-term environmental safety that these cementitious materials will not be harmful to barrier system, such as bedrock, bentonite and other engineered barriers. Then the investigations for the development of lower-pH cementitious material have been operated world-widely.

In this study, two types of low-pH cementitious materials, ‘LAC’ and ‘SAC’, were investigated about these initial properties and hardened physical properties, and these properties of low-pH cements were compared with that of ordinary Portland cement.

7.2 Materials

Table 7-1 shows the chemical composition of low-pH cementitious materials used in this investigation. LAC was developed by CRIEPI and Taiheiyo Consultant Co., Ltd. (Thaiheiyo Cement Grope), aiming to avoid forming of calcium hydroxide in hardened matrix. Then LAC is composed mainly of calcium-sulfo-aluminate type clinker and water granulated blastfurnace slag. As for the high reaction ability of LAC, citric acid were added to mixing water as retarder.

SAC was developed by Kiev national university of civil engineering and architecture. The main component of SAC is water granulated blastfurnace slag. Then, meta-sodium-silicate solution is used as a hardening. And the concentration of mata-sodium-silicate solution was controlled by its density of solution. In this study, the density of 1.05, 1.10 and 1.16 g/cm^3, were applied as mixing water (alkali solution).

Table 7-1. Chemical composition of low-pH cementitious materials and OPC (mass%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO
LAC	37.7	18.6	16.8	0.9	22.3	2.4
SAC	41.5	39.1	8.4	1.43	0.6	4.8
OPC	65.5	22.7	4.8	1.7	2.8	1.4

7.3 Experimental procedure

Physical properties of cement, flow-ability, consistency, setting time (initial and final), soundness, and compressive strength were measured in conformity to Japanese Industrial Standard (JIS R5201 2002, Physical testing methods for cement). Here the testing methods of consistency, setting time and compressive strength were in conformity to ISO 9597 and ISO 679 respectively. The amount of bleeding water was also measured at 3.5 hours and 24 hours after mixing. Soundness were measured by the pat method; Two pats of cement are immersed, as attached to the glass plate, which have been cured for 1 day in the wet box at 20°C. In the water of scalder, heat is gradually increased to boil for 90 minutes and after cooling down naturally, examine for the presence of cracks or distaortions due to expansion. The test results were expressed as "good" for the cement which presented neither crack nor distorted due to expansion , and as "failed" for the cement which presented those features.

Shrinking properties (autogeneous shrinkage and drying shrinkage) were also measured. The size of mortar specimens was 40·40·160 mm, and the bench mark balls were embedded into the both end sides. The specimens were prepared according to procedure of ISO 679 using a standard sand with cement to sand ratio= 1:3. After the initial curing on 20°C of humid air for 1 day, the hardened specimens were sealed, and the amounts of autogeneoue shrinkage of these specimens were measured by predetermined time, Figure 7-1. The specimens for measuring of drying shrinkage were pre-cured in water of 38°C for 28 days to accelerate the hydration. These specimens were cured in 60°C, 80°C and 110°C drying for 27 days after pre-drying for 1 day.

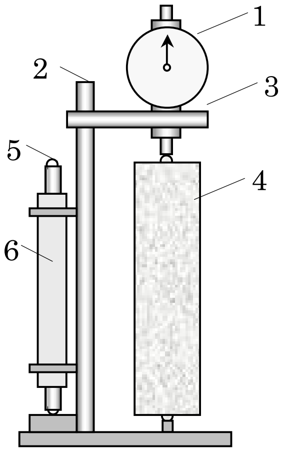

***Figure 7-1**. Scheme of a device for determination of shrinkage deformation.*

1 - a digital indicator 2 - a device frame 3 - an arm 4 - a testing specimen 40x40x160 mm with bench mark balls 5 - a reference steel rod (160 mm) 6 - a wooden casing

Water permeability was measured by input method with permeability tester (shown in Figure 7-2. ϕ 150·150 mm specimens were prepared in conformity to ISO 679. Water permeability was calculated with following equation:

$$K = \rho \cdot g \cdot \frac{q \cdot l}{t \cdot A \cdot P} \tag{1}$$

where, q :quantity of injected water (m^3), l :average permeation depth (m), t :injecting time (s), A :injected cross-section area of mortar(m^2), P :water pressure (Pa), ρ :density of water (kg/m^3), g: gravitational acceleration (m/s^2) K :water permeability (m/s)

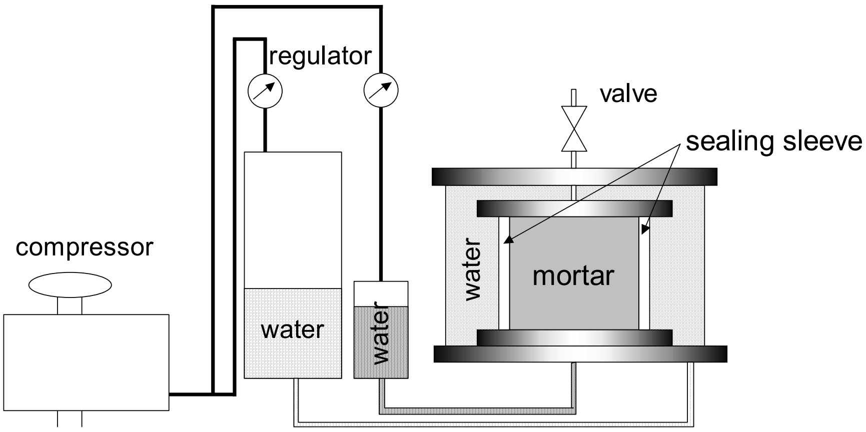

***Figure 7-2.** Schematic diagram of water permeability tester*

7.4 Results and discussion

Table 7-2 showed the results of initial physical properties of low-pH cement. The initial setting time of SAC was fast in all mixing solution cases, so the use of retarder was needed from the viewpoint of workability. The setting time of LAC showed also early, but it depended on the dosage of citric acid. The flow values of SAC and LAC mortar showed some relation to the concentration of meta-sodium-silicate solution and the dosage of citric acid, respectively. LAC and SAC mortar system show high resistance to segregation that obtained by the bleeding test.

Table 7-2. The results of early physical properties of low-pH cement.

Cement type			Soundness*1) /mass%	setting time		Flow value /mm	Bleeding /%	
				initial /h-min	final /h-min		3.5h	24h
LAC	Dosage of citric acid (mass%)	0	29.0	0-30	1-00	130	-	-
		0.1	26.2	0-15	1-15	153	-	-
		0.3	24.2	0-46	1-15	171	-	-
		0.5	24.4	1-12	1-52	167	0.00	0.00
		0.7	24.2	3-03	4-03	165		-
SAC	Solution concentration (g/cm^3)	1.05	29.4	0-32	2-22	181	0.00	0.00
		1.10	30.0	0-22	2-33	166	0.00	0.00
		1.16	30.6	0-23	1-13	151	0.00	0.00
OPC			27.6	2-00	3-10	178	0.25	0.00
OPC (JIS R5210)			-	over 1-00	under 10-00	-	-	-

*1) Values were described in solution/cement ratio.

*2) Dosage of citric acid were described with mass ratio to cement

Figure 7-3 shows the compressive strength of each mortar. The strength development of LAC mortar with 0.3 and 0.5 mass% dosage of citric acid seemed to be similar to that of OPC system. While the strength development of SAC system showed different strength development comparing with that of OPC. The compressive strength of SAC was influenced strongly by the concentration of mixing solution. In the case of much high concentration, the compressive strength rises up higher.

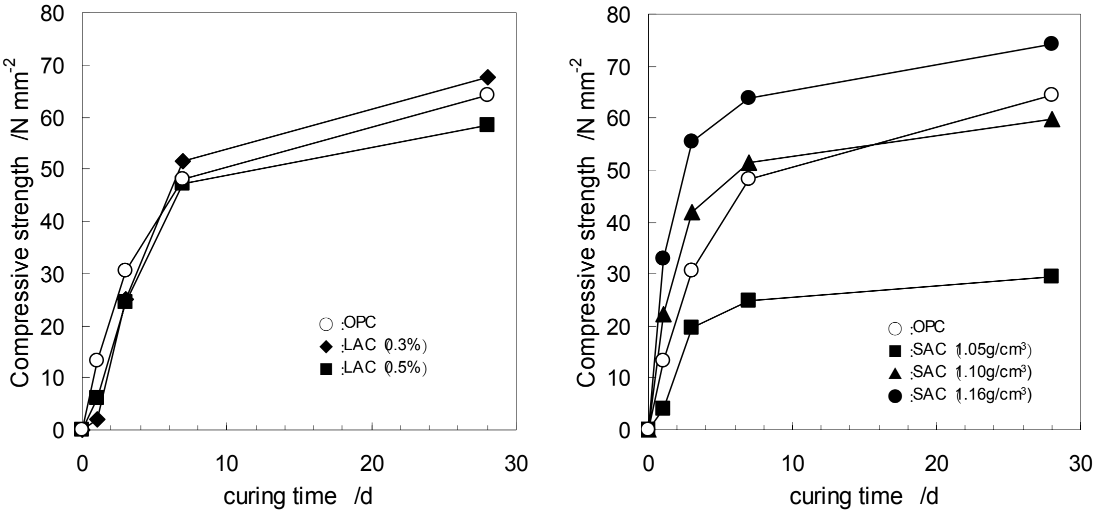

Figure 7-3. Strength development of LAC, SAC and OPC mortar

Shrink values of each mortar are shown in Table 7-3. The autogeneous shrinkage of SAC and OPC mortars showed almost the same tendency, but the LAC mortar showed expansion. It was thought that the expansion was derived from the formation of ettringite, which were produced by the reaction of calcium-sulfo-aluminate clinker. In this point, we must have some investigation if that expansion will bring harmful fractures in the LAC mortar and concrete. The drying shrinkage of LAC mortar was lower than that of SAC and OPC mortars in the case of drying at 60°C and 80°C. The difference was thought to be derived from each characteristic hydration products. SAC was slag based cement, and that main hydration product is composed with C-S-H. On the other hand, the hardened matrix of LAC, which was based on calcium sulfo alminate clinker, contained much amount of ettringite. In applying low-pH cement to structural member in HLW repository, we must avoid initial defect mainly as cracks. So, our future study is important to investigate the effect of the type of hydration phases on the shrinkage.

Table 7-3. The shrinkage of each mortar（$\times 10^{-6}$）

	autogeneous shrinkage /28d	**drying shrinkage /after 28d**		
		60°C	**80°C**	**110°C**
LAC(0.5%)	130	-407	-520	-1018
SAC (1.10g/cm^3)	-59	-836	-811	-895
OPC	-66	-926	-962	-917

Figure 7-4 shows the relationship between permeability and total pore volume measured by mercury intrusion porosimetry (MIP) There was linear correlation between permeability and total pore volume. There was no relationship between the pore size distribution and permeability from the results. The permeability was thought to be depending on the total pore volume. But the far more study is needed by applying other permeability measuring method.

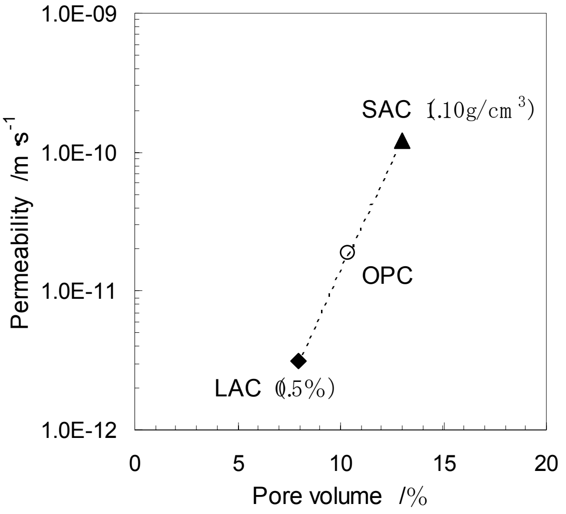

***Figure 7-4**. Relationship between total pore volume and permeability*

7.5 Conclusions

- The setting time of LAC and SAC mortars was earlier than OPC. So, early setting time must be controlled by the retarder.
- The strength development of SAC depends on the concentration of its mixing solution.
- Hardened LAC mortar, which cured enough, showed better dimensional stability than SAC and OPC mortar.
- LAC has lower permeability than other cement which were investigated in this study.

8 Low-pH grouting cements – results of leaching experiments and modelling

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8.1 Introduction

The possibility of a high-pH plume resulting from ordinary grouting material has been a concern to the long term safety of a repository. Another risk is imposed by the organic cement admixtures, which are able to complex radionuclides and thereby enhance their transport. In order to overcome such effects by designing a new type of injection grout a co-operation project, "Injection Grout for Deep Repositories", was set up between three organizations, Posiva Oy, Swedish Nuclear Fuel and Waste Management Co (SKB) and Nuclear Waste Management of Japan (NUMO). The work discussed here encompasses Task 5 ("Leach testing of the most promising low-pH grout mixes developed") in Subproject 1 (SP1) ("Low pH cementitious injection grout for larger fractures").

The acceptable target pH resulting in the leach solutions used was set at a value ≤ 11, which would limit the OH-alkalinity of the leachate to a value of about 1 mmol/L in pure water. The preferred characteristics of the grout were a known chemical composition with tested properties and without added organics. Two types of leach solutions were selected; fresh and saline simulated groundwaters representing the current lower and deeper bedrock groundwater conditions at Olkiluoto, the site for the Finnish underground rock characterization facility ONKALO. For comparison reasons it was felt necessary to include a reference grout in the leach tests, as well. The reference grout represented a conventionally used grout with high-pH.

To aid evaluation of the long-term safety of the tested mixes leach testing was planned to provide various analytical data, for estimating the leachable inventory and the remaining leachable fraction of the analysed solutes as a function of time, as well as for performing thermodynamic equilibrium modelling of the chemical behaviour of cement phases.

Leaching of cementitious materials has been extensively studied, but in general experiments have been primarily concerned with the degradation of structural materials, with a consequent loss of strength and integrity. Here the main objective was to assess the pH in the leachates in contact with the low-pH grout materials. More details and results are presented in Vuorinen et al. /2005/.

8.2 Leach testing

A variety of test procedures are used in characterization of materials with respect to their leaching behaviour for regulatory purposes, e.g., waste management purposes, environmental impact assessment, and for scientific purposes, are available /van der Sloot 1996, 1998, van der Sloot et al.1996, Wahlström 1996, Fällman and Aurell 1996, MCC Nuclear Waste Materials Handbooks, Saito and Deguchi 2000, Hohberg et al. 2000/. However, test procedures may often have to be altered or combined in order to fulfil the aim of the test and to take account of the local environmental conditions. In this work two leaching methods were used; one method for assessing the maximum equilibrium pH deep in the bedrock with slow turnover of groundwater, and another test (diffusion controlled release), which would facilitate the assessment of long-term safety by derivation of leach rates. Tests were run inside an anaerobic glove-box (nitrogen atmosphere with low CO_2 ($\leq$ 0.01ppm)) in order to avoid the interference of CO_2 on the high-pH solutions.

8.2.1 Equilibrium test

In the equilibrium test (EQ-test) a part of the leach solution was extracted and replaced with the same amount of fresh leach solution periodically. The amount of leach solution replaced periodically was evaluated on the basis of the groundwater flow-rate in Olkiluoto bedrock. The turnover rate of groundwater was chosen to meet the effective flow per area in a potential grouted area at Olkiluoto. According to Vieno et al. /2003/ the characteristics of a grouted zone could be 20 m in diameter with 250µm aperture of an injected fracture. Based on these choices it was assessed that the leachate in the test vessel needed to be changed with a rate of 0.26 L/yr in order to reach the flow per area of $100L/(yr\cdot m^2)$.

This periodic replacement of the leach solution was considered necessary in the equilibrium test because the development of a low pH grout material aimed at binding alkalies to CSH (calcium silicate hydrate) phases and thereby to reducing the pH of the pore solution /Kronlöf 2004/. Without any replacement of the leachate the highly soluble high-pH alkalis , NaOH and KOH, as well as $Ca(OH)_2$ (even if considered solubility limited), when sufficiently available in the pore solution of the grout could have kept the pH higher than the longer term pH controlled by the CSH phases (pH ≈ 10.5).

Completed EQ-tests were carried out for 20 or 25 weeks and the amount of leachate replaced was about 104 mL.

8.2.2 Diffusion test

In the diffusion tests (DIFF-test) the entire leachate volume was replaced at each exchange point. In the beginning of the test the leachates were exchanged more often and later on the exchange frequency was decreased. Generally the exchange of leachates occurred twice on the first day, 3h and 6h, thereafter daily up to day 6 and continuing day 8, 11 and 15, after which the exchange was made at 7 day intervals up to the 20th exchange point. However, some modifications had to be made to the schedule due to holidays etc. The duration of the entire testing period was 70 and 79 days for mixes 52 and L8, respectively, whereas mixes 44 and f63 were tested up to 25th exchange point reaching up to 106 and 109 days of testing, respectively. In a complete DIFF-test the amount of leachate exchanged was 600 or 750 mL (20 or 25 exchange points).

8.2.3 Experimental

The grout mixes were cast in plastic pipes and after an adequate curing (at 20°C) period suitable disks were sawn (diamond blade) for leach testing. In each sample vessel two 1cm thick specimen slices (∅ 2.84 cm) were placed with 30 mL of leachate. This gave a value of ~0.85 cm to the ratio of sample surface area to leach solution volume (A_S/V_L). The leach tests were performed in tightly closed polyethylene vessels inside the anaerobic glove-box. The leached specimens were kept immersed in the leachates without stirring until each sampling point, and only then, before extracting any solution samples, the system was stirred. All solution samples extracted were filtered (0.2 µm) in order to remove possible fragments or larger colloidal particles present in the leachates. After each leachate exchange the remaining solutions, not needed for the measurement of pH, titration of alkalinity or determination of sulphide concentration, were taken out of the glove box into a freezer to be stored for the purpose of chemical analysis to be performed later.

Leach solutions

The compositions of the two simulated groundwater solutions, saline (OL-SR) and fresh (ALL-MR), are given in Table 8-1. The CO_2-free leach solutions were prepared inside the anoxic glove-box at least two weeks before starting the leach testing. The test temperature was the ambient box-temperature, which was kept at 25 °C ±1 °C, but due to fluctuations in the laboratory air-conditioning system the temperature range may have been larger for shorter time periods.

Table 8-1. Nominal compositions of the two leachates used.

		Fresh (ALL-MR)	Saline (OL-SR)			Fresh (ALL-MR)	Saline (OL-SR)
pH		8.8	8.3	**HCO_3^-**	mol/L	$1.1\cdot10^{-3}$	

Na^+	mol/L	$2.3 \cdot 10^{-3}$	0.21	**Cl^-**	– ″ –	$1.4 \cdot 10^{-3}$	0.41
Ca^{2+}	– ″ –	$0.13 \cdot 10^{-3}$	0.10	**Br^-**	– ″ –		$1.3 \cdot 10^{-3}$
K^+	– ″ –	$0.10 \cdot 10^{-3}$	$0.54 \cdot 10^{-3}$	**J^-**	– ″ –		$0.01 \cdot 10^{-3}$
Mg^{2+}	– ″ –	$0.03 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	**F^-**	– ″ –		$0.06 \cdot 10^{-3}$
Sr^{2+}	– ″ –		$0.40 \cdot 10^{-3}$	**B^-**	– ″ –		$0.09 \cdot 10^{-3}$
SiO_2	– ″ –	$0.03 \cdot 10^{-3}$		**SO_4^{2-}**	– ″ –	$0.10 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$

Tested grout mixes

Different grout mixes were designed and their technical performance was tested before any mixes were chosen for leach testing. An exception to this was mix L8 (Japanese low alkali cement, LAC), which was not suitable for grouting but was tested for comparison purposes. Detailed information on the materials, mix characteristics, designing of the mixes and results from their performance are found in Kronlöf /2004/. Two types of pozzolan were used to reduce the pH of the grout mixes; blast furnace slag (SL) and silica fume (SF). The compositions of the mixes chosen for leach testing are given in Table 8-2 for the OPC-silica mixes and in Table 8-3 for the slag and Japanese LAC mixes. The composition of the reference mix (R52), a conventional grout mix with high pH, is included in both tables. The chemistry of the grout mixes tested is given in Table 8-4.

Table 8-2. **The mix compositions of the OPC-silica mixes and the reference mix /Kronlöf 2004/.**

Mix	**Binder**	**OPC -type**	**SF type**	**OPC /DM**	**SF /DM**	**Gypsum /OPC**	**HAC /OPC**	**SF /OPC**	**Superplasticizer/DM**	**Water /DM**
12	UF16-SF	UF16	Grout Aid'	0.77	0.23	0.000	0.000	0.30	0.00	1.26
f63	UF16-SF with ETTA	UF16	Grout Aid'	0.56	0.38	0.027	0.075	0.69	0.00	2.48
f64	UF16-SF with ETTA	UF16	Grout Aid'	0.49	0.46	0.027	0.075	0.94	0.00	2.91
w1	WCE-SF with ETTA	WCE	Grout Aid'	0.56	0.38	0.027	0.075	0.69	0.00	2.48
w2	WCE-SF with ETTA	WCE	Grout Aid'	0.49	0.46	0.027	0.075	0.94	0.00	2.91
R52	UF16-SF-SPL	UF16	Grout Aid	0.925	0.070	0	0	0.075	0.01	1.21

OPC = Ordinary Portland Cement SF = Silica Fume WCE = Egyptian White Cement
DM = dry matter SPL = Superplasticizer ETTA = Ettringite Acceleration
UF16 = commercial cement Grout Aid = commercial slurry of SF HAC = High Alumina Cement

Table 8-3. The mix composition of the slag, LAC and reference mixes /Kronlöf 2004/.

Mix	**Binder**	**OPC type**	**SF type**	**OPC /DM**	**SF /DM**	**SL /DM**	**G /DM**	**SF /SL**	**OPC /SL**	**G /SL**	**Superplasticizer/DM**	**Water /DM**
44	Slag-RC10-SF	UF16	Grout Aid'	0.04	0.16	0.80	0.00	0.20	0.05	0	0.00	1.36
S14	Slag-RC10-Gypsum-SF	RC10	GroutAid	0.029	0.29	0.59	0.093	0.50	0.05	0.16	0	1.6
S20	Slag-RC10-SF	RC10	GroutAid	0.031	0.31	0.63	0.000	0.50	0.1	0	0	1.6
L8	LAC						0.000				0	1.0
R52	UF16-SF-SPL	UF16	GroutAid	0.925	0.070	0	0.000				0.01	1.21

RC10 = commercial cement LAC = Low Alkali Cement SL = Blast furnace slag G = Gypsum

Table 8-4. The chemical composition of the mixes tested, given as weight unit per volume unit of grout /Kronlöf 2004/.

Mix	CaO	SiO_2	Na_2O eq. OPC+ SL + SF	Na_2O eq. OPC+SL	Na_2O eq. OPC	Al_2O_3	MgO	Fe_2O_3	SO_3	S	Other	Tot	Ca/Si
	w%	w%	W%	w%	w%	w%	w%	w%	w%	w%	w%	w%	mol/ mol
12	49.7	39.5	0.84	0.38	0.38	2.69	0.69	3.23	1.85	0.00	1.55	100	1.35
F63	37.8	49.3	1.06	0.30	0.30	4.87	0.50	2.36	2.03	0.00	2.08	100	0.82
F64	33.2	54.9	1.18	0.26	0.26	4.28	0.44	2.07	1.78	0.00	2.19	100	0.65
W1	39.6	50.0	0.83	0.06	0.06	4.43	0.15	0.12	2.12	0.00	2.75	100	0.85
W2	34.8	55.5	0.97	0.05	0.05	3.88	0.13	0.11	1.86	0.00	2.78	100	0.67
44	33.8	44.8	1.57	1.25	0.06	7.80	7.74	1.08	0.12	1.04	2.04	100	0.81
S14	27.7	49.5	1.50	0.91	0.04	5.71	5.66	0.79	4.41	0.76	3.99	100	0.60
S20	28.4	53.5	1.64	1.02	0.09	6.26	6.16	0.93	0.19	0.81	2.13	100	0.57
L8	38.1	18.2	0.22	0.22	0.00	16.92	2.25	0.82	22.63	0.00	0.91	100	2.25
R 52	63.1	27.8	0.20	0.07	0.07	2.51	0.24	0.19	2.38	0.00	2.36	100	2.32

Measurements

The measurement of pH was performed with a commercial glass combination electrode (Orion ROSS) inside the anoxic glove-box. In the calibration of the pH measurement commercial pH buffers of adequate pH values were used. Titration of total alkalinity (HCl solutions of adequate strength, Gran plot method /Stumm & Morgan 1996/ was also performed inside the glove-box.

High pH values are due to high alkalinity but the nature of alkalinity can not be determined merely from the pH value. By definition alkalinity is the acid neutralising capacity of solutes in a water sample and consists of the sum of titratable carbonate and noncarbonate chemical species in a filtered water sample. Important noncarbonate contributors may include organic ligands (especially acetate and propionate) as well as hydroxide, silicate, borate, ammonia, sulphide /Hem, 1989/, phosphate and arsenate /Stumm and Morgan, 1996/ when found in high concentrations.

$$\text{Alkalinity}_{TOT} = -(H^+) + (OH^-) + (HCO_3^-) + 2(CO_3^{2-}) + (NH_3) + (HS^-) + 2(S^{2-}) + (HSiO_3^-) + (B(OH)_4^-) - (H_3PO_4) + (HPO_4^{2-}) + 2(PO_4^{3-}) \quad (1)$$

After completing leach testing the chemistry of some leachates was analysed /Vuorinen et al. 2005/. The analysed substances were Na, K, Ca, Mg, Al, Si, Cl^-, SO_4^{2-}, S_{TOT} and Fe. In Japan CRIEPI performed analyses of some solid specimens /Imoto et al. 2004/: Qualitative phase analyses by XRD (X-Ray Diffractometry), the chemical composition by XRF (X-Ray Fluoresence), the amount of $Ca(OH)_2$ in the solids by TG-DTA (Thermo Gravimetric-Differential Thermal Analysis), the profile of Ca/Si ratio by EPMA (Electron Probe Microanalysis), specimen surfaces with SEM (Scanning Electron Microscopy) and the pore structure by MIP (Mercury Intrusion Porosimetry).

8.2.4 Results on leachates

The pH values measured in the saline leachates (OL-SR) were constantly lower than in the fresh leachates (ALL-MR), and therefore the measurements in the saline leachate were stopped, as the results in the fresh leachate gave an upper limit. The pH values measured in the equilibrium tests are shown in Figure 8-1.

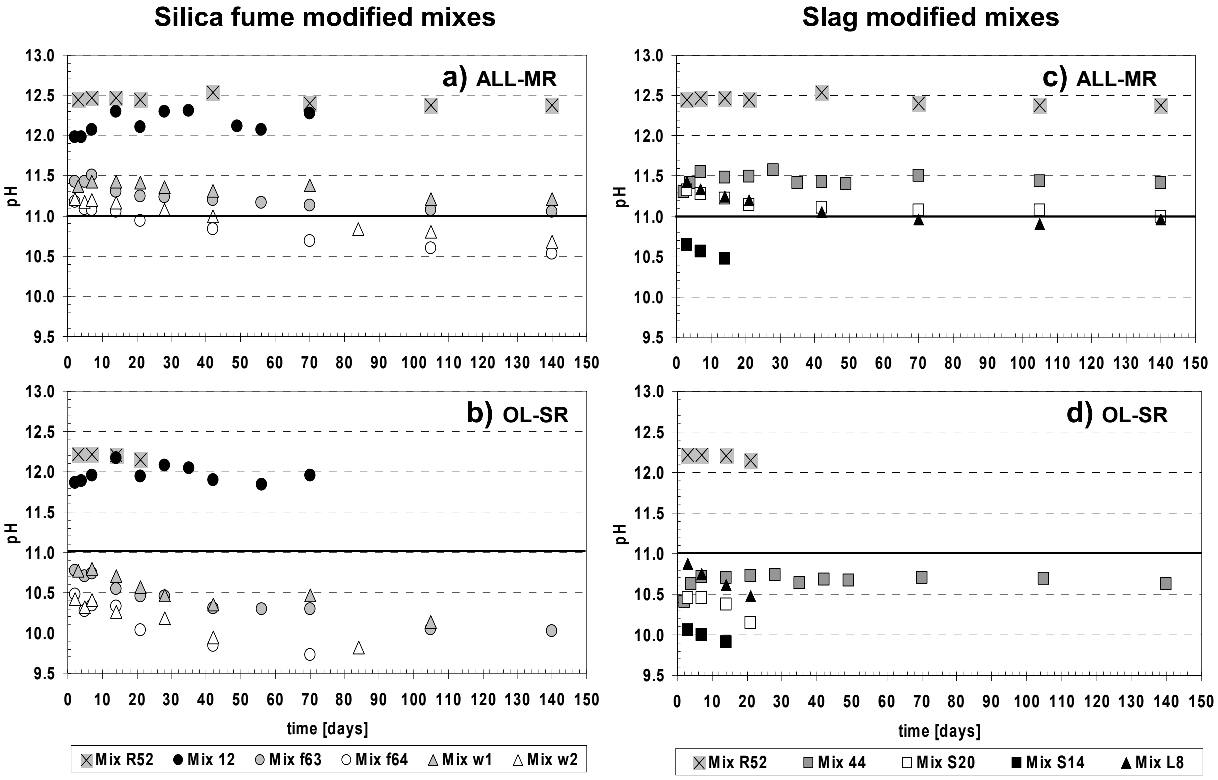

Figure 8-1. pH values measured in EQ-test. The left sub-figures are for the SF modified mixes a) fresh leachate and b) saline leachate, and the righ side sub-figures for the slag modified mixes, c) fresh leachate and d) saline leachate. Both figures in include values for the reference mix as well. The target pH of 11 is depicted with a heavier line across the sub-figures.

The reference mix (R52) exhibited, as expected, high pH values (EQ-test), around 12.5, and accordingly also high alkalinity (Alk_{TOT} ~ 35-50 mmol/L), Figure 8-2. The alkalinity was due to high concentrations of hydroxide in the leachates originating mainly from the dissolution of portlandite (c.f. Ca in Figure 8-4a), strongly supported by the analytical results of the solid specimen /Imoto et al. 2004/. In the case of the low-pH mixes the target pH ≤ 11 was reached in the saline leachates right from the beginning of leach testings except in the case of mix 12 (pH>12) (Figure 8-1b and d). Slag mixes, even though exhibiting low pH values had an unfavourable attribute in respect of long term safety of the repository; leached sulphide, which is detrimental to copper, whereas mix L8 leachates contained high concentration of sulphate (Figure 8-4a), which is a potential source of sulphide produced by SRB (Sulphate Reducing

Bacteria). The presence of sulphide also increased the total alkalinity values especially in the case of mix S14 (Figure 8-2a).

Lowest alkalinities in the fresh leachate (ALL-MR) at the end of EQ-test were measured for mixes w1 and f63 (Figure 8-2b). Both mixes nearly reached the target pH at the end of testing, whereas mixes w2 and f64 reached even lower pH values, below 11 (Figure 2-1a), despite of the slightly higher alkalinities (Figure 8-2b).

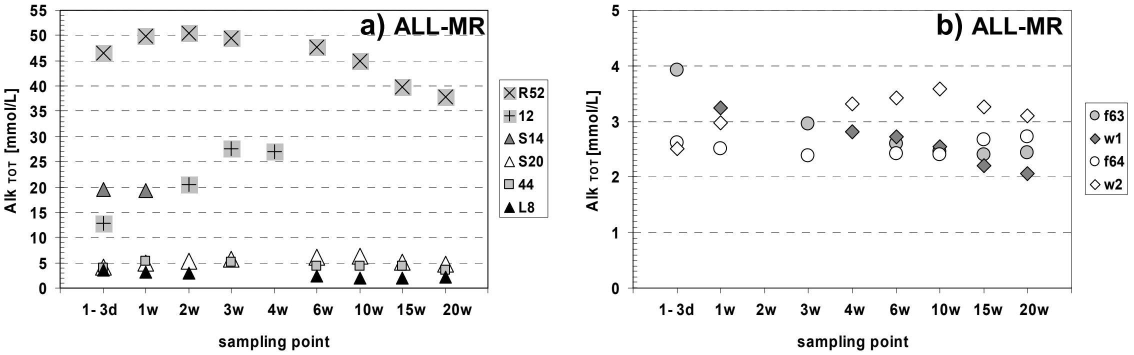

***Figure 8-2**. Titrated total alkalinities in EQ-test in the fresh leachate (ALL-MR). (The figure is split in two for reasons of clarity).*

Only a few analytical results of the saline leachates were available for the equilibrium tests and in the case of mix w1 the results were even better than for mix f63. Comparison of the results for f63 and w1 showed that the last pH (10.05 and 10.14, respectively) and total alkalinity (0.91 mmol/L and 0.73 mmol/L, respectively) values were about the same but the leached K, SO_4^{2-} and Si concentrations for w1 were distinctly lower (52 vs. 150 mg/L, 29 vs. 250 mg/L, and 7.6 vs. 15 mg/L, respectively), whereas the other element concentrations (Na, Ca, Mg, Cl) did not differ much.

DIFF-testing was performed only on five mixes, R52, f63, w1, 44 and L8, representing basic compositions of the different types of mixes. The pH values measured for the low-pH mixes varied at the end of testing between 10.9 and 11.3, while the reference mix R52 showed a pH of 12.3 (Figure 8-3). Alkalinities were measured only at the end of DIFF-test; 33 mmol/L, 2.1 mmol/L, 1.9 mmol/L, 1.4 mmol/L and 1.2 mmol/L (R52, 44, f63, w1 and L8 respectively).

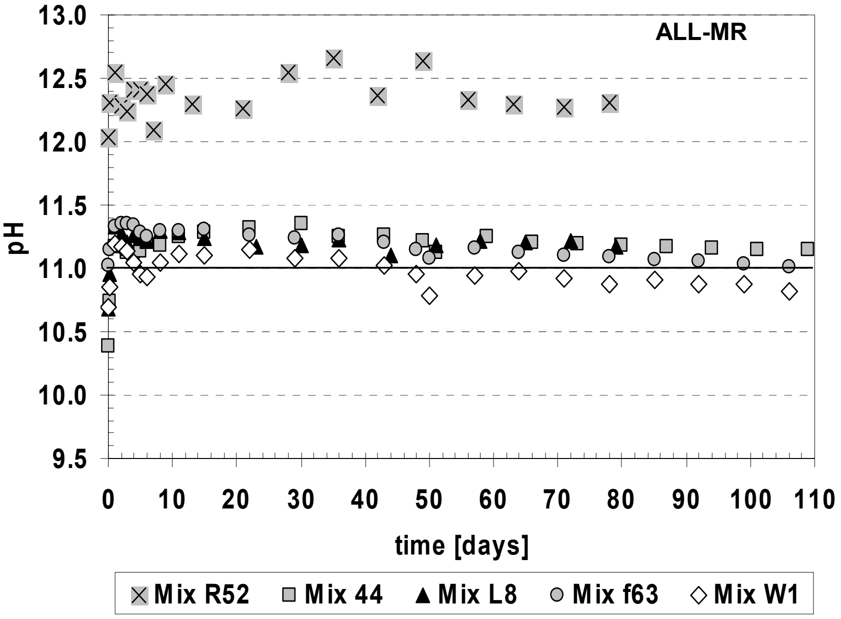

Figure 8-3. *DIFF-test pH values in the fresh leachate for the five mixes tested.*

Analyses of the fresh leachate samples were performed for four mixes: R52, 44, f63 and L8 (Figure 8-4). In the case of some substances the concentrations were at or below the concentration of the initial leach solution (Table 8-1) indicating e.g., indiffusion, sorption or precipitation (e.g., *Mg*: R52, 44, f63 and L8; *SO_4*: R52 and 44; *Na*: f63; *Si*: R52) and therefore are not present in Figure 8-4. Ca was the main alkaline substance released to all the leachates throughout testing. Na and K were released in R52 leachates as well, but the concentrations were at the level of the initial leach solution in the end of testing. Also in L8 leachates Na and K concentrations decreased to the level of the initial leach solution at the end. In the leachates of the low-pH mixes Ca was also the main alkaline substance (L8, Figure 8-4a; f63 and 44, Figure 8-4b), except at the beginning of testing K was in the case of mix f63 (Figure 8-4). In the end of testing K concentration exceeded that of the initial leach solution only in mix 44 leachates. Furthermore, all the low-pH mixes showed increasing Si concentrations, less in the case of mix L8 (Figure 8-4b), whereas in R52 leachates Si decreased below the initial leach solution concentration. Small amounts of Al were present in all the low-pH mix leachates, about four times more in L8 leachates. Distinctly SO_4 was leached from mixes f63 and L8, but decreased in the case of f63 to the level of the initial leach solution at the end, whereas in L8 leachates the concentration initially increased and only towards the end levelled and slightly decreased but stayed at a high value.

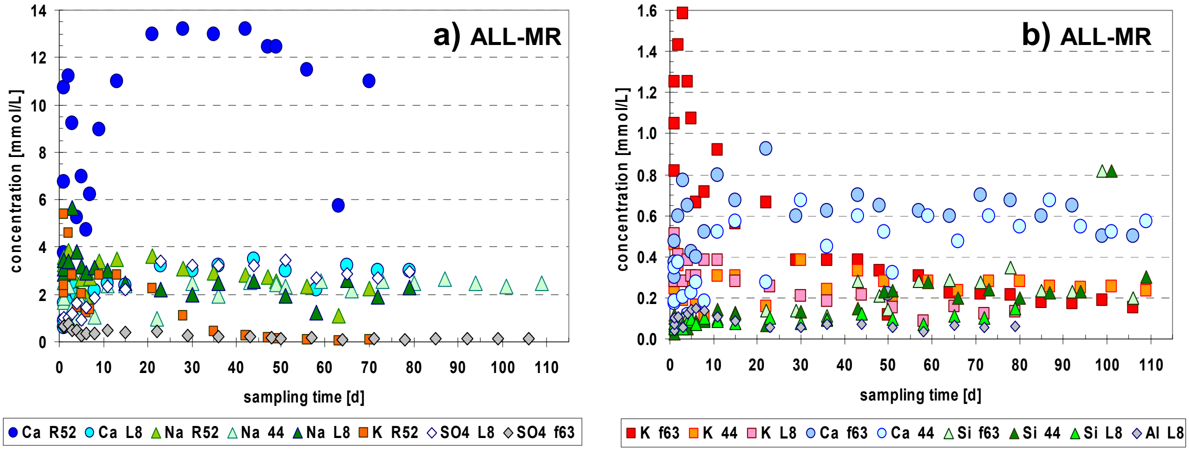

Figure 8-4. *Analytical results from DIFF-tests for mixes R52, 44, f63 and L8 in the fresh leachate (ALL-MR). (The figure is split in two for reasons of clarity).*

8.2.5 Main results from solid analyses

Solid analyses were performed on leached specimen (from DIFF-test) and original specimen not subjected to leaching /Imoto et al. 2004/. The qualitative phase analysis (XRD) results are gathered in Table 8-5. AFt was present in all specimens, as well as C-S-H phases (confirmed by SEM results as well). $Ca(OH)_2$ was only detected in mix 52, in both original and leached specimens, but the amount of $Ca(OH)_2$ decreased in the leached specimen from 14.9 g/100mL to 10.6 g/100mL, as determined by TG-DTA analysis. The presence of $CaCO_3$ was suspected to result from precipitation due to the small amount of bicarbonate initially present in the fresh leach solution.

Table 8-5. Results of qualitative phase composition by powder XRD /Imoto et al. 2004/.

Cement type	Initial/ Altered	Hydration products				C_4AF	Calcite ($CaCO_3$)
		AFt	AFm	CH	C-S-H		
f63	Original	++	(+)	–	++	–	(+)
	Altered	++	(+)	–	++	–	(+)
44	Original	+	++	–	++	–	(+)
	Altered	(+)	++	–	++	–	(+)
R52	Original	++	(+)	+++	++	+	(+)
	Altered	++	(+)	++	++	+	(+)
L8	Original	+++	–	–	++	+	–
	Altered	+++	–	–	++	+	–

– not detected (+) very week + weak ++ medium +++ strong

AFt (Al_2O_3-Fe_2O_3-tri) = Ettringite, $3CaO·Al_2O_3·3CaSO_4·3·2H_2O$

AFm(Al_2O_3-Fe_2O_3-mono) = $3CaO·Al_2O_3·CaX·nH_2O$ (X=SO_4, CO_3 or $(OH)_2$)

CH = Calcium Hydroxide ($Ca(OH)_2$), C_4AF = tetra calcium aluminoferrite

C-S-H = cakcium silicate hydrate

EPMA results: In the leached specimens the Ca/Si mole ratio decreased only at the solution contacting interface. An exception was mix R52, where the altered zone reached a depth of about 1.5 mm. This deeper alteration was suggested to be a result of $Ca(OH)_2$ leaching supported by the high content of Ca in the leachates Figure 8-4.

Rather slight increase of total pore volume (from MIP) in the leached specimens was observed for mixes f63 and L8 (~ 0.4% and ~ 1%, respectively), whereas a decrease was observed in the case of mixes 52 and 44 (~ 0.8% and ~ 5%, respectively). The greater decrease in mix 44 could possibly result from the hydration of slag or pozzolan. The porosity decreased (∅ from 0.1 to 0.2 micron) only in the case of mix 52, due to leaching of $Ca(OH)_2$.

8.3 Modelling

The simplified thermodynamic model calculations performed on slag mix 44 using the MEDUSA software /Puigdomènech 2004/ were successful in qualitatively reproducing the experimentally observed (XRD) cement phases in the initial state and during the early phases of leaching. It is conceivable, although not definite, that during the leaching phase, a redox buffer within the mix renders chemical conditions reducing enough to sustain sulphide in the aqueous solution until total depletion of sulphur.

The experimental XRD results of the mix f63 were also adequately explained by thermodynamic model calculations. Figure 8-5 depicts the calculated equilibrium phase diagrams for calcium and silica. The experimental leach results for Si were found to be below the solubility limit, which was calculated to lie between 10-3.2 M and 10-2.1 M at pH <11.4, depending on the sulphate concentration in the system. The former value represents the depletion of sulphur in the mix, which is shown by the experimental leach results to occur relatively rapidly. Above pH 11.4, the solubility of Si was calculated to steadily rise up to 10-0.7 M at pH 12.3–12.5.

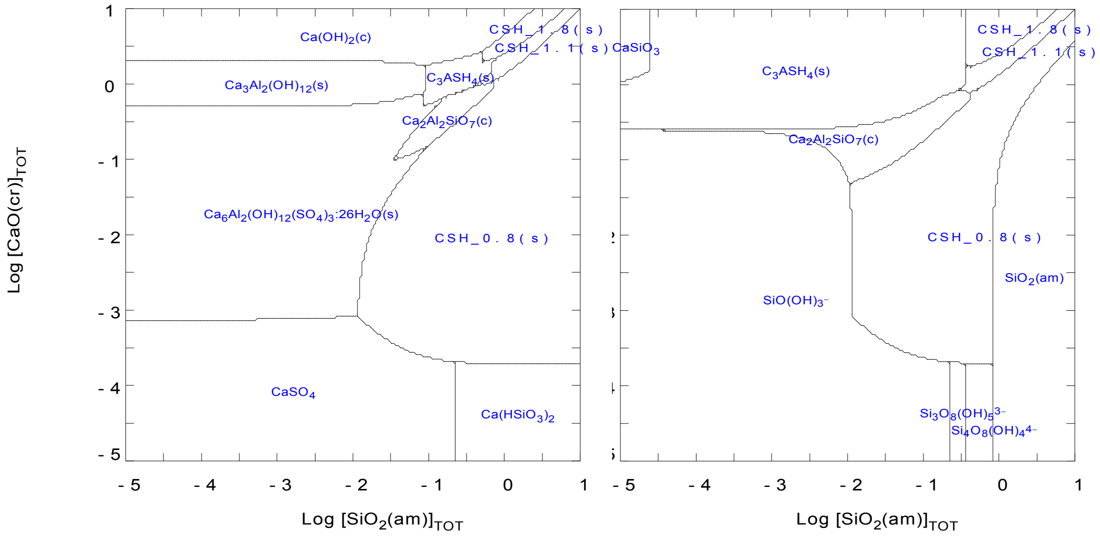

Figure 8-5. Initial phase predominance area diagrams of Ca (left) and Si (right) for mix f63. Oxidizing conditions assumed, pH = 11.5, total sulphur concentration, 0.12 mol/L of pore fluid (calculated from the initial inventory of SO_3 and the initial inventory of SO_3 and the initial porosity).

Leach rates or/and diffusion coefficients of Ca, K, S_{TOT}, Si and Al from the cementitious mixes were calculated using two different Fickian diffusion models. Based on the model results (see Table 8-6 for the shrinking-core-model fits), the order of leach rates was found to be the following:

Ca: 44 < f63 < L8 < R52
K: 44 << f63 ≈ L8 < R52
S_{TOT}: 44 < L8 << f63
Si: L8 < 44 ≈ f63
Al: 44 ≈ f63 < L8

The chemical speciation of excess sulphur in the equilibrating solution (ALL-MR in Table 8-1) for mix 44 was 100% sulphide, whereas for mixes f63 and L8, it was mainly sulphate.

Table 8-6. Leach rate fitted to a shrinking core model /Paul and McSpadden, 1976/

	Leach rate ($mmol/m^2/\sqrt{d}$)			
Leachant	**mix 44**	**mix f63**	**mix L8**	**mix R52**
Ca	14.1	25.9	112.1	523.3
K	9.0	–	–	–
S_{TOT}	15.2	–	143.4	×
Si	4.8	5.9	2.9	×
Al	0.7	1.1	4.9	×

× Not fitted. No cumulative excess concentration in the leachate.

More reliable estimates of the long-term leaching rates for some substances would require longer duration of experiments. Unfortunately, allowance of longer times makes predictions of chemical equilibria increasingly difficult due to the fact that e.g. the major cement phases (CSH) begin to crystallize with time, thus giving rise to new phases. Furthermore, explicit coupling of transport with chemistry would undoubtedly result in a more lucid picture of the long-term evolution of the system.

8.4 Main conclusions

The blast furnace slag containing mixes were rejected due to leached sulphide, which is detrimental to copper. Thus in this study the most promising mixtures from the chemical point of view were the OPC-silica mixes with one exception, mix 12, which exhibited high pH values, around 12.

Cau Dit Coumes et al. /2004/ have shown that the equilibrium pH of the pore solution mostly depends on the silica content of the binding whatever the added pozzolan is, because the added silica lowers the Ca/Si ratio in CSH and thereby enhances sorption of alkalis and decrease of the equilibrium pH of the pore solution. The Ca/Si ratio was high in mix 12 (1.35) when compared to the other OPC-silica mixes, f63 (0.82), w1 (0.85), f64 (0.65) and w2 (0.67). Three mixes (f63, f64, and w2) with ettringite acceleration fulfilled the pH≤11 in equilibrium testing. The most promising mix for further development was mix f63 when taking into considering also the technical performance /Kronlöf 2004/. Furthermore the pH values of mix f63 fresh leachates slowly decreased and almost reached the target value of 11 at the end of the diffusion test. Other favourable chemical aspects were the rather fast depletion of K, Al and SO_4^{2-} and no release of Na, as well as, the declining trend of Ca concentrations with continued leaching. However, the increasing release of Si might be an unfavourable aspect in regard to bentonite stability. The corresponding mix (by composition except the cement used) to f63, mix w1, also showed decreasing pH values in the fresh leachates and reached the target pH already before completion of the diffusion test. However, additional chemistry results of the mix w1 fresh leachates were not available. Only a few analytical results in saline conditions were available from the equilibrium test of mix w1, which could be compared with those of mix f63; the last pH and total alkalinity values were about the same but the leached K, SO_4^{2-} and Si concentrations for w1 were distinctly lower, whereas the other element concentrations (Na, Ca, Mg, Cl) did not differ much.

8.5 References

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9 Low-pH grouting cement testing at the laboratory and in the field

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9.1 Background to the low-pH grouting cement project

A joint project "Injection grout for deep repositories" was implemented for development of low- pH grouting cement between Posiva, SKB and NUMO. The project was divided into four separate subprojects:

1. Low-pH cementitious injection grout for larger fractures (hydraulic aperture > 100µm)
2. Non-cementitious low-pH injection grout for smaller fractures (hydraulic aperture < 100µm)
3. Field testing in Finland
4. Field testing in Sweden

The aim of this paper is to describe the development work done in Finland, where the target was to find a suitable low pH cementitious injection grout for larger fractures (>100 µm). The development of the technical properties on the laboratory was carried out mainly by Anna Kronlöf, VTT Building and Construction. Leaching properties of developed recipes and the pH in leachates were analyzed by Ulla Vuorinen and Jarmo Lehikoinen, VTT Processes. As a background for laboratory work the requirements were settled by Reijo Riekkola, Saanio & Riekkola Consulting Engineers and Ann Emmelin, SKB. Environmental acceptance of low pH cementitious grouts were studied by Ursula Sievänen, JP-Suoraplan and long term safety related issues were considered by Margit Snellman, Saanio & Riekkola Consulting Engineers. Testing of the most promising recipes in the field was reported by Ursula Sievänen, JP-Suoraplan and Pauli Syrjänen, Gridpoint. The works done in Finland were managed by Tapani Lyytinen, ELY Management.

9.2 Requirements

The following requirements were determined during the planning face of the project (Table 9-1). The requirements worked as a guideline for laboratory determinations. All desired properties could not be measured quantitatively, like stability and durability of the mass. These properties have been discussed during the whole project and the knowledge will increase with time and experiences gained from the laboratory and from the field. The prioritizing of the requirement has been made so that the long-term safety should not be impaired. But ranking the requirements is not the best way while they interact with each other. If pH requirement is very strict, it may cause weakened properties for workability properties of the developed grout, which may increase leakages to the facility with long time. High pH and increased leakages may both be undesirable for long-term safety. The measurement the pH of leachates is somewhat time dependent, but this project had a time limit. Penetration ability was measured with penetrability meter, but there are several methods available and they should be used combined to get more information about the workability of mass. The workability time requirement was set from the practical reason, it should prevent fast setting of the mass, so that grouting equipment do not get broken during grouting operation. Compressive strength was measured to ensure that admixtures do not impair the strength development. What is the required compressive strength for micro cement grout is not defined properly. The fluidity of the mass increase the spreading of the grout into the bedrock, but measurement and understanding of behaviour tixotrophic masses is difficult.

Table 9-1. The requirements used for the development of low pH grout on the laboratory. Kronlöf 2004

Order of Importance	Property	Requirement	Measuring method
Required Properties	pH	≤ 11	Leaching tests
	Penetration ability b_{min} Penetration ability b_{crit}	≤ 80 µm ≤ 120 µm	Penetrability meter at 60 min
Desired Properties	Viscosity	≤ 50 mPas	Rheometry at 60 min
	Bleed	≤ 10%	Measuring glass at 2 hours
	Workability time Shear strength Yield value	≥ 60 min ≥ 500 Pa ≤ 5 Pa	Determined by penetration ability and viscosity Fall cone at 6 h Rheometry at 60 min
	Compressive strength	≥ 4 MPa	Uni-axial compressive strength at 28 d

9.3 Laboratory work

9.3.1 Methods

Following properties were measured: temperature; filtration stability with filter pump; penetration-ability with penetrability meter; bleeding (water separation); early shear strength (fall cone test); rheology; Marsh cone; compressive strength and pH of leachates. The continuation of the work based on the gained results. The practical problem was that determination of compressive strength and pH could be done only for aged samples so it slows down the efficiency of development work. All other measurements were done by A. Kronlöf except pH leaching analyses.

9.3.2 Different systems and materials

Mixes were based on the four different preliminary systems that were modified experimentally.

1. Ordinary Portland Cement + Silica Fume (OPC+SF)
2. Blast furnace slag (Slag)
3. Super sulphate cement (SSC)
4. Low Alkali Cement (LAC)

The materials used in this project are described in Kronlöf's report /2004/.

9.3.3 Development of low pH grout recipes

Anna Kronlöf based the experimental studies of physical properties of the mass on stepwise development, which is described in this chapter /Kronlöf 2004/.

9.3.4 Development of low pH grout recipes

Anna Kronlöf based the experimental studies of physical properties of the mass on stepwise development, which is described in this chapter /Kronlöf 2004/. The composition of development mixes and mix numbers are described in the previous presentation by Vuorinen (see Table 8-2Table 8-3).

Step 1 – First tests on OPC+SF and Slag systems

The first systems examined were OPC+SF and Slag. The amount of SF (GroutAid) was kept to minimum due to its

- detrimental effect to penetration-ability at large quantities,
- tendency to increase water demand and retard strength development and
- cost.

Slag was activated by OPC only and its content was also kept to minimum for pH reasons. SP additions and different mixing orders were tested.

Step 2 – First penetration ability and pH measurements

A few most promising mixes out of the ones tested in step 1 were chosen to be tested for penetration ability by penetrability meter. Two mixes were later chosen for the pH test. The penetration ability of OPC+SF mix (12) was good and the slag mix (44) was unsatisfied. The shear strength at 6 h OPC+SF mix (12) was too low (poor) and slag mix (44) was good The preliminary pH of both mixes was too high (poor).

The low shear strength was disturbing, because the early age strength development is temperature sensitive and mix temperature in field conditions might be lower than 12 ºC, which would lower the shear strength respectively. On site the temperature of materials may be lower than 12 ºC and the agitation period shorter. The later would give the reactions less time to proceed at the “agitation temperature” that is slightly higher than the ambient temperature. Therefore in the laboratory a few extra kPa of shear strength over the given requirement was preferred to avoid grouting problems on site.

Step 3 and 4 – Checkpoints and ETTA

Something needed to be done to lower the pH. Increase of SF was the first obvious choice. Also lower alkali content through material selection was considered. Something needed to be done to increase the shear strength at the age of 6 h. Typical accelerators (Cl^- and NO_3^-) were ruled out due to long-term safety reasons. Shotcrete accelerator (Meyco SA 161), which is based on aluminium salts and produces ettringite, was suitable from the long-term safety aspect, but it reacted too fast and the mix lost the penetration ability altogether. SPL was not used due the desire of avoiding organics. The filter pump was replaced with penetrability meter. Fly ash system was ruled out without testing (due the possible quality risk reason). A special ettringite acceleration (ETTA) system for low-pH grouting purpose was developed.

Step 5 - OPC+SF system + ETTA

OPC+SF system mixes were developed by using:

- • increased content of SF (silica fume/OPC over 0.69) for lowering the pH,
- • increased water to dry materials ratio (W/DM 1.62 → W/DM 2.5) for penetration-ability and viscosity to compensate the silica fume admixture
- • ETTA for setting (6h shear strength).

Two mixes with differing SF contents (f63 and f64) were tested for pH, which was within the requirements in both cases.

Step 6 - WCE

Low alkali white cement from Aalborg White Sinai (Egyptian) plant (WCE) was introduced and the two mixes were tested for pH. Alkali content of the cement was found not to be the pH-determining factor.

Step 7 – Pre-mixing

Pre-mixing of components by jet mill was tested with and without dry SF (un-densified, type 938). The aim was to produce a single product and reduce the number of materials to be handled on site. Premixing the un-densified SF with cement instead of using GroutAid deteriorated the penetration ability.

Step 8 - Low Alkali Cement (LAC)

LAC tested and completed. Low penetration ability was achieved and therefore LAC was not suitable for grouting.

Step 9 - pH

Correlation between the chemical composition of the mixes and the results of the pH tests was examined. As modelling was outside the scope of this work, this study did produce neither modelling nor validation of any existing model. Yet, the observations offered valuable guidelines for further mix modification.

Step 10 - Compressive strength

The requirement for uniaxial compressive strength at 28 days was set to ≥ 4 MPa. Setting the requirement was somewhat contradictory because unreasonably high requirement would jeopardise the penetration ability achieved and a too low requirement might possibly jeopardise the durability of the grout. Further, for the time being there is no knowledge about long-term durability and compressive strength of grouts in different environments. Therefore the requirement bears neither theoretical nor empirical background. It merely expresses that the mixes should differ as little as possible from “ordinary” grout mixes.

Determining the properties vs. water to dry material ratio (W/DM) was added to the testing program.

Step 11 - OPC+SF system completed

The development of OPC+SF system with ETTA was completed. All properties were tested against W/DM.

Step 12 - Slag activation

Slag and SSC activation were developed. The SF content was increased in order to lower pH compared to that of the slag mix 44. Lower pH is detrimental to slag activation, which delays or stops strength development. Activation with both OPC (Slag system) and gypsum (SSC-system) were studied.

Step 13 – Slag and SSC systems completed

The development of slag and SSC systems was completed with a slag batch of relevant fineness. All properties were tested against W/DM.

Step 14 – Reference

A reference mix (superplasticized UF16-SF mix) of known good performance in practical field conditions was tested. The composition differed largely from the low pH UF16-SF mixes.

Step 15 - First pilot test

Mixes f63 and S20 were tested in field conditions in Finland in Sub-Project 3 /Sievänen et al 2004/ /Kronlöf, 2004/.

9.3.5 Results from the laboratory work

The mechanisms which may influence to the grout behaviour was analysed based on the gained results. Grinding and mixing the materials is very sensitive to the defects and that influenced to the interpretation of results, Table 9-2.

Table 9-2. The most promising mixes, which were sent to the pH measurements. /Kronlöf 2004/

Mix	Binder	Bleeding 2 h %	Shear strength 6 h kPa	B_{crit} µm	B_{min} µm	Visco-sity Bingham mPas	Yield value Bingham Pa	Visco-sity Casson mPas	Yield value Casson Pa	W/DM	Comp strength 28 d MPa
Require-ment.		≤ 10	≥ 0.5	≤ 120	≤ 80	≤ 50	≤ 5	≤ 50	≤ 5		≥4
12	UF16-SF	0	0.2	108	63	55	22	18	15	1.26	
f63	UF16-SF with ETTA	0	3.7	65 2)	44 2)	50	21	16	15	2.48	3.3
f64	UF16-SF with ETTA	0	3.4	63 3)	44 3)	40	16	12	12	2.91	2
w1	WCE-SFwith ETTA	0	1.3	103	49	35	8	13	5	2.48	
w2	WCE-SF with ETTA	0	1.0	102	47	28	7	9	5	2.91	
44	Slag-RC10-SF	0	1.3	136	61	32	8	11	5	1.36	
S14 1)	Slag-RC10-Gypsum-SF	0	1	139	40	50	18	14	13	1.6	7.1
S26 1)	Slag-RC10-Gypsum-SF	0	1	135	47	52	22	15	16	1.6	9

Mix	Binder	Bleeding 2 h %	Shear strength 6 h kPa	B_{crit} µm	B_{min} µm	Viscosity Bingham mPas	Yield value Bingham Pa	Viscosity Casson mPas	Yield value Casson Pa	W/DM	Comp strength 28 d MPa
S20c	Slag-RC10-SF	0	2.8	99	40	63	24	20	17	1.6	4.4
L8	LAC	0	1.6	-	-	27	7	9	5	1.0	16.5
Ref 52.	UF16-SF-SPL	0	2.6	63	201	23	5	8	3	1.21	9.3

9.4 Field testing of most suitable recipes

Field testing of developed masses is needed for qualification of workability. The aim of the pilot field tests is to determine the pump ability and practical properties for grouting. The pilot tests verify the work done in the laboratory and gives indication of modification needs. During this project two pilot field tests were done: first in Helsinki, multipurpose tunnel construction site in May 2004 and second in Olkiluto, ONKALO access tunnel construction site in January 2005.

9.4.1 First pilot test without superplastisizer

The rock type in the tunnel is mica gneiss with granite/pegmatite veins. Depth of the tunnel floor was -45 m below sea level. Measured ground water pressure was 4.0 bars. Measured groundwater and air temperatures were +13°C. The test grouted grouting fan was the same as originally designed for the tunnel section. The grouting fan included 14 grouting holes, each of them 24 m long and the maximum distance between the grout holes was 3 m. The overlap of grouting fans was 4-5 m. The grouting pressure varied between 40-50 bar. /Sievänen 2004/. The recipes used in the tests are presented in Table 9-3.

Table 9-3. Tested recipes. /Sievänen 2004/

Recipe S20c **hole 1**		**Recipe S21** **holes 2-5 and 13-14**		**Recipe f63** **holes 6-12**	
Water/Dry Materials	1.6	Water/Dry Materials	2	Water/Dry Materials	2.5
Water	81 l	Water	105 l	Water	75 l
RC10	4 kg	RC10	4 kg	UF16	20 kg
SL10	40 kg	SL10	40 kg	AC10	1.5 kg
GroutAid	26 l	GroutAid	29 l	Gypsum slurry	0.5 l
				GroutAid	20 l

Results from Pilot field test 1

None of the test mixes showed totally satisfying results. All mixes showed good penetrability abilities (filter pump) but fluidity was often too poor (Marsh cone).

Slag-based mix S20c was too stiff and the W/DM had to be raised. Slag-based mix S21 (higher water to dry material ratio) was better grout able, but the development of strength was not good. The grout ability of OPC-silica-based mix f63 was the most promising, but the development of strength was the worst: Some reaction started before 1 h, but the mix was not hardened after 5 days. According to the measured densities (mud balance) fluid components was overdosed and this have had an effect on the strength development. The measured and theoretical densities were compared afterwards. It seemed that the water flowmeter was not calibrated.

Grout take was about same with S21 and f63 (~2 kg/m). The water losses in these holes did not vary remarkably. This indicates that penetration abilities are at the same level with both mixes. With recipes S20c and S21 the grouting operation was slower when compared to the normal grouting. Grouting time was shorter with f63 due to lower viscosity /Sievänen 2004/.

However, grouting of quality control holes showed that the penetration ability of the test mixes was poor when comparing to ordinary good quality grouting mixes. Grout take to the already grouted (with test mixes) rock was 8 kg/m, much higher than the intake of test mixes.

It has to be possible to accelerate (and possible retard) the mixes. The further development has to focus on the development of strength and the acceleration (e.g controlling the grout inflow back to tunnel). Also the viscosity should be better to enable better penetration into fractures. It seems that for high quality mixes W/DM should be near 1 but then viscosity is not high enough without superplastizicers.

The grouting equipment, and especially dosing and mixing are very important factors. The studied mixes did not tolerate inaccuracy in dosing. It was found that tested mixes were not ready for use in ONKALO and that more research work had to be made to find high quality low-pH grout mixes. /Sievänen 2004/.

9.4.2 Continued development work after first pilot test

Based on the experiences got from the pilot test 1 and observations in leaching tests the following guidelines in the further development of the low pH cementitious grout were chosen:

- the continuation is to be based on the development of OPC-silica-system (blast furnace slag-system were ruled out due to leaching of sulphide),

- water to dry material ratio have to be lower in order to get satisfying development of strength,
- the use of superplastizicer was regarded necessary in order to lower the water content without jeopardising viscosity (and possible penetration ability),
- the number of the components to be used in field have to be minimised.

Further laboratory work was done with OPC-silica-superplastizicer –mixes. Based on these results several recipes were preliminary tested in field in batch mixing test. Based on the mixing test the recipe(s) for the pilot field test 2 in ONKALO access tunnel were chosen. /Sievänen 2004/

9.4.3 Second pilot test with superplastisizer

Test site was selected based on pilot hole results and hydraulic conductivity measurements. The rock type based on tunnel mapping is veined migmatite with pegmatitic veins and gneiss inclusions. The test fan is located at tunnel station 214 m-240 m, and the last part of the tunnel section is altered and fractured. The fan consists of 22 holes of 26 m length with a maximum distance 2.5 metres. Results are shown in Table 9-4.

Table 9-4. The following recipes were used in second pilot test. P3 is the developed low-pH cementitious grout. /Sievänen 2004/

Left side: Holes 1, 3 ,5, 7, 9, 11, 13, 15, 17, 18, 19, 21, 22, OL-PR0214B	Right side: Holes 2, 4, 6, 8, 10,12, 14, 16, 20, OL-PR0214A, OL-PR0214 C, OL-PR0214D and extra hole (27)
Recipe P3 W/DM = 1,6 SPL 2% (weight% from dry materials) = 10 g/l	Reference grout Normal grouting recipe in ONKALO W/DM = 1,0 SPL 1% (weight% from dry materials) = 8 g/l
Water 40 l Ultrafine 16 20 kg Mixing 2 min GroutAid 20 l SP40 0,55 l Mixing 3 min Agitating	Water 60 l SetControl II 0,8 l Mixing 30 s Ultrafine 16 60 kg Mixing 4 min

Results from second pilot field tests

Tested grout was OPC-silica-superplasticizer based recipe P3. About half of the fan was grouted with the test mix, and half with reference grout (grout used in ONKALO). This enabled a comparison between the test grout and ordinary grout with known good performance. The behavior of the test mix P3 was poorer than reference grout with regard to the penetration ability and Marsh fluidity. The results were promising but not satisfying. The bleeding of P3 was good. The development of strength was acceptable, and the uniaxial compressive strength at 28 d was good. One reason could be the low temperature, which may have had an effect on this silica rich test mix. This possible problem could be solved in other ways (water supply with even temperature). The reference grout does not show any remarkable difference in behavior in different temperatures.

Clear differences in grout take between test mix P3 and reference grout cannot be seen. Also the sealing effect can be regarded satisfying, because the prognosis for the studied tunnel section was 0.8 l/min without grouting and after grouting only moisture and one dropping leakage were observed. However, it may have happened that the sealing effect of reference grout was better than that of P3. The amount of data obtained from one grouting fan is too limited to draw exact conclusions.

The use of this low pH cement could be considered for repository production grouting. However, more field experiences are needed in order to verify the behavior of the grout. Technical performance could be better, so further optimizing is recommended. /Sievänen 2004/.

9.5 Conclusions

This work was development of low-pH cementitious injection grout for larger fractures, which was joint project for SKB-NUMO-Posiva. The work consisted of laboratory part where the suitable ways to decrease pH of grouting cement was analyzed. Field-testing was made to verify the results of development work. The workability of developed grout did not fulfill the target, which was sealing and tightening the leakages in grouting fan. The development work continued on the laboratory and a new field test was made. Based on the second field test the grout seems to be promising but still optimization is needed to improve penetrability of mass and use of more long-term safe superplastisizer. The grouting procedure will also be taken account when planning the field test.

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10 Selective stabilisation of deep core drilled boreholes using low-ph cement

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Summary

This paper concerns the use of low-pH cement for selective stabilisation in deep boreholes and injection (gap grouting) along the entire steel casing in the upper 100-200 m of percussion drilled or/and core drilled boreholes.

Different cases and scenarious requires different materials and techniques. The two major scenarious are injection grouts that stabilises the rock in the fractured zones and a stabilisation concrete that replaces excavated or sections that has collapsed. In both cases material has to be transported to the actual section for which an equipment is designed and tested.

A conclusion of a literature review overall work is that there are few documented studies concerning grout injection at substantial depths that actually shows the improvement of the mechanical properties of solid rock or fault zones.

The basic requirements of the materials are that they shall not give a pH higher than 11, which is achieved by a mixture of Portland cement and silica fume. Moreover, the material shall contain no or minor amount of organic substances like superplasticizer (SP). The results showed that it is difficult to get a strong hardened material without SP. The water/binder ratio had to be very high and there were problems with water dilution in the tests. To some extent this was solved by using gentle mixing and granulated silica fume. In laboratory the grouts achieved the target strength of 5 to 10 MPa but in the field test dilution lowered this. Further work has to be done on the application technique to avoid dilution. The grout was, however, successful in filling and stabilising steel casing as this only required pumping in a tube and filling of a relatively wide gap.

For stabilising rock section a method of widening of the bore hole, filling this borehole with concrete and redrilling to the original size was chosen. This gives a remaining tube that requires high strength. In this case it was not possible to avoid SP but the amount of used concrete will be low. Successful experiments were done with ultrahigh

performance concrete with glass fibres. The concrete is based on a concept from reactive powder concrete but with more silica fume and glass fibres instead of steel fibres. The basic concept is apart from a low pH binder combination based on fine quartz aggregate (<0.5 mm) and ultrafine quartz filler that with short fibres (6 mm) gives a self compacting flow. In the field tests the strength was between 50 and 100 MPa which is enough for the application. The entire chain of casting and in-the-hole equipment for completed selective stabilisation has been tested. The cementing pipe needs to be trimmed a little more.

A high strength low pH concrete with SP, which is fairly resistant against water dilution, with variable aggregate size has also been developed. This concrete has been tested for stabilisation and will be tested for filling of wide open gaps where a grout will give inferior properties.

10.1 Introduction

Various types of drilling are an essential part of SKB’s site investigation programme for deep storage facilities in Sweden to establish the basis for a geological site description. The drilling shall be made to predetermined depths sometimes through more or less disrupted zones. These zones have to be stabilised and thus it is important that the drilling contractor has a "toolbox" approved by SKB to master the difficulties. One way to do this is to use cementitious materials, but these cementitious materials have to be low-pH not to interfere with the ground water in such a way that it may harm safety barriers in the future repository.

SKB’s site programme for a deep repository for spent nuclear fuel and waste is running in Oskarshamn and Forsmark. The drilling programme will primarily be concentrated on investigation of a crystalline granitoid rock volume.

Two main types of boreholes in bedrock are utilized in the investigation:

- Cored boreholes, for investigating the rock down to a depth of about 1,000 metres /eg, Claesson and Nilsson, 2003b/.
- Percussion boreholes, drilled through soil layers and the superficial part of the bedrock, down to a maximum depth of about 300 m /eg, Claesson and Nilsson, 2003a/.

The major part of deep cored boreholes are performed as telescopic boreholes, entailing that the upper 100 metres are percussion drilled with diameter of about Ø 200-250 mm, whereas section 100-1000 metres is cored drilled with a diameter of approximately Ø 76 mm. Stainless steel casing is installed through the soil layers and a short distance, no more than 100 m, into the rock. To prevent superficial water from leaking down and mixing with deeper lying groundwater, the gap between the casing and the borehole wall is generally grouted.

To be able to stabilise a damaged zone the bore hole has to be assessed and described. There are several ways to stabilise the zone and each scenario requires a special technique and material.

Together with Swedish Cement and Concrete Institute (CBI), Royal Institute of Technology (KTH) and drilling contractor Drillcon, SKB has formed a group with the task of creating such a "toolbox" for selective stabilisation mainly of deep core boreholes and gap injection of casing using low-pH cementitious materials.

KTH made the experiments with injection grouts, CBI made the experiments with gap grouting and stabilisation concrete and Drillcon developed the in-the-hole equipment.

10.2 Basic concepts

10.2.1 Scenarios and rock description

For its work the group has established five rough borehole scenarios in which treatment using low-pH may be required.

- Fractured zones or crushed rock with secondary weak crack fillings like clay.
- Fractured zones or crushed rock with open water bearing cracks.
- Discrete wide water bearing cracks
- Fall out of rock due to released tension or friable rock.
  Detected at instrumentation of boreholes and attended to after drilling.
- Gap injection of casing that is installed through soil layers down into solid rock.

This lecture will demonstrate the progress made by the group and the status of its work with low-pH grouting.

10.2.2 Basic methods for stabilisation

There are several ways to stabilise depending on the situation.

- Open cracks can be injected. Small thin cracks can be injected with cement paste grouts while wider cracks need mixtures with aggregates to increase the stability. Wider gaps need coarser aggregate.
- Fractured weak zones with crack filling can not be injected. Instead the weak material has to be removed and replaced with stronger new material.

- Loose debris can be removed or glued to keep in place. This may be difficult and either of the two methods described above must be used. Which type depends on the situation and the reason for the loose debris.

10.2.3 Low-pH cementitious materials

The basic requirements is that the low-pH product shall not give a pH higher than 11 to the ground water. Moreover it shall contain a minimum of organic constituents.

The basis of the low pH cementitious products is to use a binder that is composed of cement and a pozzolana. A pozzolana is siliceous materials that reacts with the cement and cement paste and change the composition of it.

This highest pH comes from the alkali ions in the cement that do not bind to any hydrate phases and thus becomes accumulated in the pore solution as alkali hydroxide. Thus low alkali cement must be chosen. Of the hydrate phases the highest pH comes from calcium hydroxide crystals (portlandite) that in contact with water gives a pH of around 12.4. Next in order is the cement gel the calcium silicate hydrate (C-S-H), a semi crystalline phase that gives a pH between 12, 4 and around 10. Thus to get a pH below 11 one must eliminate the CH. The CH reacts with the pozzolana and forms more C-S-H. Around 15 % fully reacted silica from the pozzolana is required to eliminate the CH. With more pozzolana than required to eliminate the CH the C-S-H will change composition. With between 30 and 40 % replacement of the cement with reacted pozzolana the C-S-H get a composition that gives a pH of 11 when in contact with ground water. The basic reactions are as follows:

(1) $Ca\,(OH)_2 + SiO_2 + H_2O = C–S–H$

(2) $C–S–H\ (1) + SiO_2 = C–S–H\ (2)$ where the Ca/Si ratio is lower in (2)

When the Ca/Si ratio of the C-S-H is around 1 it will give a pH of 11. The most efficient pozzolana is silica fume that consist of nano-sized amorphous pure silica.

Hydration of cement occurs through a series of complex, kinetically controlled chemical reactions. With a normal pozzolana CH is first formed and later it reacts with the cement paste to get the equilibrium required to get a pH of 11. Silica fumes react rapidly, to a large extent before the cementitious material hardens, and thus the cement paste gets low-pH properties fast within a year. (Lagerblad et al 2004). To get a low-pH concrete the binder of the composite must contain between 30 and 40 wt. % silica fume. In the mixes we have 40 % to be on the safe side. Some mixes also contains ultra fine ground quartz that also acts like a slow pozzolana and thus the mix requires less silica fume.

The silica fume is amorphous and extremely fine. This gives some problems with proportioning and mixing. The concrete must flow to be able to fill a form and large amounts of silica fume hinder flow ability. This is due to the fine grain size and that the silica fume gelates in contact with the high pH in the pore solutions. To overcome this problem organic surface active agents called superplasticizer are commonly used. Without a superplasticizer the amount of water has to be high and as a consequence of this the concrete becomes porous and physically weak. Moreover it will leach and lose its integrity faster.

By using compacted silica fume, which is silica fume in large aggregates, the water demand can be lowered but it will take some time before the paste is fully homogenised and it will thus give a higher pH for some years. To get a high strength concrete a superplasticizer is necessary. Higher strength requires less water and thus more superplasticizer. One good thing is, however, that only a minor part of the superplasticizer is water soluble and thus the large amount of it will not be assessable until the concrete is fully degraded. The amount of the superplasticizer that is available for leaching is investigated at the moment.

As been mentioned above one must consider the time frame as regard both pH and organic contamination of the ground water. Especially the high strength concrete will contain remaining unhydrated cement grains for a considerable time. In contact with ground water these cement grains will give a higher pH for the first time period. The leaching is a result of interaction (ion diffusion) between the pore solution of the concrete and the ground water. Later the cement hydrates reeqilibrates with the pore solution but the first batch gives somewhat high pH than the bulk. The drill holes will be open for some time and there will be some water changes. Thus the pH after a couple of water changes will be most appropriate for the pH measurements.

10.3 Materials and tests

10.3.1 Grouts

The intentions with the grout are that they shall penetrate cracks and glue rock fragments together and thus hinder debris from falling out. There are two extremes in answering the question of whether a cement based injection grout can improve the mechanical properties in a fractured zone:

- The fault zone is regarded as friction material. Studies of injecting in friction-material show that the cohesion, c, can be improved or created in loose friction soils (i.e., have no cohesion to begin with). Unfortunately, the effect decreases with increased in-situ tension and the content of clay (Karol, 1999).
- The fault zone consists of intact blocks of rock and fracture planes. A comprehensive study of injection in fracture planes and of their mechanical properties has been made at the Chalmers University of Technology, Gothenburg (Swedenborg, 2001). The conclusion of this study is that improved mechanical properties in the fracture planes are negligible.

Scenario I, severely fractured and water-bearing zone

The zone is described as being moderate to extensive water bearing with severely broken rock mainly of friction character. RQD is low, about 10 to 30. The one to ten metre wide zone is classified as "Very poor rock" according to the Q-system (Stille & Nord, 1990). The wall of the borehole is not stable and it collapses due to inferior mechanical properties of the zone, in combination with high tension from the surrounding mass of rock and/or shearing between the fracture planes. The hydraulic conductivity is estimated at $1\text{-}10\cdot10^{-7}$m/s.

The stability calculation for zone I has been made using a rough estimate according to the principle "Ground reaction curve" (Stille & Nord, 1990). The calculations are based on the fracture zone acting as an elastic plastic material and the borehole radius being much smaller than the thickness of the zone. The zone is at a depth of 1000m and the horizontal tensions in the fracture zone are isotropic and correspond to the dead weight of the rock. Stabilisation of the borehole is achieved by injection in the zone. Re-drilling the borehole is started after the grout has hardened. Improved mechanical properties of the zone round the borehole shall be able to absorb tangential tension surrounding the borehole at a theoretical final strength of 3.7MPa in the stabilised zone.

Requirements on compressive strength of the injected zone are 3-4MPa and penetration of grout into the zone should be about 0.3m. The grout is to be in position within one (1) hour after mixing is completed. The injection pressure should lie between double the groundwater pressure and at least the smallest main-tension value (Brantberger, 2000). Example: at 500 m depth and smallest main tension 12MPa (Äspö conditions) gives an injection pressure between 10 and 12MPa.

Scenario II, loose falling fragments and non-water bearing zone

Stability problems in this scenario are often detected after completion of drilling to full length of the borehole, for example in connection with measuring or instrumentation of the borehole.

The zone is described as non-water bearing and with frequent falling fragments from the wall of the borehole. The rock is often initially hard and favourable. The RQD-value is high 80-100. The cause of fracturing can be high rock tension combined with a brittle type of rock, resulting in overload and fracturing of the rock.

A rough estimate of how thick an injection layer is needed to stabilise the borehole suggests that a remaining thickness of six millimetres would cope with a load of about 1.5MPa. The presumption for the project is a borehole diameter of 76mm and final strength of the grouting layer at about 10 MPa. A borehole of at least 88mm in diameter is required to achieve this, created for example by selective broaching. The grouting should be cured after one day.

Laboratory testing

Some factors were examined in a laboratory environment to study their influence on the curing sequence. KTH tested in several trials how the mixing of saltwater, disturbance of the grout during the curing sequence and dilution effects could interfere with the actual curing process.

Initial tests were made on grout mixtures based on Cementa's injection cement 30 (IC30) and Ultrafine 16 (UF16). These cement are based on clinkers from Cementa´s Anläggningscement that has relatively low content of CaO (64.2 wt. %). The requirement on pH<11, however, still requires that the grout should contain at least 30 % silica to cement weight. In the concept organic constituents were to be avoided. In the first concept granulated silica fume was selected to be able to keep the water/binder down and the strength up. In the second grout aid was used. GroutAid is silica fume premixed in water. It is a commercial product from Elkem A/S. In this case the water binder has to be higher.

An accelerator is needed to achieve faster curing. The choice fell on calcium chloride. A series of different mixing ratios were tested in trials containing varying amounts of $Ca\ Cl_2$.

Grout properties that are strived for are:

- Low separation (<2%) even following disturbance and separation.
- For scenario I, pressure strength of about 4MPa even when dilution and salt admixture is considered.
- For scenario II, pressure strength of about 10 MPa even when dilution and salt admixture is considered.
- The pressure strengths should be achieved after about one day.

Two mixtures were recommended after the trials:

- A stabilising; Construction cement (AC) with 30 % compacted silica, w/b at 0.6 with 3 % addition of $CaCl_2$.
- An injecting; Injection cement (IC30) with 30 % grout aid, w/b at 1.2.

Results from field tests

In the field tests grout was taken down to the desired depth. For techniques and equipment, se later. After the injection test the section was cored and the core was examined.

In the tests some problems turned up. The major problem was that the grout was diluted by ground water at site. This in turn affected the binding time and the strength as the w/b increased. The tests indicated binding time of 2-3 days. Thus to apply this technique another method for application has to be developed. The information comes from the fillings in the hole thus we do not know if grout penetrated the cracks

An important aspect is that the grout should be applied as quickly as possible, preferably within one hour. To maintain quality and traceability it is also imperative that a requirements specification and a work schedule are established for each stabilisation operation. Injection equipment such as mixer and pumps is not critical but should be in good condition.

10.3.2 Gap grouting of steel casing

The gap injection grout shall stabilise the steel casing against soil at the top of the drill hole. The width of the gap is around 20 mm and the physical demands are low. Thus it is possible to formulate a grout without superplasticizer. In the other recipes (se later) undensified silica fume was used. With this silica a water/binder of more than 2.0 was needed for the pump ability. Moreover, a water separation was observed. Test was also made with co-ground cement and silica but the water/binder needed for good pump ability was still too high. Thus compacted silica fume was used. Compacted silica fume are small grains with agglomerated silica fume grains. In normal concrete these aggregates disperse due to impact during mixing from aggregates (Lagerblad & Utkin 1995). In a cement slurry, however, there will be no impact and thus granulates will remain intact and they will not disturb the rheology. By the use of compacted silica fume and a smooth mixing it was possible to reduce the water/binder to around 0.8 and the strength was sufficient. Field tests were made with a mix with 30 wt% granulated silica fume (based on amount of binder) and a water/binder ration of 0.78.

Results from field tests

The grout slurry was tested in field. The grout was pumped in a tube to the bottom from where it filled the gap. The pumping stopped when grout could be observed at the surface. The initial tests, however, showed that the hardening was slow and thus the grout was thus accelerated with Calcium Chloride. The compressive strength of the hardened grout was around 5MPa (cube strength) after 5 days and around 13 after 28 days. The gap is 20mm and thus the grout can be mixed with aggregate. For simplicity, however, a grout based only on binder and water was used.

A microscope examination showed that one could observe undispersed silica fume in the hardened paste. These grains were only partly reacted and one could still observe some portlandite crystals. Consequently leaching tests showed that the pH of the water was more than 11. Presumably the portlandite crystals will with time equilibrate with the silica fume nodules /Lagerblad & Utkin 1993/ and the pH will drop. It will, however, take some time. One can increase the amount of the silica fume in this grout but this will decrease the strength of the grout.

Materials and recommended recipe (m^3)

Aalborg Portland white cement 603 kg/m^3, Granulated silica fume, Elkem 920-D, Water 671 kg, Calcium Chloride to give a desired hardening time. The properties of fresh grout depend on the mixer speed and temperature. Sedimentation should be controlled after mixing. A test procedure for application was developed.

10.3.3 Stabilisation of wide cracks, cavities and collapsed parts of borehole

With wide cracks, cavities or collapsed part of the bore hole a strong grout that do not dilute with water is needed. Thus the concept with a high w/b grout does not work. The w/b has to be lower and the grout must contain aggregates to be stable. Laboratory experiments showed that to be stable when poured through water the w/b has to be very low and it will improve if mixed with ultrafine particles (Lagerblad & Vogt 2004). The recipe used for stabilisation (se later) without fibres performed well in the experiments. Thus this recipe was adjusted by increasing the aggregate size and removing the fibres.

Depending on the estimated crack width or packing density of the collapsed material the maximum particle size of aggregates can be adjusted. The developed concrete contains relatively high amounts of cement combined with low water content. To secure a low pH of the surrounding ground water the binder contains up to 40 wt. % silica fume. This gives a good stability when cast through water. As a result of the extreme high content of fine grains and low water content, this type of concrete demands effective super plasticizers. Thus the injection depth and used material must be restricted.

Recipe for the test calculated on a cubic meter. Portland cement 557.1kg/Silica fume in compacted 300kg, ultrafine quartz filler 107.5kg, Quartz sand (< 0.5mm) 494.7kg, granitic aggregate (<1mm) 494.7kg, Water 250.63kg, Plasticizer (carboxyl on dry weight) 5.25kg.

Field test

Using this concrete, the stabilisation of a collapsed section of a percussion drilled bore hole close to the bottom (circa 100m depth) was successful. The concrete was pumped into the water filled bore hole approximately 2m above the collapsed zone and after 3 days hardening the core drilling was continued.

Stabilisation of a deformed part of the steel casing close to the bottom of the percussion drilled part of another bore hole was not successful. Nevertheless, this test showed the importance of using the appropriate technique to fill the concrete into the hole. The failure resulted out of heavy water dilution of the concrete, using the wrong pumping technique.

The recipe can be changed and different aggregate sizes can be used. Thus it can be modified to fit the situation. This concrete will be tested on vide open gaps where the aggregate size will be adjusted to the gap and openings.

10.3.4 Stabilisation by remaining tube

One concept of stabilising bore holes is to widen the critical section of the drill hole, fill this extended hole with concrete and then drill with the original drill size again, Figure 10-1. This will result in a remaining "tube" that will stabilize the rock. It is expensive and difficult to widen the hole thus it is favourable to have very strong concrete for thin tube thickness. In the concept a widening and thickness of 10 mm of the remaining tube is assumed. The concrete must be possible to transport to a fairly deep position in water filled holes, which apart from strength also puts high demands on equipment, rheology and D-max of the aggregates. The concrete should have a compressive strength of 30 MPa after 24 hours considering the fact that the concrete may be diluted with ground water when cast. Moreover, the cementitious material must be formulated in such a way that the contamination to the ground water is minimal. The amount of cementitious material in the rock shall be small. To avoid a pH plume the cement paste shall be difficult to dissolve and the amount of organic material shall be at a minimum.

The demands on the physical properties of the concrete can not be fulfilled with normal concretes, thus ultrahigh performance concrete is needed. Reactive powder concrete can fulfil many of the demands. This concrete has small size aggregates and it is very strong both as regard compressive and flexural strength. Moreover, already in its basic concept this concrete contains rather large amounts of silica fume. The application method also requires a concrete with high flow ability, long opening time, high stability against separation in water and fast hardening. A concrete that can fill a chosen borehole segment is shown in Table 10-1.

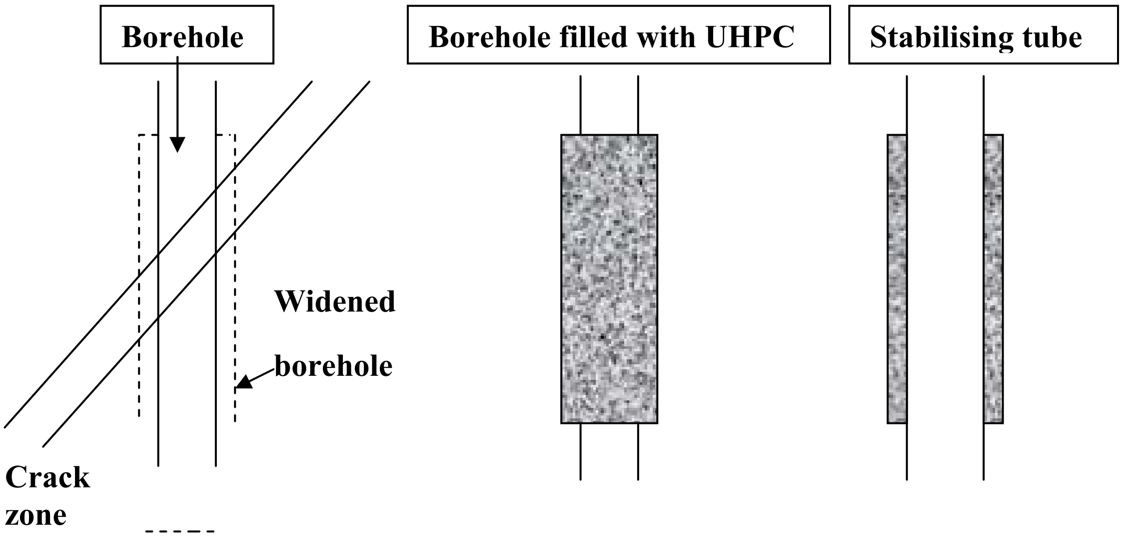

***Figure 10-1**. Sketch showing the concept with a tube of UHPC stabilising the borehole.*

Materials and laboratory tests

To lower the pH the amount of silica fume was to 40 wt % of amount of binder. Moreover the mix contains ultrafine quartz that will lower the pH further. As a result of the extreme high content of fine grains and low water content, this type of concrete demands effective super plasticizers. The composition of the concrete was optimized to give sufficient workability at minimum plasticizer content. To get good flow ability 6-mm steel fibres (Bekaert) were used in the first instance. The steel fibres, however, caused problems both during casting and drilling due to water dilution and sedimentation, thus in another set we tested 6-mm glass fibres (CEM-FIL, Saint-Gobain) that have a density similar to the fresh concrete matrix. The concrete needs to be mixed in a forced mixer. The concrete was designed to be self compacting, as vibration is difficult in the boreholes.

Table 10-1. Composition and mechanical properties of glass fibre concrete

Composition	**kg/m^3**	**Fresh concrete properties (spread flow):**		
White cement		200 mm after mixing, 165 mm after 4 hours		
Silica fume, undensified				
Quartz filler		Hardened concrete properties:		
Quartz sand (< 0,5 mm)			Compressive strength [MPa]	Flexural strength [MPa]
Glass fibres (6 mm)		1 day	50,2	-
Plasticizer (dry content)		2 days	74,1	-
Water		28 days	127,5	24,1
Water/binder	0,285	91 days	138,6	25,4

Shrinkage was tested on beams cured under water as this represents the realistic conditions in the boreholes. Additionally the autogeneous shrinkage was measured in sealed plastic tubes at 6°C and 20°C. Shrinkages are shown in Figure 10-2.

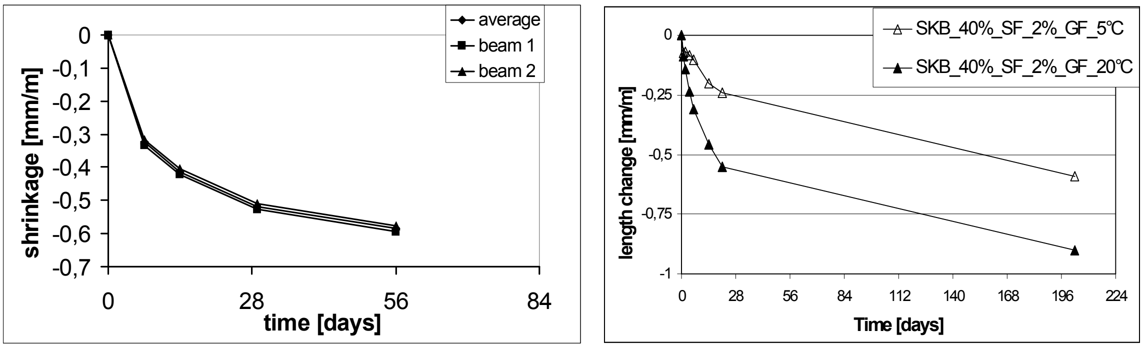

***Figure 10-2.** Shrinkage under water (left) and autogenous shrinkage (right)*

Field test

One of the big problems is to fill the boreholes with concrete of sufficient quality. Thus a series of dilution tests were done. It was tested both laboratory and in field conditions. No organic compounds, often used in under water casting, can be used. Depending on the depth of the bore hole, the opening time of the concrete needs to vary but after casting fast hardening is desired. These parameters can be influenced by the type of plasticizer.

Small scale field tests in short water filled bore holes with different concrete compositions and fibres types were performed and the results from these tests were used to optimize concrete recipe and application technique. Steel fibres were exchanged with glass fibres after observed separation and problematic drilling. In a new test hole of realistic scale and depth, tests were done with concrete containing glass fibres (Table 10-1). The actual application equipment and methods are described in Chapter 10.4. So far four transmissive zones in the hole were stabilised using this concept. Drilling was continued as early as 22 hour after casting for test 3. A sample from an over cored "tube" can be seen in Figure 10-3. Compressive strength of cored concrete is shown in Table 10-2.

Table 10-2. Compressive strength of UHPC-GF from the full scale test hole, the tests were done at 17 m (test 1), 105 m (test 2) 342 m (test 3) and 344 m (test 4) depth.

Position within the core	**Compressive strength in MPa (tested at)**			
	Test 1 (6days)	**Test 2 (2 days)**	**Test 3 (3 days)**	**Test 4 (5 days)**
Top	92.9	58.4	56,7	-
Middle	-	72.9	-	76,5

Position within the core	**Compressive strength in MPa (tested at)**			
	Test 1 (6days)	**Test 2 (2 days)**	**Test 3 (3 days)**	**Test 4 (5 days)**
Bottom	112.9	55.0	52,8	-

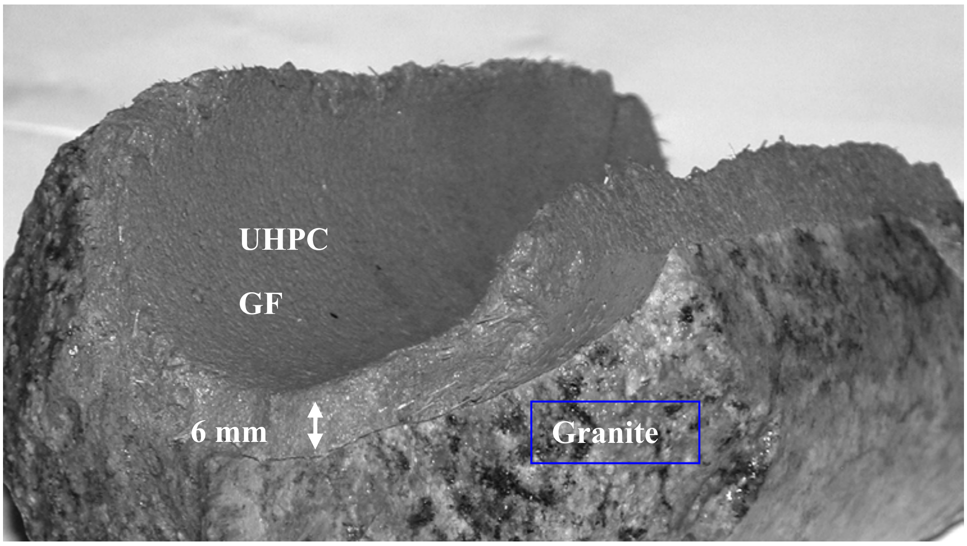

***Figure 10-3**. Sample from short bore hole with glass fibre UHPC. Thickness of tube/shell is 6 mm. Ove cored after 3 days.*

The field tests showed that it is necessary to pump concrete from bottom of the hole. It is not possible to simply pour the concrete into the water filled holes. That would lead to extreme fibres separation as the concrete is not stable enough in water. Underwater compounds might increase the stability but are not allowed in this application. The tests also demonstrated that glass fibres are superior to steel fibres. Glass fibres make it easier to handle the concrete and do separate less when cast into water filled bore holes. Glass fibre reinforced concrete is much easier to drill than steel fibre concrete. The UHPC has the ability to fill smaller cracks and forms a stable inner tube in the holes.

10.4 Equipment and practical tests in boreholes Drillcon, SKB

Stabilisation of boreholes can be made in several different ways. The SIT-project has developed a method that is based on a concept in which the borehole is expanded selectively at depth, is filled with a cement mixture and re-drilled to the initial diameter of the hole. A strict and accurate procedure is required to ensure desired properties of the mixture. Implementation and handling of the formula and equipment shall conform to approved instructions and manuals.

A programme for testing of equipment was carried out in core borehole KAS17 at Äspö HRL in 2004. The object of the procedure was to develop and ensure methods, technique and peripheral equipment for applying the low-pH grouts prepared by KTH and CBI, Sweden. Some selected critical equipment for cementing of boreholes is listed below.

10.4.1 Milling tool for selective broaching of rock section

A milling tool has been developed to facilitate broaching a section of the borehole from Ø 76 mm to Ø 98 mm. The tool is mounted on wire line drilling rods and lowered to the desired depth. By rotating the pipe string at the same time as the string is pressurised by flushing water, segments fitted with diamond bits are pushed out against the wall of the borehole. The rotating segments broach up the wall of the borehole to about Ø 98 mm.

10.4.2 Cementing pipe

The next step is to prepare a special cementing pipe with a predetermined cement mixture and lower it using wire line technique. The cementing pipe is an adapted inner core pipe that can be jointed up to 21 metres in length. When the inner pipe has landed, the water pressure can be increased to pump the cement out of the pipe.

10.4.3 Top packer

Cementing by top packer has been tested. The difference is that a packer is placed at the lower edge of the cementing pipe and when the cement mixture has theoretically displaced all the water below the packer it is tightened and seals against the wall of the borehole. The coupling between packer and pipe string has an integrated valve that closes when the pipe string is unscrewed from the mounted packer. When the injected grout has cured, the packer and cement are drilled away by the core drilling equipment.

10.4.4 Bottom packer

Mechanical bottom packers can be utilised when the bottom of the borehole cannot be used. The mechanical wedges at the bottom of the collar spring out as the collar leaves the boring pipe. The collar expands as pressure of the water increases and it fastens to the wall of the borehole. The top and bottom collars are of different design because they must seal from below and from above respectively.

10.4.5 Summary of the field tests

Experience of trials carried out with the broaching tool show that the tool works well.

Fine trimming of the cementing pipe remains at present because a valve does not close fast enough when using coarse grout. Consequently, the down transport of grout needs to be tested further to ensure that no contamination of formation water occurs.

All collars/packers that have been tested worked satisfactorily and remained in position until they were over cored. Mounting is simple and fast, they appear to remain in position regardless of load, and not least they can be over cored using wire line technique and retrieved with the inner core tube. Neither does the collar appear to release until the entire length has been over cored, i.e., no parts of the collar fall down to the bottom of the borehole.

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11 ESDRED & technology development

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11.1 Introduction

Geological disposal of high-level long-lived radioactive waste has been studied by various organisations, notably radioactive waste management agencies and major research organisations, for the last 30 years. The feasibility of such geological disposal, from a scientific viewpoint, has reached a very mature level. European research works have generally been carried out in the framework of international cooperation programs. Most of the outcomes resulting from these research works are shared by the scientific community of the concerned countries.

On the other hand the technological aspects of geological disposal have not yet been addressed with the same degree of shared international effort. However the feasibility of deep geological disposal depends not only on scientific studies but also on engineering ones. As a matter of fact the scientific component is mainly linked to the long term nuclear safety performance assessment whereas the technological one is linked to the industrial feasibility and the operational safety. Thus the existing body of knowledge must now be complemented with engineering and technological developments

When developing the ESDRED project (Engineering Studies and Demonstrations of Repository Design) proposal a review of the various activities involved in the construction and closure of a repository was performed in order to identify the key technological issues. Although disposal concepts vary from country to country depending, for instance, on the type of waste to be disposed and the nature of the receiving medium or host rock, this review exercise highlighted a number of common elements that are of importance to the various European waste management agencies. These include, among others, heavy load transportation technology, waste canister emplacement technology, buffer design and construction, monitoring activity and temporary sealing using specific types of cements. These now constitute the main technical themes within ESDRED

11.2 Nature and scope of the project

The ESDRED (***Engineering Studies and Demonstrations of Repository Design***) Integrated Project is a joint research effort by major national radioactive waste management agencies (or subsidiaries of agencies) and by research and development organisations. The project is born from the initiative of 9 European countries (13 Partners in all) which decided to work together on engineering and technology.

ESDRED is co-ordinated by the French national radioactive waste management agency (ANDRA) and is part of the European Union's 6th EURATOM Framework Programme for Nuclear Research and Training (Contract nº FI6W-CT-2004-508851). The five year project has a total budget of EURO 18.7 million, of which 7.3 million is a grant from the EU's Framework Programme.

ESDRED is focused on technology and has three main objectives.

- To fabricate full scale technological demonstrators and to demonstrate their feasibility.
- To promote a shared European vision in the field of technology.
- To disseminate widely the objectives and the knowledge developed within ESDRED.

11.2.1 First Objective

The first objective is to demonstrate, at an industrial scale, the technical feasibility of some very specific activities related to the construction, operation and closure of a deep geological repository for high level radioactive waste. The work is organised inside four (4) Technical Modules and essentially involves the conception, design, fabrication and demonstration of equipment or products for which relevant proven industrial counterparts (mainly in the nuclear or mining industry) do not exist today. This work is to be carried out within the framework of compliance regarding the requirements for operational safety, long term safety, retrievability and monitoring.

Each of the four technical Modules, shown below, involves from 3 to 7 Partners and a total of 7 different national disposal concepts are represented within ESDRED.

Module # 1: Buffer Construction Technologies
- for horizontal disposal concepts
- ONDRAF/NIRAS (Belgium) is Module Leader

Module # 2: Waste Canister Transfer and Emplacement Technology
- for horizontal and vertical disposal concepts
- DBE TECHNOLOGY (Germany) is Module Leader

Module # 3: Heavy Load Emplacement Technology

- for horizontal disposal concepts
- SKB (Sweden) is Module Leader

Module # 4: Temporary Sealing (using low pH cement) Technology

- for construction of sealing plugs and for rock support using shotcrete techniques
- ENRESA (Spain) is Module Leader

11.2.2 Second Objective

A second and equally important objective is to promote a shared European vision in the field of radioactive waste disposal technology. This is accomplished through the INTEGRATION process, which is one of the key objectives that identify Euratom's 6th Framework Programme. Among other things integration involves working together within Work Packages and/or Modules; sharing information; comparing one another's input data and functional requirements for consistency; ensuring that, where possible, fabricated components are compatible; and coordination of demonstration activities.

All 13 Partners are involved in the Module shown below.

Module # 6: Integration

- covers all of the technical modules
- ANDRA (France) is Module Leader

11.2.3 Third Objective

The third objective involves communication and training and is deemed to be sufficiently important to merit a separate Module. Among other things it involves the dissemination of knowledge by way of press releases, pamphlets, technical articles and presentations, videos and eventually an international event. Training, with a focus on New Member States, is to be accomplished via workshops, courses and possibly some secondments. Activities in this Module are primarily the responsibility of the 4 Technical Module Leaders, the Project Coordinator and NAGRA.

Module # 5: Training and Communication Activities

- covers all of the technical modules
- ANDRA (France) is Module Leader

11.2.4 ESDRED Consortium

The 13 Partners included in the ESDRED consortium are:

Radioactive Waste Management Agencies:
ANDRA, France
ENRESA, Spain
NAGRA, Switzerland
NIREX, United Kingdom
ONDRAF/NIRAS, Belgium
POSIVA, Finland
SKB, Sweden

Technological R&D Organisations:
AITEMIN, Spain
CSIC, Spain
DBE TECHNOLOGY, Germany
ESV EURIDICE GIE, Belgium
GRS, Germany
NRG, The Netherlands

11.2.5 Project Schedule

The general schedule of the project is shown in Figure 11-1.

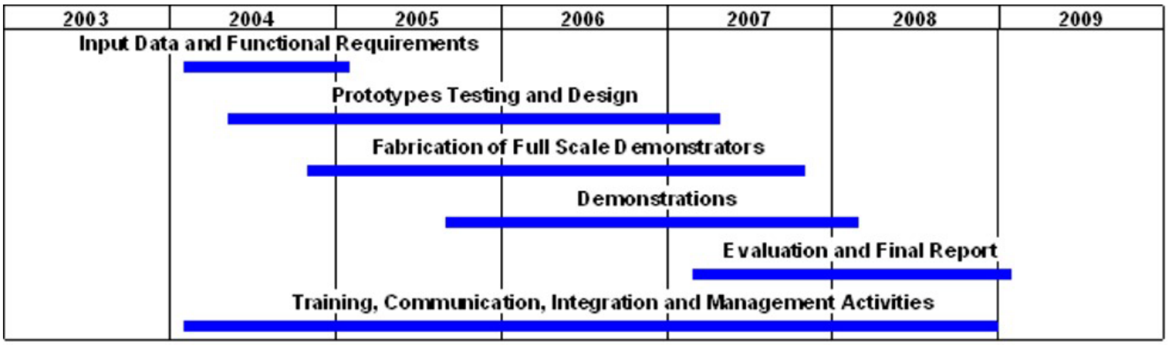

***Figure 11-1**: General schedule of the ESDRED project*

11.3 Project activities

11.3.1 Module # 1 - Buffer Construction Technology for Horizontal Disposal Concepts

In this work the buffer is an engineered barrier, usually made of material such as cement or bentonite (possibly mixed with sand), which is placed between the radioactive waste container and the geological formation surrounding the disposal drift.

Within ESDRED, three engineering options for waste/buffer emplacement are considered leading to three designs and therefore three prototypes:

1. the buffer is prefabricated in a surface facility, then transported to the underground repository and positioned in the disposal drift ; then the waste canister can be emplaced,
2. the waste canister is inserted into a large container, (so-called “super-container”) which includes part of the buffer; once the super-container is emplaced in the disposal drift, the annular space between the super-container and the drift is filled with a granular buffer,
3. the waste canister is placed on a prefabricated solid buffer cradle and then a granular buffer material is used to fill (backfill) the disposal drift.

The two last options look rather similar, but the volume of granular buffer material required and the emplacement technology used (including the possible compaction) are quite different, see Figure 11-2.

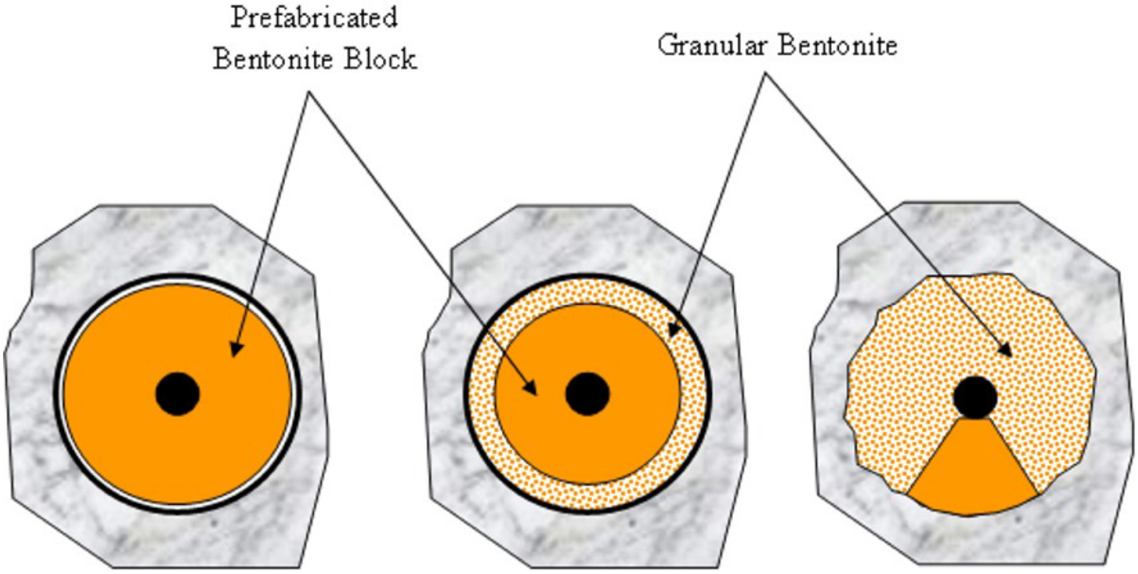

Figure 11-2*: Three Buffer Concepts*

11.3.2 Module # 2 - Waste Canister Transfer and Emplacement Technology for Horizontal and Vertical Disposal Concepts

Although surface transportation of radioactive waste is a routine activity, transport and emplacement in an underground environment presents unique challenges. Among other things:

- spaces are more confined and a shielding cask is required for transportation in order to ensure the radiological protection of workers
- in addition to the shielding cask, remote control operating techniques may have to be used

- during transportation of the waste container and while docking at the disposal location
- during the transfer operations into the disposal location (drifts or boreholes)
- and finally during closure of the disposal drift or borehole.

Within ESDRED emplacement equipment for both the horizontal and vertical options will be designed, fabricated and demonstrated. Two examples of design are shown in Figure 11-3 and Figure 11-4.

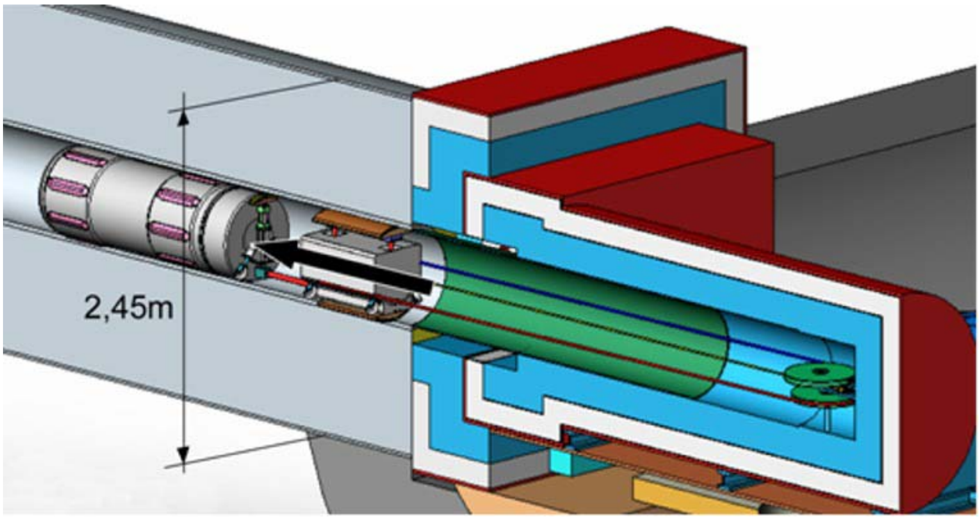

***Figure 11-3**. Layout of ANDRA's Repository Concept for Horizontal Emplacement - showing a remote-controlled pushing robot (black arrow) emplacing a waste canister while a shielding cask (in red) ensures the radiological protection of workers present in the access drift.*

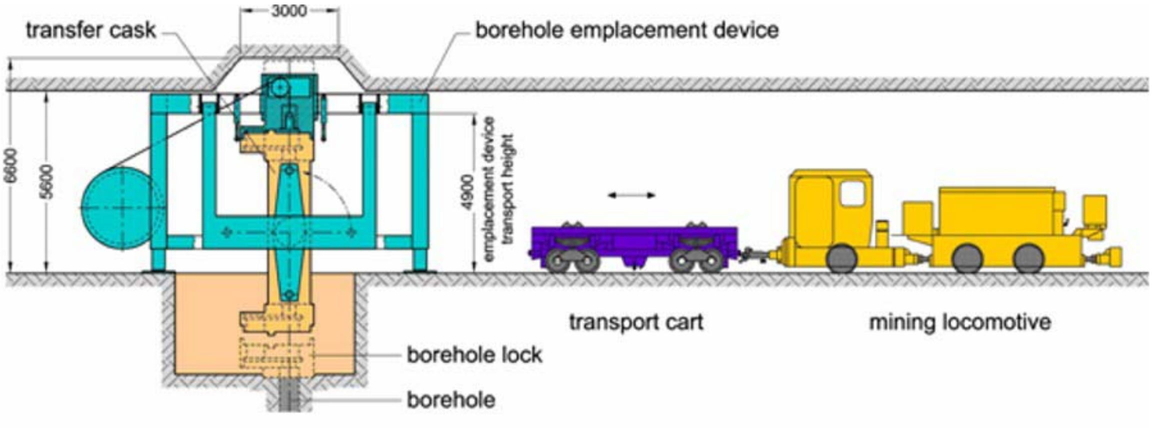

***Figure 11-4.** Layout of DBE-TEC's Repository Concept in Salt for Vertical Emplacement of waste canisters in a Borehole - showing transfer mechanism in blue*

11.3.3 Module # 3 - Heavy Load (15 to 50 metric tons) Emplacement Technology for Horizontal Disposal Concepts

Horizontal emplacement of very heavy spent fuel canisters, of super-containers (including buffer material and the waste canister) or of a large assembly of prefabricated bentonite buffer rings (see Module # 1) is required in some disposal concepts, see Figure 11-6 and Figure 11-7.

In order to minimize friction, which must be overcome when moving such heavy cargoes, the option of using air or water cushion technology is considered. This technology is widely used in civil engineering when pressurised air or water is injected between two flat horizontal surfaces, Figure 11-5.

The challenge is to demonstrate the feasibility of this technology, for heavy cargo emplacement, when pressurised air or water is injected between two cylindrical surfaces. It is already known that the cylindrical shape of the surfaces will reduce the uplift force which can otherwise be obtained between two horizontal surfaces in the classical application of this technology.

The type and flow-rate of the fluid must also be compatible with the repository environment so that, for example, the use of water in a clay host rock is not practical whereas it is perfectly acceptable in granite.

Within ESDRED both the air cushion and the water cushion technology will be demonstrated as a means of moving loads up to 50 tonnes within relatively small diameter disposal cells/drifts.

1° The cargo rests on the lifting device

2° Pressurised fluid is expelled through the lifting device and the cargo is lifted up

3° Once the cargo is lifted up by the fluid cushion, the friction is reduced and a small force can move the cargo horizontally

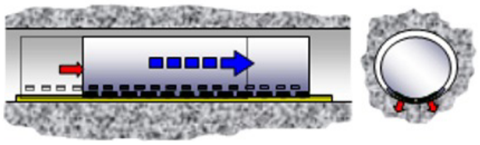

Figure 11-5. General Fluid Cushion Emplacement Concept Application of air or water cushion technology for cylindrical container emplacement

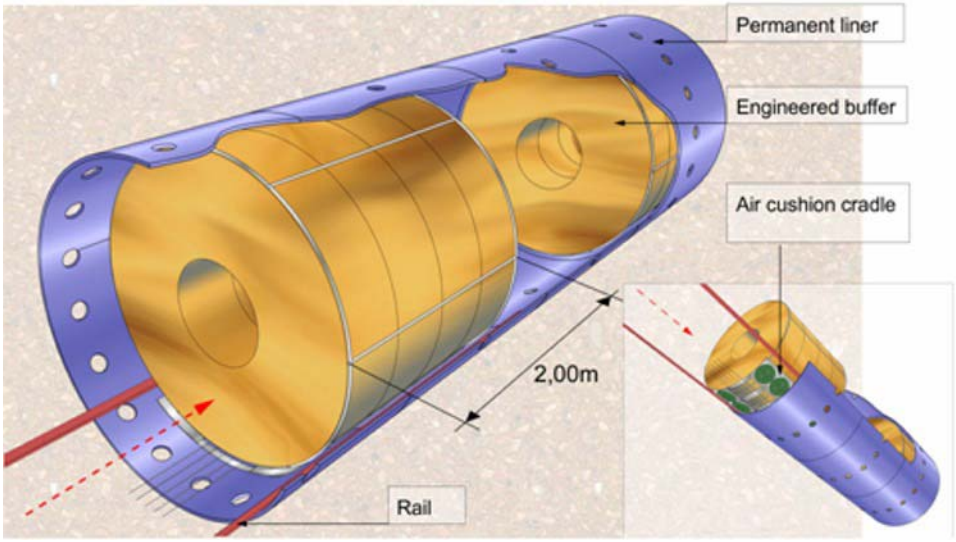

Figure 11-6. *Illustration from ANDRA's repository concept in clay showing emplacement of a 15t set of prefabricated bentonite rings (from Module 1) in a disposal cell equipped with a steel liner*

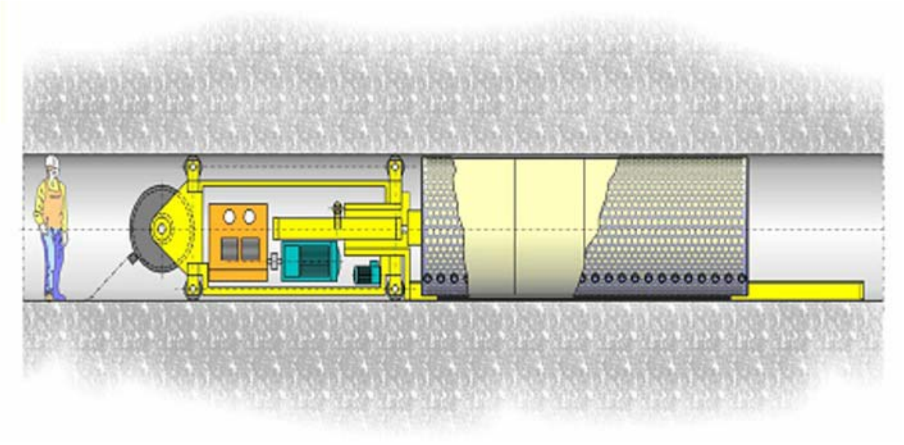

Figure 11-7. *Illustration from SKB's repository concept in granite showing emplacement of a 45t super container into a horizontal disposal tunnel*

11.3.4 Module # 4 - Low pH Cement for Shotcrete and Sealing Plug Construction Technology

Cementitious materials are widely used in underground engineering. For radioactive waste disposal, specific consideration is given to the applicable geochemical phenomena in the long term safety analysis, including for instance the possible interaction of the cement with the vitrified waste matrix or with the surrounding geological medium via a so-called plume effect.

In order to reduce these interactions, new cement formulations are considered, which are more neutral with respect to the waste matrix or underground environment, while retaining the necessary mechanical and sealing properties.

Within ESDRED the development of low pH cements is complemented by the formulation of concrete mixes which may be placed at an industrial scale, using the shotcrete technique, for the construction of disposal drift sealing plugs and for ground support, i.e. rock-wall lining.

A full-scale demonstration test is planned at the underground Äspö Hard Rock Laboratory in Sweden, Figure 11-8.

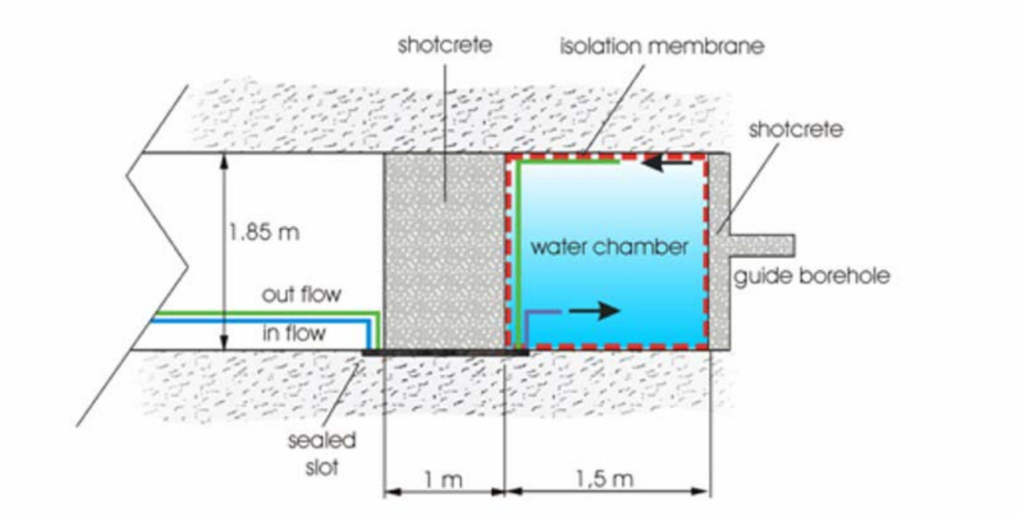

Figure 11-8 *Layout for testing (to failure) a short disposal drift sealing plug constructed using the shotcrete technique.*

11.4 Major technical work accomplished to date

11.4.1 Module #1: Buffer Construction Technology

Input data and functional requirements were developed in a first deliverable report. Bids were solicited for the design, fabrication and testing of bentonite buffer rings. A contract was signed which includes utilising, at 65 000 tons, the most powerful press available in Western Europe today. The basic design and laboratory testing of buffer configurations to be used for surface and insitu demonstrations of seals constructed in vertical bore holes, was completed. Field work is planned to start in 2005.

11.4.2 Module #2: Waste Canister Transfer and Emplacement Technology

Input data and functional requirements were developed in a first deliverable report. A contract has been awarded for the design, fabrication and testing of prototype pushing robots to be used for the horizontal emplacement of spent fuel and vitrified waste canisters. The conceptual and basic design of the equipment intended for the industrial demonstration of the horizontal (2007 in situ) and vertical (2007 in a workshop) emplacement concepts has begun. Finally a compilation of data describing the various National repository concepts or variations thereof, as they relate to reversibility/retrievability, is underway. This will result in a desk study deliverable.

11.4.3 Module #3: Heavy Load Emplacement Technology

Input data and functional requirements were developed in a first deliverable report. This is the module with the most visible sign of progress as shown in the Figure 11-9. Bertin Technologies, a French firm, has successfully completed the design, fabrication and testing of a 1/3 scale prototype air cushion device for the emplacement of heavy loads up to 43 tons. Experiences gained here are being incorporated into the design and fabrication of a similar full scale industrial demonstrator to be tested in 2006. ANDRA and SKB have both awarded contracts for the design, fabrication and testing of the full scale industrial demonstrators.

Figure 11-9. *Prototype Test of the Air Cushion Principle Applied to Small Diameter Canister*

Figure 11-10. *Sealing Plug Construction Site – Full face bored demonstration drift at Äspö.*

11.4.4 Module #4: (Temporary Sealing)

Input data and functional requirements were developed in a first deliverable report. This Module has made a lot of progress with respect to the laboratory work needed to be able to design the demonstration work which is to follow in the next 2 years. First a methodology for the rapid determination of pH in cements was tested and selected. An important Milestone was achieved upon the completion of the characterization and formulation of low pH cements suitable for further testing as part of shotcrete mixes using site specific aggregates. The design of the test plan for the *in situ* construction of a sealing plug at Äspö is into final review and the construction of the plug should take place in late 2005 or early 2006. Following the construction and curing this plug will slowly be loaded to failure (slippage) using water pressure as shown in Figure 11-8. The excavation of the 15m long borehole, where the sealing plug construction demonstration will take place, has already been completed, see Figure 11-10 above.

11.5 Expected results & outlook

The ultimate objective of the ESDRED demonstration activities is the fabrication, testing and working demonstration of full scale first generation prototype equipment and/or systems. The demonstrations will be performed in surface facilities simulating underground geometries as well as in three or four different Underground Research Laboratories (URLs). The technologies developed and the operational experience obtained will contribute directly and indirectly to the evolution of the various European national waste disposal concepts. It will also contribute specifically to the ongoing development and improvement of industrial equipment/systems which will be incorporated at sites selected to become final repositories.

ESDRED aims to demonstrate that feasible techniques are available for the implementation of deep geological disposal thereby contributing to an increase in stakeholder confidence particularly where the public at large is concerned. The ESDRED website (www.esdred.info) is adapted to a variety of audiences providing information at several levels of detail, notably from short abstracts to more complete descriptions of the technical activities as described in the Contract between the European Commission and the Contractors.

12 Potential applications of shotcrete techniques in hlw repositories. engineering aspects and chemical implications

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Abstract

Shotcrete may be used for different applications in an underground repository, and in some cases it can be more convenient and cost-effective than conventional concreting techniques. However, the number of uncertainties associated to the long term chemical interaction of this material with the rock and the bentonite barrier is higher than in the case of conventional concrete, due to the formulation of the shotcrete and the need of using a number of additives. The paper describes the potential uses of shotcrete in HLW repositories, and the benefits of this technique from the engineering point of view, and makes a preliminary analysis of the chemical aspects derived from the use of this material, from the point of view of the long-term safety assessment of the repository.

12.1 Concrete uses in HLW repositories

Concrete, on its various forms, is being considered in most repository designs as the basic construction material for different purposes:

- Rock reinforcing in tunnels and caverns
- Construction of platforms, sills, fundaments, and other structures
- Plug construction
- Grouting and sealing

Some of these uses may be temporary, as for instance some platforms and plugs that may be removed before the repository closure, but an important amount of concrete remains in the system along its entire life. Indeed, cementitious materials are also being proposed recently as main components of alternative engineered barrier systems.

In the particular case of the Spanish AGP concept for underground repositories, the total volume of concrete needed for structural purposes has been estimated in about 266.000 m^3 in the case of clayish formations, and 40.000 m^3 in granite, according to the distribution shown in Table 12-1. These figures exclude potential grouting needed for sealing fractures.

Table 12-1. Concrete volumes in the AGP Concept (in cubic metres)

Use	**Area**	**AGP - Clay**	**AGP - Granite**
Structural	Access shaft, ramps, and service galleries	209 227	36 000
	HLW deposition galleries	53 438	----
Plugs	Access and ventilation shafts and ramps	1 019	1 689
	Access and ventilation galleries	1 312	1 110
	Central area	393	492
	HLW deposition galleries	1 140	377
	MLW storage area	225	128
TOTAL		**266 754**	**39 796**

12.2 Applicability of shotcrete techniques in HLW repositories

12.2.1 Shotcreting principles

Shotcrete, also called “sprayed concrete”, is a well-known construction technique based in spraying concrete on a rigid surface (rock or soil), using a concrete pump and compressed air. The compressed air projects the concrete mix at high speed against the surface, so that it sticks to such surface. Once sprayed, the concrete starts to set immediately, thanks to an “accelerant” additive, forming a self-supported layer. The setting speed determines both the self-supporting capacity and the rate of development of structural strength in the shotcrete layer, and is controlled by the dosage of accelerant and also by the shotcrete formulation. In normal conditions, the typical thickness of shotcrete layers ranges from 5 to 15 cm.

Due to the characteristics of the formulations used and the spraying process, shotcrete is normally a high density and low permeability material, compared to an average standard concrete. It shows also lower surface cracking.

12.2.2 Methods and equipment

There are two basic types of shotcreting techniques, called “wet mix” and “dry mix”, depending if the water is added at the mix before the pump stage (wet mix), or at the end of the pipe, just before the spraying nozzle (dry mix). Figure 12-2 shows schemes of both processes. Nowadays, practically all shotcrete works are made using the wet mix system, as this provides a more uniform flow and therefore a more consistent quality in the final product.

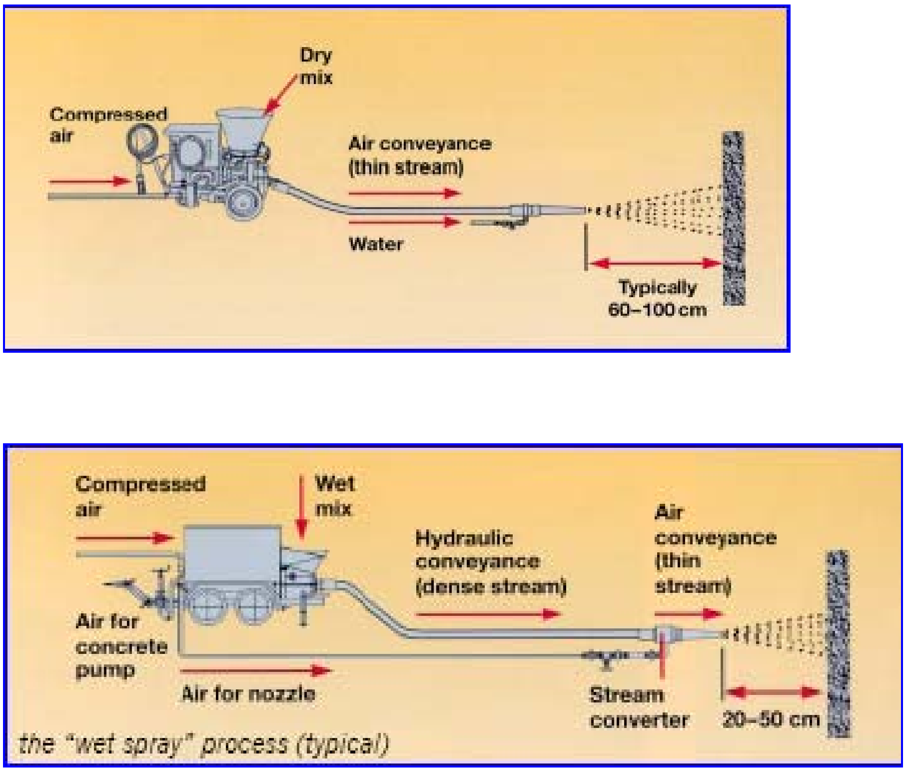

Figure 12-1. *Typical dry-mix (above) and wet-mix shotcrete processes (after SCA)*

Shotcrete operation can be performed either manually or using articulated arms commonly known as “robots”, that can perform some movements in automatic or semi-automatic mode. In galleries of small cross-sections, as the ones planned in many repository designs, the operation must be carried out so far manually, as the dimensions of the robots existing in the market are made larger spaces. This makes the operation more difficult, especially if radiation protection is needed. However, special shotcreting equipment has been designed for other specific applications, as for example the systems embedded in tunnel boring machines, and therefore the design of a low profile, teleoperated shotcreting arm should not be too difficult.

Pumping distances may reach several hundred metres using the wet mix method, and selecting the adequate equipment and shotcrete formulation. This would enable to apply shotcrete techniques at any point in deposition galleries and drifts. Longer distances may be achieved, however, using special equipment or double stage pumping.

12.2.3 Shotcrete formulations

As in any other concrete, the formulation of shotcrete depends on the specific requirements and the work site conditions. In principle they are not too different from standard modern concretes, however there are a number of considerations to be made:

Binders

Ordinary Portland Cement (OPC) is the most commonly used cementitious material in shotcrete formulation; however other types of cements can also be used. Other pozzolanic materials, such as Fly Ash, Blastfurnace Slag, or Silica Fume, can be added for improving certain properties in the plastic or in the hardened state. Silica Fume, in particular, improves pumpability, cohesiveness, and adhesion, and is very commonly used in high-quality shotcrete mixes. The addition of silica fume enables the construction of thicker shotcrete layers in a single pass, and also reduces the pH.

Aggregates

The grain size distribution of aggregates is a critical factor in the shotcrete formulation. It must comply with the curves specified in the applicable standards, in order to prevent segregation of the material along the pipe. Maximum grain size is usually 4, 8, or 16 mm, depending on the fineness of the shotcrete. In comparison with standard concrete, shotcrete requires a higher proportion of fine sizes, especially if using wet mix. Basically any type of aggregate can be used, but rounded, natural washed gravels and sands provide a better behavior at the pumping stage. In general, selecting the adequate aggregate for each mix requires considerable experience and testing.

Fibres

Steel and polymer fibres can be added to the shotcrete mix for different purposes. Steel fibres improve the tensile and flexural strength of the hardened shotcrete and also reduce shrinkage and cracking. Polymer fibres have a similar effect in terms of reducing shrinkage, and also improve other properties like ductility, fire resistance, etc.

Admixtures

Shotcrete requires a number of admixtures. They may vary from one mix to other, depending on the application and the specific requirements, but the most important ones are:

- Superplaticizer: These are always required in order to improve pumpability, reducing at the same time the amount of water required, thereby improving the final quality

- Accelerant: The accelerants increase the setting speed, providing early strength development and enabling the construction of self-supported layers. These products are added at the last moment, just at the spraying nozzle.

Other admixtures such as retarders, hydration control compounds and curing agents may be required, depending on the application and the work site conditions. In particular, curing compounds may be relevant in a HLW repository application, as they prevent the evaporation of water from the mix, reducing shrinkage and cracking.

12.2.4 Potential applications

Rock support

The most usual application of shotcrete is rock support, in which a layer of shotcrete is sprayed on top of the rock surface immediately after excavation, to create a support arch that at the same time prevents rock expansion. Typically, shotcrete is combined with bolting and a wire mesh for improved efficiency. This method, widely used in the "New Austrian Tunelling Method" (NATM) is applied to medium to soft rocks, in tunnels, mines, and other underground constructions. Shotcrete is also applied in hard rocks on highly fractured or weak areas, although in this case its function is rather preventing the falling of loose blocks than structural support.

In comparison with standard concrete lining for roof support, shotcrete is time and cost efficient, and can be used in most host rocks considered for HLW repositories. The only difference is that the final surface obtained is more rough and irregular than with standard lining, which could be perhaps a problem in the zones that must be backfilled with pre-shaped blocks or packages.

In principle, only in the case of repositories in clay formations the shotcrete used for this application would be in direct contact with the engineered barrier. In granite, basically all shotcrete used for rock support should be in access and service galleries and vaults, at longer distances from the EBS.

Plugs

Plugs are required in HLW repositories in a number of places. The plugs in the deposition galleries have basically a mechanical function, which is transferring to the rock the thrust of the swelling bentonite, but in some repository designs they must have also a hydraulic seal function (especially the interruption of the EDZ).

Shotcrete has a number of advantages, from the engineering point of view, for the construction of plugs:

- Forms not required
- Fast construction

- Early mechanical strength
- Excellent bonding to the rock surface
- Low permeability material
- Reduced shrinkage
- Easy to construct with teleoperated/robotized systems

All these benefits make shotcrete a good candidate for the construction of plugs in the repository area, both for temporary and final ones.

A first experience in this field has been the plug constructed in the FEBEX project after the partial dismantling carried out in the "in situ" experiment in 2002. In this case, a parallel plug, without any recess excavated in the rock, has been built, with a total length of 3 m (Figure 12-2. Design of the FEBEX II shotcrete plug Figure 12-2).

The plug was constructed in two phases: A first section with about 1 m thickness was built in 2002, and a second section of about 2 m was later one year later in 2003. The mix formulations were very similar in both cases, and are shown in Table 12-2.

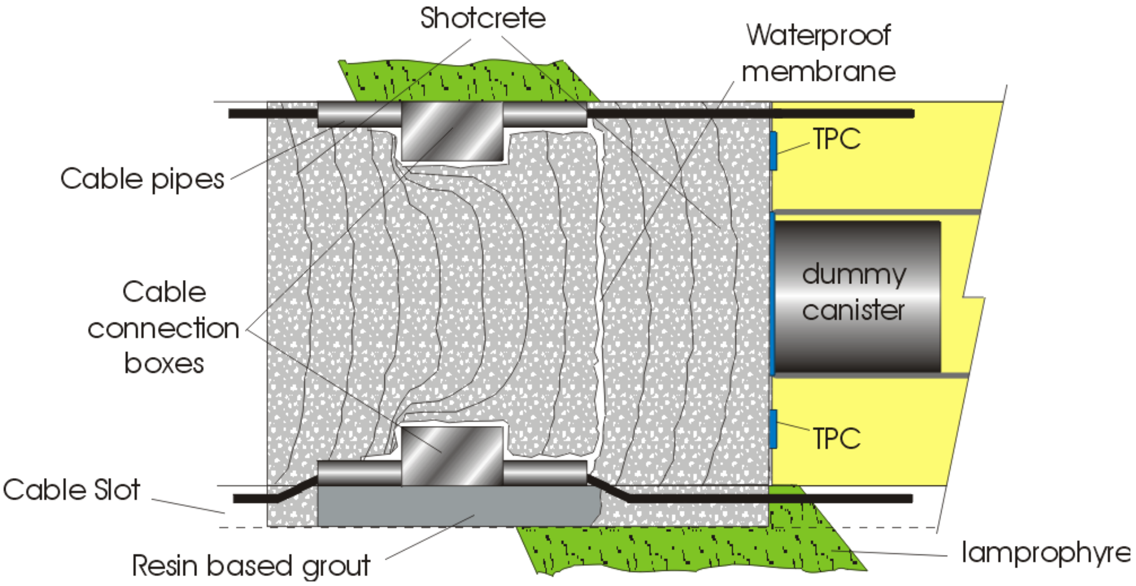

Figure 12-2. *Design of the FEBEX II shotcrete plug*

Table 12-2. Shotcrete characteristics in FEBEX II plug

Component	**Section 1**	**Section 2**
CEM II A-L 32,5 R	430 kg/m^3	475 kg/m^3
Nanosilica MEYCO MS 660	30 Kg/m^3	60 Kg/m^3
Steel fibres Dramix ZP 306	50 Kg/m^3	----
Polypropylene fibres	800 g/m^3	----
Superplasticizer GLENIUM T803	1.5 %	1.5 %

Component	Section 1	Section 2
W/C	0.40	0.46
Aggregate 0-8 mm	1 700 Kg/m^3	1 700 Kg/m^3
Curing compound MEYCO TCC 735	1 %	1 %
Accelerant MEYCO SA 160 E	6 %	6 %

The main difference between both formulations is that in section 2 both steel and polypropylene fibres were eliminated, as it was considered that this type of materials would not be desirable in a real repository, because of the difficulty of assessing their behavior in the long term. The proportions of cement and silica fume were also modified in Section 2 to compensate some variations found in the grain size distribution of the aggregates /Fuentes-Cantillana, 2003/.

Both sections were constructed by layers with a thickness raging from a minimum of 5 cm, to a maximum of 67 cm. However, some shrinkage cracks were observed in the thicker layers, so the standard thickness was finally set to 25-30 cm. Figure 12-3 shows the final appearance of the plug, and Table 12-3 lists the main technical characteristics of the shotcrete obtained on each phase.

Figure 12-3. *Final aspect of FEBEX II shotcrete plug*

Table 12-3. Technical characteristics of shotcrete in FEBEX II plug

Parameter	Section 1	Section 2
Uniaxial strength (mean value)	32.00 MPa	39.66 MPa
Hidraulic Conductivity (mean value)	4.3 E-11	9.4 E-11

The behavior of this plug has been so far excellent. The first section, with a thickness of only 1 m, was in place for one year, supporting a peak pressure of 3.13 MPa. The complete plug, with a total thickness of 3 m, is currently supporting a pressure of 5 MPa, with no apparent deformation or movement.

12.3 Chemical implications

As seen from the figures in Table 12-1 concrete, and in particular cement, are the main artificial material introduced in the repository, in terms of volume. Some concerns have been raised about the chemical impact of such large volumes of cement in the long term assessment of the repository. In particular, the most critical zone would be the concrete in the deposition galleries, as it is in direct contact with the engineered barrier system.

There are several aspects of the problem to be considered:

12.3.1 Effect of pH

Pore water in standard concrete and shotcrete formulations has an alkaline character. For example, analysis made on samples from the FEBEX II shotcrete plug has shown a pH of 12.55 in the first section, and 12.85 in the case of the second section. High pH values may interact with the near field in two ways:

Concrete-bentonite interaction

During the development of ECOCLAY phase-I and phase-II projects (Huertas et al., 2000; ANDRA, 2005) several alteration experiments were conducted with the aim of testing FEBEX and MX-80 bentonite against the effects of hyperalkaline (K,Na,Ca-OH) fluids. Two general conclusions could be extracted from the experiences.

- Although high reactivity is observed at pH >12.5, this early alkaline phase can be neglected concerning buffer alteration, due to its overall limited duration and also to the overall limited quantities of alkalis in the cement. A reduced extent of buffer would be affected (<2 cm), considering mass balance and experimental effects.
- Montmorillonite reaction at pH < 11 is not observed, either by the slow reaction rate or by the equilibrium attained with CSH phases.

At pH 12.5-11, the reaction rate, mainly for dissolution of montmorillonite, is very slow also, but these pH values (portlandite equilibrium - high Ca/Si CSH equilibrium) will stand for very long times in contact with OPC cements. Several simulations are available, considering MX-80 bentonite and OPC evolved pore waters (De Windt et al., 2004; Gaucher, 2005). Based on 10.000 y-100.000 y calculations, the buffer will be affected in a 20-30 cm thickness, and pH will be buffered at <10 by bentonite-CSH-Mg-hydroxide/silicate products.

Very similar conclusions can be applied to stiff clays /Mäder and Adler, 2005/ and shales /Gaucher, 2005/.

Granite-concrete interactions

Experiments and simulations concerning granite, marls or consolidated shale emplacements have been done considering the existence of preferential pathways along fractures or vein fillings /Adler, 2001; Soler & Mäder, 2002/.

Minerals and altered mineral phases in granites have much larger crystal size than the usual constituents of bentonite buffers or clay host rocks. This leads to little amounts of reaction produced in minerals like muscovite or quartz. Albite and microcline partially dissolves at pH 13.4-12.5 and CSH phases precipitate. The results from small-scale laboratory experiments with Grimsel granodiorite and Opalinus Clay support the progressive permeability reduction due to the closure of flow paths /Adler, 2001/.

This fact can be taken as a retardation and buffering positive effect when the migration of alkaline plume is thought in hard-rocks emplacements.

12.3.2 Additives and admixtures

Polyolefins or steel fibres are quite inert in alkaline-reducing environment /Tagnit-Hamou et al., 2005/, and nano-silica materials have the positive effect of reducing pH of concrete, so these materials are not expected to produce negative impacts.

The main problem for the long term analysis are the additives, as there are a number of different products, and the manufacturers are extremely reluctant to provide information about their exact chemical composition..

For example, accelerants of the calcium sulfoaluminate (ettringite) type can induce the formation of more ettringite in the cured cement paste. Hydrated CSH can be dissolved and porosity can be increase /Paglia, C., Wombacher, F., and Böhni, H. 2003/. This effect will be negative to the durability of concrete, but does not change basically, the chemistry of alteration. Modern alkali-free accelerants, however, are claimed to have less impact in the durability of the concrete.

On the other hand, superplasticizers (polycarboxilates, polymetacrylates) and curing compounds (acrylic polymer, sodium silicate, or chlorinated rubber based) normally contain organic functional groups (carboxylic) or organic solvents (COVs: Carbon organic compounds) that can migrate in the porous media (COVs) or act as complexing agents for metals (Al, Fe, radionuclides). In this sense, superplaticizers of the polycarboxilates type have the lowest densities of functional groups in relation to polyolefin side chains, having therefore a lower potential for providing metal-complexing agents.

12.4 Conclusions

Shotcrete has important engineering and technological benefits as for being considered a good candidate for rock support and plug construction applications in HLW repositories. The chemical implications of using shotcrete refer to the potential impact of the high pH of this material, and the difficulty to assess the long term behaviour of the additives that are required in the mix.

The problem of the pH is similar in case of using standard concrete, and according to experimental results, the impact is probably limited to the area in the close vicinity of the shotcrete. In any case, it is expected that the activities being currently carried out under the EU “ESDRED” Integrated Project may provide a solution. Preliminary results are promising and show that it may be possible to provide a valid formulation for a shotcrete with pH 11 or lower.

The problem of assessing the long term effects of the additives must be yet studied in detail, but this requires a better knowledge of their chemical composition. The analysis should in any case take into account the actual quantities of these products available in the shotcrete.

Acknowledgments

Data and experiences included in this paper have been in a large part taken from the FEBEX I, FEBEX II, ECOCLAY I, ECOCLAY II, and ESDRED projects, funded by the European Commission under the Nuclear Fission Safety program.

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13 Shotcrete development for low-pH cements

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Abstract

The use of low pH-cements to design and produce a structural shotcrete represents a rather complex task because of the special characteristics of the binder. The requirements for the mix are many, both in the fresh and hardened state, as it has to fulfil the requirements associated to the structural design in addition to "pumpability" and "projectability".

Wet-mix shotcrete operation requires an accelerator admixture to be used at the pumping nose, thus its compatibility with the other constituents in the mix (low-pH cement, water-reducer admixture) must be evaluated.

The design and optimisation of the concrete to be pumped and shotcreted must be carried out taking into account the performance specified for the hardened concrete as well, i.e., compressive strength, elasticity modulus, coefficient of permeability, etc.

This paper deals with the design and optimisation process of a mix which would be used for a low-pH shotcreted concrete plug. Thus, the design was performance-oriented, according to the functional requirements set for this particular case.

13.1 Introduction

The design of a shotcrete-base concrete on a performance basis is a complex process, as many conditions arise: properties at the fresh state, such as consistency, pumpability and projectability and at the hardened state as well. The use of chemical admixtures is current practice and the compatibility between them and the binder must be assessed.

When regular components are employed, general rules for mix design can be applied and, as a general rule, shotcrete execution induces an increase in porosity as compared to the same shotcrete-base concrete and thus, a decrease in mechanical properties must be expected. Nevertheless, the hydration processes and further strength evolution vs. time are equivalent to a conventional concrete.

The use of a low-pH cement formulation, made of commercially available cement and high percentages of mineral additions, is more challenging, because each case has to be considered as unique. Neither the compatibility between the low-pH cement and the chemical admixtures nor the hydration processes and strength evolution vs. time are known, thus an extensive characterisation process has to be performed.

This paper shows the design of a concrete mix to be shotcreted at a concrete plug where a low-pH is mandatory. Moreover, the functional design of the plug imposes further requirements to the material, and so, the design must be done accordingly.

13.2 Considerations about functional requirements

The main requirement for the concrete plug is its low-pH, which must be around 11, to prevent the bentonite in contact from deteriorating. This requirement strongly conditions the use of low-pH cement, which must be designed considering only commercially available constituents.

At the concrete design stage, only pre-selected low-pH formulations are used. In the pre-selection process, different considerations such as the water demand, the compatibility with chemical admixtures, setting time and compressive strength come into consideration, and only a brief comment will be made on the matter.

As the design of the concrete plug involves different characteristics of the concrete (mechanical strength, deformation, hydraulic permeability, heat of hydration, shrinkage, potential durability, etc.) and other technological properties, such as consistency, pumpability and a low-loss in workability with time, the design and optimisation of the concrete must be carried out on a performance-basis. Table 13-1 summarises the main functional requirements for the shotcreted concrete.

Table 13-1. Functional requirements for the shotcreted concrete

Requirement	Target	Complementary considerations
Maximum pH	< 11	Measurement technique (1) Age of measurement
Hydraulic conductivity	K < 10^{-10} m/s	
Final mechanical properties Young Modulus Poisson ratio	< 20GPa	Final means: long-term. The age of testing to assess final properties will be established from test results.

Requirement	Target	Complementary considerations
Tensile Strength Friction angle Cohesion Compressive strength	0.2 a 0.3 1 MPa > 37° 2 MPa 10 MPa	
Workability	> 2h	Negligible workability loss for at least 2 hours
Pumpability	500m	A long pumping distance can be expected
Peak of hydration	< 40°C	Temperature rise is influenced by the accelerating admixture added at the shotcrete nozzle.

(1) The measurement technique is dealt with in another paper

13.3 Relationships between conventional concrete and shotcrete

As it was mentioned in previous paragraphs, the shotcreted concrete differs from the base-concrete, which is transported, pumped and shotcreted. Thus, a reduction in strength and elasticity modulus and certain increase in water permeability have to be taken into account when considering the targeted values. The actual reduction in strength must be experimentally determined from the comparison between cores and cylinders but for mix design purposes, it can be estimated in about 50 %, i.e., if a target value for compressive strength in shotcrete is 10 MPa, the base-concrete should be designed for a strength of about 20 MPa.

Additional considerations have to be taken into account when considering the influence of the on-site production as compared to the very controlled conditions of laboratory made concrete. Thus, a further reduction of 10 to 15 % in compressive strength has to be expected.

Taking into account these considerations, the target value of the compressive strength for the base concrete at laboratory stage was set in the range 20-25 MPa. Once the results from testing shotcrete cores are obtained, minor adjustments are possible with changes in the water/binder ratio and/or cement content in the mix.

13.4 Preliminary tests on mortar

Once different low-pH cements were formulated, the selection was refined by tests on mortar. At this stage, 1:3 (binder: sand) mortars were prepared, with different w/binder ratio, with and without superplasticizer. Thus, the mortars were tested for their fluidity, stability, water demand and compressive strength a different ages.

In some selected mixes, accelerating admixture was also included, to assess the compatibility between the low-pH cement, high-range water reducing admixture and the accelerator. Setting time was considered of utmost importance, as it might determine the stability of the shotcrete once it has been projected on vertical surfaces.

As a result, three low-pH cement formulations were selected to be used in concrete mix design. Two of them are portland cement based while the other is calcium-aluminate based. All low-pH formulations content a high percentage of mineral additions: fly ash and/or silica fume.

13.5 Aggregate grading and characterisation

The use of local aggregates, crushed granite obtained from Äspö, was also required, although this was not considered fundamental. The use of crushed granite as fine aggregate was challenging as far as pumpability is concerned.

Aggregate grading was adjusted according to the recommendations of the SCA, UK, because the limits suggested by EFNARC are intended to be used for dry-shotcrete applications. The adjusted limits for 12 mm maximum size aggregate are shown in Figure 13-1 where the dashed line indicates the targeted grading for the aggregate.

Aggregate from Äspö came in three fractions: 0-4 mm (sand), 4-8 mm (medium) and 8-12 mm (coarse). Their mineralogy and texture were the same but there was a greater percentage of flaky particles in the fine fraction, as can be seen from Figure 13-2.

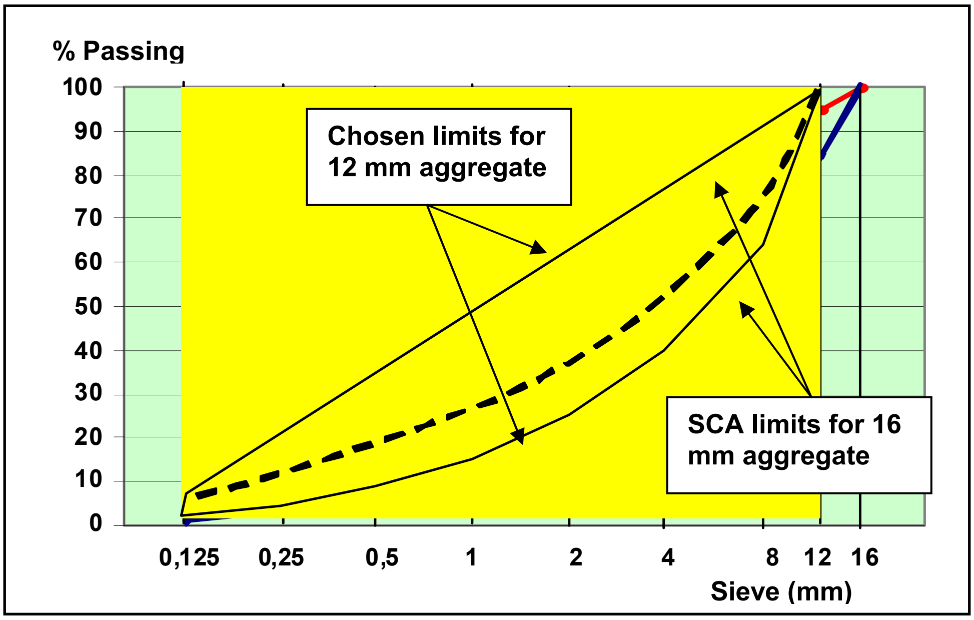

Figure 13-1. *Selected grading for the aggregate (crushed granite)*

Figure 13-2. *Aggregate fractions: fine, medium and coarse aggregate (MS: 12 mm)*

Trial mixes showed that improvements in the aggregate grading was needed to improve workability. As a result, the grading curve was displaced towards the fines, slightly increasing the amount of mortar from the theoretical optimum value. The grading use is sketched in Figure 13-3.

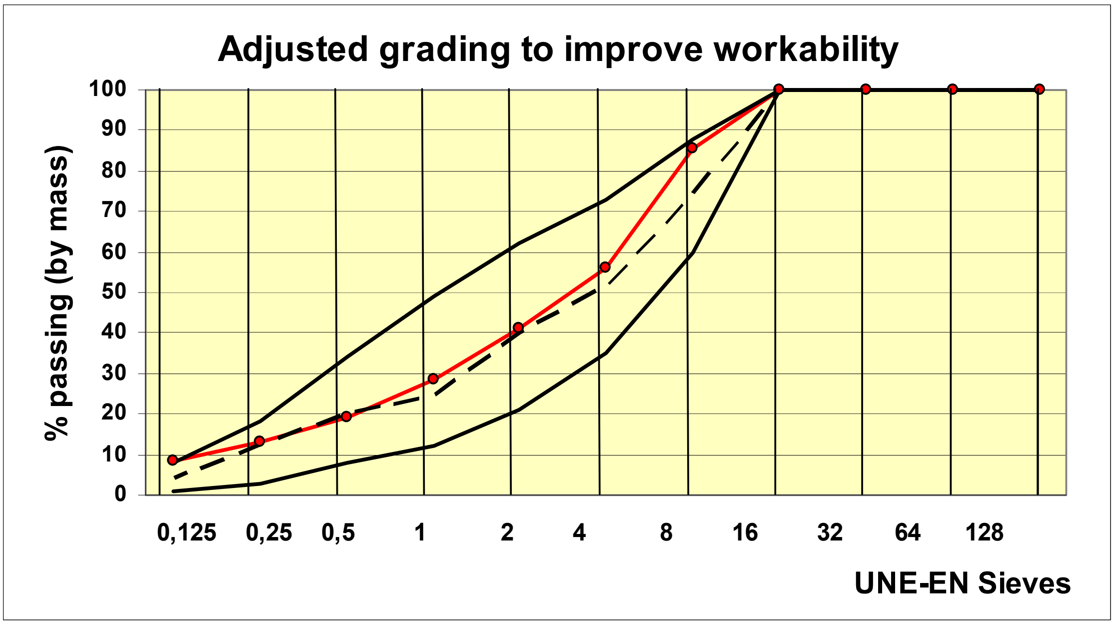

***Figure 13-3**. Total aggregate grading (red line)*

13.6 Mix design and testing at the fresh state

Mix design was performed according to the absolute volume method. The initial cement and water content were established from the results obtained on mortars but they were further adjusted according to the results from the trial mixes.

13.6.1 Materials

- Low-pH cement formulation: three low-pH formulations were tested, named B.1.2, B.3.4 and A.3.1. The later correspond to a calcium-alumina cement based formulation, while the other two correspond to a Sulphate Resistant Portland Cement.
- Water: tap water was used for all concrete tests
- Aggregates: The three fractions, all made from crushed granite, were used in the following proportion (by weight): 51 % sand, 37 % coarse aggregate and 12 % medium aggregate.
- Water reducing admixture: SP 1: Policarboxylate. pH = 4.25

  - SP 2: Naphtalene Formaldehyde; pH = 7.50
  - SP1 was chosen for CAC based low-pH cement, while SP2 was chosen for OPC based low-pH cement concretes.

- Air entraining admixture: conventional air-entraining admixture for concrete was used to improve workability, at very low dosage. Nevertheless, the increase in air content of the mixes was negligible.
- Accelerator: No accelerators were used when designing the mixes.

The use of very fine materials in the low-pH cement formulation imposes the use of a high-range water reducer admixture. Nevertheless, according to the dosage used, the actual content of organic compound in the hardened concrete would be about 2 kg / 2200 kg of concrete, equivalent to a 0.09 % (mass by mass).

13.6.2 Test methods

Two tests were used to characterise workability: slump test and inverted cone test. The former characterises the fluidity of the mix and it is very sensitive to water content, while the latter can be considered as an indication on potential pumpability. In order to evaluate slump-loss, the slump was measured at 15 minutes and at 45 minutes after mixing. Unit weigh at the fresh state was also measured. Air content of the mixes was measured with a type-A air meter, according to ASTM C 231. Cohesion and bleeding were not evaluated in a quantitative but qualitative way.

Table 13-2 shows the proportions of the concretes and

Table 13-3 summarises their properties at the fresh state.

Table 13-2. Mix proportions and properties at the fresh state. OD: oven-dried condition

	A.3.1	**B.1.2**	**B.3.4**
Constituent	**(kg/m^3) OD**	**(kg/m^3) OD**	**(kg/m^3) OD**
Cement	309,7	307	337
Water	262,3	277	316
w/c	0,85	0,9	0,75
Coarse agg	621	615	635
Medium agg	201	200	205
Sand	825	818	843
HRWRA (1.8%)	5,58	5,5	5,7

	A.3.1	**B.1.2**	**B.3.4**
Constituent	**(kg/m^3) OD**	**(kg/m^3) OD**	**(kg/m^3) OD**
Air entrainer (0,2%)			0,6

Table 13-3. Properties at the fresh state

	A.3.1	**B.1.2**	**B.3.4**
Unit weight	2,23 t/m^3	2,23 t/m^3	2,25 t/m^3
Slump	17 cm	12 cm	13 cm
Cohesion	Good	Good	Good
Aspect	Good	Good	Good

From each concrete, 7 cylindrical samples were prepared, to be tested at 7, 28 and 90 days in compression. Concrete samples were cured under standard conditions (T = 20° ± 2 °C; RH > 95 %) until de age of testing.

13.7 Properties of the basic concrete in the hardened state

In order to assess the “final” properties for these concretes, the information obtained from mortars gave as a useful guidance. Strength evolution with time strongly depends on the cement type.

The comparison between samples cast with different w/c ratios and different cement types can be made from the percentage of the compressive strength at any age vs. the 28-day strength. Thus, no matter the actual the strength level, all samples exhibit the same relative value at 28 days: 100 %.

Figure 13-4 represents the relative strength (to 28-day) vs. log. age. From the figure, it is clearly seen that the strength evolution of Calcium-Aluminate based low-pH cement is negligible over 7 day-curing while Portland-cement based low-pH cements exhibit an increase of about 40 % at 90 days.

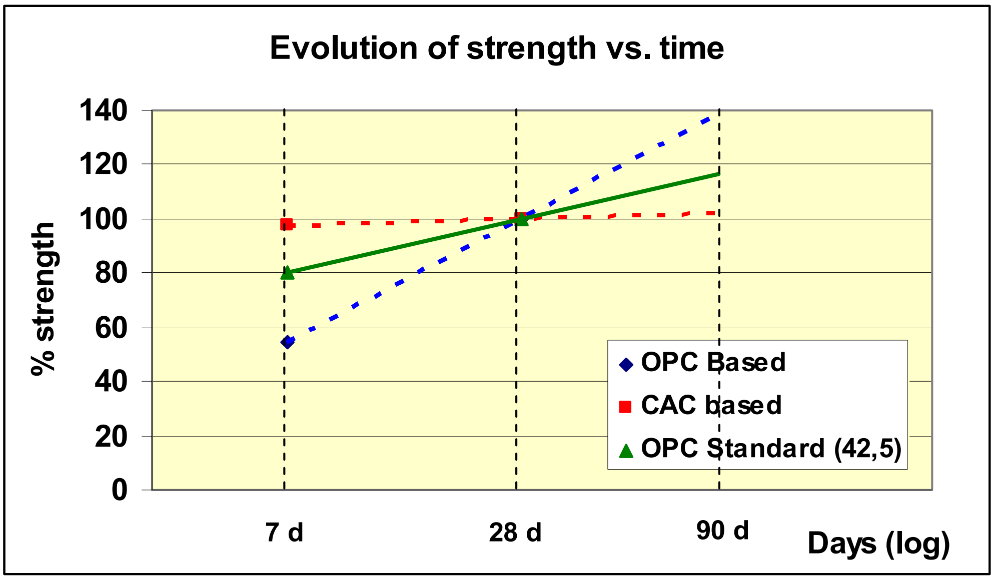

***Figure 13-4**. Relative strength evolution vs. log. time for different cement types*

Table 13-4 summarises the results obtained for the different low-pH cement concretes, at different ages.

Table 13-4. Mechanical properties of base-concrete for shotcrete

	A.3.1	**B.1.2**	**B.3.4**
Compressive strength	**MPa**	**MPa**	**MPa**
7 days	18,3	16,2	11,8
28 days	---	29,0	22,3
35 days	18,7	---	---
90 days	---	20,2 (1)	29,4
Elasticity Modulus (GPa)	15,5 (35 days)	21.7 (90 days)	18.3 (90 days)

Note: (1) this value shows an unexpected decrease of strength. More data are required to give a comprehensive explanation on the matter.

13.8 Large-scale trials. Pumpability and projectability

At Santa Barbara Mining School B12 concrete was prepared at a large scale, using the available facilities. A concrete plant was used to weight aggregates and cement and the chemical admixtures were dosed on a weight basis, using a suitable scale.

The components of the low-pH cements were added separately, i.e, they were not pre-blended in advance. This procedure might ease on-site operations it was supported by experimental evidences.

A statistical analysis of the comparison between pre-blending technique and separately addition to the mixer, evaluated in mortars at the IETcc showed that the difference between both procedures is negligible, as can be seen from **Figure 13-5**, which represents the t-Student distribution for the compressive strength of mortars, made using both procedures: premixed (or pre-blended) and separate addition of the low-pH cement constituents.

Mixing time lasted for more than 5 minutes, and it the total amount of water was established according to the consistency of the mix, in order to consider the humidity of the aggregates.

Concrete was transported with a mini-truck mixer to the pump and samples were taken at the discharge chute, by the concrete pump. The concrete was very workable and cohesive and no difficulties arose related to its pumpability.

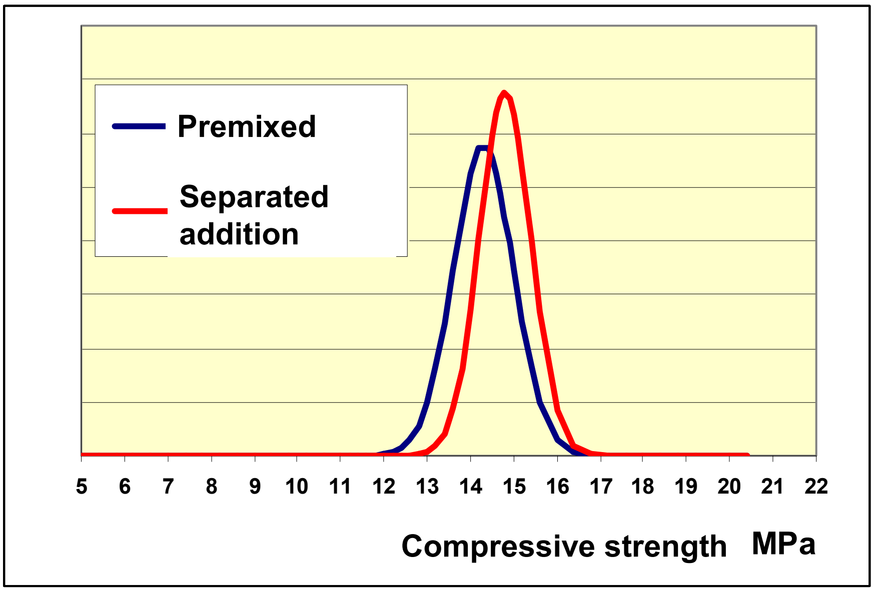

Figure 13-5. *Density distribution (t-Student) for premixed and separated addition in mortar testing*

Fresh concrete samples have been taken and the material was characterised by its slum and the inverted-cone test. The slump measured on site for the B12 concrete was the same as the one measured at the lab. Figure 13-6 shows the fresh concrete at the discharge point and the aspect of the cylinders cast.

The concrete prepared with B12 low-pH cement showed a good projectability, and although the accelerating admixture effective dosage was lower than expected (2 % instead of 6 %), the concrete remained stable on a 13° tilted (from the vertical) panel.

Fresh concrete discharge from the truck mixer to te pump

150 x 300 mm cylinder cast at Santa Barbara

***Figure 13-6**. B12 concrete at the discharge point and aspect of a specimen cast.*

13.9 Conclusions

The designed low-pH cements are suitable to produce concrete, which can be pumped and projected, according to the requirements at the fresh state. Not only the concretes show a good workability and pumpability but the mixes are stable, with a negligible slump-loss and they showed to be robust, i.e., slight changes in mixture proportions and/or batching conditions do not alter essential characteristics.

The results show that it is possible to reach a compressive strength at 90 days in the range 20-25 MPa for conventional concrete, which could lead to a final value in shotcrete of about 10 MPa.

The elasticity modulus obtained is according to that prescribed as functional requirement. For conventional concrete, the final elasticity modulus is about 20 GPa and it is expected a reduction for the shotcreted material.

As far as permeability and temperature rise, further tests are still needed. The results obtained from drilled cores from panels will provide a more accurate figure on the properties of the shotcrete and they will definitely establish its suitability to be used for the low-pH shotcrete plug.

14 Materials for sealing of small fractures

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14.1 Background

In 2001 Posiva from Finland and SKB from Sweden carried out a pre-study on low-pH cementitious material for deep repositories. The next stage was a feasibility study carried out in 2002-2003 in which also NUMO from Japan participated. The feasibility study focused on low-pH cementitious injection grout. As a result of the feasibility study, Posiva, SKB and NUMO found it necessary to separate the development of injection grouts into two types, one for larger fractures, i.e. hydraulic aperture ≥ 100 µm, and one for smaller fractures, i.e. hydraulic aperture < 100 µm. This paper summarises the results of the studies on smaller fractures.

Injection grouts that have been investigated are colloidal silica and periclase (MgO). Swedpower carried out a short review on periclase grouting, which then was deemed to be unreliable as grout. A literature review on silica sol was carried out by NUMO and environmental acceptance and long-term safety studies were carried out at The Royal Institute of Technology (Stockholm) and Swedpower AB (Stockholm). The laboratory work was carried out at the Chalmers University of Technology (Göteborg).

14.2 Silica sol

14.2.1 General

Colloidal silica is a stable dispersion of discrete nonporous particles of amorphous silicon dioxide (SiO_2). The particles have a diameter of 1-500 nm. The colloidal silica can be seen as a base material that can be refined into various products. The product used for grouting purposes is silica sol and the interval of the particle size has been narrowed to range from 5 to 100 nm. To prevent uncontrollable aggregation of the particles the silica sol is stabilised with ions (e.g. aluminium).

The silica sol used in the laboratory tests at Chalmers was Eka® Gel EXP36. It consists of an aqueous solution with SiO_2 35% by weight and is stabilised with aluminium, which is strongly bound to the silica particles. The aluminium concentration (Al_2O_3) is approximately 0.8% of the weight of SiO_2 and 0.26% of the total silica solution. The accelerator is 2.9% by weight $CaCl_2$ and the pH of the silica sol solutions is <10.

When used as injection grout, the silica sol particles shall aggregate and form a strong and solid gel within a predictable time. This is controlled with salt, normally sodium chloride (NaCl) or calcium chloride ($CaCl_2$). The gelling time depends on the amount of salt added and the environment in the grouted rock (e.g. temperature, pressure, groundwater flow and groundwater salinity). The higher salt concentration and temperature is, the shorter gelling time for the sol.

14.2.2 Laboratory work

Since there was little, if anything, known about the basic mechanical properties of silica sol, these were investigated using standard methods for concrete and geotechnical testing at Chalmers in Göteborg (Sweden).

The test specimens were cured in four different environments:

1. +8°C, 100% relative humidity (RH), fully saturated
2. +8°C, 95% RH
3. +8°C, 75% RH
4. +20°C, 50% RH

The reason to choose those environments was to imitate ordinary tunnel conditions. The temperature of 8ºC is common in shallow rock in Sweden. Towards the depth the temperature increases and higher temperatures could also exist as external heat sources, such as nuclear waste. A humidity of 75% is very low in a tunnel and can almost be considered as a lower value that can occur occasionally. Relative humidities of 95% and 100% are more likely to occur in tunnels. The reason for storage of silica sol in 20ºC and 50% RH was to use the standards for cement as much as possible. It was revealed that this was not a relevant environment for investigation of a grout such as silica sol.

Tests of the specimens were done over a period of six months, more often at the beginning of the period and less often at the end of the period. The drying shrinkage measurements were conducted with a slide calliper, a simple and robust method. The shrinkage of the silica sol is larger at low humidities than at high humidities. The drying shrinkage seems to initially have a relatively slow development but after less than approximately one week the shrinkage accelerates. After six months the shrinkage is 2 % for specimens stored at 100 % RH and 25 % for specimens stored at 75 %.

Flexural strength was tested according to the European Standard EN 12390-5:2000 (SIS 2002) for testing the flexural strength of hardened concrete. The tests show a faster increase in flexural strength on specimens stored in a dry environment than a humid.

After determining the flexural strength, the same specimens were used for compressive strength measurement according to European Standard EN 12390-3 (SIS 2002) for concrete. In general, the spread in result between different measurements was small. The compressive strength increased from 0.6 kPa after one day to approximately 5 kPa after a week. Thereafter specimens stored at low humidity showed a more rapid increase in strength development than specimens stored at high humidity. The stress/strain curves showed an initially linear elastic relationship.

To begin with, the failure of silica sol appears to be ductile but when the strength increases the failure becomes brittle.

The shear strength was measured with a fall cone, according to the Swedish Standard SS 027125 for geotechnical tests. The penetration of the fall cone into the test specimen gives an empirically based value of the shear strength. The shear strength was approximately 10 kPa after one day and increased more rapidly for specimens stored at low humidity at similar temperature. The fastest increase in shear strength was noted for specimens stored at 20°C and 50% relative humidity.

At the beginning the increase of strength for silica sol is slow but steady. After a week, the compressive strength is around 5 kPa, irrespective of the storage environment and grows steadily. After some time, depending on the humidity, the increase in strength accelerates. When this rapid increase happens, depends on the humidity. For the specimens stored at 75% relative humidity (RH) the increase appears after 1000 hours and for the specimens stored at 95% RH the increase becomes obvious after 2000 hours. For the specimens stored at 100% RH this rapid increase did not appear during the six months test period.

A drying-out test was carried out to test the hypothesis that some shrinkage occurs near the tunnel due to drying from the air, but the shrinkage is stopped further out in the rock due to the surrounding water. A specially designed test specimen was used, where the water acted on the silica sol with a predetermined water pressure and the leaking water was measured in a measuring bucket. Breakthrough of water was noted after 4-6 days. After breakthrough, the specific flow decreased with time.

The reason why the flow decreased over time is not fully understood. It can depend on either a swelling mechanism of silica sol or that a re-watered silica surface appears thirsty and is then self-healing.

So far, silica sol seems suitable for grouting of smaller fractures. Still there is a need for further investigations of silica sol properties, e.g. behaviour of silica sol under different climatic conditions.

14.2.3 Environmental acceptance and long-term safety

Environmental impact of silica sol

The Swedish producer of silica sol, Eka Chemicals, has prepared a risk assessment /Jansson, 2001a/ where it is concluded that colloidal silica is harmless to the environment. The main risk for workers handling the product is that it is slightly alkaline (pH 9.5-10). Resulting waste can be left as non-burnable waste at the community refuse dump, or left together with concrete waste.

A general description on hazards, safety measures and properties is given in Eka Chemicals Safety Data Sheet /Eka Chemicals, 2004/, where Eka® Gel EXP36 is defined as “Not classified as Dangerous for Health or as Dangerous to the Environment”. In /Jansson & Lindblom, 2003/ it is stated that one advantage of using colloidal silica is that it approved for food contact in USA by the Food and Drug Administration (FDA).

Colloidal silica has been tested in the USA for groundwater protection against infiltration of non-aqueous-phase liquids or other impurities, see e.g. /Persoff et al, 1998/ and /Durmusoglu & Corapcioglu, 2000/.

Banverket, the administrator of the Swedish railway network, has carried out some tests in Hallandsås railway tunnel and evaluated the use of silica sol (Cembinder U22).The evaluation was based on information from the producer Eka Chemicals and on Banverket’s own investigations. Banverket’s environmental risk assessment showed very little environmental impact from the silica sol on the surrounding groundwater and a nearby river. Even with an anticipated loss of 10 % of the injection grout directly to the surrounding water, only a minor change in the chemical composition of the surrounding groundwater is expected. At some sampling points downstream, close to the injection point, an increase in silicon and a small increase in chloride were observed during grouting. No significant increases in calcium or aluminium content were measured, i.e. the natural variation of the groundwater aluminium content was higher than the calculated maximum increase of aluminium caused by injection of silica sol Cembinder U22.

Banverket’s tests verified the estimates of the risk assessments, i.e. less than 50 metres from the injection point all measured concentrations were below the limit accepted for drinking water.

For a gel submerged in water, as a worst case, it is assumed that all the salt (accelerator) will leach out within one week, regardless of whether sodium or calcium chloride is used as accelerator. Thus, if a calcium chloride concentration of e.g. 0.24 M /Persoff et al, 1998/ is used and the mix is 5 parts colloidal silica and 1 part accelerator for each litre of the mix, slightly less than 3 grams chloride per litre mix is released to the surrounding water.

There are worries that aluminium in colloidal silica might be released to the groundwater after gelling. In tests performed by Eka Chemicals on Cembinder U22 the aluminium concentration was measured in a permeate to 0.03 mg/L, as compared to 0.1 mg/L which is the maximum acceptable concentration in drinking water in Sweden.

The release of colloids has been investigated in laboratory experiments at the Royal Institute of Technology in Stockholm, and the results showed that the release of colloids was in all cases < 1 mg/L. This is in agreement with results from groundwater investigations in Sweden, e.g. /Laaksoharju et al, 1995/, showing that the colloid concentration will be insignificant in water containing more than 4 mg/L Ca. The expected calcium concentration in granitic bedrock in a repository will be approximately 10-2000 mg/L. Further, calcium chloride as accelerator will increase the calcium concentration in fractures when grouting.

The bentonite around the canisters can be affected from salt. With the use of calcium chloride as accelerator, silica sol will contribute to transfer sodium bentonite to calcium bentonite. All calcium in the accelerator is “free” in the silica sol and will be released to the surrounding water at a rate depending on the concentration gradient and the surrounding water flow. The impact of calcium in the silica sol compared to calcium in the groundwater and from concrete is dependent on the proportion of available silica sol, concrete and groundwater.

In laboratory leaching experiments the pH of the water in contact with silica sol was in all cases below 11 except for experiments using distilled water, an unlikely situation in the field. Thus, the requirement that the pH should be below 11 is fulfilled /Jansson, 2001b/.

No effects caused by the colloidal silica are foreseen to have any significant influence on the bentonite properties. As mentioned above, no significant release of colloids is foreseen because the calcium concentration in the groundwater is expected to be high enough to suppress colloid formation.

Long-term safety

The compressive strength of a silica sol gel increases over time. Jansson & Lindblom /2003/ refers to experiments by Yonekura showing that the compressive strength increased for up to about 3 years (and continued to increase) from around 0.35 MPa directly after gelling to 1.2 MPa after ca 3 years stored at 20ºC and 100% relative humidity. At the same time practically no dissolution or changes in permeability were observed. Persoff et al /1998/ observed that samples immersed in water continued to gain strength for 1 year.

The stability of the gel is not expected to be significantly influenced by variations in the groundwater salinity. Possible variations in groundwater salinity would however influence the gelling time, thus, it is important to perform sufficient tests with the correct groundwater salinity prior to applying the silica sol in situ.

If the gel is dried, the material will be brittle and have low resistance to mechanical movement. If for some reason the gel dries after being applied in the rock, then rock movements would seriously degrade the gel. If a dried undisturbed gel is resaturated quick tests have shown that it becomes even more brittle and falls apart, but this behaviour and how it affects the properties of the gel is yet to be studied.

14.2.4 Japanese experience

Some Japanese papers were reviewed in the co-operation project between NUMO, Posiva and SKB.

Since 1974 the Japanese government has prohibited the use of all chemical grouts, except sodium silicate (liquid glass). The Japanese studies /Yonekura, 1996/ and /Yonekura & Shimada, 1999/ are mainly focusing on ground improvement, not on grouting of hard rock. The chemical structure and basic characteristics of the materials are well explained in his papers.

14.3 Periclase

Periclase (magnesium oxide) has been suggested as injection grout. A number of databases was searched in order to verify if periclase could be used as injection grout for smaller fractures. In general, the results of the searching were poor. Most results from the searches were from other areas where periclase is used, like pharmaceutics, food, cosmetics, paint, plastics, rubber and elastomers.

The use of periclase as a sole agent in rock grouting seems unusual. Elkem A/S manufactures a product ”Thermax”, consisting of 70 – 100% periclase. They recommend the use of Thermax (periclase) as a temporary water blocker to be able to grout with micro cement after blasting (post grouting).

A general view on Thermax, given by different people, is that it is difficult to steer the set time. When Thermax sets, it sets very quickly, thus it’s a great risk of spoiling the equipment.

The conclusion of the survey on magnesium oxide (periclase) was that it has not been used as a sole agent in rock grouting. The indication from the literature search and discussions with grouting experts was that it couldn’t be recommended to go on with further research in order to develop magnesium oxide as an injection grout for smaller fractures in a deep repository. If magnesium oxide had had a potential as grout for smaller fractures, it seems reasonable to believe that it would already have been marketed as such.

14.4 Conclusions

The construction and operation of a nuclear waste repository requires grouting stability for tens of years, perhaps up to one hundred years. The long-term stability of silica sol gel has not yet been clearly demonstrated. The studies presented in this report have given a better understanding of the gel behaviour, but those studies need to be supplemented with other types of long-term stability tests, e.g., leaching tests, dry-out/wetting tests and behaviour of silica sol under different climatic conditions.

Colloidal silica seems to be a suitable material to seal very small fractures (<0.05 mm). The gel is sufficiently stable to prevent water flow through the sealed fractures. No chemicals are foreseen released in concentrations that would be harmful to the environment. An immediate release of either sodium or calcium and chloride during injection is anticipated, and a small long-term release of silicon cannot be excluded. However, compared to the concentration of these elements in the surrounding water, the effect of these releases is assumed to be insignificant in the long-term perspective. The release of colloids after grouting has been found to be negligible. Silica sol can in all important aspects be considered to pose no threat to human health or the environment.

Magnesium oxide (periclase), which has also been proposed as a low-pH material for grouting, was abandoned because it appears difficult to control its setting time, and it has so far been used only for temporary grouting applications.

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15 Silica sol for sealing of finer rock fractures – field testing

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15.1 Introduction

Sealing demands for deep repositories for used nuclear fuel in crystalline bedrock will be very strict. Although sites with host rock of good quality will be chosen, the high water pressures mean that even small fractures will carry a lot of water. The sealing demands are related to the factors present in ordinary tunnelling projects – a requirement to preserve the ground water table and have an acceptable climate in the tunnel, but also to specific factors related to the use as repository. Up-coning of saline water as an effect of large leakage would give an environment that is not favourable for the bentonite buffer. Local leakages must be kept low so as not to erode buffer and backfill in deposition tunnels.

It has been assumed that fractures down to 50 µm have to be sealed. This is on the limit of what can be achieved with normal cement grouting. In the low-pH project, a cooperation project between SKB, Posiva and Numo, with the task to develop injection grouts with pH below 11, two working lines were pursued; One to develop cementitious grouts for fractures wider than 100 µm, the other to develop non-cementitious grouts for smaller fractures. One obvious choice was silica sol, as investigations on silica sol as sealing agent had already begun at Chalmers.

In the low-pH cooperation project, silica sol was first tested in laboratory, then under controlled conditions in a small field test at the Äspö Hard Rock Laboratory, in an earlier cement grouted pillar. Results showed that the behaviour and penetration was predictable /Funehag, 2004-1/. Based on those results, and earlier results from a test at Hallandsås tunnel /Funehag, 2004-2/, silica sol was taken into production at a road tunnel, the Törnskogstunnel, in the Stockholm area. The performance and results of the Äspö and Törnskogstunnel groutings are here presented.

15.2 Field test at Äspö

15.2.1 Aims and method

A field study was carried out in order to investigate whether the penetration of a Newtonian fluid, as silica sol, can be predicted and verified using numerical models, based on grout properties and hydraulic tests. The field study was conducted in a rock pillar 100 m below surface at Äspö HRL.

The overall methodology was divided into three parts, Figure 15-1:

- Characterisation of the fracture,
- Grouting the fracture with silica sol, design based on the characterisation, and
- Verification of grouting result and evaluation of the penetration length.

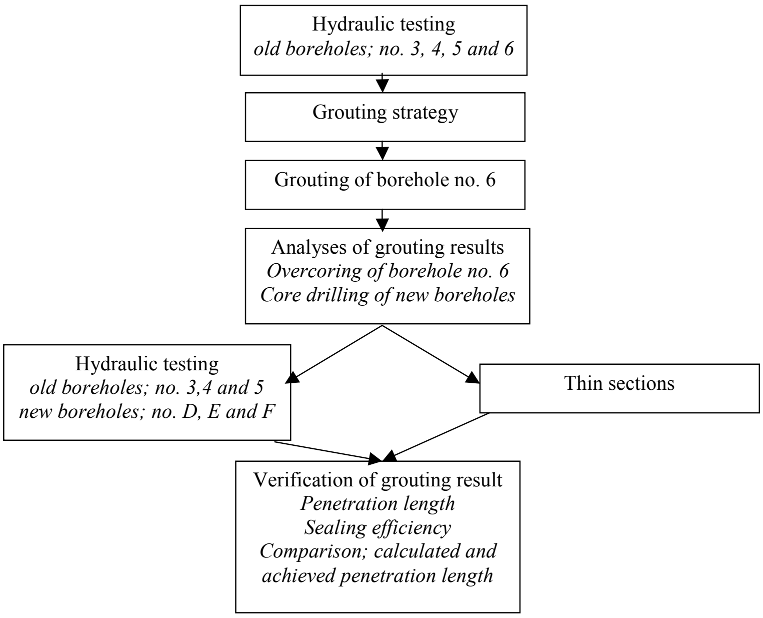

Figure 15-1. *Flow scheme of the used grouting methodology. /Funehag, 2004-1/.*

15.2.2 Site conditions and characterisation

The selected pillar carries water but with low (atmospheric) pressure and was earlier grouted with cement grout, resulting in very limited penetration. It is most likely that only one fracture intersects the grouted section. The evaluation by Fransson /2001/ resulted in a hydraulic aperture of 45 µm. To check the current conditions of the fracture constant head tests were conducted in old boreholes nos 3, 4, 5 and 6, see Figure 15-2. Transmissivity of the fracture was estimated and the hydraulic aperture was calculated by cubic law. Funehag /2004-1/ achieved almost the same results, a hydraulic aperture of 50 µm was assumed.

15.2.3 Grouting design and performance

Essential parameters for silica sol grouting are viscosity and gel time. Given a specific fracture width and pressure, the viscosity decides the “reference time”, i.e. the time it will take to reach a set “reference penetrability length”. Reference length and the connected reference time together with the gelling time decide how far the sol can reach before gelling starts and penetration stops.

Using a one dimensional model; gel time, grouting pressure (0.2 MPa) and time were set to achieve a penetration length of 2.2 metres at 46 minutes not considering tortuosity of the fracture. The grout mix was 8 parts by weight of silica sol (35%) Eka® Gel EXP36 and 1 part $CaCl_2$ (2.9%). An optical brightener was added to the grout in order to make it possible to verify the grout penetration with UV-light.

Grouting was done in borehole no 6 at section 1.1-3.0 m. The first 10 minutes was used for mixing, adjusting pressure and deairation of the borehole. Gel time was checked in the field by taking reference samples of the grout. The grouting continued until the gel time was reached (51 minutes). During grouting, the inflow of the fluorescent grout into borehole 2 was detected with the help of a handheld lamp.

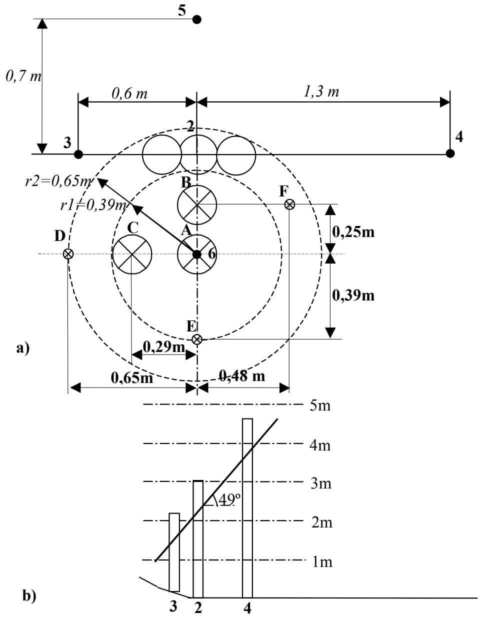

Figure 15-2 *a) A front view of the boreholes in the rock pillar at section 0/670 in the access tunnel at the Äspö HRL. The boreholes 2 through 6 are boreholes drilled in an earlier test /Fransson, 2001/ and /Eriksson, 2002/. Borehole 2 is the location of the cement-grouted hole in the earlier test. Borehole 6 is the silica sol grouted borehole in this test, which was later over cored. The new core drilled boreholes are A (over cored), B, C, D, E and F. b) A schematic plan of how the actual fracture intersects with borehole 2, 3 and 4.*

15.2.4 Verification of grouting results and models

Core drilling parallel to the existing holes was used to verify the penetration. The silica sol in the fracture was detected by visual observation and microscopy. In cores from boreholes B, D, E and F (but not in C) traces of silica sol were detected, which indicates a penetration length of at least 1 m in the fracture.

The microscopy analyses verified that silica sol was apparent in the fracture but did not completely fill it, see Figure 15-3. This might have been a result of stress release when drilling the cores. The methods of preparing the macro specimen could also have degraded the gel. This is indicated from analyses of cross sections of macro specimens where gel was found as a more complete fracture filling towards the depth of the fracture.

Hydraulic tests give additional, more direct information about the effect of grouting. The method and evaluation was the same as used in the hydraulic tests before grouting.

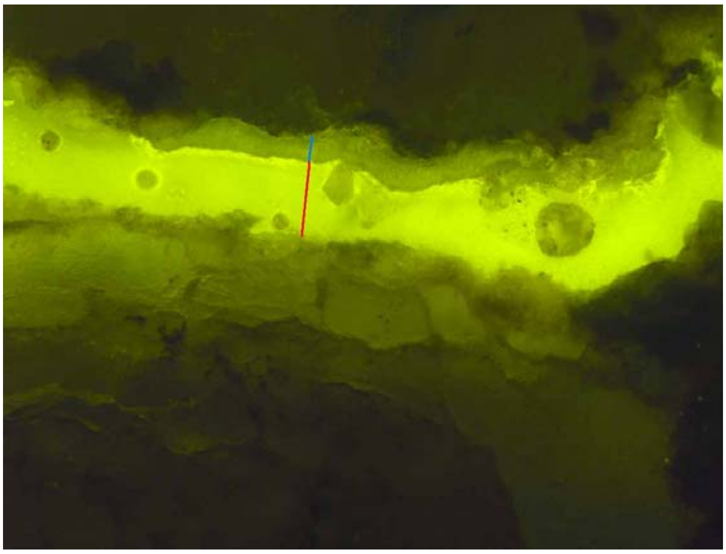

***Figure 15-3**. Microscope photo 50 mm from grouted borehole. The analysed fracture is partly filled with silica sol (transparent dark green) and partly filled with epoxy (fluorescent light green). The measurement profiles are marked with a blue line for the silica sol and red for the epoxy. /Funehag, 2004-1/.*

The median value of the transmissivity before grouting was $1.5 \cdot 10^{-8} m^2/s$. The values of the transmissivities are here seen as representative values of the rock mass before grouting. After grouting the transmissivity was $4.8 \cdot 10^{-9} m^2/s$ representing the transmissivity of the affected boreholes D, E and F. This implies a sealing efficiency of approximately 70%.

The penetration of sol was calculated using a 2-dimensional model. The breakthrough of sol into borehole 2 situated 0.39m away from the grouting hole, appeared after 2 min 30 s grouting. According to the calculations, penetration at 2 minutes would be 0.3m. From the numerical 1-D model it is concluded that the penetration stops long before the gel time is reached. While agreement between observed and calculated penetration was found for the first part of the grouted time, it was found necessary to consider the viscosity development of the sol as modelled penetration was overestimated. The 2-D model considers only constant viscosity of the grout and therefore the penetration was calculated as the average of viscosity for the first 18 minutes of grouting, see Figure 15-4. The same mechanism, that the penetration stops before the gel time is reached, is observed in a sand column test and verified with theory development /Funehag, 2005/.

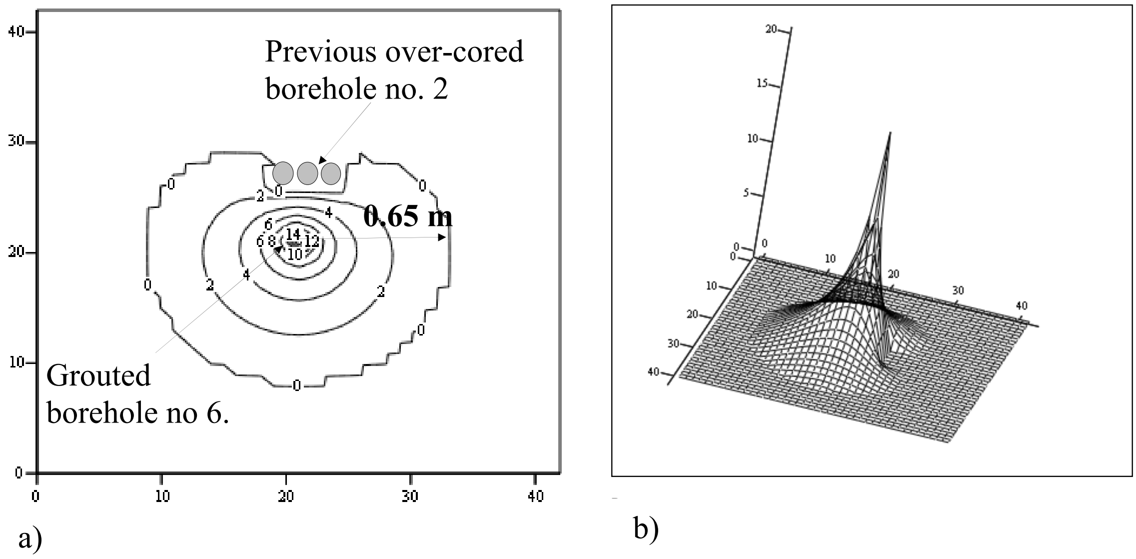

***Figure 15-4**. Calculation of penetration length in the 2-D model. a)The grout front after 18 minutes. The figure shows contour lines of the pressure. The zero pressure line indicates the grout front; in the centre, the 14 pressure line is the grouting hole. The grout has penetrated 13 cells or 0.65 m. b)Figure showing the pressure distribution net after 24 minutes grouting. The penetration has nearly reached 1.15 m.*

15.3 Silica sol in production at Törnskogstunneln

15.3.1 Törnskogstunneln

The Törnskogstunnel is part of a new16 km long road under construction, connecting two major roads just north of Stockholm. The Törnskogstunnel will consist of two 2.1 km long tunnels spanning 11–13 metres. Rock cover is normally 15–25 metres, but passing under depressions down to 5 metres. Those depressions are filled with soil and sensible to settlements as housing and roads are situated here. Thus the requirements on grouting are very high, allowing inflows of only 3 litres/minute and 100m of tunnel.

Given the very strict requirements, it was discussed how to perform a grouting that would achieve the requested tightness. Employer Swedish Road Administration and contractor Oden Anläggningsentreprenad with subcontractor Besab AB having an open dialogue permitting new solutions to be tested, could soon vote for silica sol to be tested at a 100 meter long section under Solängsvägen. Grouting design was awarded Chalmers, representing current knowledge gained in laboratory, at Hallandsås and in Äspö. Follow up was to be conducted jointly by Chalmers and Besab as responsible for the grouting.

15.3.2 Geologic pre-investigations

At Solängsvägen previous results from a core drilled hole were available for further evaluation. Although changes in rock conditions were expected to change rapidly along the tunnel while passing the depression, core mapping, water loss measurements at 3 m sections and Bips – camera survey and mapping of core hole, were considered to form a good basis for judging the fractures that had to be sealed.

15.3.3 Grouting design

Although sealing of tunnels by means of pre-grouting is the traditional way in Scandinavia, the design of the grouting is often primarily set based on experience as the understanding of the system rock mass – grout – technique is not fully developed. Requirements have however become stricter to get acceptable climate in the tunnels and so as to avoid unwanted lowering of ground water table. This has led to development of materials as well as research on how to describe rock properties in a way that is relevant for grouting and on how to predict penetration and sealing results.

The description of the fractures in the rock mass is essential for the grouting design. Based on the water-loss measurements the transmissivities of the measured 3m sections were estimated. However, transmissivities are not known to correlate to the number of fractures, which was also shown in this case. To be able to make use of the data available, they were transformed into a fracture transmissivity distribution assuming a pareto-distribution. Choice of distribution can be discussed; the pareto distribution is chosen as it is characterised by a few extreme values, here signifying a situation, where a few fractures represent a major part of the sections transmissivity, see e.g. Fransson /2001/.

Based on the transmissivities, the hydraulic apertures were calculated. The hydraulic aperture gives a reasonable value of the width possible to penetrate. As seen from Figure 15-5, no less than 98% of the fractures were smaller than 100µm, and thus normally not considered groutable with ordinary cementitious injection grouts. The fractures being wider than 100µm were representing 61% of the leakage before grouting, and by completely sealing them the permeability would be efficiently reduced. However, to achieve the required inflow of 3 litres/minute and 100m it would be necessary to seal fractures down to 0.014mm, according to calculations.

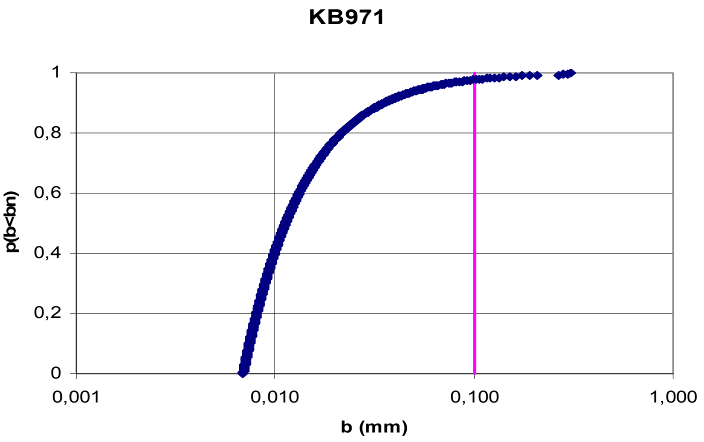

Figure 15-5. *Calculated aperture distribution for borehole KB971.*

In the test grouting at Hallandsås /Funehag, 2004-2/, it was shown that fractures at least down to 0.01mm could be sealed with silica sol. The models used for predicting the penetration were the ones earlier verified at Äspö. Thus, having selected grouting pressure and a sol with known viscosity and a gel time of 45 minutes, it was calculated that the maximum penetration was 1.2 metres for the 0.014mm fracture and the maximum distance between holes was set at 1.5 metres giving a 50% overlap in penetration. The hole geometry and criteria for stopping of the grouting was adjusted giving a fan consisting of 42 holes, but otherwise the original design based on cementitious grout was kept, see Figure 15-6.

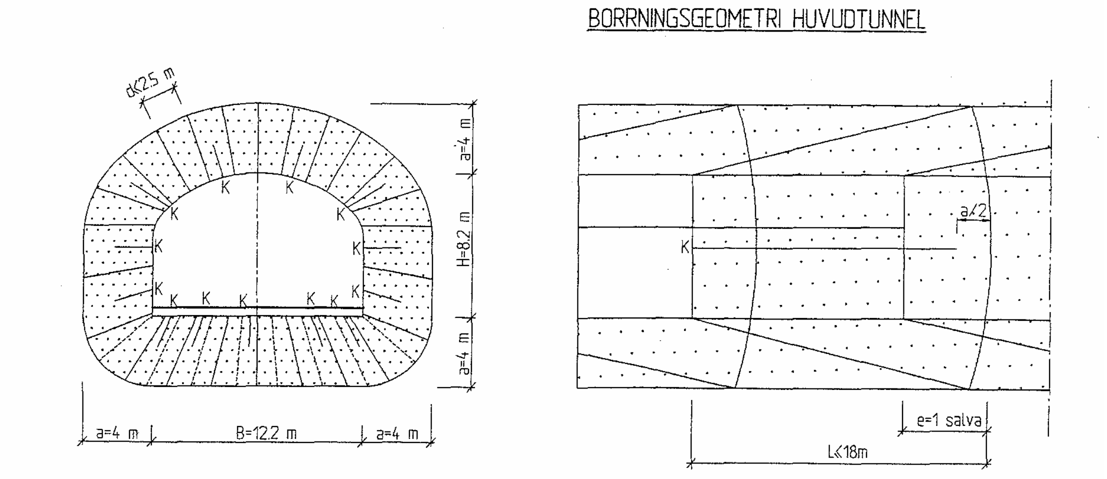

Figure 15-6*. Geometry for grouting, original design based on cementitious grout.*

15.3.4 Performance of grouting

Totally nine fans were grouted with silica sol. Fans 1 and 2 were 42-hole fans, the prognosis being very fractured rock. Grouting time for each hole was 30 minutes after the pressure had stabilised at 1.1 MPa, or the volume of 289 l was reached. However, conditions were much better than anticipated, and as the grouting result was very good, it was considered that the drilling of 42-hole fans was overdoing it.

Fans 3-6 were subsequently drilled using the design originally set for cement grouting with 2.5 metres hole distances, resulting in a total of 25 boreholes in one grouting fan. The standard refusal criterion for grouting was used, being zero-flow at the pressure of 1.1 MPa or having consumed 1000 litres. Fans 3-5 proved successful, while fan 6 hit the poorer rock and gave leakages up to 1 L/min in five of the ten control holes. Staying in the more fractured rock, fans 7-9 subsequently were 42 hole fans.

15.3.5 Results

The inflow from the holes into the tunnel before and after grouting for fan 4 is presented in Figure 15-7. The median inflow for the 25 grouting holes was 0.5 L/minute tested at a pressure of 0.5 MPa. Water losses were measured in five control holes, all being tight, the measure limit set at 0.005 L/minute. Thus sealing the already relatively tight rock lowered the inflow with a factor 100. This corresponds to permeabilities before grouting $k = 1.2 \cdot 10^{-8}$ m/s, and after grouting $k = 1.2 \cdot 10^{-10}$ m/s.

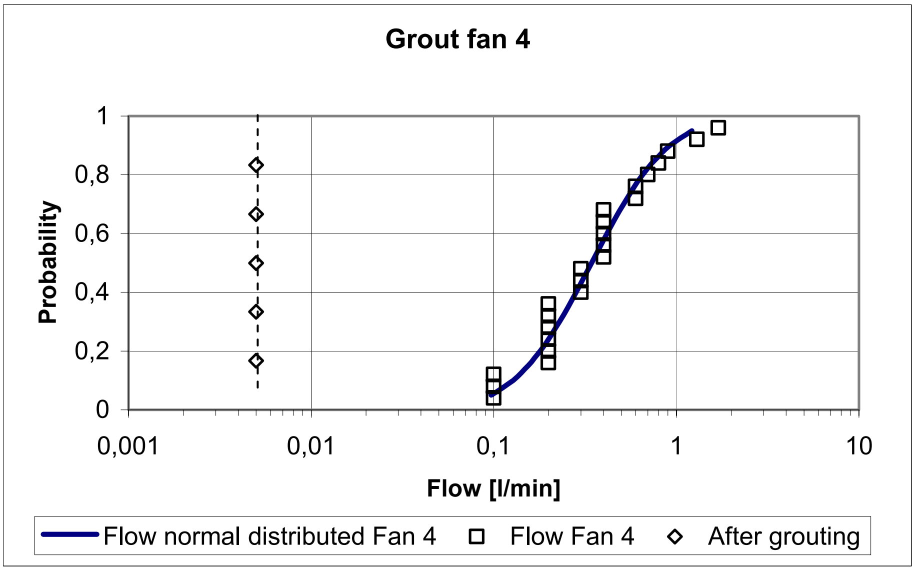

Figure 15-7. Water loss measurements in fan 4, before and after grouting. All five control holes were tight.

Results in the more fractured parts were not as good as for the earlier fans, especially fan 8 which had a much larger inflow before grouting than the other fans. A major part of the grouting holes in fan 8 had inflows around 2-4 L/min and 0.5 MPa, with a highest recording of 10 litres, see Figure 15-8.

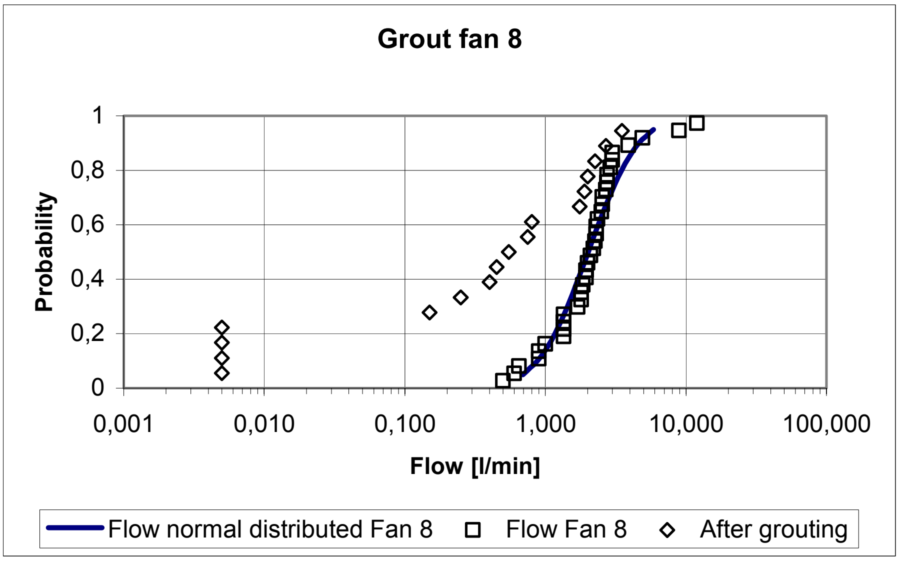

***Figure 15-8**. Water loss measurements in fan 8, before and after grouting. Only 4 out of 17 control holes were tight. Note: Water losses before grouting also being relatively high.*

All inflows, presented as log-normal flows, for the nine grout fans are found in Figure 15-9. As can be seen the inflows are relatively homogeneous for all fans, or around 100 m of the tunnel, except for fan 8.

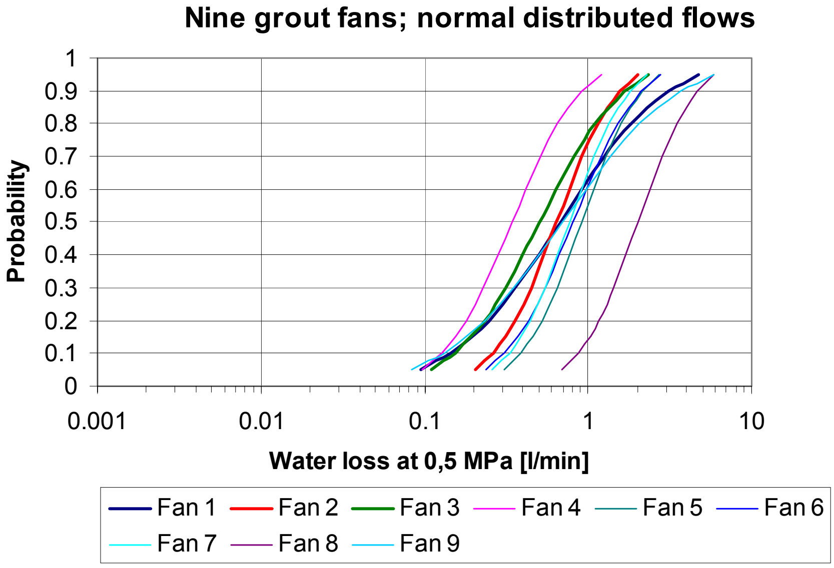

Figure 15-9. *Normal distributed inflows before grouting for all nine grout fans. Note that the inflow from fan 8 is higher than the rest of the fans.*

15.4 Observations and discussion

In the low-pH cooperation project, silica sol was first tested in laboratory, then under controlled conditions in a pilot field test in Äspö, in an earlier cement grouted pillar. Results showed that the behaviour and penetration was predictable. Based on those results, and earlier results from a test at Hallandsås tunnel, silica sol was taken into production at a road tunnel, the Törnskogstunnel.

After an introduction for the workers, the grouting started and was carried out with ordinary grouting equipment. Sol and salt was easily mixed in the agitator. After a couple of fans working procedures went smoothly. It was found important to be careful with the dosage and that the sol and salt should have the same temperature as the rock, as gelling times are easily affected and control of the grouting procedure is depending on gelling times. Due to the low viscosity of the silica sol it is easy to pump and makes the total pumping time per borehole faster than with ordinary cement. The total cycle times for silica sol grouting is the same or faster than for cement due to easy and fast mixing and the relatively short pumping time. The tunnel running parallel to the silica sol grouted tunnel was grouted with ordinary injection grout. A comparison of results for the two tunnels is yet to be done.

In all, silica sol seems to be a promising material, both allowing an effective design and grouting procedure and having good sealing properties. From an environmental and long-term safety point of view objections seem to be few, if any. There is judged to be a potential for improvement by testing different sol-mixes – design and optimising the equipment. Combinations of grouting with cement and with sol could also be considered for more heavily fractured rock. A better knowledge on the material's behaviour related to climate and to durability is also due, before it can be recommended for use in deep repositories.

15.5 References

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16 Programme, June 15, 2005

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9.30 – 10.20 (incl. 20 min discussion)	Margit SNELLMAN (Saanio&Riekkola): **Safety case aspects on use of low pH cement.**	
10.20 – 11.10 (incl. 20 min discussion)	Ola KARNLAND (Clay Technology) Siv OLSSON (Geochemica), Ulf NILSSON (Lund University, Geol department), Patrik SELLIN (SKB) **Experimental study on changes of bentonite mineralogy and physical properties as a result of exposure to high pH solutions.**	
	BREAK	
11.30- 12.20 (incl. 20 min discussion)	Bernhard SCHWYN, Peter BLÜMLING, Lawrence JOHNSON, Urs MÄDER, Wolfgang KICKMAIER (Nagra): **Use of cement in Opalinus Clay and its consequences.**	
	FUNDAMENTALS	
12.20 – 13.00 (incl. 20 min discussion)	Ana HIDALGO, Jose Luís GARCIA, , Maria Cruz ALONSO, Luis FERNANDEZ-LUCO and Carmen ANDRADE (IETcc): **Testing methodology for pH determination of cementitious materials. Application to low pH binders for use in HLNWR.**	
	LUNCH	
14.30-15.20 (incl. 20 min discussion)	Céline CAU DIT COUMES (CEA), P. LE BESCOP (CEA), Maud CODINA (ANDRA), Xavier BOURBON (ANDRA), Stephanie LECLERQ (EDF): **Formulation and characterization of low-pH, high resistance and low-heat concrete.**	

Time	Topic	Chairman/Responsible
	LUNCH	
	FUNDAMENTALS, cont'd	
15.20- 16.10 (incl. 20 min discussion)	Harutake IMOTO, Takeshi YAMAMOTO, , Michihiko HIRONAGA (CRIEPI) and Hiroyoshi UEDA (NUMO): **Properties of low-pH cementitious materials developed and tested by CRIEPI and NUMO.**	
16.10-17.00 (incl. 20 min discussion)	Ulla VUORINEN (VTT Processes): **pH leaching experiments and modelling of results for low-pH grouting cements.**	
	BREAK	
17.10 – 18.00 (incl. 20 min discussion)	Johanna HANSEN (Posiva), Tapani LYYTINEN (ELY Management): **Low-pH grouting cement testing: on the laboratory and in the field.**	
	APPLICATIONS	
18.00 – 18.50 (incl. 20 min discussion)	Torbjörn HUGO-PERSSON (SKB): **Stabilisation and sealing of deep boreholes using low-pH cement.**	
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17 Programme, June 16

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10.20- 11.10 (incl. 20 min discussion)	José L. FUENTES-CANTILLANA (AITEMIN), Fernando HUERTAS (ENRESA): **Potential applications of shotcrete techniques in HLW repositories. Engineering aspects and chemical implications.**	
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11.30 – 12.20 (incl. 20 min discussion)	Luís FERNANDEZ-LUCO, Maria Cruz ALONSO, Jose Luís GARCIA and Ana HIDALGO (IETcc): **Shotcrete development for low-pH cements.**	
	BREAK	
	ALTERNATIVE MATERIALS	
12.20 – 12.40 (incl. 5 min discussion)	Anders BODÉN (Swedpower), Ignasi PUIGDOMENECH (SKB): **Materials for sealing of small fractures.**	
12.40 – 13.00 (incl. 5 min discussion)	Ann EMMELIN (SKB), Johan FUNEHAG (CTH): **Field-testing of silica sol.**	
	COLLABORATION AND FUTURE ACTIONS	
13.00 – 13.20	**Discussions**	Göran BÄCKBLOM
13.20 – 13.30	**Summary** **Closure**	Fernando HUERTAS
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15.00 – 16.00	**Tour of the laboratory facilities**	Maria Cruz Alonso

18 Participants

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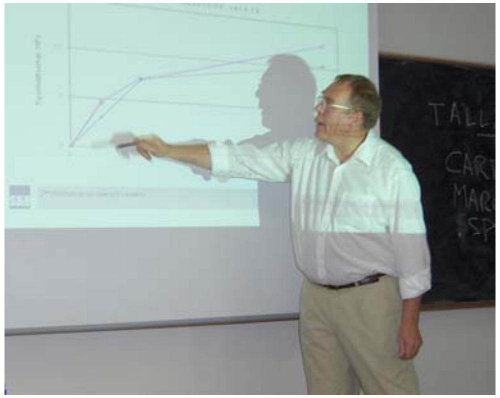
Xavier Bourbon

Russell Alexander

Harutake Imoto

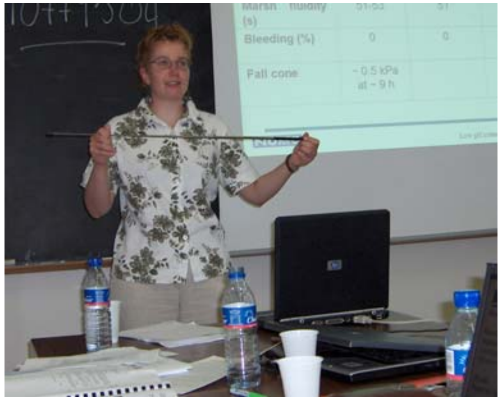
Göran Bäckblom

Wolf Seidler



Torbjörn Hugo-Persson

Ulla Vuorinen



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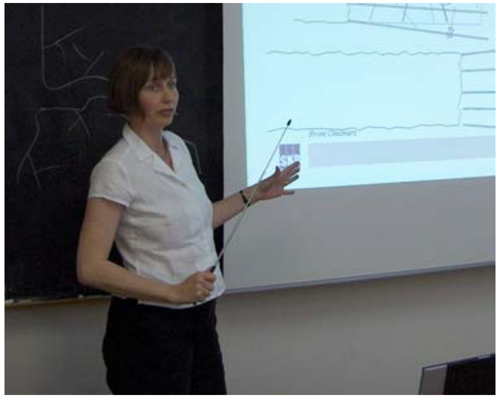

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