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Low-pH injection grout for deep repositories

Summary report from a co-operation project between NUMO (Japan), Posiva (Finland) and SKB (Sweden)

Anders Bodén, SwedPower AB

Ursula Sievänen, JP-Suoraplan Oy

June 2005

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

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Keywords: Low-pH grout, Grout, Repository, Silica sol.

This report concerns a study which was conducted for SKB, Posiva and NUMO. The conclusions and viewpoints presented in the report are those of the researchers and do not necessarily coincide with those of the clients.

This report is also published as Posiva working report No 2005-04.

Preface

This report summarises results achieved in the joint SKB, Posiva and NUMO project "Injection grout for deep repositories". The work has been carried out in four sub-projects with SKB and Posiva as responsible for two sub-projects each. This report summarises the original reporting. Facts within the original reporting have been examined within each sub-project and the reports then approved by the project steering group.

The authors/researchers responsible for the work carried out and the original reporting are: Anna Kronlöf (VTT Building and Transport) – programme, recipes and execution of laboratory work on cementitious grout, Ulla Vuorinen (VTT Processes) – leaching of cement specimens, Reijo Riekkola (Saanio & Riekkola Oy) – requirements on low-pH cementitious grout, Jarmo Lehikoinen (VTT Processes) – modelling on cementitious grout, Harutake Imoto and Taskeshi Yamamoto (CRIEPI) – analysis of solid phases of cement specimens, Maria Cruz Alonso, IETcc – pH measurements of some cement specimens, Aino Heikkinen (CT Group) – grinding and laboratory testing of cementitious grout, Martti Hakanen (University of Helsinki) – effects on radionuclide mobility by organic cement additives, Ursula Sievänen (JP-Suoraplan Oy), Pauli Syrjänen and Susanna Ranta-Aho (Gridpoint Finland Oy) – field-testing of cementitious grouts, Magnus Axelsson and Åsa Fransson (Chalmers University of Technology) – mechanical tests on silica sol, Johan Funehag and Åsa Fransson (Chalmers University of Technology) – field-testing of silica sol, Hiroyshi Ueda (NUMO) – Japanese literature review on silica sol, Kalle Pettersson (SwedPower AB) – literature review on magnesium oxide (periclase) as grout, Börje Torstenfelt (SwedPower AB) – Swedish laws on the environmental aspects on the use of cement and environmental acceptance and long-term safety of silica sol, Mats Jansson and Maria Atienza (KTH, the Royal Institute of Technology) – investigations on colloid releases from silica sol gel, Ursula Sievänen (JP-Suoraplan Oy) – Finnish regulations on the environmental aspects (cement).

Anders Bodén (SwedPower AB) and Ursula Sievänen (JP-Suoraplan Oy) have done the compilation of this report. In some cases whole parts or sections from the original reporting are copied directly into this report, sometimes the information is re-written. References to the persons/organisations that have carried out the work and original reporting (including possible reference to referable report) are only done at the beginning of each chapter in this report. However, for figures copied from a report, a name reference is always given in the figure text.

Each author of the original reporting has reviewed the facts originating from their respective work in this report. The report is approved by the steering group (Stig Pettersson, Ann Emmelin and Ignasi Puigdomenech for SKB; Johanna Hansen, Margit Snellman and Tapani Lyytinen for Posiva and Hiroyoshi Ueda for NUMO) and the project owners at NUMO, Posiva and SKB respectively.

Stockholm June 2005

Stig Pettersson
Chairman of the steering group

Summary

The use of standard cementitious material creates pulses of pH in the magnitude of 12–13 in the leachates and release alkalis. Such a high pH is detrimental and also unnecessarily complicates the safety analysis of the repository, as the effect of a pH-plume should be considered in the evaluation. As no reliable pH-plume models exist, the use of products giving a pH below 11 in the leachates facilitates the safety analysis. Also, according to current understanding, the use of low-pH cement (pH ≤ 11) will not disturb the functioning of the bentonite, although limiting the amount of low-pH cement is recommended.

In earlier studies it was found that shotcreting, standard casting and rock bolting with low-pH cement (pH ≤ 11 in the leachate) should be possible without any major development work. It was also found that the development of low-pH injection grouts had to be divided into two types, one for larger fractures, i.e. hydraulic aperture ≥ 100 μm, and one for smaller fractures, i.e. hydraulic aperture < 100 μm.

Posiva was responsible for the studies on low-pH cementitious grout, while SKB was responsible for the studies on non-cementitious grout.

A result of the project is that there are both low-pH cementitious material for grouting larger fractures (≥ 100 μm) and non-cementitious material for grouting smaller fractures (< 100 μm) that will, after further optimisation work, be recommended for grouting of deep repositories.

This project concentrated on the technical development of properties for the low pH grouts. Long-term safety and environmental aspects and durability of materials were preliminarily considered. Continued evaluations have to be carried out.

The development of low-pH cementitious grout consisted of several tasks. First the potential systems were selected, based on the outcome of the earlier studies and on expert judgement, and the technical properties of some two hundred recipes were tested. The most promising recipes were then selected for pH and leaching tests. Based on these results, the most promising recipes were tested in two small pilot field-tests in Finland.

The material requirements were also considered from an environmental acceptance and long-term safety point of view.

Numerical requirements for the low-pH cementitious grout were set before the grout development started. Based on the experiences achieved in laboratory and in the field, these requirements were later revised.

Five systems, e.g. material combinations, were studied in the project:

1. Ordinary Portland Cement + Silica Fume. “OPC+SF” denotes a binder system that is based mainly on OPC+SF. SF was used in a few commercial forms. The OPC used in this system was mainly UF16 and in some cases Rheocem 900 or white cement.
2. Blast furnace slag. “Slag” denotes an OPC activated slag based system. Alkali and water glass activation were not examined, because of long-term safety reasons. OPC used in this system was rapid hardening Portland cement.
3. Super sulphate cement. “SSC” is a slag-based system activated with gypsum and OPC. The OPC used was rapid hardening Portland cement and the gypsum was a very fine grained slurry product.

4. Low-Alkali Cement "LAC" was introduced to the project by NUMO as a product, ground to fixed fineness by the producer. Neither the mineral composition nor fineness, were modified in the present experiments.
5. Fly ash system was ruled out at an early stage due to expected problems concerning the availability and stability of the raw material properties as well as expected difficulties with the setting time of the mixes.

The grouting related properties tested in laboratory (and methods) were penetrability (filter pump and/or penetrability meter), bleeding (measuring glass), early age shear strength (fall cone) viscosity and yield value (rheometry measurements). For some selected mixes fluidity (Marsh cone) was also measured. The uniaxial compressive strength was also measured, but it is not a grouting property.

The methods for testing pH and the leaching behaviour were "equilibrium tests" and "diffusion tests". Two simulated groundwater solutions were used at the beginning, one saline (OL-SR) and one fresh (ALL-MR). It was soon found that the saline water gave lower pH than the fresh water; so later only fresh water was used, because it gave the conservative values.

The tests on cementitious grouts begun with tests on OPC+SF and slag systems. Slag was activated by OPC only and its content was kept to minimum for pH reasons. SF dosage was based on preliminary calculations and kept to a minimum. Different mixing orders were tested. Penetrability check (filter pump), rheology, bleeding and setting time were tested. The most promising mixes were then tested for pH and penetrability. The penetrability (filter pump) of the chosen OPC+SF mix was within requirements, but the penetrability of the slag mix was slightly above the requirement. The shear strength at 6 h of the OPC+SF mix was too low, while the shear strength of the slag mix was within requirements. The measured pH was too high for both mixes.

In order to get satisfying early strength development, ettringite acceleration (ETTA), using High Alumina Cement (HAC) and gypsum (G) was developed. The OPC+SF system mixes were improved by using large content of SF for pH, high W/DM ratio for penetrability and viscosity and ETTA for setting.

Egyptian low alkali white cement (WCE) was introduced and two mixes were pH-tested, but the alkali content of the cement was found not to be the pH-determining factor.

In order to simplify the number of materials to be handled on site, premixing of components by jet mill was tested with and without dry SF. Premixing the dry SF with cement instead of using GroutAid (silica slurry) deteriorated the penetrability.

Correlation between the chemical composition of the mixes and the results of the pH tests was examined. This gave valuable guidelines for further mix modification.

Slag and SSC activation were developed. The SF content was increased in order to get lower pH. Low pH is detrimental to slag activation, which delays or stops strength development. Activation with both OPC (Slag system) and Gypsum (SSC system) were studied. Two slag batches were not quite as fine and the reactivity not quite as high as it was supposed to be. The results explained how to activate slag to yield the required compressive strength in low-pH mixes and the importance of quality assurance of materials.

A reference mix, UF16, SF and superplasticiser, of known good performance in practical field conditions was included in the studies in order to find a comparison to the cementitious grout mixes developed in this study.

As a result of the laboratory tests, two mixes, one OPC+SF+ETTA and one slag mix, were tested in a pilot field test in a multi-purpose tunnel in Helsinki.

After this first pilot test, slag was ruled out due to high leaching of sulphide observed in leaching experiments. OPC+SF was found too slow in field conditions. Superplasticiser (SP) was regarded necessary in order to decrease the W/DM-ratio and to speed up the setting time. Further mix modification in laboratory was needed and some tens of different mix modifications were tested.

Based on laboratory tests, a few new mixes were selected for batch mixing test in field conditions. Based on those results, one OPC+SF+SP mix was selected for pilot field-test in ONKALO. However, the overall conclusion was that this kind of mix combination could, with further development, be considered for repository grouting.

Japanese low-alkali cement (LAC) was also tested. The supplier recommended the use of citric acid, if retarded hydration is needed. It was found that the penetration ability of LAC was poor. From a long-term safety point of view, the addition of citric acid needs to be evaluated. However, LAC seems to be unsuitable for grouting purposes.

The laboratory tests on the systems showed that alkali content originating from OPC does not directly influence the measured pH in the leachates. In order to achieve $\text{pH} \leq 11$ for the OPC+SF, WCE+SF and slag based mixes, the minimum content of SiO_2 in mixes should be close to or above 50 weight-% of total binder materials or Ca/Si molar ratio should be close to or less than 0.80.

Evaluation of the environmental acceptance was based on a literature study, manufacturers product information specifications, national and European standards as well as Finnish and Swedish laws.

In Finland laws do not directly regulate grouting, but some laws can be interpreted to be connected to grouting via pollution of water or soil, or via using new materials. In Sweden cement is considered a traditional material with well-known properties. The laws that deal with cement are applying to workers health. The national/European standards associated to grouting include no certain regulations, only overall instructions for grouting works. From environmental acceptance point of view, none of the systems were considered to be unacceptable for grouting.

The key uncertainties identified with respect to the use of cement in a repository are related to the uncertainties in the estimation of the range and effect of the pH-plume on the rock, as well as the possible detrimental effects on bentonite due to cement/bentonite interaction. In the present study the potential effects on the repository performance and the rock have been evaluated based on the composition of the materials and leaching tests, expert judgement and some simple mass balance and diffusion calculations. A first review of the potential effects of organic cement additives on the radionuclide mobility has also been done, although the preference at the outset of the project was to develop an injection grout without organic additives. Based on the review, any use of SP needs further evaluation for the specific grout and organic additive being used. Also the long-term durability of the low-pH cementitious material and the long-term phase changes/degradation and leaching of the grout is not yet known and need to be evaluated. All the potential harmful components for long-term safety, in addition to organics, phosphates and nitrogen compounds present, need to be evaluated with respect their potential harmful effect on the long-term safety.

The non-cementitious candidate materials were investigated regarding basic properties and long-term safety aspects in order to form the basis for the decision whether silica sol can be used in the deep repository and whether periclase (MgO) should be further investigated.

In a small field-test it was also investigated if the penetration of silica sol (a Newton fluid) can be predicted based on hydraulic tests, transmissivity and hydraulic aperture.

Silica sol, colloidal silica, is a stable dispersion of discrete nonporous particles of amorphous silicon dioxide (SiO_2). The product tested in this project, Eka Gel EXP36, has a particle size of around 14 nm. When used as injection grout, the silica sol particles shall aggregate and form a solid gel at the set time. This is controlled with addition of salt, normally sodium chloride (NaCl) or calcium chloride ($CaCl_2$). The concentration of the accelerator (salt) depends on the properties of the environmental conditions, e.g. groundwater flow, water temperature, salinity of the surrounding water, etc and on the time required for the sol to gel. When using NaCl, the concentration of the accelerator in solution is normally around 10%. If calcium chloride is used as accelerator, the total chloride concentration is reduced some 75%. Both a higher salt concentration and a higher temperature give a shorter gelling time.

Rock grouting with silica sol is a relatively new application. Silica sol has been used for soil grouting in e.g. Japan. The Japanese experience is that colloidal silica is a durable grout. Test results show that samples were impermeable during a test period of more than 11 years, and that it achieved increasing strength in saline water.

Since there was little known about the basic mechanical properties of silica sol, these were investigated at Chalmers University of Technology using standard methods for concrete and geotechnical testing and the test specimens were cured in four different environments.

The testing of the specimens continued for a period of six months. The tests carried out were drying shrinkage, flexural strength, compressive strength and shear strength. Drying-out tests were carried out in a specially designed test specimen. Strength increase and shrinkage are highly depending on ambient temperature and humidity.

Colloidal silica seems to be a feasible material to seal very small fractures (< 0.05 mm). The gel is sufficiently stable to prevent water flow through the sealed fractures. Colloidal silica can be considered to pose no threat to human health or the environment. No significant release of colloids is foreseen because the Ca and Na ion concentration in the groundwater is expected to be high enough to suppress colloid formation. The salt used as accelerator will not affect the salt levels in the groundwaters expected in the Finnish and Swedish sites.

The long-term stability of silica sol gel has not been clearly demonstrated and it’s favourable to gain a better understanding of its durability and mechanical properties before it can be recommended for repository grouting.

Experiments with silica sol and sand columns show that by assuming that the hydraulic aperture is a good estimate of the aperture of a fracture, the results from the sand column test can be applied to interpret both the penetration length in fractures and the grout characteristics themselves.

A literature review on periclase (MgO) and discussions with grouting experts show that, based on present knowledge, periclase couldn’t be recommended for further studies.

Contents

Abbreviations

ALL-MR = fresh water used in leach tests

b_{crit} = Critical aperture. Mesh width where no clogging occurs (when measured with penetrability meter)

b_{min} = Minimum aperture. Mesh width where practically no grout passes (when measured with penetrability meter)

DIFF = Diffusion test

DM = Dry materials

EQ = Equilibrium test

ETTA = Ettringite acceleration

G = Gypsum

GA = GroutAid

HAC = High alumina cement

LAC = Low alkali cement

NOM = Natural organic material

OL-SR = Saline water used in leach tests

OPC = Ordinary Portland cement (ground in these tests)

RC = Rapid cement, RC10 = Rapid cement ground to d_{98} = 10 µm

SF = Silica fume

SL = Slag (Blast furnace slag), SL10 and SL15 = Slag ground to d_{98} = 10 µm and 15 µm respectively

SP = Superplasticiser

SSC = Super sulphate cement

UCS = Uniaxial compressive strength

UF16 = Ultrafin 16, commercial microcement by Cementa, Sweden

W = Water

WC = White cement

WCE = Egyptian white cement

1 Introduction

When constructing a deep repository, the use of common construction materials, as steel and concrete, are foreseen. With respect to the repository long-term safety, a suitable chemical environment is vital. The use of low-pH products is necessary in order to get leachates with a sufficiently low pH (≤ 11). Hence Posiva from Finland and SKB from Sweden carried out a pre-study in 2001.

In the pre-study, not reported in a referable report, it was found that standard casting and rock bolting with low-pH cement should be possible without any major development work. So, it was concluded that focus should be on grouting. However, there are other international low-pH projects running, for applications other than grouting.

The next stage was a feasibility study, focusing on low-pH cementitious injection grout. The feasibility study was limited to studies on increasing the basic understanding of the properties of low-pH cement, long-time repository function and safety, methods to fabricate cement paste and the technical feasibility of using low-pH grout for rock bolts and for grouting. There were also plans to carry out a small field-test and to plan for a major verifying field-test, but as no usable grout recipe was available, the field-testing was cut out from the project.

The feasibility study was carried out in 2002 – mid 2003. Apart from Posiva and SKB also NUMO from Japan sponsored the studies. The feasibility study is not reported in a referable report.

As a result of the feasibility study, the participating companies 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. In June 2003, the three participating companies NUMO, Posiva and SKB launched the here reported project “Injection grout for deep repositories”. The results in this report are based on research mainly performed at Chalmers University of Technology, Sweden and VTT (Technical Research Centre of Finland), Finland.

2 Objectives

Cementitious grouts are commonly used in conventional tunnelling. The use of standard injection cement paste will create pulses of pH in the magnitude of 12–13 in the leachates and release alkalis. Such a high pH is detrimental and also unnecessarily complicates the safety analysis of the repository, as the effect of a pH-plume should be considered in the evaluation. No reliable pH-plume models exist to define a safety distance. Risks associated with a high pH-plume are related to enhanced dissolution of uranium oxide and impairment of bentonite functioning, and possible alterations in fracture fillings. The use of products giving a pH below 11 in the leachates facilitates the safety analysis.

According to current understanding the use of low-pH cement ($pH \leq 11$ in the leachate) will not disturb the functioning of bentonite, although limiting the amount of low-pH cement is recommended. In the preceding feasibility study it was also found that the development of injection grouts for both larger and smaller fractures as well as testing of them in field was needed. Only the materials with presumable low pH in the leachate were aimed to be studied in this project, and some possible grout systems had been identified in the feasibility study. The current project aimed at achieving some well quantified, tested and approved low-pH injection grouts to be used from the start of the construction of Posiva's underground rock characterisation facility ONKALO, summer 2004, and deep repositories in Japan and Sweden later.

The objectives of the current project were to

- Develop cementitious grout recipes for larger fractures, i.e. hydraulic aperture ≥ 100 μm that gives a $pH \leq 11$ in the leachate. Further the grout should be verified in the field, showing that it fulfils requirements on workability and penetration.
- Develop low-pH non-cementitious grouts for smaller fractures, i.e. hydraulic aperture < 100 μm.
- Test grouting with silica sol in earlier cement grouted fracture at the Äspö HRL.

In order to facilitate a good progress, the project was divided into four sub-projects (SP):

- SP1 – Low-pH cementitious injection grout for larger fractures.
- SP2 – Non-cementitious low-pH injection grout for smaller fractures.
- SP3 – Field testing in Finland (cementitious grouts).
- SP4 – Field testing in Sweden (silica sol).

Posiva was responsible for the execution of SP1 and SP3, while SKB was responsible for SP2 and SP4. The results from the laboratory and field-tests of cementitious grouts (SP1 and SP3) are presented in Chapter 3, and the results of the research, laboratory tests and field-tests of non-cementitious grouts (SP2 and SP4) are presented in Chapter 4.

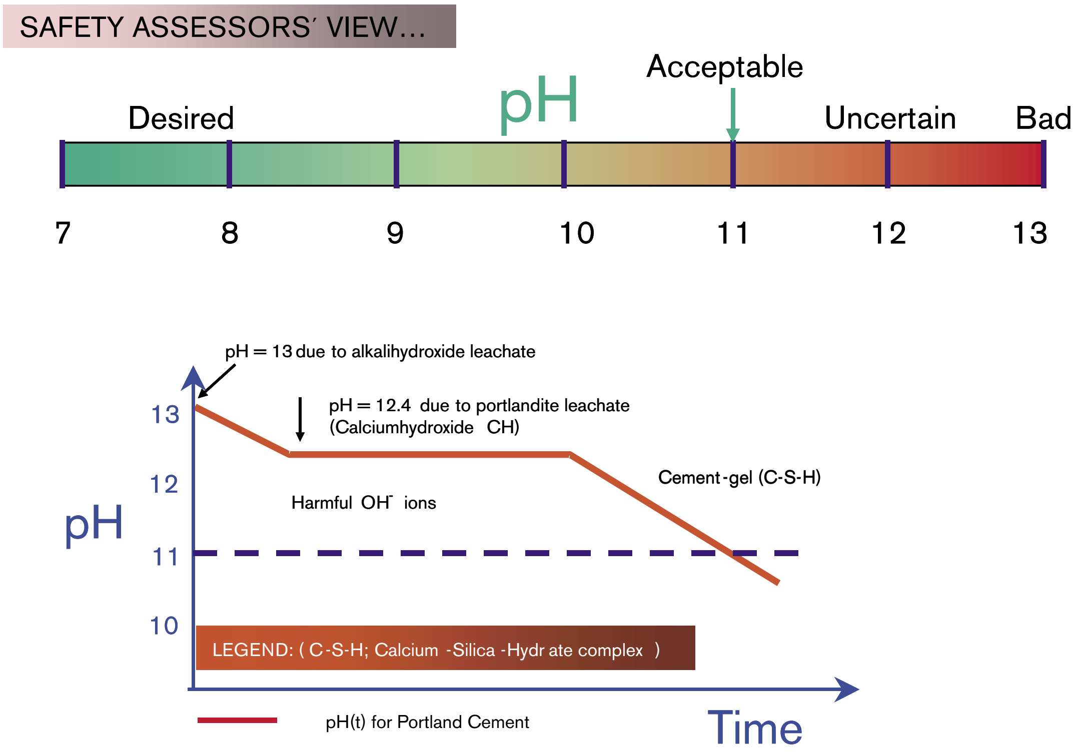

Figure 2-1. *Safety assessor's view on pH, principles for the pH-evolution for Portland cement. Figure by Göran Bäckblom, Conrox AB.*

3 Low-pH cementitious injection grout for larger fractures

The text in this chapter is based on Posiva Working Reports by /Kronlöf, 2004; Kronlöf, 2005; Vuorinen et al. 2005; Sievänen et al. 2005; Imoto et al. 2005/ and work carried out by Aino Heikkinen (CT Group), Reijo Riekkola (Saanio & Riekkola Oy), Martti Hakanen (University of Helsinki), Ursula Sievänen (JP-Suoraplan Oy), Pauli Syrjänen and Susanna Ranta-Aho (Gridpoint Finland Oy) and Börje Torstenfelt (SwedPower AB).

3.1 Introduction

The development of low-pH cementitious grout consisted of several tasks. First the potential systems were selected based on the outcome of the earlier feasibility study and on expert judgement. The laboratory tests consisted of testing the technical properties of the grouts at VTT Building and Construction (VTT, Technical Research Centre of Finland), and testing the most promising mixes for pH and leaching behaviour at VTT Processes. Solid phase analyses were performed at CRIEPI in Japan, and some reference pH measurements were performed at IETcc in Spain. The recipes were planned based on the chemical calculations and recommendations by manufacturers, and then further modified according to the results. The modification included both chemical modification (changes of recipes) as well as modification of the grain size distribution of some components. Grinding and grading was done by CT Group and by VTT. The most promising recipes were tested more comprehensively than those not so promising. In total, some two hundred recipes were tested for technical properties, and ten recipes for their leaching behaviour.

Based on laboratory testing some of the most promising recipes were tested in field conditions in two pilot field tests in a tunnel under Helsinki city and in ONKALO access tunnel.

As a part of sub-project SP1, evaluations of the environmental acceptance and the long-term safety were made.

3.2 Material requirements

The grout requirements were considered from the viewpoints of environmental acceptance, long-term safety, the aimed sealing result and the practicability.

3.2.1 Properties to assure the long-term safety

The basic requirement is leachates with a $\mathrm{pH} \leq 11$. In addition, the amount of organic materials must be minimised and the composition of the grout mixture and its components, especially the content of any harmful components for the long-term safety, must be known to enable the analysis of their impact on the long-term safety.

3.2.2 Properties to assure the environmental acceptance and occupational safety

Grouting materials may cause harmful effects on the environment (or man-made structures) if setting process does not take place properly or if leachates include harmful chemical compounds.

The requirements to assure the environmental acceptance were to use known and acceptable components in the grouts, to achieve enough short setting time and to have acceptable strength of the hardened grout. The occupational safety is assured by using components that are known to have no toxic effects and by using the materials as instructed.

3.2.3 Technical properties to enable reasonable excavation work

A precondition for a reasonable excavation work is that the grout must be practical and economical to use, which is mainly proved in field tests. It is important that the excavation can be continued within reasonable time frames after pre-grouting is completed. The grouting material needs to have sufficient strength to withstand the outward water pressure and to enable continuation of construction activities after pre-grouting. These goals can be achieved by designing the working procedures and by controlling the early strength development of the grout.

Based on calculations, the desired shear strength was set to 500 Pa. This was desired to be reached at 6 hours to enable the continuation of the excavation work at reasonable schedule. While grouting, the viscosity of the grout has a great impact on the time needed to fill the fractures, whereas the yield value has an influence on the grouting pressure. The desired viscosity was set to $\leq$ 50 mPas and the desired yield value to $\leq$ 5 Pa.

Blasting of the tunnel produces vibrations in the rock and pre-grouted zone. It would be good if the grout has plastic properties during the most critical blasting rounds within the first few days after grouting. When the hardening process continues after blasting, the grout is foreseen to possess some self-healing capability for obtaining an intact structure and sufficient strength. The property to affect this is the development of the strength. No requirement was set related to this aspect.

3.2.4 Technical properties to enable good sealing result

To obtain good sealing results the grout should penetrate and fill different kind of fractures and the hardened grout should have low water conductivity. Present understanding is that the lower limit of the apertures into which cementitious grouts can penetrate are in the scale of one tenth of a millimetre. The requirement for the critical aperture b_{crit} was set to $\leq 120\ \mu m$ (measured by penetrability meter). The requirement for b_{min} does not have that much impact on the total tightness of the grouted zone but has an important role in sealing the very small fractures that the grouting holes penetrate. The requirement for b_{min} was set to $\leq 80\ \mu m$.

When the grout has been pumped into a fracture it should fill the fracture as completely as possible to achieve a tight grouted zone. If the cementitious particles of the suspension settle under gravity, a passage for water may be formed. Generally, grouts with a bleed less than 5% are favoured. However, in small fractures the bleed is not considered to be such a critical factor and the value of $\leq$ 10% was desired for bleeding.

The need for a uniaxial compressive strength (UCS) requirement is not clearly understood. In tunnel project specifications, an UCS-requirement on the grout is often set. The requirement was set, because one target was that grouts to be developed should not deviate from standard grouts. It was decided to set a desired value of UCS within the lower range of other more standard grout recipes, and a value of 4 MPa at 28 days was chosen. In cement technology it is found to be a relation between UCS and water conductivity. If this applies to grout in a fracture is not known. There may be a connection between UCS and the groutability to prevent water leakage trough the grout matrix, leading to deterioration of the grout.

3.2.5 Other requirements

The grout was aimed to fulfil other, more general requirements that cannot so far be expressed by numbers:

- The material must be available during the construction and operation of the repository.
- The material or at least its components must have a history of use in cement technology or practical engineering.
- The durability (chemical and physical) properties of the material need to be sufficient so that the grouted zone maintains its required properties during the expected lifetime (which cannot be proven for the new materials within the length of the project duration).
- Material costs (and construction costs) should be reasonable.

The aimed numerical requirements for the low-pH cementitious grout are summarised in Table 3-1. They are classified as required properties and desired properties. During the project these requirements were revised on the basis of the experiences.

The desired workability time practically meant that some properties were measured at 1 h (= workability time). The idea was that the grout should not set too fast and it should tolerate some waiting after mixing before grouted into the bedrock. However, during the project this was regarded unnecessary long and a doubt was raised that some properties suffered from too long workability time. Some mixes were perhaps ruled out although their behaviour may have been acceptable within shorter time frame. This should be reconsidered in further development work.

Table 3-1. Required and desired properties of low- pH cement based grouts.

Order of importance	Property	Requirement	Measuring method
Required properties	pH	≤ 11	Leaching tests.
	Penetrability b_{min}	≤ 80 μm	Penetrability meter at 60 min.
	Penetrability b_{crit}	≤ 120 μm	
Desired properties	Viscosity	≤ 50 mPas	Rheometry at 60 min.
	Bleed	≤ 10%	Measuring glass at 2 hours.
	Workability time	≥ 60 min	Determined by penetrability and viscosity.
	Shear strength	≥ 500 Pa	Fall cone at 6 h.
	Yield value	≤ 5 Pa	Rheometry at 60 min.
	Uniaxial compressive strength	≥ 4 MPa	Uniaxial compressive strength at 28 days.

3.3 Tested systems and used products

The five systems, e.g. material combinations, studied in the project were:

1. Ordinary Portland Cement + Silica Fume. "OPC+SF" denotes a binder system that is based mainly on OPC+SF. SF and cement were used in a few commercial forms. The OPC used in this system was mainly UF16 and in some cases Rheocem 900 or white cement.
2. Blast furnace slag. "Slag" denotes an OPC activated slag based system. Alkali and water glass activation were not examined, because of long-term safety reasons. OPC used in this system was rapid hardening Portland cement.
3. Super sulphate cement. "SSC" is a slag-based system activated with gypsum and OPC. The OPC used was rapid hardening Portland cement and the gypsum was a very fine grained slurry product.
4. Low-Alkali Cement "LAC" was introduced to the project by NUMO as a product, ground to fixed fineness by the producer. Neither the mineral composition nor fineness, were modified in the present experiments.
5. Fly ash system was ruled out at an early stage due to expected problems concerning the availability and stability of the raw material properties as well as expected difficulties with the setting time of the mixes.

The following products were used in the experiments (abbreviations in brackets, number after the cement abbreviation refers to d_{98} value (µm)).

- Ultrafin 16 (UF16), sulphate resistant OPC developed for grouting purposes by Cementa.
- White Portland cement (WCE), ground low-alkali cement from Aalborg Sinai plant.
- White cement (WC10), ground low-alkali OPC from Aalborg plant.
- Rheocem 900, OPC microcement for grouting by Master Builders.
- High Alumina Cement (HAC), ground Secar 71 by Lafarge aluminates.
- Rapid hardening Portland cement (RC10), ground.
- Injekipsi 1 (G), gypsum slurry by Kemira.
- Slag (SL, SL10, SL15), ground blast furnace slag from Raahen Kuonajaloste.
- GroutAid (GA), slurry made of silica fume for grouting purposes by Elkem.
- Silica fume UN 920 (SF 920), condensed (dry) silica fume by Elkem.
- Silica fume UN 938 (SF 938), condensed (dry) silica fume by Elkem.
- G3, dry mix of WCE, HAC, G and SF 938, ground and pre-mixed.
- G4, dry mix of WCE, HAC and G, ground and pre-mixed.
- LAC coarse, low-alkali cement by NUMO, coarse grinding.
- LAC fine, low-alkali cement by NUMO, fine grinding.
- SP40, melamine based superplasticiser by Scancem.
- Meyco SA 161, aluminium salt, shotcrete accelerator by Master Builders.

3.4 Grinding and grading of blast furnace slag and some admixtures

CT Group was responsible for grinding some of the components to desired grain size distribution. Such components were white cement, high alumina cement, rapid cement and blast furnace slag. Dry mixing, i.e. grinding all the materials together was also done in co-operation with CT Group.

Pulva FP micronizing method patented by Micropulva Ltd was used in grinding. Pulva Rex equipment consisted of an opposed jet mill and a micro classification system. Also a compressor and a processor gas drier were needed. The grain size distributions were measured with a laser diffraction method, Cilas Alcatel 850 analyser in Micropulva Ltd.

The target was, that of the raw materials 98% should pass 15 µm and 50% should pass 2.1–2.5 µm.

3.5 Course of experiments and methods

3.5.1 Course of the experiments

The research was planned to proceed in a stepwise manner so that the most interesting systems were to be taken into closer research and the less promising were to be ruled out. The results were examined shortly after testing and the decisions about developing/modifying the systems were made continuously. The pH and leaching tests were made only to the most promising grout mixes.

The work proceeded through a 19-step procedure each giving the necessary knowledge for the next step as listed below (Table 3-2). During the process a number of additions were made to the original testing program.

Table 3-2. The course of the experiments.

Step 1	First tests on OPC+SF and Slag systems	Slag was activated by OPC only and its content was kept to minimum for pH reasons. SF was kept to minimum. Superplasticiser additions and different mixing orders were tested. Penetrability by filter pump, rheology, bleeding and setting time were tested.
Step 2	First penetrability and pH measurements	Most promising mixes were tested by penetrability meter. Based on their overall injection properties one OPC+SF mix and one slag mix were later chosen for the pH test. • The penetrability of the chosen OPC+SF mix was within requirements but that of the slag mix was slightly too poor. • The shear strength at 6 h of the OPC+SF mix was too low, while that of the slag mix was within requirements. • The preliminary pH of both mixes was too high. The shear strength requirement was considered too low as early shear strength development is temperature sensitive. The laboratory temperature was selected based on the conditions, which are normal in the repository (+12°C). However, temperature might vary, and a few extra kPa of shear strength over the given requirement was preferred.

Step 3	Check points	• Something needed to be done to get the pH lower and to increase the shear strength at the age of 6 h (Typical accelerators and superplasticisers were ruled out). • Filter pump was found to be too approximate and penetrability meter was introduced throughout the mix development. • Fly ash was ruled out without testing, other systems were continued.
Step 4	Ettringite acceleration, ETTA	Ettringite acceleration (using HAC and G) procedure was developed, because early strength development was problematic.
Step 5	OPC+SF system + ETTA	OPC+SF system mixes were developed by using • Large content of SF for pH. • Large water to dry materials ratio for penetrability and viscosity. • ETTA for setting (6 h shear strength). Two mixes with differing SF contents were tested for pH, and both were within the requirements.
Step 6	WCE	Egyptian low alkali white cement (WCE) was introduced and two mixes were tested for pH. Alkali content of the cement was found not to be the pH-determining factor, based on the measurements during three months.
Step 7	Premixing	Premixing of components by jet mill was tested with and without dry SF. The aim was to produce a single product and reduce the number of materials to be handled on site. Premixing the dry SF with cement instead of using GroutAid deteriorated the penetrability.
Step 8	Low Alkali Cement (LAC)	LAC tested and completed. The specimens were found not suitable for grouting.
Step 9	pH	Correlation between the chemical composition of the mixes and the results of the pH tests was examined, which offered valuable guidelines for further mix modification.
Step 10	Compressive strength	The requirement for uniaxial compressive strength was set to ≥ 4 MPa. First the testing age was not defined because the strength development rate was not considered critical. The testing age was initially 28 d. Later also 91 d was added to the program. Determining the properties vs. water to dry material ratio (W/DM) was added to 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. 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. The slag was not quite as fine and the reactivity not quite as high as it was supposed to be. The results explained how to activate slag to yield the required compressive strength in low pH mixes and how important is the quality assurance of materials.
Step 13	Slag and SSC systems completed	The development of slag and SSC systems was completed with a slag batch of proper fineness. All properties were tested against W/DM.
Step 14	Reference	A reference mix (UF16+SF+superplasticiser) of known good performance in practical field conditions was tested for comparison.
Step 15	Pilot field test 1	One OPC+SF+ETTA mix and one Slag mix were tested in field conditions.
Step 16	Checkpoint	Slag was ruled out because of too high leaching of sulphide. OPC+SF was too slow in field conditions.
Step 17	Further modification of OPC+SF system with superplasticiser	Superplasticiser was needed to get W/DM lower. A few mixes were found promising based on laboratory tests and they were selected for mixing test in field conditions.
Step 18	Mixing test	As a part of pilot field test 2, the promising mixes were mixed and tested for technical properties in field conditions. No test grouting performed.
Step 19	Pilot field test 2	One OPC+SF+superplasticiser mix was tested in grouting test.

3.5.2 Methods for testing of grouting related properties in laboratory

Testing temperature in laboratory was 12°C, except for compressive strength, which was tested in 20°C. Testing of recipes in laboratory included the following tests:

- Penetrability check by filter pump (100 µm filter).
- Bleeding (water separation) measured by 100 ml measuring glass.
- Early age shear strength measured by fall cone.
- Viscosity determined by co-axial rheometry.
- Yield value determined by co-axial rheometry.
- Penetrability (b_{min} and b_{crit}) of the promising recipes was also tested by a penetrability meter (with different sieve openings).
- Compressive strength determined by measuring the uniaxial compressive strength.

For some of the mixes special properties were determined by the below mentioned methods:

- Fluidity measured by Marsh cone.
- Shear strength (24 hours and 1 week), was done also but these results are not reported here. The testing was mainly done as a guide in which direction to continue further investigations for the different systems.

3.5.3 Methods for testing pH and leaching behaviour

According to the results of technical testing, the samples of the most promising recipes were cast and cured (at 20°C and at 50°C, 50°C was later ruled out). The cured samples were immersed in a CO_2-free leach solution. All samples were tested in duplicates (later the duplicates served as reserve samples in case of doubtful results). Two simulated groundwater solutions were used in leaching tests, one saline (OL-SR) and one fresh (ALL-MR) (Table 3-3). Leaching in saline water was later stopped, because it systematically gave lower pH-values than those in fresh water. Therefore, leaching of samples cured at 20°C in fresh water was thought to give the upper limit for pH. Tests were run inside an anaerobic glove-box (nitrogen atmosphere with low CO_2 ($\leq$ 0.01ppm)) in order to avoid the interference of atmospheric CO_2 on the high-pH solutions.

Table 3-3. Nominal compositions of the two leach solutions used.

		Fresh (ALL-MR)	**Saline (OL-SR)**			**Fresh (ALL-MR)**	**Saline (OL-SR)**
pH		8.8	8.3	HCO_3^-	mol/L	1.1×10^{-3}	
Na^+	mol/L	2.3×10^{-3}	0.21	Cl^-	mol/L	1.4×10^{-3}	0.41
Ca^{2+}	mol/L	0.13×10^{-3}	0.10	Br^-	mol/L		1.3×10^{-3}
K^+	mol/L	0.10×10^{-3}	0.54×10^{-3}	J^-	mol/L		0.01×10^{-3}
Mg^{2+}	mol/L	0.03×10^{-3}	2.3×10^{-3}	F^-	mol/L		0.06×10^{-3}
Sr^{2+}	mol/L		0.40×10^{-3}	B^-	mol/L		0.09×10^{-3}
SiO_2	mol/L	0.03×10^{-3}		SO_4^{2-}	mol/L	0.10×10^{-3}	0.04×10^{-3}

Leach testing of the chosen materials was started with the equilibrium leach test (EQ). A part of the leach solution was extracted and replaced with the same amount of fresh leach solution periodically. The extracted leach solution was filtered and used for measuring the pH-value and, if necessary, also for titration of alkalinity. The amount of leach solution changed periodically was decided on the basis of the groundwater flow-rate in Olkiluoto bedrock. This periodic replacement of the leach solution was considered necessary in the equilibrium test in order to remove the highly soluble initially released alkalis. 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). Equilibrium tests were carried out for 20 to 25 weeks. Equilibrium test was done to 10 mixes, 3 slag based mixes, 3 OPC+SF mixes, 2 WCE+SF mixes, one LAC and reference mixes.

Based on the results of the equilibrium tests – if a low enough pH-value was reached after some weeks of testing – the product was subjected also to the "diffusion test" (DIFF). In the diffusion tests the entire leachate volume was replaced at each exchange point. The exchange frequency decreased with time. DIFF-testing was performed only on five mixes, R52, f63, w1, 44 and L8, representing each type of mix in tests.

The nature of alkalinity (OH^-, or other) in leachate cannot be determined merely from pH, therefore titrations of total alkalinity and some analysis of chemical composition of the leachates were performed. OH-ion content of the solution needs to be known, as it is one main component affecting e.g. the bentonite. The analysed substances were Na, K, Ca, Mg, Al, Si, Cl^-, SO_4^{2-}, S_{TOT} and Fe. Ion chromatography (IC) was used to determine Cl^- and SO_4^{2-} concentrations, K was determined by Flame Atomic Absorption Spectrometry (FAAS) and the rest by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Furthermore solid specimens of four mixes (leached and unleached), R52, f63, 44 and L8, were studied in Japan (CRIEPI) and Spain (IETcc). CRIEPI performed solid phase analyses for four mixes /Imoto et al. 2005/. Qualitative phase analyses were performed by XRD (X-Ray Diffractometry), the chemical composition was analysed by XRF (X-Ray Fluoresence) and the amount of $Ca(OH)_2$ in the solids by TG-DTA (Thermo Gravimetric-Differential Thermal Analysis). EPMA (Electron Probe Microanalysis) was used in analysing the profile of C/S ratio, sample surfaces were surveyed with SEM (Scanning Electron Microscopy) and the pore structure was analysed using MIP (Mercury Intrusion Porosimetry). IETcc measured pore fluid pH values with different methods.

As part of the project thermodynamic equilibrium modelling of the chemical behaviour of cement phases were performed. 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.

3.5.4 Evaluation of environmental acceptance

Evaluation of the environmental acceptance was based on a literature study. Manufacturers' product information specifications were collected. National and European standards were studied as well as the Finnish and Swedish laws.

In Finland grouting is not directly regulated by laws. However, some laws can be interpreted to be connected to grouting via pollution of water or soil, or via using new materials. No Swedish law rules the use of cement or cementitious material. Cement is considered a traditional material with well-known properties. The laws that deal with cement apply to workers health. When using cement, the user must be familiar with the material and know how to handle it. The national/European standards associated to grouting include no certain regulations, only overall instructions for grouting works.

3.5.5 Evaluation of the long-term safety

The feasibility study revealed that low-pH cement can be accepted as a material to be used during the construction of a repository, but it will probably be necessary to set a limit on the quantities to be used. The key uncertainties identified with respect to the use of cement in a repository are related to the uncertainties in the estimation of the range and effect of the pH-plume on the rock, as well as the possible detrimental effects on bentonite due to cement/bentonite interaction. In the present study on low-pH cementitious injection grouts (pH ≤ 11), the potential effects on the repository performance and the rock have been evaluated based on the composition of the materials and leaching tests, expert judgement and some simple mass balance and diffusion calculations. A first review of the potential effects of organic cement additives on the radionuclide mobility has also been done, although the preference at the outset of the project was to develop an injection grout without organic additives.

3.5.6 Pilot field testing

The pilot field tests included a small geological and hydrogeological characterisation (water loss measurements) of the area to be grouted, test groutings, testing of grout properties and observations during grouting (workability, pumpability) and after grouting (quality control by water loss measurements and observations of the leakages after excavation). The grout properties were tested using the following methods:

- Filter pump test to check penetrability (63, 75 and 100 µm sieve openings).
- Marsh cone test to measure fluidity.
- Measuring glass test to measure bleeding.
- Fall cone test to measure shear strength.

3.6 Tests on system 1 – Ordinary Portland cement and silica system

3.6.1 Grouting related properties

OPC+Silica system – First tests

Grouting mixes based on the sulphate resistant cement UF 16 and silica in the form of GroutAid (GA) were modified to reach the required injection properties. The SF/OPC ratio was held constant at 0.30. The mixing order was varied. The first experiments gave information about the effect of W/DM, mixing order and shotcrete accelerator. Also comparative tests with rapidly reacting OPC micro cement were done. The accelerator and the more rapid micro cement were applied to overcome the problem of too slow setting, but they decreased the penetrability.

As W/DM was increased the mix became very clearly more fluid and the shear strength decreased as well. The three highest shear strength values were higher than the requirement but there raised a suspicion if the strength development is enough for practical grouting. The large variation of composition in the mixes barely had an effect on the filter pump values.

This was due to insensitivity of the method when using 100 µm sieve. This observation lead into using the penetrability meter in all tests. The mix chosen to be the most promising and also subjected to leach testing was mix 12 (W/DM = 1.26). All promising (also leached for pH) OPC+SF-mix compositions are given in Table 3-4, and the test results are given in Table 3-5.

Delayed addition of silica made the mix clearly more fluid. Yet, such a procedure was considered too laborious in practice in the field and so "mixing everything together" was preferred. The effect of 1% superplasticiser addition was negligible. Again the modifications did not affect the filter pump results for the reasons given above.

The use of shotcrete accelerator deteriorated penetrability and had none or minor unwanted effect on the other properties. The acceleration did not offer a solution to the slow setting rate problem.

The relatively rapidly reacting OPC micro cement (Rheocem 900) was tested in order to find a solution to the slow setting problem. It was found that Rheocem 900 was not compatible with GroutAid. The penetrability was poor even with high W/DM.

None of the mixes could provide acceptable properties in all respects. The slow setting was not good from the practical point of view.

OPC+Silica system – First penetrability and pH measurements

Four mixes from the previous tests were remixed and tested for penetrability by the penetrability meter. The results were within the requirements. Even though the alternative mixing order (delayed SF addition) made the mixes more fluid it did not affect the penetrability, neither did the addition of the superplasticiser. The setting was too slow. Mix 12 was the most promising one and was chosen to be leach tested for pH.

OPC+Silica system – Ettringite acceleration (ETTA)

An acceleration system based on an early age ettringite reaction was developed for the OPC+SF mixes in order to increase and control the setting rate at the relatively low ambient temperature of 12°C. Typical commercial accelerators such as nitrates NO_3^- were ruled out due to their long-term safety risks (e.g. nitrate is harmful for copper corrosion) and shotcrete accelerator was ruled out due to penetrability reasons. The system was developed for UF16+GA mixes, which were used throughout the experiments. The ETTA components were aluminium cement (HAC) and gypsum slurry (G).

The basis of the system was the accelerating effect of HAC on OPC. The options of either adding or not adding gypsum to the mix were examined. Both ETTA components were applied as fine particles. Different mixing orders were tested.

The ETTA system was first developed with a constant SF/OPC ratio of 0.26, which is relatively low. W/DM was 1.62. Later higher SF/OPC ratios were examined along with higher W/DM.

Increasing the HAC content (HAC/OPC) without gypsum accelerated the strength development. The highest values were more than 100 times as high as the requirement. The penetrability (by filter pump) decreased. The simplest mixing order (water+dry materials, 2 min mixing, (superplasticiser), GA, mixing 3 min) gave the best mixes. The effect of mixing order was more dominant with gypsum present. Again the simplest mixing order was the best. Other mixing orders deteriorated especially the penetrability.

When comparing the results with the best mixing, the penetrability of the mixes with gypsum was better. Increasing the SF content while using ETTA also gave promising results. The shear strength vs. W/DM was not quite as high as with smaller SF/OPC. A similar test was also made with higher HAC dosage, but the results with the lower dosage were slightly better.

OPC+Silica system – Penetrability and pH measurements with ettringite acceleration (ETTA)

To reach the required pH-value the OPC+SF mixes were further modified by increasing the SF content. The SF/OPC ratios applied were 0.69 and 0.94. The mixing order was: water + dry materials, 2 min mixing, GA, 3 min mixing. No superplasticiser was used. The studies gave information about the SF/OPC and W/DM with ETTA (HAC/OPC = 0.075 and 1, G/OPC = 0.027) and also without gypsum.

The results showed that several mixes met the requirements except the yield value. Especially the penetrability results (b_{min} and b_{crit}) were excellent. The mixes f63 and f64 were chosen to be leach tested for pH. The mix compositions and results are given in Tables 3-4 and 3-5.

OPC+Silica system – Effect of W/DM with ettringite acceleration (ETTA)

When the compressive strength requirement was set, the effect of W/DM was preliminarily tested with specimens originally cast but not used in the pH experiments.

After the preliminary compressive strength tests all the properties of the f63 and f64 type of mixes were tested against the W/DM ratio. The b_{min} values ranged from 32 to 63 µm. Both values were within the requirements. The value of W/DM ratio that gives the mix the required properties is about 2.5. Yet, the compressive strength would be slightly too low. Decreasing the W/DM ratio to 2 would increase the viscosity sharply up to 100 mPas, which clearly exceeds the requirement.

The dosage of ETTA can be increased or decreased depending on the needs. As the effect of gypsum alone was found relatively small, ETTA dosage could be regulated with HAC only, while keeping the gypsum content constant.

OPC+Silica system – Low alkali white cement (WCE)

The very low alkali white Portland cement (WCE) was ground to micro cement fineness and tested for all the injection properties. SF in the form of GroutAid was used. The aim was to find answers to the following questions:

- How is pH affected by the low alkali content of the cement material?
- Is it possible to make a penetrable mix with WCE+SF? OPCs are known to behave very differently in the presence of SF.
- Does ETTA work with WCE?

The mixes met the requirements except the yield value. Yet, the yield values were better than in the case of similar UF16+SF+ETTA mixes whereas the setting was worse. More ETTA would be needed on site conditions. Mixes w1 and w2 were chosen to be leach tested for pH. Mix compositions are given in Table 3-4 and results in Table 3-5.

The low alkali cement (WCE) did not produce a mix of lower pH compared to the higher alkali cement (UF16) Thus, the alkaline element content of the cement is not alone the decisive factor for the pH of the leachates. For mix w1 equivalent to mix f63 a pH value of 11.2 was reached after 20 weeks. Mix w2 reached the required pH value, as did the corresponding OPC+SF mix f64.

OPC+Silica system – Effect of premixing of SF with cement

In order to produce a single dry product, the possibility of pre-mixing the ETTA components and dry un-densified SF with cement was examined. Low alkali SF type 983 was used in the experiments.

The results showed that premixing of SF is clearly detrimental to the injection properties. The only exceptions were the viscosity and yield value, which decreased when pre-mixing dry SF. Yet, the reason for this was the agglomeration of SF on cement particles during the pre-mixing, which is not wanted. The result showed quite clearly that GroutAid couldn't be substituted by dry un-densified SF without deteriorating the penetrability.

3.6.2 Summary of technical tests on OPC+SF system

The mix compositions of the most promising grout mixes of OPC+SF system are gathered in Table 3-4. These samples were also sent to leach testing. The results of technical tests in laboratory are presented in Table 3-5.

Table 3-4. The mix composition of the most promising OPC+SF and WCE+SF mixes. Those were also tested for pH.

Mix	Binder	OPC type	SF type	OPC /DM	SF /DM	Gypsum /OPC	HAC /OPC	SF /OPC	SP /DM	Ca/Si molar ratio SiO_2 wt-%	Water /DM
12	UF16-SF	UF16	Grout-Aid	0.77	0.23	0.000	0.000	0.30	0.00	1.35 Ca/Si 39.5 wt-%	1.26
f63	UF16-SF with ETTA	UF16	Grout-Aid	0.56	0.38	0.027	0.075	0.69	0.00	0.83 Ca/Si 49.3 wt-%	2.48
f64	UF16-SF with ETTA	UF16	Grout-Aid	0.49	0.46	0.027	0.075	0.94	0.00	0.65 Ca/Si 54.9 wt-%	2.91
w1	WCE-SF with ETTA	WCE	Grout-Aid	0.56	0.38	0.027	0.075	0.69	0.00	0.85 Ca/Si 50.0 wt-%	2.48
w2	WCE-SF with ETTA	WCE	Grout-Aid	0.49	0.46	0.027	0.075	0.94	0.00	0.67 Ca/Si 55.5 wt-%	2.91

Table 3-5. The results of the technical tests of the most promising OPC+SF and WCE+SF mixes.

Mix	Bleeding (%)	6 h Shear strength (kPa)	b_{min} (μm)	b_{crit} (μm)	Viscosity, Bingham (mPas)	Yield value, Bingham (Pa)
12	0	0.2	63	108	55	22
f63	0	3.7	44	65	50	21
f64	0	3.4	44	63	40	16
w1	0	1.3	49	103	35	8
w2	0	1.1	47	102	28	7

3.6.3 Leaching and pH

The leach tested OPC+SF mixes were 12, f63, f64, w1 and w2 (compositions given in Table 3-4).

The equilibrium testing of mix 12 was interrupted, as a descending trend in the pH-value was not observed after ten weeks (Figure 3-1). The pH in ALL-MR water showed values between 12–12.3 and in OL-SR water the values were between 11.8–12.2. Total alkalinity in EQ-test was high in both leachates and for both curing temperature specimens; increasing from the initial 10 mmol/l up to about 27 mmol/l after four weeks of leaching. High alkalinity was expected, as the pH was also high.

In EQ-tests in both OPC-silica-ETTA mixes f63 and f64 (cured at 20°C) the target pH of about 11 was reached in the fresh ALL-MR, after 20 weeks with mix f63 (Figure 3-2) and after 2 weeks with mix f64 (Figure 3-3). In the saline OL-SR the corresponding pH values were about 10 for both mixes. Samples cured at 50°C were also tested for pH and the results were clearly below the target value.

DIFF-test was performed on mix f63 (Figure 3-2). In ALL-MR (20°C specimen) an increase was observed in the beginning of testing and only towards the end of testing the pH values gradually declined during the last equifrequent leachate exchange period. The target pH-value of 11 was reached at the end of testing. The pH values in OL-SR were about 0.5 pH units lower than in ALL-MR and already from the beginning of testing well below 11, around 10.5. The last value measured was about 9.7. The specimen cured at 50°C showed a different behaviour. In ALL-MR for mix f63 the trend was increasing, whereas in OL-SR it varied slightly around 9.8. At the end of testing the pH values increased slightly.

In EQ-testing mixes f63 and f64 were tested for total alkalinity in both leachates with both curing temperature specimens. The alkalinities varied between 1 and 4 mmol/l for mix f63 and between 1 and 3 mmol/l for mix f64. Lower alkalinities were measured in OL-SR. However, in the case of mix f64 the total alkalinities of both curing temperature specimens showed slightly increasing or at least constant value in ALL-MR even if the corresponding pH-values slightly decreased.

In DIFF-testing of f63 only a few alkalinity values were measured in both leachates for the lower curing temperature specimens. The alkalinity values in ALL-MR increased to about the same level (2.4 mmol/l) as in the equilibrium test after staying in the leachate for a longer period after the more intense equifrequent exchange period, while in OL-SR the values were a little lower, about 0.5 mmol/l.

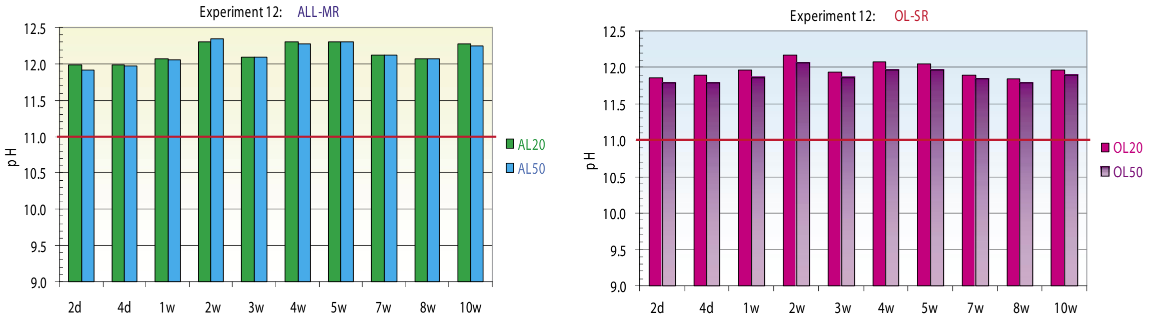

Figure 3-1. pH results of mix 12 in equilibrium tests /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL to the fresh water (ALL-MR) and OL to the saline water leachate (OL-SR).

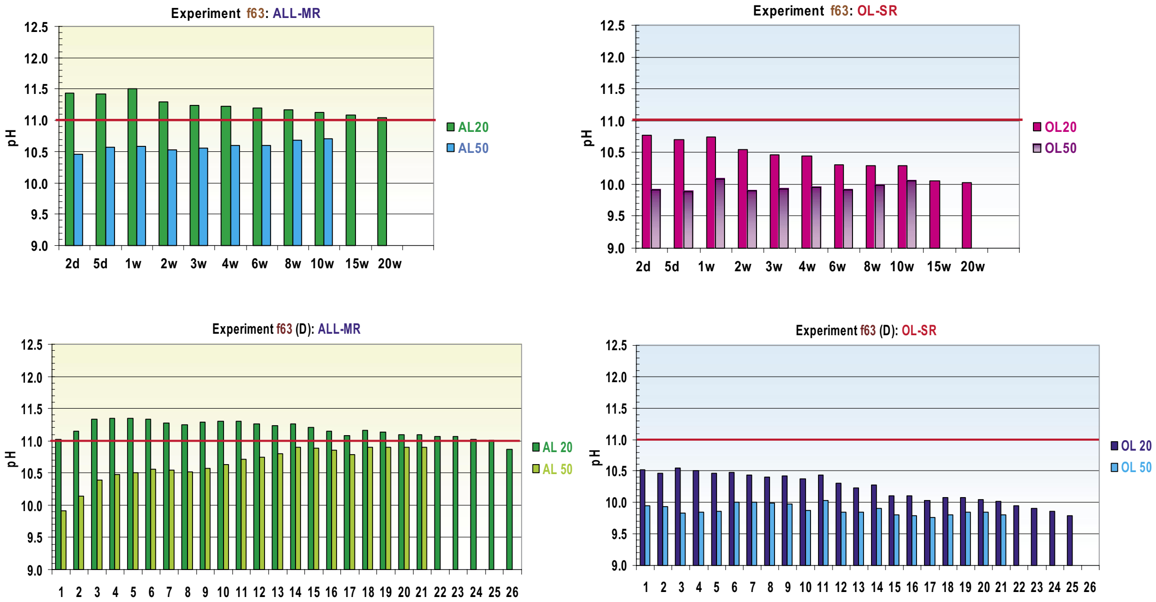

***Figure 3-2.** pH results of mix f63 in equilibrium tests (above) and in diffusion test (below) /Vuorinen et al. 2005/. The x-axis in each histogram gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL and OL to the leachates.*

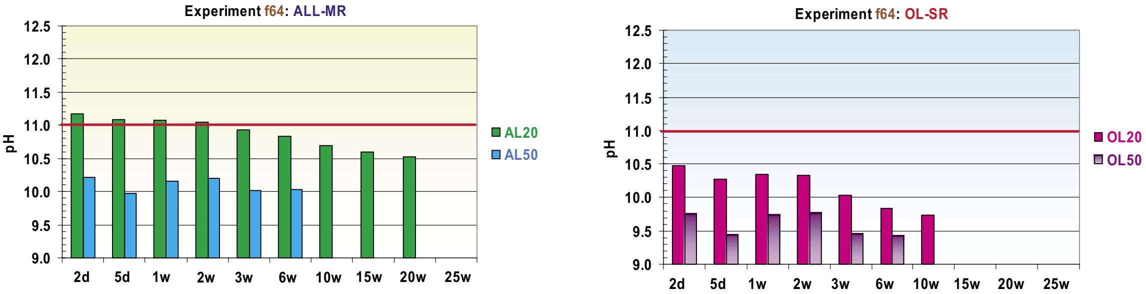

***Figure 3-3.** pH results of mix f64 in equilibrium tests /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL and OL to the leachates.*

For WCE-SF-ETTA mixes w1 and w2 pH values in the leachates were anticipated to be lower than those for mixes f63 and f64, due to lower alkali element content, but the values measured in EQ-test (Figures 3-4 and 3-5) in both leachates were about the same in the beginning for the specimens cured at 20°C, but higher for specimens cured at 50°C. The pH values reached at the end of testing remained slightly higher for these mixes than for the f63 and f64 mixes. This indicates that the alkaline element content of the cement is not alone the decisive factor in the resulting pH of the leachates. The target pH value of 11 was reached in all other cases except in ALL-MR for mix w1. The last pH value measured after 20 weeks of testing was 11.2 (cured 20°C). Generally the pH level measured was higher for the samples f63 and w1 with a higher Ca/Si molar ratio and lower SiO_2 wt-% (Table 3-4) as compared to the samples f64 and w2 with a lower Ca/Si molar ratio and higher SiO_2 content.

The alkalinities varied between 0.8 and 3 mmol/l for mix w1 and 0.8 and 3.6 mmol/l for mix w2. Mix w2 alkalinities showed a different behaviour as the total alkalinities increased with decreasing pH values and the alkalinity values at the end of testing were higher, especially in ALL-MR, than for mix w1 even if the SF/OPC ratio was higher.

Mix w1 was subjected to diffusion test (Figure 3-4). In DIFF-test in ALL-MR (20°C specimen) an initial increase in pH was observed in the beginning of testing and only towards the end of testing the pH values gradually declined during the last equifrequent leachate exchange period. The pH values for mix w1 were slightly lower than for mix f63. The pH values in OL-SR were about 0.5 pH units lower than in ALL-MR and already from the beginning of testing well below 11, around 10.5. Similar declining trend at the end of testing was observed as in ALL-MR. The last value measured was about 9.5 for mix w1. In DIFF-test the total alkalinity values were at the end slightly lower, 1.5 mmol/l in ALL-MR and 0.4 mmol/l in OL-SR when compared with the results from EQ-testing.

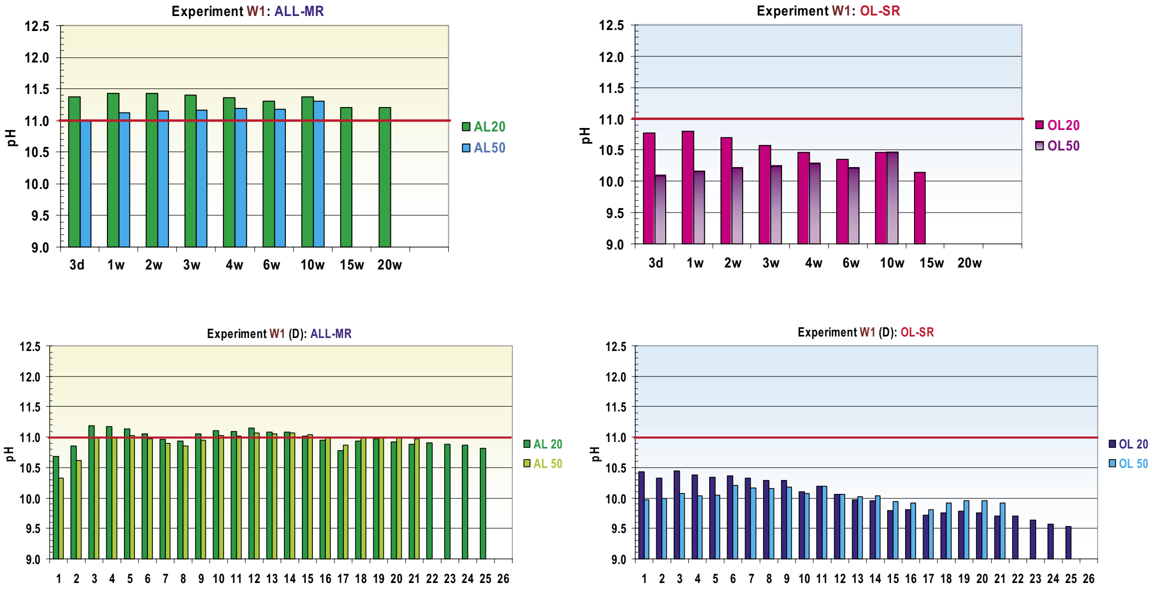

Figure 3-4. *pH results of mix w1 in equilibrium tests (above) and in diffusion test (below) /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL and OL to the leachates.*

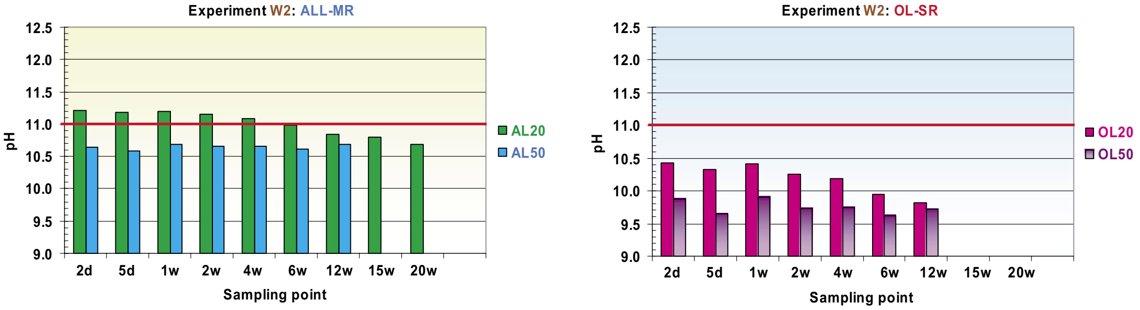

Figure 3-5. *pH results of mix w2 in equilibrium tests /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL and OL to the leachates.*

3.7 Tests on system 2 – Slag (first tests)

3.7.1 Grouting related properties

A number of preliminary tests were run to study the basic injection properties of ground slag (SL). The OPC was ground Finnish rapid hardening cement (RC). SF was used in form of GroutAid. The following items were studied: The effect of OPC/SL, the effect of superplasticiser (SP), the effect of OPC-type, the effect of mixing order with and without SP and the effect of W/DM.

The tests on OPC/SL ratio showed that the setting was too slow. The attempts to accelerate setting by increasing the OPC/SL ratio while keeping the W/SL ratio constant showed that increasing OPC content did not accelerate setting but made the mixes stiffer.

Superplasticiser reduced viscosity as expected. The most striking effect was that of the mixing order: The delayed GroutAid addition clearly gave a more fluid grout. This was most pronounced in the more silica rich mixes. However, further studies on mixing order were not carried out.

Some mixes were selected to penetrability meter tests. The mixes were relatively fluid, but the penetrability was poor as well as the setting. The setting was within the target, but too slow for practical grouting. Mix 44 was selected to the pH test. The mix composition of mix 44 is presented in Table 3-6 and the results of technical tests of mix 44 are gathered in the Table 3-7.

Table 3-6. The mix composition of the Slag mix 44.

Mix	Binder	OPC type	SF type	OPC /DM	SF /DM	SL /DM	G /DM	SF /SL	OPC /SL	Gypsum /SL	Superpl /DM	Ca/Si molar ratio SiO_2 wt-%	Water /DM
44	Slag-RC10-SF	UF16	Grout-Aid	0.04	0.16	0.80	0.00	0.20	0.05	0	0.00	0.81 Ca/Si 44.8 wt-%	1.36

Table 3-7. The results of the technical test of the Slag mix 44.

Mix	Bleeding (%)	6 h Shear strength (kPa)	b_{min} (µm)	b_{crit} (µm)	Viscosity, Bingham (mPas)	Yield value, Bingham (Pa)
44	0	1.3	61	136	32	7.9

3.7.2 Leaching and pH

The composition of the leach tested slag mix 44 is shown in Table 3-6.

With the slag mix 44 the measured pH values (EQ-test) stayed at quite constant level throughout the test period of 20 weeks; in ALL-MR around 11.5 and in OL-SR 10.7 for the specimens cured at 20°C and for higher curing temperature around 11.3 and 10.5 respectively (Figure 3-6).

In EQ-testing the total alkalinity values were determined for both curing temperature specimens in both leachates. The obtained total alkalinities varied between 1.5 and 5.5 mmol/l. One reason for the higher values could be sulphide. The alkalinities initially increased and thereafter gradually declined. However, deviating from the behaviour of

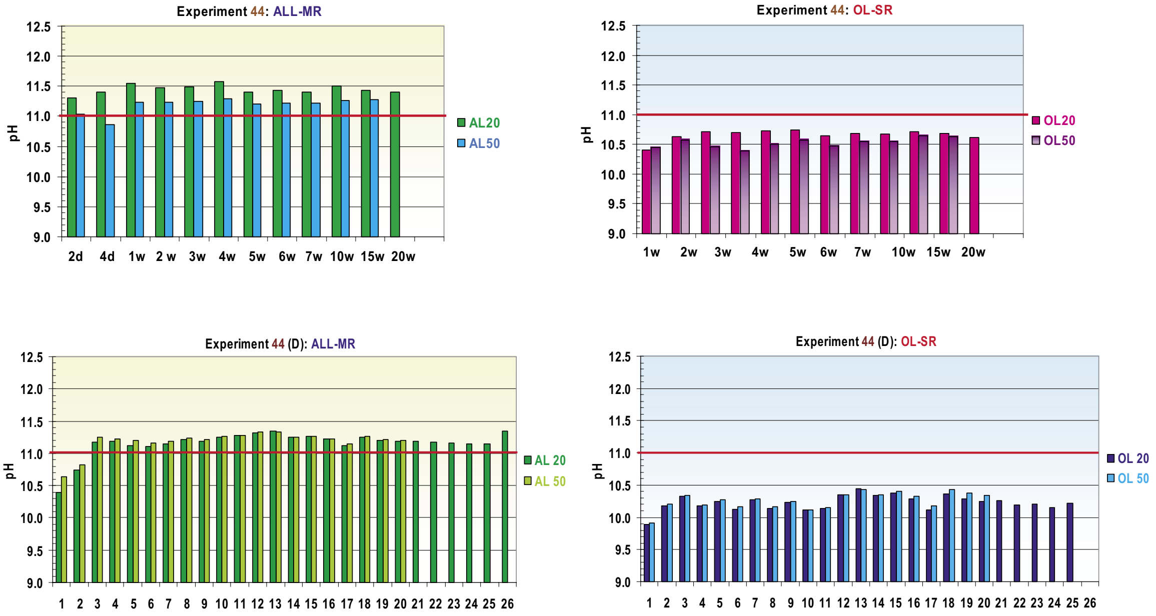

Figure 3-6. *pH results of mix 44 in equilibrium tests (above) and in diffusion tests (below) /Vuorinen et al. 2005/. The x-axis in each histogram gives the time of sampling in days or weeks. 20 and 50 refer to the curing temperature and AL and OL to the leachates.*

all the other mixes similarly tested, the specimen cured at 50°C showed distinctly higher alkalinities in the saline OL-SR than the lower curing temperature specimen. Also in ALL-MR the alkalinity values show a similar behaviour at the end of EQ-testing.

In DIFF-test the pH values initially increased above 11 and remained around 11.3 in ALL-MR and between 10.2 and 10.5 in OL-SR without any clear trend. The higher temperature specimens of mix 44 did not behave differently from the lower temperature ones. During the more intense exchange period the alkalinity values were slightly lower than in EQ-testing, about 2 mmol/l in ALL-MR and 0.4 mmol/l in OL-SR. But at the end of testing the alkalinity increased in ALL-MR even to a higher value, 4.6 mmol/l, whereas in OL-SR it remained at the low value.

3.8 Tests on systems 2 and 3 – Slag and super sulphate cement

3.8.1 Grouting related properties

Once the requirement for the compressive strength was set, the work was focused on the activation of slag, because the strength gain and the low pH of the final product are conflicting requirements. Earlier experiments on slag showed that besides for compressive strength the mixes needed to be improved also for penetrability, setting and pH. Lowering the pH with more silica would inactivate slag even more, and SF would also increase the water demand and thus retard setting. The aim of the slag experiments was to find answers to the following questions:

- What would be the safe SF dosage from the pH point of view?
- Can slag be activated with OPC only while using dosages that would produce the low pH required?
- How can ETTA be applied to the slag system in order to accelerate setting?

- Is super sulphate system needed to increase the strength development?
- What is the gypsum content needed in the super sulphate system?
- Is NaOH activation needed to start the reactions?
- What is the effect of W/DM on the properties?

The SF content was increased to ensure the total SiO_2 content of 50.5–54.5% by weight throughout the series. SF/DM ratio was about 0.3 throughout the series. OPC/SL ratios used were 0.05 and 0.1.

Two ground slag batches were used namely SL15 and SL10/3. The OPC used in these tests was Rapid cement (RC) ground to d98 = 10 µm. SF was used in form of GroutAid. The mixing order was: water+slag+OPC+gypsum, 2 min mixing, (superplasticiser,) GA, 3 min mixing.

The following studies were made with Slag SL15: the effect of ETTA, the effect of aluminium cement, the effect of gypsum and the effect of gypsum and NaOH. With Slag SL10 the following studies were made: the effect of OPC/SL, the effect of gypsum and the effect of W/DM.

The mixes with ETTA (HAC) showed that by increasing the ETTA content while keeping their ratio constant accelerates setting quite clearly. Unfortunately there was no compressive strength development what so ever by the age of 28 d. Testing the effect of excluding OPC in the presence of HAC proved that OPC is needed for setting. Again no compressive strength gain was observed at the age of 28 d. Experiments on increasing gypsum content led again to similar result. The overall conclusion was that any presence of HAC depresses slag strength development.

The mixes without ETTA (HAC) all showed strength development. The effect of gypsum on strength development was positive. Yet, there was an unexplained minimum at the 3% gypsum dosage. NaOH showed no acceleration, which ended the interest to the originally questionable alkali activation. The setting of all mixes was relatively slow. Gypsum seemed to depress it even more.

The b_{crit} values were generally slightly over the requirement while the b_{min} values were within the requirements. Mix S14 was selected to closer examination as the new finer slag batch arrived. The identical mix with the finer slag batch was named S26. Mix S14 was also sent to pH tests. The mix compositions of the most promising mixes are presented in Table 3-8 and the results of them in Table 3-9.

The super sulphate system was found to be an effective way of activating slag with the relatively low OPC/SL ratio of 0.05:

- The compressive strength was doubled compared to the mixes without gypsum.
- On the contrary, setting was delayed by gypsum.
- Increasing the gypsum content over the G/SL ratio of 0.16 did not produce any benefits.

When using the higher OPC/SL ratio of 0.1, the behaviour of the mixes did not differ significantly from that of the mixes with the lower OPC/SL ratio of 0.05. Actually higher OPC-content did not provide any benefits to the mix properties. Only a slight acceleration of setting (shear strength) was observed, but it was not significant.

A fluidity measurement with the Marsh cone was introduced to some slag experiment. The results referred to the high yield values of the studied mixes. The Marsh cone values were not further examined.

The slag batch SL/2 was also tested, but the penetrability results were fluctuating in a random manner due to material failure: A certain amount of oversized particles were present, which were able to block the sieves of the penetrability meter very efficiently. The fraction of large particles (> 63 μm) was 0.3%. The observation of oversized particles is significant, while planning the quality control of ground grouting products:

Table 3-8. The mix composition of the most promising Slag and super sulphate cement mixes.

Mix	Binder	OPC type	SF type	OPC /DM	SF /DM	SL /DM	G /DM	SF /SL	OPC /SL	Gypsum /SL	Superpl /DM	Ca/Si molar ratio SiO_2 wt-%	Water /DM
S14 and S26 1)	Slag-RC10-Gypsum-SF	RC10	Grout-Aid	0.029	0.29	0.59	0.093	0.50	0.05	0.16	0.00	0.60 Ca/Si 49.5 wt-%	1.57
S20c	Slag-RC10-SF	RC10	Grout-Aid	0.063	0.31	0.63	0.000	0.50	0.100	0.000	0.00	0.57 Ca/Si 53.3 wt-%	1.58
S21 2)	Slag-RC10-SF	RC10	Grout-Aid	0.063	0.31	0.63	0.000	0.50	0.100	0.000	0.00	0.57 Ca/Si 53.5 wt-%	2.00

1) Mix S26 was nearly identical to the mix S14, the only difference was the fineness of the ground slag batch, which was finer for mix S26. S14 was leach tested for pH.

2) Mix S20c was selected to pilot field test 1, but it turned out to be too stiff, and so mix S21 (higher W/DM) was tested instead.

Table 3-9. The results of technical tests of the most promising Slag and super sulphate cement mixes.

Mix	Bleeding (%)	6 h Shear strength (kPa)	b_{min} (μm)	b_{crit} (μm)	Viscosity, Bingham (mPas)	Yield value, Bingham (Pa)
(S14)/S26	(0)/0	(0.98)/0.98	(40)/47	(139)/135	(50.3)/52.3	(17.7)/21.7
S20c	0	2.77	40	99	62.6	24.2
S21	0	1.46	37	99	36.2	8.5

3.8.2 Leaching and pH

The leach tested mixes are S14 and S20 and the composition of them are shown in Table 3-8.

Mix S14 was leach tested only with specimens cured at 20°C in both leachates. The pH values obtained already at the beginning were below the requirement of 11 and showed a decreasing trend up to the two weeks testing; in All-MR from 10.6 to 10.5 and in OL-SR from 10.1 to 9.9 (Figure 3-7).

In EQ-testing of mix S14 quite high alkalinity values were measured, about 19 mmol/l in ALL-MR and 12 mmol/l in OL-SR. The high values resulted from high sulphide concentrations and testing was stopped after 2 weeks. The obtained sulphide concentrations were considered too high (in ALL-MR about 270 mg/l and in OL-SR about 170 mg/l) and to include a risk for the long-term safety in the final disposal concept.

Mix S20 was leach tested with specimens cured at 20°C in both leachates. Similar decreasing trends in the pH values were observed in leachates as for mix S14, but the pH values were higher (Figure 3-8). In ALL-MR the pH values gradually decreased from 11.3 to 11.0 during the 20 weeks of testing and in OL-SR from 10.5 to 10.2 during three weeks of testing.

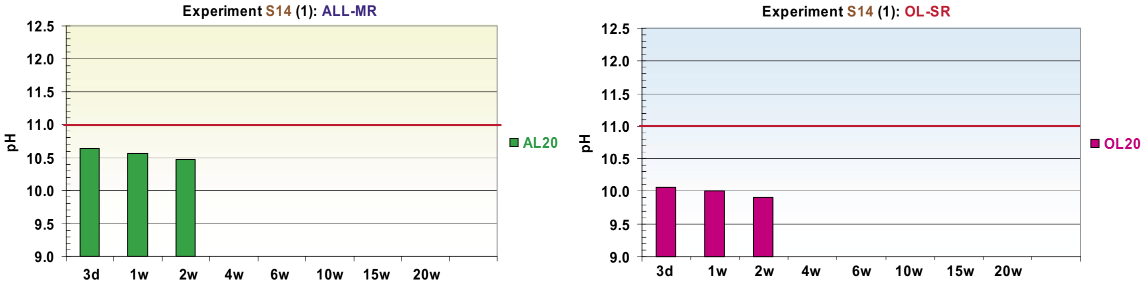

Figure 3-7. *pH results of mix S14 in equilibrium tests /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 refers to the curing temperature and AL and OL to the leachates.*

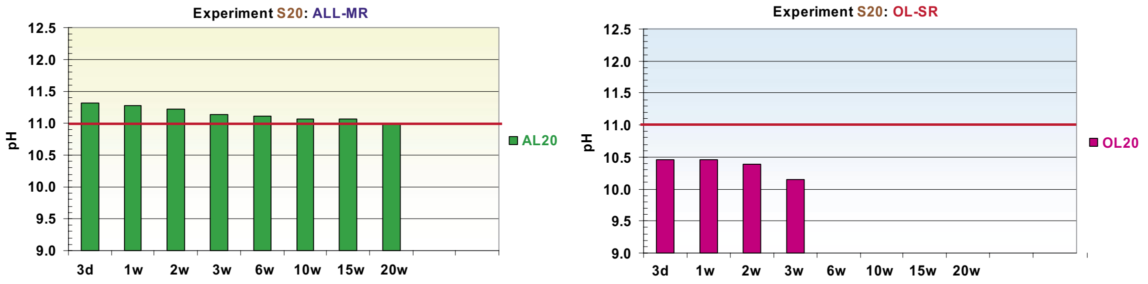

Figure 3-8. *pH results of mix S20 in equilibrium tests /Vuorinen et al. 2005/. The x-axis in histograms gives the time of sampling in days or weeks. 20 refers to the curing temperature of the specimen, and AL and OL to the leachates.*

Mix S20 was subjected to EQ-test only using the lower curing temperature specimens in both leachates. The total alkalinity values varied between 2 and 6.5 mmol/l and showed an increasing trend in both leachates. Only after 15 weeks of leaching decreased alkalinity values (about 5 mmol/l) were measured in ALL-MR. However, the leachates had a yellowish tint indicating sulphide release. The analysed sulphide concentration in ALL-MR was about 15 mg/l and in OL-SR about 19 mg/l.

3.9 Tests on system 4 – LAC

3.9.1 Grouting related properties

Experiments

NUMO delivered two batches of low alkali cement (LAC) to test the applicability of the products for grouting purposes. They were named “LAC coarse” and “LAC fine”. LAC fine was far finer than the other cements and slag used in the work. Use of citric acid was recommended by the deliverer in order to retard hydration if needed.

The LAC fine mixes were not penetrable even when the W/DM ratio was increased up to 2.5 and the citric acid content up to 1.8%. Since the LAC fine particles were very small, the reason must be a very strong gel blocking due to the material reactivity or flocculation. In this work the age of the mix at the penetrability testing has been 60 min throughout the experiments, but here an exception was made: One mix was tested immediately after mixing but no better penetrability was observed.

Modifying mix L3 by substituting LAC fine with LAC coarse while keeping W/DM ratio to 2.0 did not yield improved behaviour. The setting (shear strength) was decreased to zero and the mixes were less penetrable than mix L5.

Mix L8 was made with LAC coarse only without citric acid for the pH leach tests because it was the only "pure" LAC mix. The W/DM ratio was 1. The penetrability was known to be poor based on the above experiments. The aim of the pH tests was to get information of the pH behaviour of LAC, which significantly differed in chemical composition from the other systems in this work: The sulphate content was much higher and the silica content lower. The composition of leach tested sample L8 is presented in Table 3-10 and the results of technical tests are presented in Table 3-11.

Table 3-10. The mix composition of the LAC sample L8. /Kronlöf, 2004/.

Mix	Binder	OPC type	SF type	OPC /DM	SF /DM	SL /DM	G /DM	SF /SL	OPC /SL	Gypsum /SL	Superpl /DM	Ca/Si molar ratio SiO_2 wt-%	Water /DM
L8	LAC						0.000				0	2.25 Ca/Si 18.2 wt-%	1.0

Table 3-11. The results of technical tests of LAC sample L8 /Kronlöf, 2004/.

Mix	Bleeding (%)	6 h Shear strength (kPa)	b_{min} (µm)	b_{crit} (µm)	Viscosity, Bingham (mPas)	Yield value, Bingham (Pa)
L8	0	1.6	–	–	6.8	27

3.9.2 Leaching and pH

The composition of the leach tested LAC mix L8 is shown in Table 3-10.

LAC mix L8 was leach tested with both leach solutions and only with specimens cured at 20°C. The pH values measured showed decreasing trends in EQ-test (Figure 3-9). The initial values were a little higher in leachates, 11.4 in ALL-MR and 10.9 in OL-SR. The target pH value of 11 in ALL-MR was reached earlier, after 10 weeks.

The total alkalinity values in EQ-tests varied between 1.5 and 3.5 mmol/l. The titration curves showed two equivalent points and the fresh leachate had a yellowish tint indicating the presence of sulphide. Sulphide was analysed but the concentration obtained was very low, about 0.02 mg/l. In both leachates alkalinity showed a decreasing trend from the start, nicely following the pH trend.

In DIFF-test mix L8 was tested for pH only with specimens cured at 20°C in ALL-MR (Figure 3-9). The pH values initially increased above 11 and remained around 11.3 in ALL-MR and between 10.2 and 10.5 in OL-SR without any clear trend. The obtained alkalinities showed an increasing trend in the very beginning in both leaching solutions. However, only testing in ALL-MR was continued further and the last alkalinity values were slightly lower, about 1.5 mmol/l than in the EQ-test.

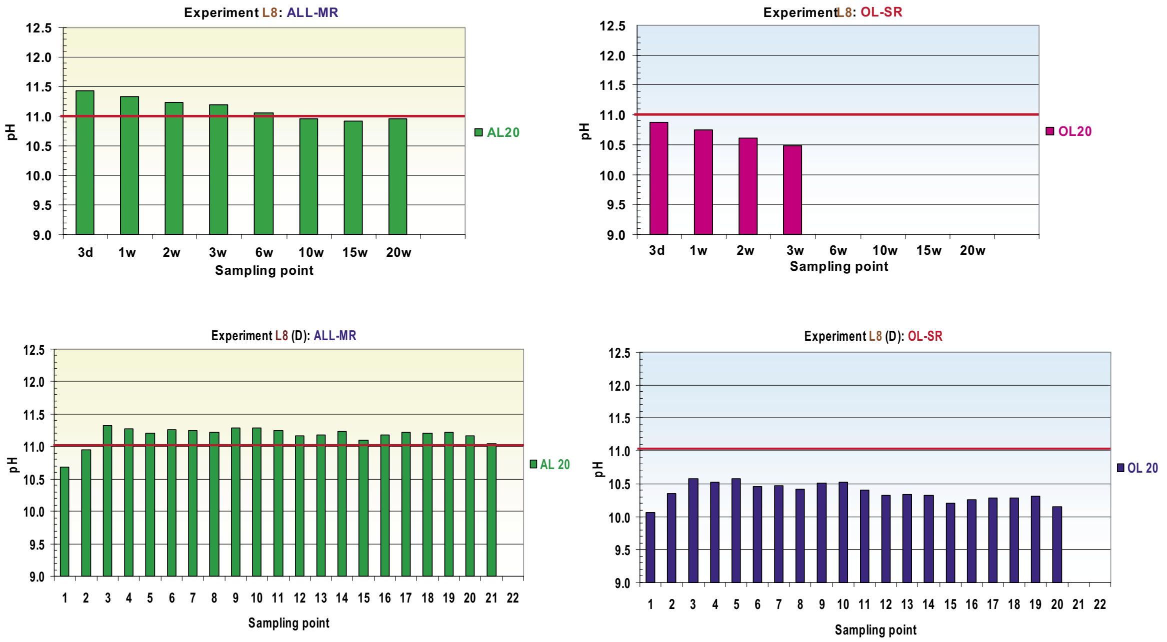

Figure 3-9. *pH results of reference mix L8 in equilibrium tests (above) and in diffusion test (below). The x-axis in each histogram gives the time of sampling in days or weeks. 20 refers to the curing temperature and AL and OL to the leachates.*

3.10 Reference grout

A reference mix (composed of UF16 and SF and superplasticiser) of known good performance in practical field conditions was included in the studies in order to find a comparison for the mixes developed in this work.

The injection properties were tested at the age of 1 hour as all mixes in this work. By that time the grout had probably already lost some of its fluidity and penetration ability. because the Marsh values on site were known to be better (the Marsh values on site have been measured from 0 up to 30 min after mixing). However, all results indicated that the reference mix was clearly more fluid than the low pH mixes made in this work. The reasons are obvious: A lot of SF and no superplasticiser were used in the low pH mixes. The mix composition and the results of reference mix 52 are presented in Tables 3-12 and 3-13.

An interesting result was that even though the reference mix was more fluid still 1 hour after mixing, it was clearly less penetrable than the low-pH mixes.

Table 3-12. The mix composition of the reference mix 52.

Mix	Binder	OPC type	SF type	SP	SF/OPC	W/OPC	W/DM	Ca/Si molar ratio SiO_2 wt-%	SP, % DM
52	OPC+SF	UF16	Grout-Aid	SP40	0.075	1.30	1.21	2.3 Ca/Si 27.8 wt-%	1

Table 3-13. The results of technical tests of reference mix 52.

Mix	Bleeding (%)	6 h Shear strength (kPa)	b_{min} (µm)	b_{crit} (µm)	Viscosity, Bingham (mPas)	Yield value, Bingham (Pa)
52	0	2.6	63	201	22.9	5.0

3.10.1 Leaching and pH

As expected of a normal grout material the pH values measured in EQ-test (Figure 3-10) were around 12.5 in ALL-MR and little less in OL-SR, about 12.3. In DIFF-test the pH values measured vary after the initial increase between 12.1 and 12.6 in ALL-MR and between 12.0 and 12.3 in OL-SR. No decreasing was observed. The pH results both indicate that mix 52 owns a lot of potential to keep the pH at high value.

In EQ-testing the total alkalinity values in ALL-MR varied between 38 and 50 mmol/L and in OL-SR between 39 and 42 mmol/L. Alkalinities in both leachates showed decreasing trends with time elapsed.

In DIFF-test the last alkalinity value in ALL-MR measured (33 mmol/l) was only slightly lower than in the EQ-test, but duration of the last period in DIFF-test was rather long (38 d). Another total alkalinity value was determined from the duplicate specimen after even a longer period (83 d) following the intense equifrequent exchanging. The total alkalinity had still increased up to 36 mmol/L. In ALL-MR the main alkaline element leached at high concentration was Ca (around 400 to 500 mg/l).

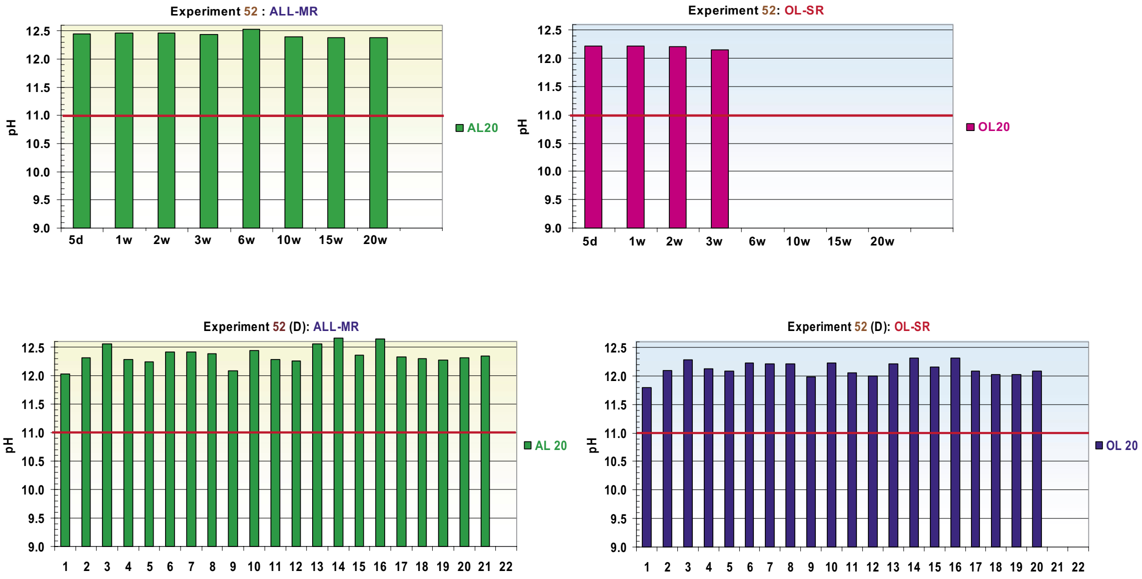

Figure 3-10. pH results of reference mix 52 in equilibrium tests (above) and in diffusion test (below). The x-axis in each histogram gives the time of sampling in days or weeks. 20 refers to the curing temperature and AL and OL to the leachates.

3.11 Main findings in the experimental laboratory studies

Laboratory tests showed that the alkali content of the raw materials could not directly be correlated to the measured pH of the leaching solutions.

Minimum value for SiO_2 content in mixes based on OPC+SF, WCE+SF or slag should be above 50 weight-% of total binder materials or Ca/Si molar ratio close to or less than 0.80 in order to yield pH 11 or lower. Also it was found that the sum of CaO+MgO is an important factor affecting the pH.

Increasing W/DM improves penetration ability of grouts but only up to the W/DM ratio of about 2. The penetration ability of OPC+SF mixes sharply became worse with W/DM below 2 but the penetration ability of some slag mixes was relatively good down to value of 1.6. Larger values still decrease (improve) viscosity. Generally viscosity and yield value were unrelated to penetration ability. The correlation was weak.

W/DM ratio controls the setting. ETTA (aluminium cement and/or gypsum) accelerated OPC+SF system clearly.

The strength of slag system mixes was lower than that of other systems. SF increases the strength in OPC+SF systems. The slag system set almost as fast as the OPC+SF system without ETTA. The setting of super sulphate system was slower than the slag system while the 28 d compressive strength of the super sulphate mixes was clearly higher.

3.12 Main conclusions of the experimental laboratory results

OPC+SF system met the requirements in laboratory quite well. In order to obtain good penetrability, the W/DM ratios had to be so high that the setting and compressive strength suffered. An ettringite acceleration method was developed to control setting. The target pH was achieved with the OPC+SF-mix f64 and WCE+SF mix w2, and the pH target was nearly achieved with f63 and w1, which had a Ca/Si ratio slightly above 0.80 and a SiO_2 wt-% slightly below 50%. Mix f63 showed so promising behaviour with regard to the grouting related properties that it was selected for pilot field test 1, instead of f64, of which the leaching behaviour was better. Mixes based on Egyptian white cement did not show any significant advantages in the technical tests.

The super sulphate system (slag activated with gypsum and OPC) met all the given requirements except that of yield value. Setting was relatively low but within requirements. W/DM ratios were lower (better) than those with OPC+SF system. Slag-mixes also met the given requirements except that of yield value. Mix S20c was selected for pilot field test 1. Later, however, slag-based systems were ruled out due to the high leaching of sulphide observed in the laboratory tests. LAC mix L8 showed satisfying pH values, but it was not penetrable even though the grain sizes were very small, and thus not suitable for grouting purposes.

The question how to get the pH lower was answered in the studies. To fulfil all the technical properties was challenging, because some requirements were contradictory. Possibilities to solve some problems in further optimisation work are for example: delayed GroutAid addition, use of superplasticiser, replacing part of GroutAid with ground glass and e.g. developing ETTA acceleration.

3.13 Environmental acceptance

With regard to the environmental aspects, there are no special reasons to judge OPC+SF system to be unacceptable for grouting of deep repository (superplasticiser excluded). No unwanted effects are expected as cement normally is injected to crystalline bedrock to a large part consisting of silica. The constituent's materials include or may include components, such as organics or heavy metals. These compounds have to be taken into account when designing the use of them in deep repositories. In addition to the cautions regarding environmental aspects and the long-term safety concerns there are the occupational safety questions to consider.

Blast furnace slag may under certain circumstances produce significant amounts of H_2S, and this phenomenon was clearly observed in late phase of the project in leaching tests. Due to this the testing of slag-based systems were interrupted and ruled out from further testing. Slag-based mixes are not suitable for grouting of deep repositories.

There are no special reasons to judge LAC to be unacceptable for grouting in deep repositories. The material is new and thus some unexpected phenomenon may take place. From the long-term safety aspect the effect of the addition of citric acid needs to be evaluated. However, LAC seemed to be unsuitable for grouting purposes.

3.14 Long term safety aspects

3.14.1 Material composition and leaching behaviour

The studied material combinations consist basically of mixtures of cement were the Ca/Si ratio and potential formation of $Ca(OH)_2$ (portlandite) has been reduced by replacing a large part of cement by a pozzolan. The pozzolans used to reduce the pH and alkalis leaching of the grout mixes were blast furnace slag (SL) and silica fume (SF). For reference a basic OPC product used in the field was also studied.

The potentially harmful components of OPC itself are the alkali compounds, which may be leached as hydroxides in the early state of OPC hydration, and alkali earth compounds, which will leach over much longer period. Other harmful components are especially the small amounts of organic compounds present due to the grinding aid used. Silica fume contain some phosphorous oxides, which need to be considered with respect to the potential effects on the radionuclide complexation and transport. In some instances gypsum was added for acceleration, gypsum contains small amounts of ammonia, which is considered as a potentially harmful substance with respect to stress corrosion of copper. Although bentonite as such is largely composed of silicates the potential effect of introducing an outer source (grout) with large amounts of silica on the basic properties of bentonite is not known.

The potential leachable inventory and the leached solutes as a function of time, as well as thermodynamic equilibrium modelling of the chemical behaviour of cement phases was the basis for the estimation of the product behaviour. Both maximum equilibrium pH of the leachant and diffusion-controlled release was measured.

A high concentration of sulphide was found in the leachants for the slag-based system in the different groundwater solutions (maximum sulphide concentration was 270 mg/l). The sulphide phases present in slag readily dissolved in the leachates and confirmed that sulphide in the leachates originated from slag. As the leached sulphide is a potential corrodant for copper in the repository the slag based system was considered to include such a potential long-term safety risk for the repository system that it was recommended not to continue the studies with the products containing blast furnace slag. Another identified risk is the sulphate leaching from the products as sulphate reducing bacteria (SRB) in groundwater might reduce sulphate leaching from cement. SRB are very common e.g. in Olkiluoto groundwaters.

The pH criterion was fulfilled in the equilibrium testing for the mixes with silica fume with a Ca/Si molar ratio ≤ 0.80. For all materials studied the pH values measured in the saline leachates were constantly lower than in the fresh leachates. The reason for the lower pH values in the saline leachates is the higher ionic strength (~0.5 M) compared with that of the fresh water (~0.003 M).

The most prominent characteristic of the low-pH cementitious grouts was that there was no $Ca(OH)_2$ in the hydrated paste. $Ca(OH)_2$ was only detected in the OPC reference mix, in both initial and leached specimens, but the intensity of the $Ca(OH)_2$ peak decreased in the leached specimens. Hydration products on the surface of all the specimens, mainly consisted of C-S-H phases, showed degradation after leaching and the surface of all the leached specimens became porous.

Ca was the main alkaline substance released throughout the tests. For the low-alkaline white cement product leached concentrations of K, SO_4^{2-} and Si were distinctly lower than for the UF16-based cement system, whereas the other element concentrations (Na, Ca, Mg, Cl) did not differ much. 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. Distinctly higher release of alkalis Ca, Na, K was observed for the reference ordinary UF16-cement. All the low-pH mixes showed increasing Si concentrations, though no solubility limit for Si was reached in the leachants. However, the increasing release of Si might be an unfavourable aspect in regard to bentonite stability.

Leach rates or/and diffusion coefficients were calculated for Ca, K, S_{TOT}, Si, Al, and Na using two different Fickian diffusion models. The cumulative leached fraction of Ca during the experiments was ranging from 1–2.3% for the silica and slag based systems, and was clearly lower than for pure OPC. The leached fraction of K and sulphate was calculated to be 100% for the SF system, whereas leaching fraction of Si and Al was low, a few %. Based on the experimental and model results, it is conceivable that irrespective of the mix the whole inventory of the alkaline elements, and possibly of sulphur, is leachable. However, the experimental time was far too short to get an indication of either the “total” leachable fraction or the leachable inventory of Ca, Si and Al for any of the mixes. The calculated diffusion constant for potassium was in the range of $2.2–6.5\times10^{-11}$ m^2/s for the SF based system and 7.5×10^{-11} m^2/s for the OPC system.

These relatively short-term experiments revealed that the pH criteria can be met, and that the potassium (K) and sulphate (SO_4^{2-}) are rapidly released from the product, and a declining release of calcium (Ca) with time. Silica release continues throughout the experimental time. The long-term behaviour of the product, phase changes and crystallization of CSH phases, which might have an effect on the long-term degradation and leaching of the product, remains to be evaluated.

3.14.2 Potential effects of organic additives on radionuclide mobility

A literature review was performed, which included an evaluation on the influence of organic cement additives on radionuclide mobility under cement conditions, and under groundwater conditions (non-cement conditions) based on the chemical structures of the main components in polyelectrolyte additives and on basic knowledge on metal-humic bounding.

The publications surveyed contained results only for high pH conditions (pH 12.5 to 13.3) in artificial cement water or NaCl solutions, and mainly results on the possible influence on sorption behaviour of Eu and Th.

Four types of superplasticisers: sulfonated melamine, sulfonated naphthalene, modified lignosulfonates and polycarboxylates were reviewed. The most commonly used are melamine-based and naphthalene-based superplasticisers. The additives are commercial products of fairly ill-defined composition and may contain also components other than those indicated in the product safety sheets. It follows that the compositions of candidate products should be better known before use when more certainty about their behaviour is needed. Also the knowledge on how the additives are incorporated into the grout, and release rate from the cement is not well known, as well as whether the products are degraded e.g. due to microbial activity.

Melamine-based additives contain groups with a potential for strong complex formation. In one case this type of additive contained some other compound that substantially reduced the sorption of Eu and Th on cement. The melamine structure is very different from what is known of NOM (= natural organic material) in groundwater, and these type of additives need to be studied in more detail before use in the vicinity of radioactive waste.

Naphthalene sulfonate-based additives form strong ionic compounds but their complex formation potential is low. The possibility of formation of non-sorbing compounds with nuclide cations needs to be studied. Otherwise this additive seems to be non-problematic. The structure of this compound is most probably very stable in groundwater.

The carbohydrate/carboxylate polyelectrolyte-based additives most probably bind nuclides in the same fashion as the humates (NOM). In non-cement conditions (tri-valent Ln and An) nuclides and at lower pH also An(IV) are effectively bound to NOM. Their similarity in behaviour to NOM in groundwater gives a good basis for estimating the behaviour of radionuclides in waters containing organic cement additives.

In the absence of experimental results, it was recommended that the organic cement additives should be evaluated to behave like NOM with respect to the complexation behaviour. Especially trivalent elements may be bound to NOM at low organics concentration, and thus organic cement additives may enhance mobility of especially of Ln and Ac(III) radionuclides and care should be taken in their use near radioactive waste repositories.

3.15 Pilot field testing in Finland

3.15.1 Introduction

Originally the plan was to do one pilot field test with the one or two most promising mix(es). The target of the pilot field testing was to verify that the properties developed in laboratory can be reached in field conditions and also to verify that grout(s) is/are suitable for practical work. According to the original idea the intention was to make only minor modifications before going to the small scale field test, which would include more detailed characterisation of the bedrock and analysis of the penetrability and sealing properties of the mix.

The first pilot field test was arranged as planned in Helsinki. The results were such that major modifications of the mixes were needed and also some requirements had to be updated before continuing the work and going to the next field tests. The main problems were too slow setting and too poor fluidity in field conditions.

The work continued with further laboratory testing and some possible mix combinations were found. A second pilot field test was arranged in two stages: In first stage several mix choices were mixed and tested for technical properties in field conditions (so-called batch mixing test). The most promising mixes were selected for actual grouting test in ONKALO access tunnel.

3.15.2 Pilot field test 1 in Kamppi-Kruununhaka multipurpose tunnel in Helsinki

Pilot field test 1 was arranged in Kamppi-Kruununhaka multipurpose tunnel in the city of Helsinki. The ground water pressure was 4 bars at the tested tunnel section. The rock type in the test area was quite similar to that at Olkiluoto island. The bedrock was quite tight, usually the Lugeon tests in grouting holes showed values < 0.5 Lug. Only a few holes showed values that refer to the existence of considerable water conductive fractures.

The test grouting fan included 14 grouting holes, which were 24 m long. The maximum grouting pressure was 40–50 bars. The original plan was to test two grouts, and grout the left side of the fan with one of the test grouts and the right side with the other test grout.

The mixes selected for the field test were f63 (OPC+SF-system) and S20c (SSC-system). However, soon after starting of grouting, S20c turned out to be too stiff, and it was changed to mix S21 (same, but higher W/DM). The mix compositions of them can be found in Tables 3-4 and 3-8, and the results of technical tests in Tables 3-5 and 3-9.

Testing the mix properties

Only one hole was grouted with mix S20c. The bleeding was 0–1%. According to the density the mix was dosed correctly. The penetrability with the filter pump was relatively good (the maximum is 310 ml) even after 1.5 h. The Marsh fluidity was poor. The aimed shear strength was obtained after about 3 h. This mix was regarded too stiff.

Six holes were grouted with mix S21. According to the density the amount of water was too high (density corresponded to the W/DM ratio 2.26, instead of the specified ratio 2.0). The bleeding was 1%, the penetrability with the filter pump was relatively good even after 2.5 h. The Marsh fluidity was relatively good after about 1 h. The aimed shear strength was not obtained before the test ended. According to the contractor also this mix was slightly too stiff. The grout flow was slow and the pressure rose near to the stopping pressure very soon after grouting started.

An S21-sample was cast and the uniaxial compressive strength (UCS) after 28 days was measured at VTT laboratory. The result was 1.54 MPa, which is less than measured in laboratory and also below the desired limit (≥ 4 MPa). Possible reasons are many. USC at 91 d was 2.13 MPa.

Seven holes were grouted with f63. According to the density the water dosing was too high, corresponding to W/DM ratio 2.95, instead of the specified ratio 2.5. The bleeding was 1%. The penetrability with the filter pump was good at 1 h and after that the penetrability got poorer. After 1 h clumps were observed in the mix in the latest filter pump measurement and also in the Marsh cone. The Marsh fluidity was relatively good after about 0.5 h. The aimed shear strength was not found because the sample was disturbed too early. However, it was observed that the mass started to react before 1 h.

According to the contractor mix f63 was “thin” compared to their normal starting mixes. This mix seemed to be better than mixes S20c and S21. The grouting pressure was low for most of the grouting time and the flow was faster than with other mixes.

A sample was cast and the uniaxial compressive strength (UCS) after 28 days was measured at VTT laboratory. The result was 1.57 MPa, which is less than measured in the laboratory and also below the desired limit ($\geq$ 4 MPa). UCS at 91 d was 1.75 MPa.

Test grouting

With mixes S20c and S21 the grouting times were longer than with mix f63. The pressure increased earlier with mixes including slag as the mixes were stiffer.

The grout take of the hole, which was grouted with S20c, was 10.9 l/borehole-m. The average value for S21 was 8 l/borehole-m and for f63 it was 6 l/borehole-m. The grout take was the highest in holes intersecting a small fracture zone.

When packers were opened 6 days after the test grouting the grout was flowing out from two grouting holes. The grout was not hardened in bedrock and the reason for this is not known. Practically this behaviour is considered unacceptable.

Quality control

The water loss measurements were done in quality control holes. The Lugeon values were about half of those before the test grouting. After Lugeon tests, the quality control holes were grouted with a standard grouting mix (Microcem 800, SP 0.5–1%, W/C-ratio = 0.8).

The average cement/grout take was 9 l/borehole-m, which is considered high, as the tunnel section was already grouted with test grout.

Conclusions of the pilot field test 1

The test grouting fan in Kamppi-Kruununhaka multipurpose tunnel in Helsinki was grouted with three test mixes: Two slag+SSC-based mixes and one OPC+SF-based mix. The grouting result was not satisfying enough. The quality control holes were grouted with ordinary cement and the grout take was significant.

When testing the technical properties of the mixes, none of the test mixes showed totally satisfying results in field conditions. All mixes showed good penetrability (filter pump) but fluidity was often too poor (Marsh cone). Also the development of the strength was very slow, even if taking into account the unintendidly high W/DM ratios.

The conclusion was that the further development should be focused on the development of strength and the acceleration. Also the fluidity should be better to enable better penetration into fractures. The use of superplasticisers seemed to be necessary in order to keep W/DM so low that the development of strength is not jeopardized.

It was found that the tested mixes were not ready for the small-scale field test or use in ONKALO and that more research work had to be made to find high quality low pH grout mixes.

3.15.3 Further development of OPC+SF+superplasticiser mixes in laboratory

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

- the continuation was based on the OPC+SF-system (slag-system was ruled out due to sulphide issue),
- water to dry material ratio had to be lower in order to get satisfying development of strength,
- the use of superplasticiser 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 should be minimised.

The most promising OPC+SF-mix f63 was further modified with water content, superplasticiser content, alumina cement content and gypsum content. Also the requirements were slightly modified due to the problems in viscosity and setting in pilot test 1.

The mixes were studied for penetration ability (by penetrability meter), bleeding, early shear strength (by fall cone test), fluidity (Marsh cone) and compressive strength.

The only new component in the mixes was SP40 superplasticiser by Elkem. The mix modification was done in a step wise-manner. The most promising results were obtained with the following composition ranges:

- W/DM = 1.2–1.6,
- superplasticiser dosage 2–3% (of total dry mass),
- aluminate cement dosage 0–1.5% (of cement weight),
- gypsum dosage 0%.

The recipes P3, P12 and P13 were chosen for the mixing test preceding pilot test 2. The mix compositions of them are gathered in Table 3-14 and the results obtained in laboratory are presented in Table 3-15. Leach testing was not done for these mixes, because the ratio of SF/OPC was not changed and the behaviour was assumed to be similar to that of f63.

Table 3-14. Compositions of mixes selected for mixing test preceding test grouting of pilot test 2.

Mix	G/OPC	HAC/OPC	SF/OPC	SP/DM %	Ca/Si molar ratio SiO_2 wt-%	W/DM
P3	0.000	0.000	0.69	2.0	0.79 Ca/Si 52.2 wt-%	1.61
P12	0.000	0.015	0.69	3.0	0.79 Ca/Si 51.8 wt-%	1.61
P13	0.000	0.000	0.69	3.1	0.79 Ca/Si 52.2 wt-%	1.61

Table 3-15. Laboratory results of mixes selected for mixing test preceding test grouting of pilot test 2.

	Bleed (%)	Shear strength 6h (kPa)	Shear strength 24h (kPa)	B_{min} (µm)	B_{crit} (µm)	Marsh cone (s)	Compressive strength 28 d (MPa)
Original requirement	≤ 10%	≥ ~ 0.5		≤ 80	≤ 120	*)	≥ ~ 4
Updated requirement	≤ 10%	≥ ~ 2		≤ 80	≤ 120	*)	≥ ~ 7
P3	0	1.3	> 245	46	107	136	14.4
P12	0	1.3	196	40	97	52	14.4
P13	0	0.3	130	38	67	51	14.0

*) based on general know-how and experiences Marsh fluidity values < 40 s can be seen very good and 40–50 s promising.

3.15.4 Mixing test and selection of the recipes for test grouting in pilot test 2

The aim of the mixing test was to

- verify that the required properties of the selected mix(es) can be achieved when mixing the grouts with ordinary grouting equipment,
- verify that the workability properties can be regarded satisfying,
- verify that the required properties of the selected mix(es) can be achieved also in field conditions (in different temperature),
- select one or two recipes for test grouting in ONKALO.

The above-mentioned mix compositions were tested and also mixing orders were varied for some mixes.

The mixing test was done at Olkiluoto, outside ONKALO, using ordinary grouting mixer and agitator. Outside temperature varied between < 0°C–7°C. First each mix was tested for density to verify that the dosage was correct. Then fluidity, penetrability check (by filter pump) and bleeding were tested. Also the early strength development was observed.

Filter pump results (250–300 ml with 63 µm sieve mesh) and bleeding (0–1%) were typically good for all mixes. The differences between the mixes were seen in Marsh fluidity and strength development. Regarding the overall behaviour of the mixes the most promising recipes were P3 with mixing order: water, OPC, 2 min mixing, SF, SP, 3 min mixing, and P12 with mixing order: water, OPC, HAC, SP, 2 min mixing, SF, 3 min mixing. P3 had promising strength development (0.5 kPa at about 8 h) and promising Marsh fluidity (< 50 s) and P12 showed good Marsh fluidity (< 40 s) and promising strength development (slightly over 0.5 kPa at 6 h). It was observed that different mixing orders affect the penetrability and the Marsh fluidity.

There were differences between the laboratory results and mixing test results. Usually the early shear strength in laboratory was better than that observed in field conditions. Instead, Marsh fluidity values observed in field were better than those measured in laboratory. Different temperature and different mixer may explain some differences.

P3 and P12 both have advantages and disadvantages. P3 was selected to be tested in test grouting in ONKALO. The advantages of it compared to other options are:

- promising early strength development,
- satisfying compressive strength in laboratory tests,
- promising fluidity compared to the most of the other tested mixes,
- absence of alumina cement and gypsum,
- lower superplasticiser content compared to mix P12.

Recipe P2, which is similar to P3 but with W/DM = 1.2, was originally chosen to be tested in field, because low W/DM was desired. Based on experiences obtained during grouting test, this was ruled out as mix P3 was so stiff, that the stiffer mix P2 was deemed not worth testing.

3.15.5 Pilot field test 2 in ONKALO access tunnel at Olkiluoto

Test arrangements

Pilot test 2 was arranged in ONKALO access tunnel at station 214. Based on the studies made in the core drilled hole the section to be grouted included several water conductive fractures with hydraulic apertures of 0–60 microns. The water inflow from this about 25 m long tunnel section was estimated to be 0.8 l/min without grouting. The groundwater elevation head was about 20–25 m.

A normal grouting fan was planned to be drilled and grouted. The basic fan included 22 holes of 26 m length with a maximum distance of 2.5 m. According to the original plan the left side of the fan was planned to be grouted with P3 and the right side with P2. Because P3 turned out to be relatively stiff, the stiffer mix P2 was ruled out. The left side and nearly all roof holes were grouted with P3. The right side of the fan was grouted with normal grout used at the site (here called the reference grout). The recipes are given in Table 3-16.

After the test grouting fan the next fan was not grouted because of tight bedrock.

Table 3-16. The recipes used in test grouting of pilot field test 2.

Left side and roof holes:		**Right side:**	
Mix P3		Reference grout	
W/DM = 1.6		Normal grout used in ONKALO	
SP 2% (weight-% of dry materials) = 10 g/l		W/DM = 1.0	
		SP 1% (weight-% of dry materials) = 8 g/l	
Water	40 l	Water	60 l
Ultrafin 16	20 kg	SetControl II	0.8 l
Mixing 2 min		Mixing 30 s	
GroutAid	20 l	Ultrafin 16	60 kg
SP40	0.55 l	Mixing 4 min	
Mixing 3 min			
Agitating			

Characterisation of the test area

Four probe holes were drilled and studied before grouting. The contractor made the water loss measurements in probe holes. Probe holes showed Lugeon values 0–1 Lug. The highest values were measured in the upper left corner (hole B). Also the out flowing water was measured, and it varied between 0.03–0.63 l/min per hole, upper left corner leaking the most. The probe holes were grouted when the grouting fan was grouted.

Results indicate the presence of water conductive fractures. Two probe holes (B = upper left corner and D = lower right corner) were also studied with Posiva Flowmeter. A few, main water conductive fractures were located at about 15–20 m ahead of the tunnel drift. In hole B two water conductive fractures were identified (hydraulic apertures 40–50 µm) and in hole D four conductive fractures were identified (10–20 µm).

Drilling of grouting holes showed that there were more abundant fracturing in all roof holes.

After excavation the rock was geologically mapped. The rock was moderately fractured. There were three main fracture directions. Q-value for each about 5 m section varied between 1.3 and 16.7 (Poor-Good). The highest Q-value is found between 214–220 and the lowest between 230–235.

Testing the mix properties

Three batches of recipe P3 and one batch of the reference grout were tested. The temperature during testing was about 2–3°C. For P3 the filter pump test showed values between 140–270 ml (maximum 310 ml). The lowest values cannot be regarded satisfying. Marsh fluidity varied between 51 and 54 s, which is relatively stiff for a grout, but not totally unacceptable. Bleeding was 0%, which is a very good value. According to the fall cone test the shear strength value 0.5 kPa was reached at 8 h 40 min, which is acceptable but not totally satisfying. The fall cone test was done to one batch. For P3 the uniaxial compressive strength at 28 d was 10.9 MPa, which is very good.

The results were somewhat poorer than those measured in the mixing test. This may be due to the lower temperature.

The reference grout showed the following values: filter pump: 300 ml, Marsh fluidity 36 s and bleeding 1%.

Test grouting

The grout take varied a lot between different holes. The intake of P3 did not differ remarkably from the intake of the reference grout. The largest grout takes (> 10 l/borehole-m) were observed in all roof holes (P3 and one with reference grout), and in three holes on the left side (P3). One clear explanation for differences is naturally the different characteristics of the fracturing.

The behaviour of grouting pressure and flow varied between different holes. The amount of holes is too limited to draw any clear conclusions, but there was a slight impression of poorer penetration ability of P3 than of the reference grout.

The upper left corner was known to have water conductive fractures and it was not a surprise that the grout take was great in those holes. The probe holes indicated water conductive features in the lower right corner, but not in the upper right corner. However, the grout take in upper right corner was remarkably higher than in the lower right corner (only reference grout used).

Quality control and sealing effect

After grouting, four 22 m long quality control holes were drilled and tested for water losses. Holes were dry and measured Lugeon values were 0. The grouting seemed successful and the excavation was continued.

After excavating the tunnel stations 214–240 the remaining leakages were observed. About the first ten meters of the left side (grouted with test grout) seemed to be dry or only limited moisture was observed. After that the moisture on the roof and walls increased and between 235–240 one dropping leakage was observed. After rock bolting several dropping leakages were observed. This indicates that the coverage of the fan was not enough and/or the 3 m rock bolts penetrated the grouted zone. The thickness of the zone grouted with the test grout has not been more than some 2–3 m. The right side grouted with reference grout was not that wet and only a couple of dropping leakages were observed in the end of the test grouted tunnel section. Maybe the distance between grouting holes was too long in the end of the grouting fan or the fractures were too narrow for the grout to penetrate. There was not a next grouting fan thus no overlapping, and this may have had an effect on the poorer result in the end of the test grouted tunnel section.

The fractures were more water conductive in the left side of the fan than in the right side. The fracturing explains partly the fact that the remaining leakages on the right side were low, if they originally were low. This can also be seen in grout takes.

The amount of remaining leakages is difficult to estimate. However, compared to the leakage prognosis for this tunnel section (about 0.8 l/min without grouting), it seems that some leakages were sealed, also with the test grout.

Conclusions of the pilot field test 2

The behaviour of the test mix P3 in the tests grouting in pilot field test 2 was poorer than that of the reference grout with regard to the penetrability 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. The results of P3 were better in the so called mixing tests before actual test grouting.

A reason for some unsatisfying results 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 take of the test grout was not low, which means that it penetrated into fractures. The fracture properties of the rock explain some differences between the take of P3-grout and the reference grout. After excavation one dropping leakage and moisture were observed in the area grouted with P3. After rock bolting, moisture and several dropping leakages were observed in the area grouted with test grout. The thickness of the test grouted zone seemed to be less than the length of rock bolts (< 2–3 m). The coverage of the P3-grouted zone seemed to be less than with the reference grouted zone.

When comparing the measured hydraulic apertures and the filter pump results with grout take, it is obvious that the interpretation of the measurements is not unambiguous. The grout takes in the holes in left wall were high, but according to the filter pump the grout was not able to penetrate into to those small fractures, characterised by flow meter. The reasons may be that the flow log method could not characterise transmissivities/hydraulic apertures accurately enough, and/or the filter pump method can not measure the penetrability of grout in a suitable way, and/or the grouting pressure opened fractures.

The use of this low pH cement could be considered for repository production grouting from technical performance point of view. However, more field experiences are needed in order to verify the behaviour of the grout. Technical performance could be better, so further optimising is recommended.

In grouting work the technical properties of the grout is one factor affecting the sealing effect. In the case of relatively poor penetration ability of low-pH grout, ideas to improve the sealing effect could be to increase the amount of grouting holes, to shorten the length of the grouting holes and to change the grouting pressure.

One important improvement would be if part of GroutAid could be replaced with some other silica product or some other product that lowers pH.

4 Non-cementitious low-pH injection grout for smaller fractures

The text in this section is based on the referable reports /Axelsson, 2004; Funehag, 2004a,b; Funehag, 2005/ and on non-referable reports and memos written by Dr. Hiroyoshi Ueda (NUMO), Dr. Börje Torstenfelt (SwedPower AB), Mr. Kalle Pettersson (SwedPower AB) and Dr. Mats Jansson and Dr. Maria Atienza (KTH, the Royal Institute of Technology).

4.1 Background

Grouting of smaller fractures, hydraulic aperture < 100 µm, is anticipated to be done with non-cementitious low-pH grouts. The objectives of the sub-projects SP2 and SP4 were to investigate basic properties and long-term safety aspects of the non-cementitious candidate materials, to form the basis for the decision whether silica sol can be used in the deep repository and whether periclase (MgO) should be further investigated. Further, it was investigated if the penetration of silica sol (a Newton fluid) can be predicted based on hydraulic tests, transmissivity and hydraulic aperture.

The laboratory work was carried out at Chalmers University of Technology while a literature review on silica sol was carried out by NUMO and environmental acceptance and long-term safety studies were carried out at SKB, the Royal Institute of Technology in Stockholm (KTH) and Swedpower. Further Swedpower carried out a short review on periclase grouting.

A small field-test was carried out by Chalmers at the Äspö HRL.

4.2 Silica sol

4.2.1 General

Colloidal silica is a stable dispersion of discrete nonporous particles of amorphous silicon dioxide (SiO_2). The particles have a diameter of 3–500 nm and have hydroxylated surfaces, which are insoluble in water. Colloidal silica is developed from raw glass with high silica content. The raw glass is heated and diluted with water to make it liquid after which it forms water glass (sodium silicate). The sodium silicate is diluted with water, after which acid or caustic is used to regenerate an ion exchanging resin, which excludes the sodium ions. The mixture is then processed in a reactor with high temperature and pressure to get the desired size and concentration of the particles.

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. The interval of the particle size has been narrowed to range from 5 to 100 nm. With different highly controlled techniques it is possible to manufacture particles with even narrower interval in diameter as well as specific surface. To prevent uncontrollable aggregation of the particles the silica sol is stabilised with ions (e.g. aluminium) and with respect to pH.

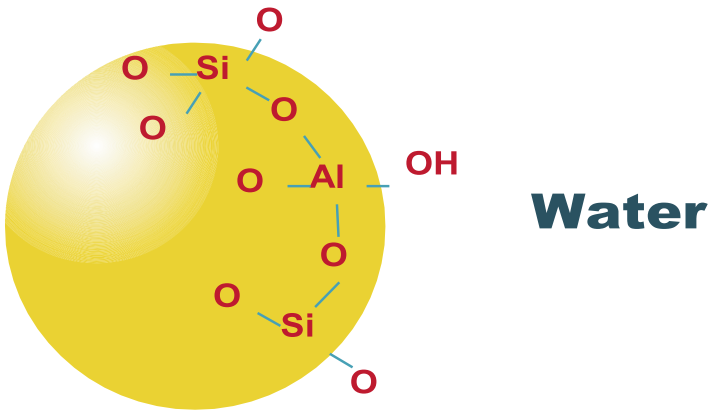

***Figure 4-1.** Schematic figure of the silica sol Eka® Gel EXP36.*

There are different types of silica sol. Chalmers University of Technology has tested Cembinder U22 as injection grout in some promising experiments at the Swedish railway tunnel Hallandsås /Funehag, 2004b/ and Eka® Gel EXP36 at Äspö HRL. Cembinder U22 is a basic, not modified, silica sol. Eka® Gel EXP36 is aluminium modified silica sol and considered to be a better (and more expensive) product.

The results at Hallandsås showed that silica sol is a feasible material for grouting fractures smaller than 0.1 mm. The non-grouted rock had a median inflow of 70 L/min, which was reduced to 2 L/min after cement grouting. After silica sol grouting the water inflow was further reduced to approximately 0.2 L/min. The hydraulic conductivity was at the same time reduced from 3.0×10^{-6} m/s (ungrouted), to 5.0×10^{-8} m/s (cement grouted), down to 1.1×10^{-9} m/s for the silica sol grouted rock mass. This can be compared to sparsely fractured deep rock where a hydraulic conductivity of 10^{-9} to 10^{-10} m/s or less is not uncommon.

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 concentration of the accelerator (salt) depends on the properties of the environmental conditions, e.g. groundwater flow, water temperature, salinity of the surrounding water, etc and on the time required for the sol to gel. When using NaCl the concentration of the accelerator in solution is normally around 10%. If calcium chloride is used as accelerator instead of sodium chloride, the total chloride concentration is reduced some 75%. However, from a public opinion point of view, sodium chloride is often more accepted than calcium chloride. The gelling time depends on the amount of salt added and the environment in the stabilised rock (e.g. temperature, pressure, groundwater flow and groundwater salinity). The higher salt concentration the shorter gelling time for the sol and vice versa. The silica sol is highly temperature sensitive; a higher temperature shortens the gel time. When the sol aggregates, it forms a network of silicon particles that encloses the present water. Depending on the environment that the sol is exposed to, some of the water will exude later on.

4.2.2 Laboratory work

The silica sol used in the laboratory tests was Eka® Gel EXP36. It consists of 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% $CaCl_2$ and the pH is < 10 /Eka Chemicals, 2004/. The particle diameter is 14 nm with a distribution range of ±3 nm.

Mechanical tests

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.

The test specimens were cured in four different environments:

- +8°C, 100% relative humidity (RH), fully saturated
- +8°C, 95% RH
- +8°C, 75% RH
- +20°C, 50% RH

The testing of the specimens continued for a period of six months, more frequent at the beginning of the period and less frequent at the end of the period. The number of performed tests differed between the different measurement sessions, mainly due to low strength at the beginning of the test period and the fact that fractures appeared at the later stages and made testing impossible.

Initially, it was planned to measure the drying shrinkage according to the Swedish Standard SS 137215 (SIS 2002) for concrete. Gage studs were mounted at each end of the prisms and the length was to be measured in a length comparator. This would have given an accuracy of ±0.005 mm. However, the adhesion between the gage studs and the silica sol prisms was too low to enable measuring. Thus measurements were conducted with a slide calliper, which has less accuracy. The results are presented in Figure 4-2.

Flexural strength measurements were done according to the European Standard EN 12390-5:2000 (SIS 2002) for concrete.

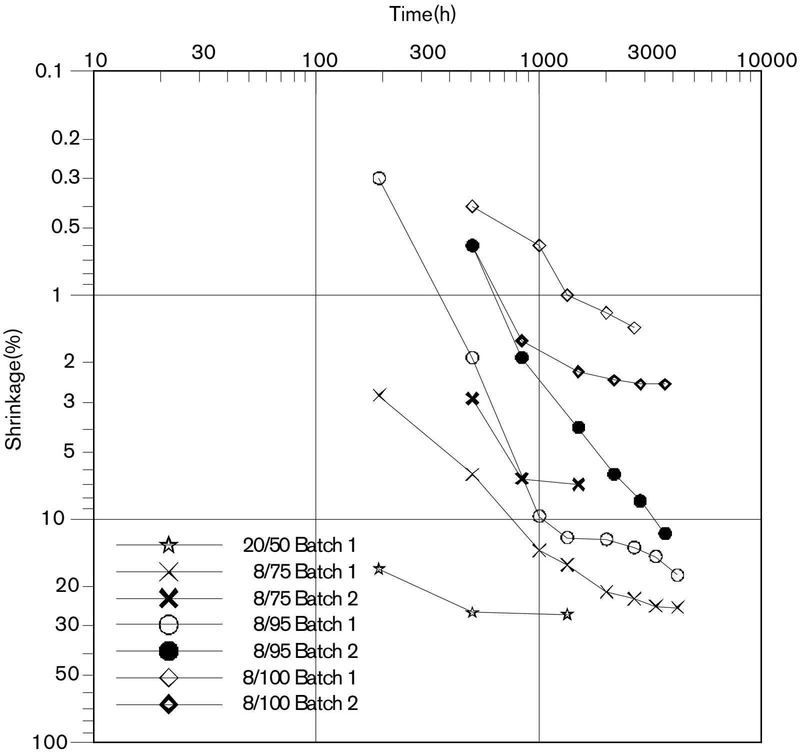

***Figure 4-2.** Drying shrinkage of silica sol during six months. The shrinkage is measured for specimens stored at four different environments. In the legend the first number denotes the temperature and the second number denotes the humidity e.g. 8/75 means that the specimens have been stored at +8°C and 75% relative humidity. /Axelsson, 2004/.*

An initially low strength and occurrence of fractures in the prisms reduced the number of prisms that could be tested, resulting in some uncertainties in the results. This is especially clear for the prisms stored at 8°C and 100% relative humidity, where the strength seems to be decreasing over time.

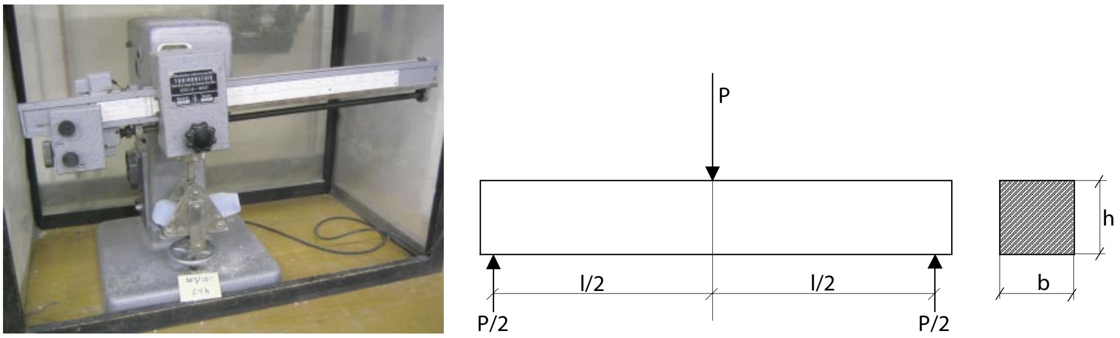

Figure 4-3. Flexural strength measurement apparatus with a tested silica sol prism (left). /Axelsson, 2004/.

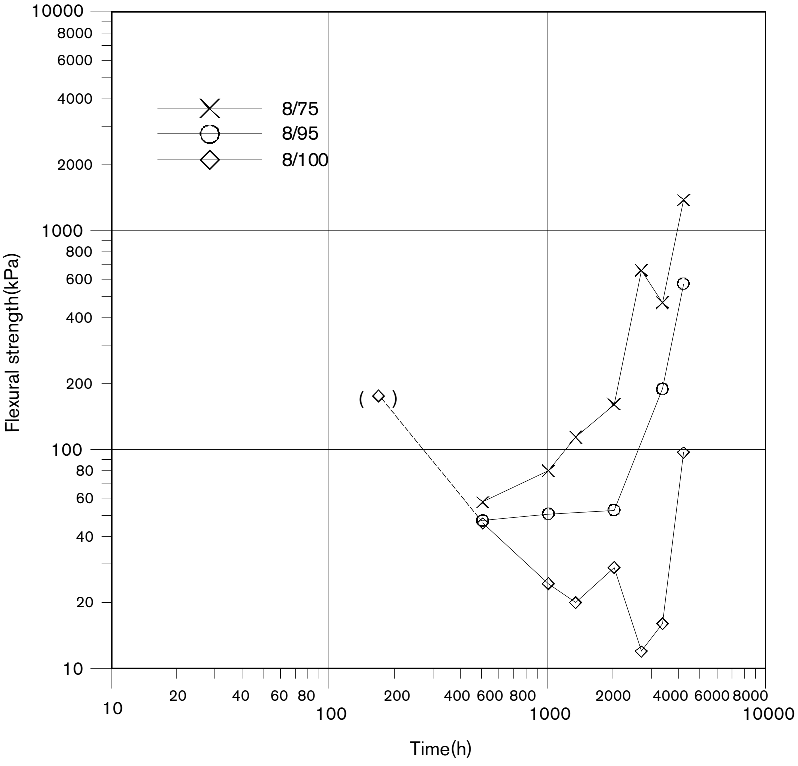

Figure 4-4. Average values of flexural strength measurements during six months. Due to failure in the prisms, some average values might only consists of one measurement. In the legend the first number denotes the temperature and the second number denotes the humidity that the specimen has been stored in. The first value of "8/100" is most certain a read-off error. /Axelsson, 2004/.

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. The measurements were done in a "Hounsfield tensometer", Figure 4-5.

Average values of the compressive strength are shown in Figure 4-6. The strength development increased faster for prisms stored at lower humidity than at higher.

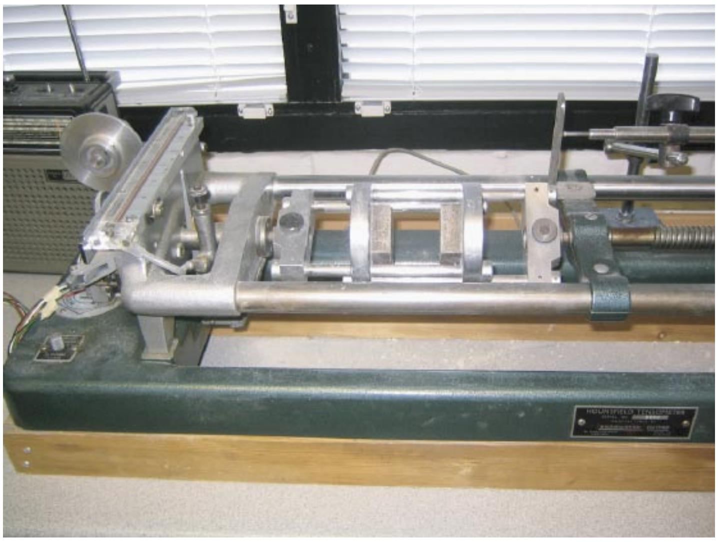

***Figure 4-5.** Hounsfield tensometer. /Axelsson, 2004/.*

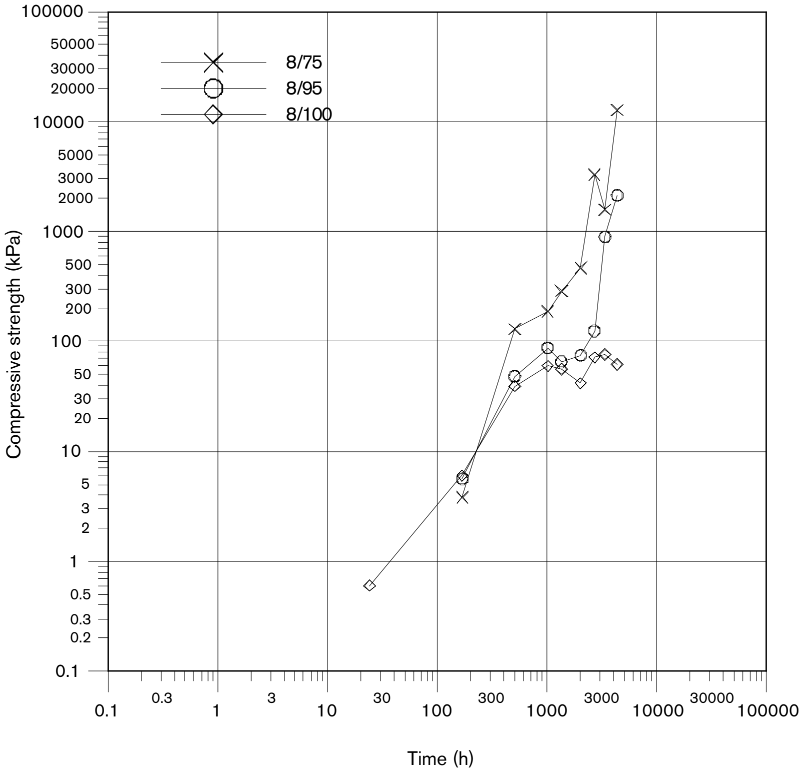

***Figure 4-6.** Compressive strength development during six months. In the legend the first number denotes the temperature and the second number denotes the humidity that the specimen has been stored in. Most values are averages over two measurements. /Axelsson, 2004/.*

The linear elastic relationship seen in Figure 4-7 shows that Hooke's law is applicable for silica sol and that it is possible to determine Young's modulus. The development of Young's modulus over time is shown in Figure 4-8.

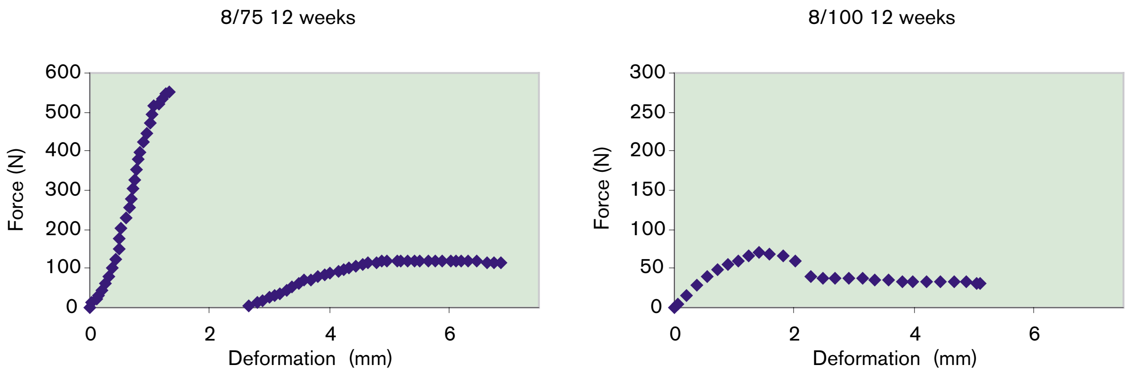

***Figure 4-7.** Example of failure curves for silica sol stored at 8°C and different humidities, after 12 weeks. To the left is a specimen stored at 75% RH that shows typical brittle failure mode. To the right a specimen stored at 100% RH that shows ductile failure. It could also be stated that both curves initially show a linear elastic relationship, which implies that Hooke's law is applicable. /Axelsson, 2004/.*

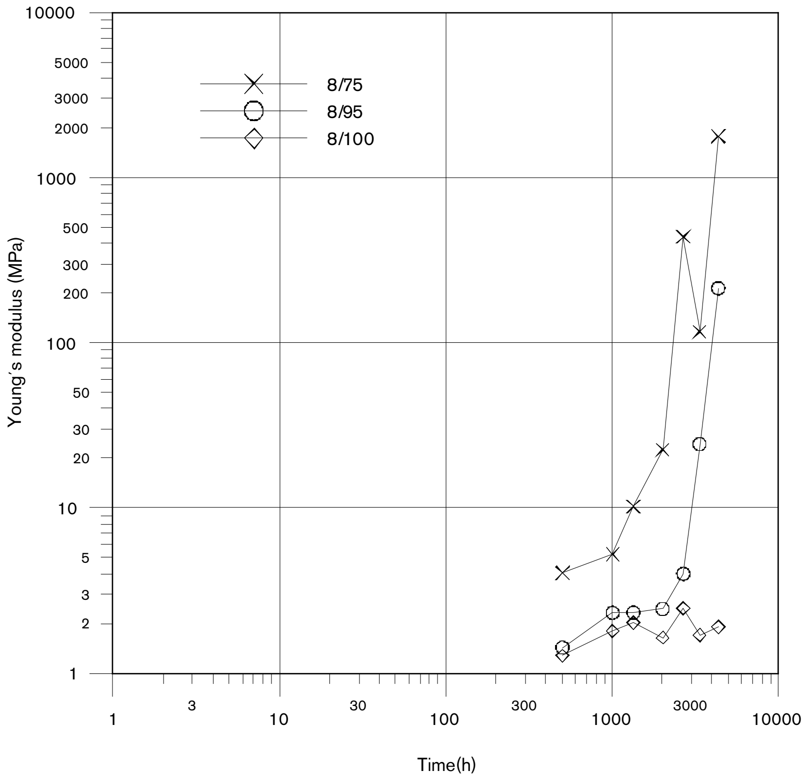

***Figure 4-8.** Development of Young's modulus during six months. Most values are averages of two measurements. In the legend the first number denotes the temperature and the second number denotes the humidity that the specimen has been stored in. /Axelsson, 2004/.*

The shear strength was measured according to the Swedish Standard SS 027125 for geotechnical tests, Figure 4-9. The shear strength was approximately 10 kPa after one day and increased faster for specimens stored at lower relative humidity than higher at the same temperature. The fastest increase in shear strength is noted for specimens stored at 20°C and 50% relative humidity.

Figure 4-9. *Fall-cone apparatus. The blue cylinder contains silica sol for shear strength test. /Axelsson, 2004/.*

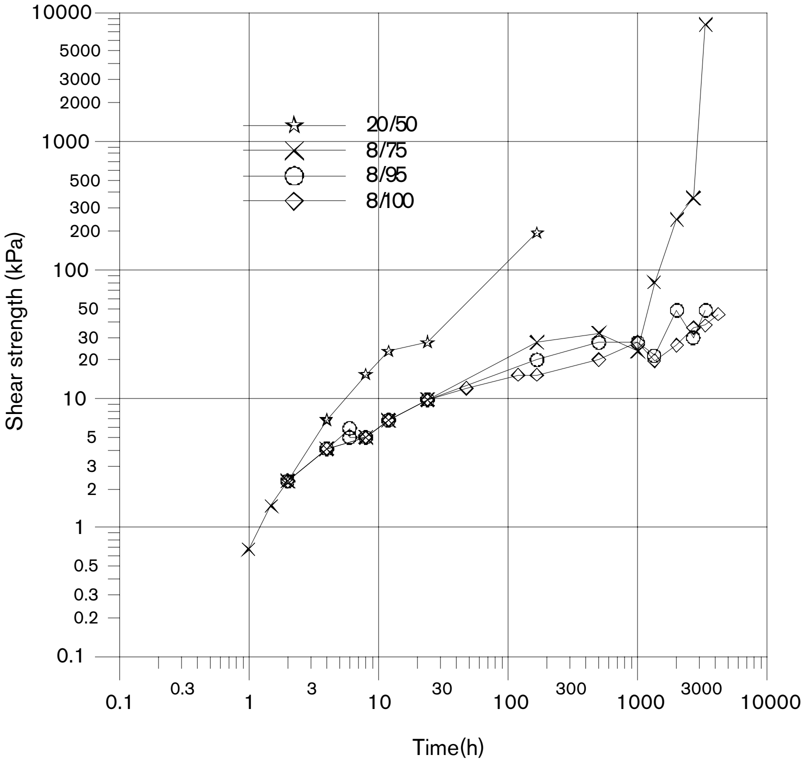

Figure 4-10. *Shear strength development of silica sol. E.g. 8/75 stands for storage at 8°C at 75% relative humidity. The recommended measuring limit for the fall-cone is around 100 kPa and this implies that the values should be seen as relative and not absolute. /Axelsson, 2004/.*

Drying-out tests

The hypothesis was that some shrinkage occurs near the tunnel due to drying out from the air, but the shrinkage is stopped further out in the rock due to the surrounding water. A specially designed test specimen was prepared, Figure 4-11. It consisted of a piece of rock core, which had a borehole that was grouted with silica sol. Water with a predetermined gradient was acting on one side and the grout was exposed to air on the other, which enabled the grout to dry out. The leakage through the grouted hole was measured in a measuring bucket.

In the first moulding the grout was exposed to a gradient of 2.1–2.5 m/m. The second moulding had an initial gradient of 2.5–3 m/m, which was increased to 8.7–9 m/m after 1,000 hours.

Breakthrough for the first moulding was after 4–6 days and for the second moulding breakthrough was noted after 5 days.

As can be seen in Figure 4-12, the specific flow (Q/dh) decreases with time. In the second moulding the pressure was increased after 1,000 hours. The increase in the pressure gradient lead to an immediate increase in the specific flow; followed by a decrease again.

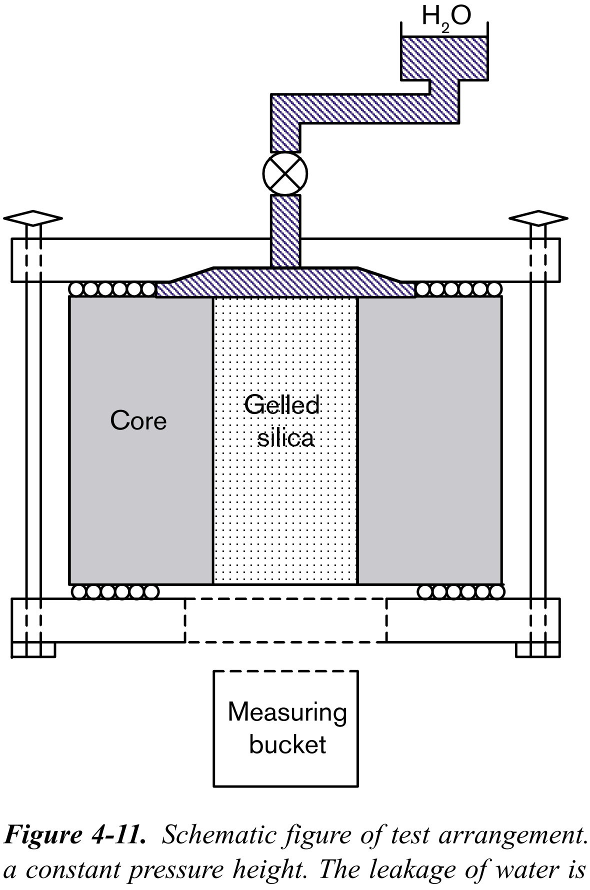

Figure 4-11. *Schematic figure of test arrangement. The water acts on the grouted hole with a constant pressure height. The leakage of water is measured in the measuring bucket. /Axelsson, 2004/.*

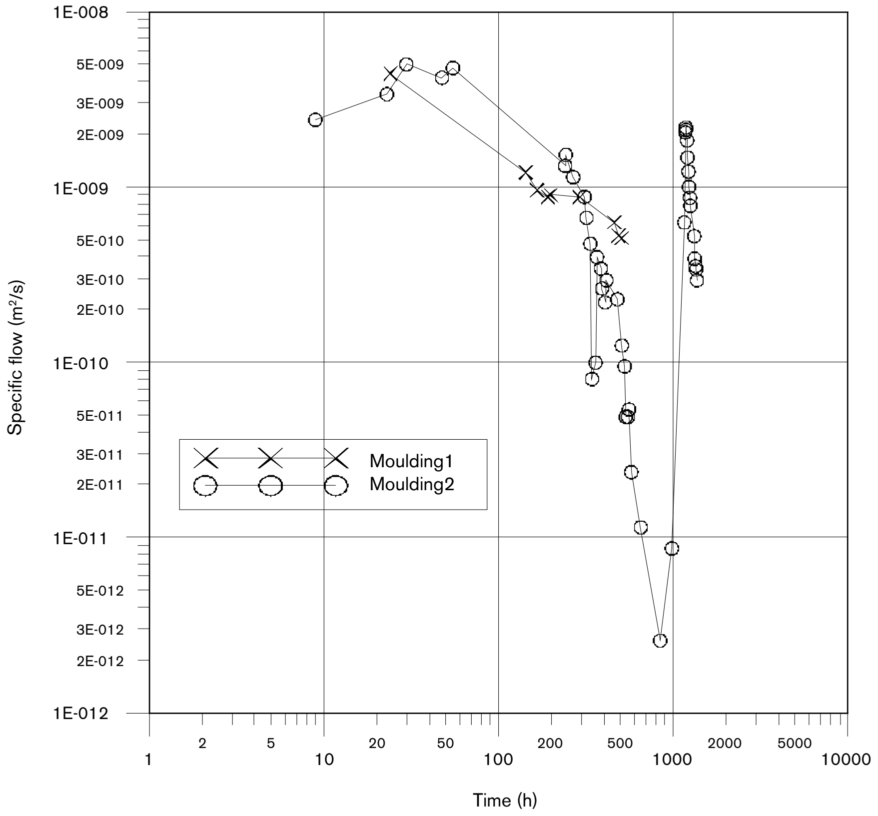

Figure 4-12. *Measured specific flow over time in the drying out test. The tests on the first moulding were stopped because the plug fell out. In the test on the second moulding, the water pressure was increased after 1,000 hours. /Axelsson, 2004/.*

4.2.3 Release of colloids from silica sol

Laboratory testing on the release of colloids from silica sol was performed at KTH. 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 and Finland showing that the colloid concentrations are insignificant in waters containing more than 4 mg/L Ca or 23 mg/L Na. The expected calcium (Ca) concentration in granitic bedrock in a repository in Sweden will be approximately 10–2,000 mg/L, while for sodium (Na) the expected concentrations range from 100 to 2,100 mg/L /SR 97, 1999/. In addition, the use of either NaCl or $CaCl_2$ accelerators will increase the ionic strength in the fractures during injection. It is therefore expected that silica sol will not contribute to the amount of colloids present in groundwaters surrounding a nuclear waste repository in Fennoscandia.

4.2.4 Sand column tests

One purpose was to investigate if the penetration length in sand could be calculated in the same way as for a fracture, i.e. by means of an aperture. A second purpose was to determine the penetration length of silica sol in the sand column. /Funehag, 2005/ made tests with two types of silica sol, Cembinder U22 with NaCl as accelerator and Eka® Gel EXP36 with $CaCl_2$ as the accelerator, both having a particle diameter of 14 nm. The sand in the sand columns was a Swedish glaciofluvially deposited sand “Baskarpsand No 20”, which consists of more than 90% SiO_2 and has almost spherical grains with a median particle size of 0.20 mm. A schematic drawing of the sand column is shown in Figure 4-13.

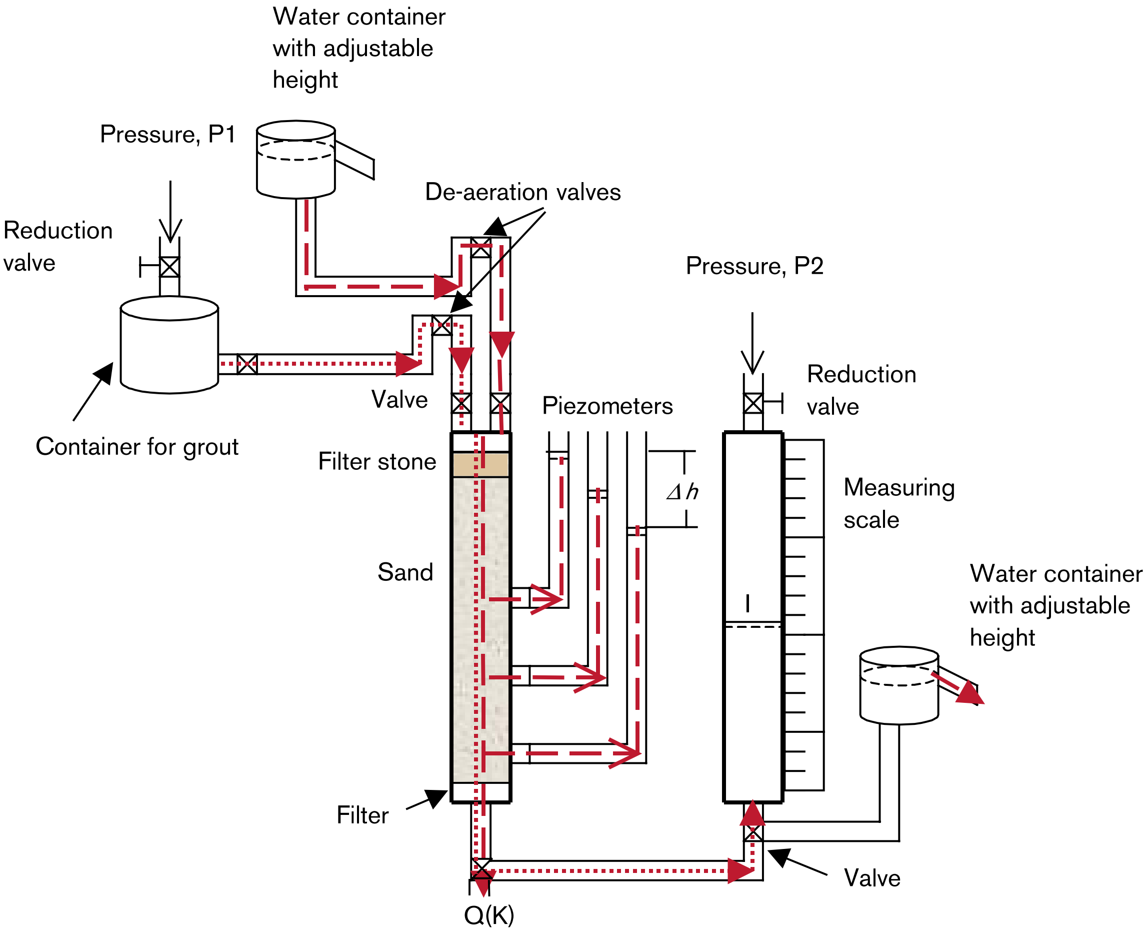

***Figure 4-13.** Schematic drawing of the sand column. The dashed lines show the water path, which determines the hydraulic conductivity, K, by measuring the hydraulic head in the piezometers and the outflow, Q. The dotted lines show the path of flow for measuring the penetration, I. /Funehag, 2005/.*

The results of the laboratory tests show that the maximum penetration of silica sol is obtained long before the gel time of the grout is reached. The penetration of silica sol in sand is shown in Figure 4-14. The grouting overpressure was 100 kPa and the penetration continued until the gel time was reached after 32 minutes (1,900 sec.). The penetration was measured with two porosities, n_1 and n_2, derived in two different ways. The figure also includes the actual viscosity development during the grouting time and the calculated penetration using an analytical 1-D model described in /Funehag, 2005/.

By assuming that the hydraulic aperture is a good estimate of a fracture aperture, the results from sand column tests can be applied to interpret both penetration length in fractures and grout characteristics. Further experiments with other types of sands are planned.

4.2.5 Japanese literature review

/Yonekura, 1996/ has described the history of the ground improvement and technical aspects of chemical grout up to around the middle of 1990's in Japan. The paper focuses on stabilisation of soft ground.

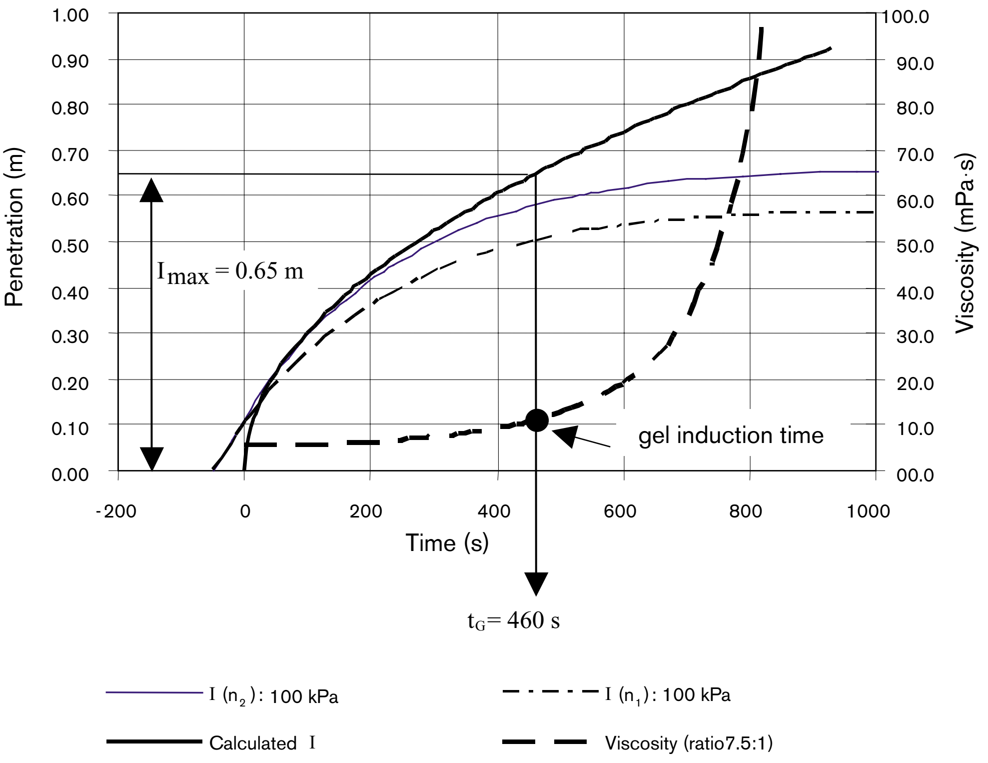

***Figure 4-14.** Measured penetration, $I(n_2)$ and $I(n_1)$, and calculated penetration (Calculated I) for Cembinder U22 at a mixing ratio of 7.51 (gel time = 32 min). The final penetration is around 0.65 m. Gel induction time indicates when the original viscosity has doubled. The actual viscosity change of the grout for the grouting time is included (heavy dashed line). /Funehag, 2005/.*

Since 1974 the Japanese government has prohibited the use of all chemical grouts, except sodium silicate (liquid glass). This is due to an accident that happened in Fukuoka prefecture in Japan, where acryl amide monomers polluted and caused health problems to people that took water from a nearby well during some 10–15 days. Different kinds of sodium silicate based grouts have been developed in Japan since the prohibition of other chemical grouts.

/Yonekura, 1996/ focuses on sodium silicate based grout. It is pointed out that durability, penetration properties and controlling of gel time are key issues for R&D of sodium silicate based grouts.

According to the pre-treatment or accelerator, sodium silicate based grouts are characterised as follows:

- Solution type
  - Sodium silicate and inorganic accelerator (JS).
  - Sodium silicate and organic accelerator (GS).
  - Acid silica sol (SS).
  - Colloidal silica (CS).
- Suspension type
  - Sodium silicate and cement or similar materials (CE).

The silica sol used in the tests at Chalmers University of Technology is comparable to the colloidal silica above, with the exception that silica sol is a refined product from colloidal silica. Chalmers University of Technology, among others, suggests that colloidal silica and silica sol should be classified as a grout-type on its own and not as a sodium silicate. This is done because the gelling mechanisms and chemistry between these two products differs.

The compressive strength (unconfined) of grouted sand is shown in Figure 4-15. The specimens were cured at +20°C and > 90% relative humidity. It is stated that, in general, solution type sodium silicate grout show lower strength under dry condition due to gel destruction. The compressive strength decreases with time, except for the suspension type (CE) and the colloidal type (CS). There is no specification on the colloidal silica studied by Yonekura. Probably there is a large spread in the material properties, depending on the type of colloidal silica.

The reasons of the strength decrease were investigated, especially focusing on silica leaching and syneresis of grout gel. Syneresis is the process by which a liquid is separated from a gel owing to further coagulation. As can be seen in Figure 4-16, there is almost no leaching from gels based on colloidal silica (CS), acid silica sol (SS) or suspension type (CE). The leaching from grout gel is due to the fact that sodium atoms remain in the gel, which reacts to decompose the silicate gel network. The acid silica sol (SS) and colloidal silica (CS) have almost no leaching because no sodium atoms remain in the gel and the suspension type (CE) does not leach because of hard crystals.

Shrinkage due to syneresis is shown in Figure 4-17. The large shrinkage of sodium silicate and inorganic accelerator (JS) is because the structure of the gel network is weak and remaining non-reacted sodium silicate. The shrinkage of sodium silicate and organic accelerator (GS) occurs for the same reason, but less remarkable than JS because the gel network is stronger.

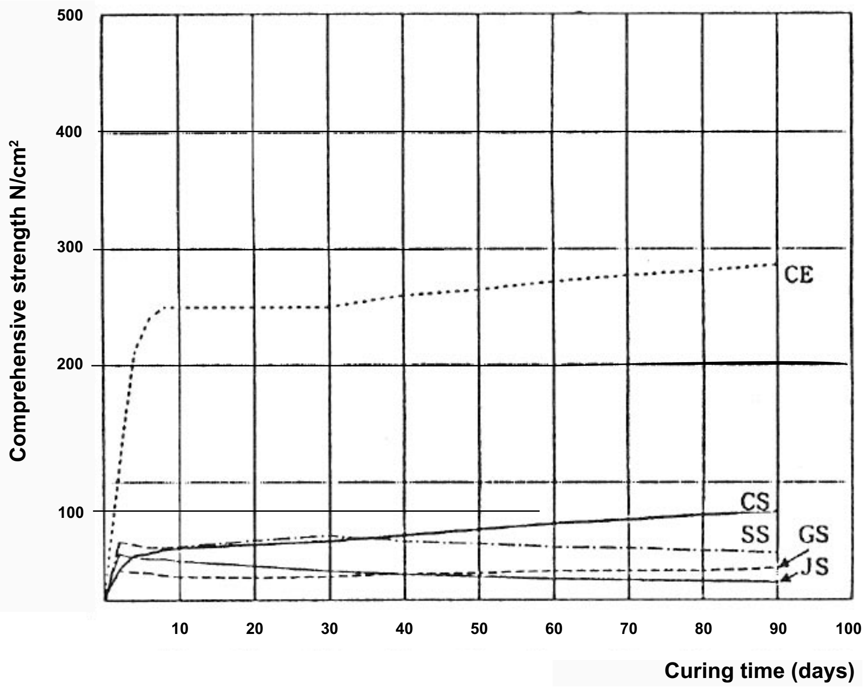

Figure 4-15. *Compressive strength of stabilised sand. /Yonekura, 1996/.*

/Yonekura, 1996/ considered colloidal silica (CS), acid silica sol (SS) and sodium silicate and organic accelerator (GS) as durable grouts and performed long-term permeability tests on samples of stabilized sand with those grouts, see Figure 4-18. The samples were placed under a hydraulic gradient of 50. The samples with sodium silicate and organic accelerator (GS) were impermeable for at least 5.5 years (2,000 days), some of them 8 years (over 3,000 days). Several of the colloidal silica (CS) samples were impermeable more than 11 years while most of the acid silica (SS) samples were started to leak within one year. Note that there is a large spread in time when leakage starts.

Chemical resistance of grout in the chemical solutions is also tested by /Yonekura, 1996/. Samples of stabilized sand have been tested in different water solutions, e.g. sulphuric acid, humic acid and seawater. In seawater, colloidal silica (CS) and acid silica (SS) achieved increasing strength while sodium silicate and organic accelerator (GS) had a tendency of decreasing strength, as in pure water. Sodium silicate and inorganic accelerator (JS) did not change in strength at all.

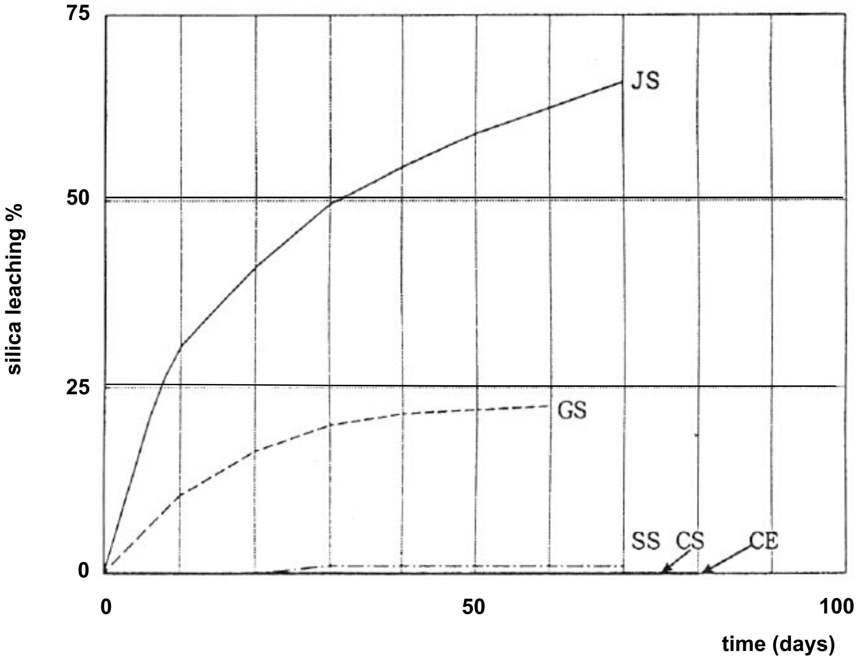

__Figure 4-16.__ Leaching of silica from gel. /Yonekura, 1996/.

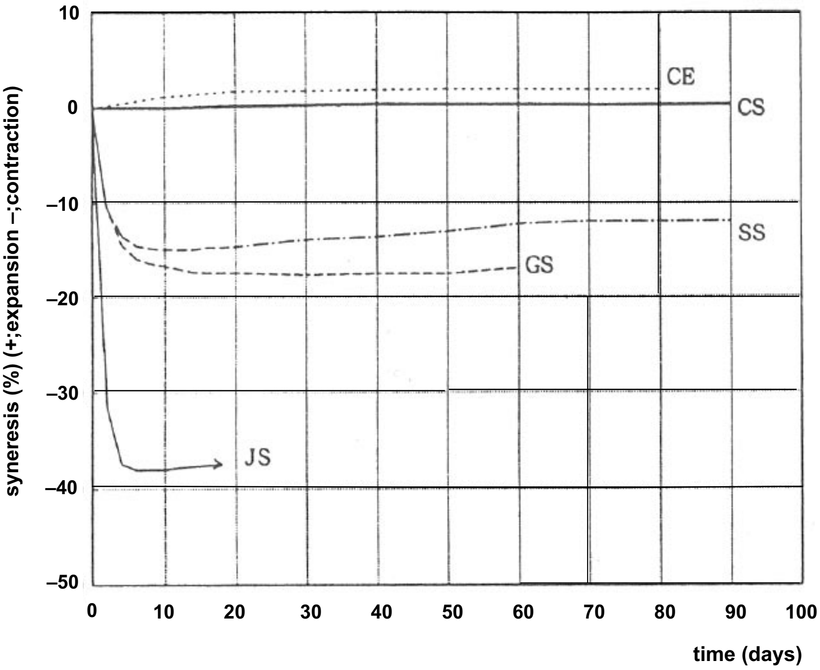

Figure 4-17. Syneresis of grout gel. /Yonekura, 1996/.

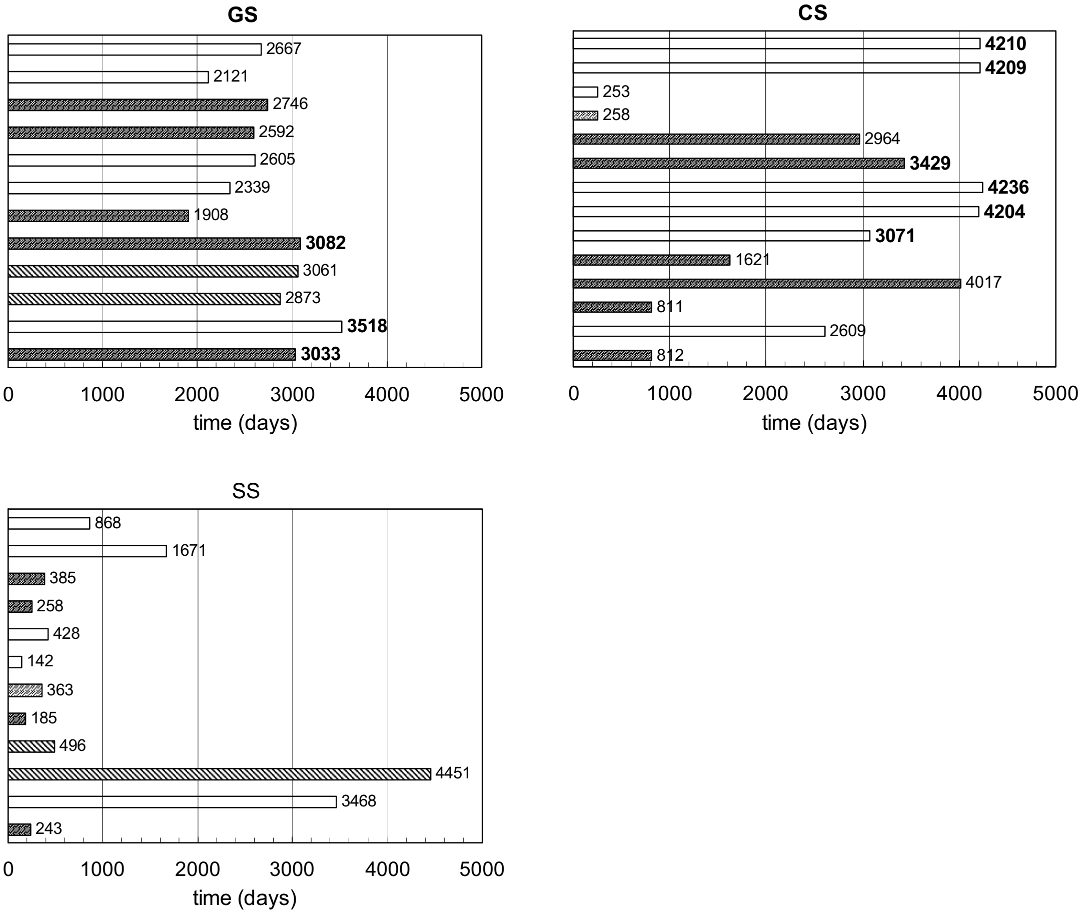

Figure 4-18. Long-term permeability test of silica-stabilised sand, showing days until leakage. Bold numbers indicates specimens still impermeable after number of days. /After Yonekura, 1996/.

4.2.6 Environmental acceptance and long-term safety

Environmental impact of silica sol

According to Swedish legislation, every producer or importer of a chemical product has to make a judgement on possible risks to health or environment when using the specific product. /Swedish Environmental Code Ds 2000:61/ stipulates that "Manufacturers and importers of chemical products or biotechnical organisms shall ensure that an appropriate investigation is carried out as a basis for assessment of the damage to human health or the environment that the product or organism is liable to cause. The investigation shall be carried out in accordance with scientific knowledge and proven experience. It shall include an assessment of the characteristics of the product in terms of health and environmental protection and shall specify:

1. the substances or organisms to which the dangerous characteristics of the product or organism are attributable,
2. the nature and degree of the dangerous characteristics,
3. any measures that are necessary in order to protect human health or the environment in connection with handling and
4. the measures that are necessary in connection with disposal of waste from the product or organism."

A general advice on how investigations of chemical products should be carried out are given by /the Swedish Chemicals Inspectorate, 1991/.

The Swedish producer of silica sol, Eka Chemicals, has prepared a risk assessment where it is concluded that colloidal silica is harmless to the environment /Jansson, 2001a/. 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". /Jansson and Lindblom, 2003/ states that one advantage of using colloidal silica is that it is 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 and Corapcioglu, 2000/.

Banverket, the administrator of the Swedish railway network, has evaluated the use of colloidal silica (Cembinder U22) in the Hallandsås railway tunnel. 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 Cembinder U22 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 Cembinder U22.

Banverket's tests verified the estimates of the risk assessments, i.e. less than 50 m 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 (non-referable memo), 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.

Long-term safety

The long-term safety aspects on the use of silica sol are related to the possible release of colloids and consequent effects on the transport of radionuclides, the potential effects of salts released from the product and the general long-term stability/durability of the grout.

Colloid formation has been found low in laboratory tests, less than 1 ppm, and is likely to be suppressed by the high enough content of ions (Ca, Na) in the groundwater. According to /SR 97, 1999/, the expected calcium concentration in granitic bedrock in a repository will be approximately 10–2,000 mg/L. Further, calcium chloride as accelerator will increase the calcium concentration in fractures when grouting.

The salt leaching from silica sol could have an adverse effect on the bentonite around the copper canisters. With the use of the 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 salt used as accelerator will not affect the salt levels in the groundwaters expected in the Finnish and Swedish sites.

The pH of the pore water released from the silica sol has been measured to be below 11 at leach tests except for experiments using distilled water, an unlikely situation in the field. Thus, the requirement that the pH should be below 11 is fulfilled if the same type of silica sol is used /Jansson, 2001b/.

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.

The overall performance of silica sol grouting over long periods of time (100 years) has not been demonstrated.

4.2.7 Field-testing in Sweden

The field-test consisted of grouting of an earlier grouted fracture in the access tunnel at the Äspö HRL, Figure 4-19.

The overall grouting methodology was divided into three parts, see Figure 4-21:

1. Characterisation of fracture with respect to hydraulic aperture, transmissivity and specific capacity, using hydraulic tests.
2. Grouting the fracture with silica sol (Eka® Gel EXP36) with a procedure based on the earlier characterisation.
3. Verification of grouting result and evaluate the penetration length.

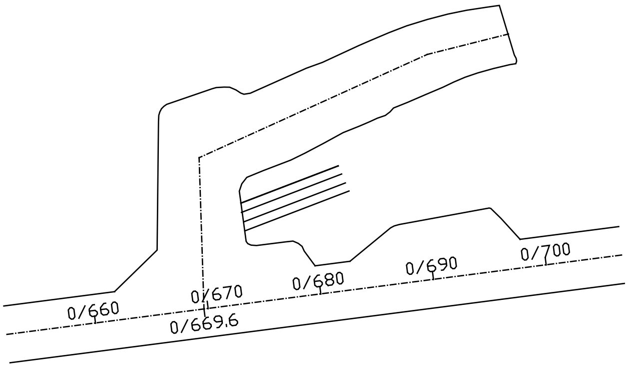

***Figure 4-19.** Sketch showing the access tunnel at the Äspö HRL and the grouted rock pillar.*

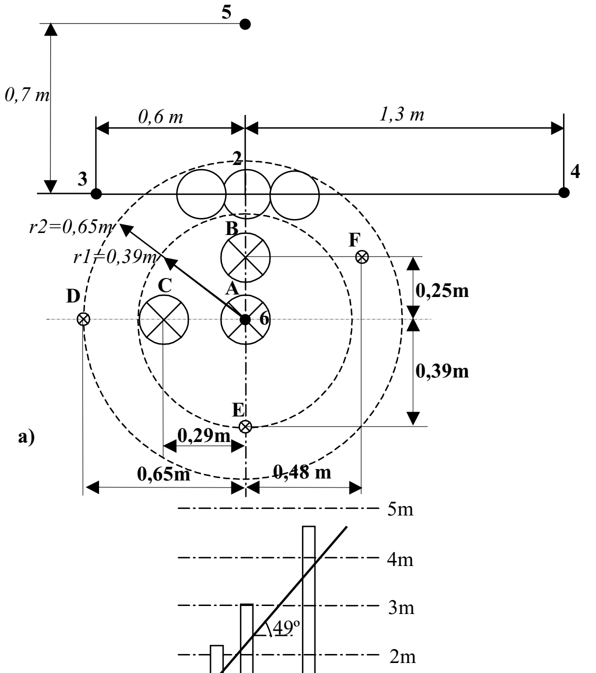

***Figure 4-20.** a) A front view of the boreholes in the rock pillar at section 0/670 in the access tunnel at the Äspö HRL. The boreholes 2 through 6 are boreholes drilled in an earlier test /Fransson, 2001/ and /Eriksson, 2002/. Borehole 2 is the location of the cement-grouted hole in the earlier test. 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.

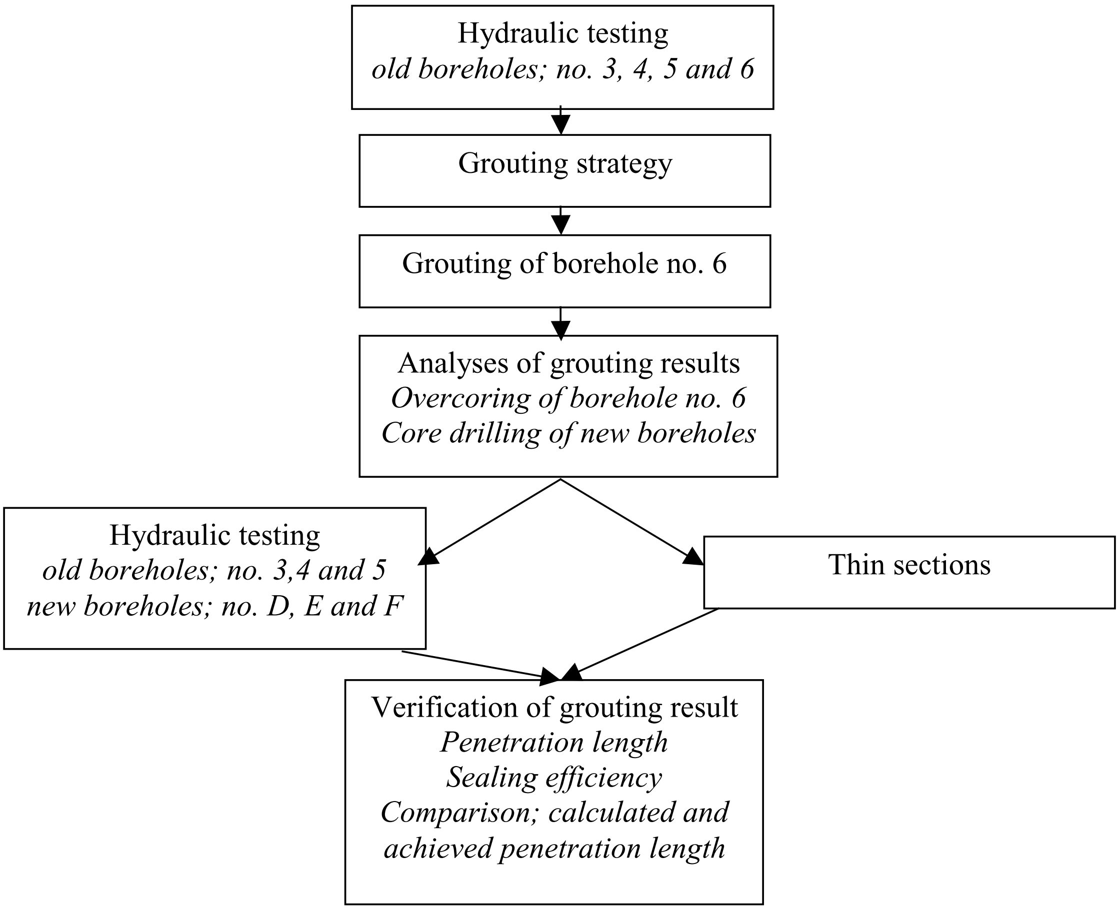

Figure 4-21. *Flow scheme of the used grouting methodology. /Funehag, 2004a/.*

Hydraulic tests before grouting

The characterisation, hydraulic testing, of the fracture consisted of constant head tests with single packer in four core boreholes over the total length and sections respectively. A typical measuring cycle was installation of packer, de-aeration of test interval and equipment, injection (~ 2 bar, 15 min), document recovery (30 min), move to next test section. The hydraulic properties of the grouted borehole differs only slightly from tests done by /Fransson, 2001/.

Grouting

Grouting with Eka® Gel EXP36 was done in borehole 6 at section 1.1–3.0 m. It is most likely that only one fracture intersects the grouted section. The evaluation by /Fransson, 2001/ resulted in a transmissivity of 6.0×10^{-8} m^2/s with a hydraulic aperture of 45 µm (one intersecting fracture only). /Funehag, 2004a/ achieved almost the same results, a hydraulic aperture of 50 µm was assumed.

The grouting procedure was (in chronological order):

- Silica sol was poured into the injection vessel and the stirring started.
- The saline solution and optical brightener was slowly poured into the vessel and the grouting time started.

- The stirring continued for 30 sec after the last amount of salt was poured.
- A reference sample of the grout was taken.
- The vessel was pressurised just enough to be able to fill the borehole (0.2 bar).
- The valve to the packer was opened and filling of the borehole started.
- The packer was tightened when some grout had evacuated and the valve was shut.
- The grouting pressure was set to 2 bars.
- When around 9 minutes had elapsed since mixing the valve to the packer was opened and the grouting started.
- The grouting continued for around 40 minutes totally or until the reference sample had gelled.

The grout mix was 8 parts by weight of silica sol (35%) and 1 part $CaCl_2$ (2.9%). Further the grout was mixed with 30 ppm of optical brightener, which is fluorescent in UV-light in order to verify the grout penetration on cores. The gel time achieved in laboratory was 46 minutes and it was checked in the field by taking reference samples of the grout. The grouting continued until the gel time was reached (~ 50 minutes).

Verification of grouting results

Verification of grouting result consisted of detecting silica sol in the fracture by visual observation and microscopy to verify the penetration length, and hydraulic tests to evaluate the achieved sealing efficiency.

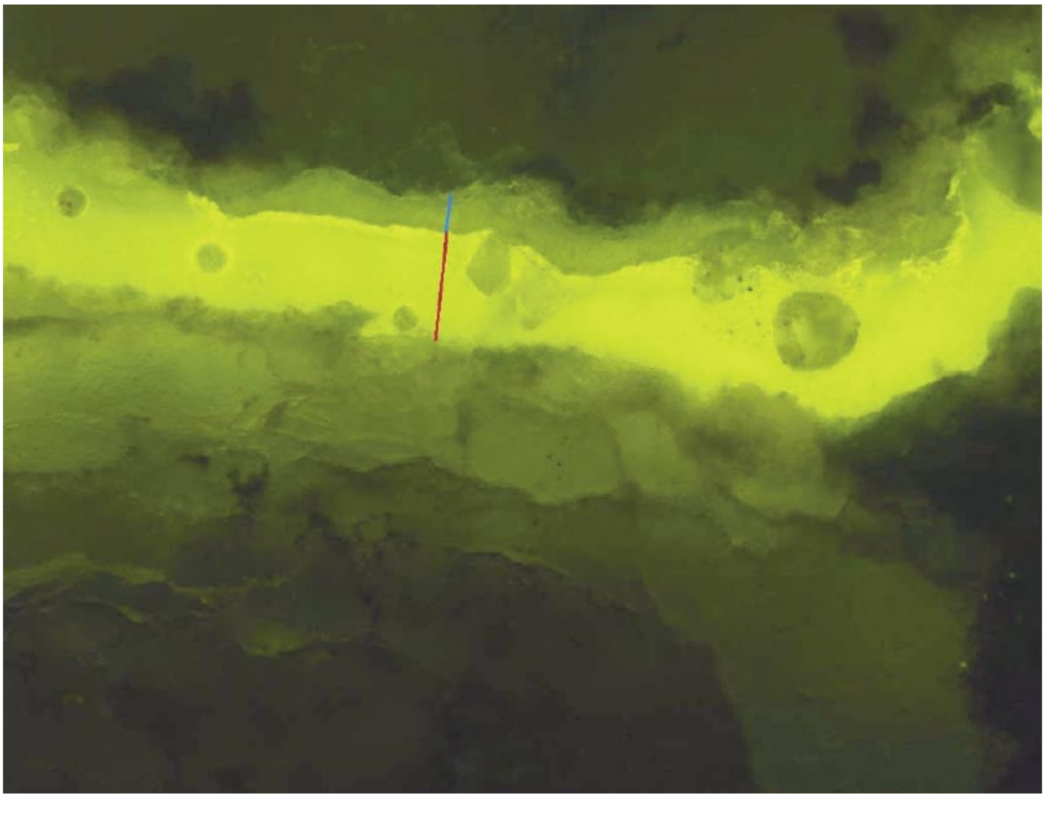

Figure 4-22. *Microscope photo 50 mm from grouted borehole. The analysed fracture is partly filled with silica sol (transparent dark green) and partly filled with epoxy (fluorescent light green). The measurement profiles are marked with a blue line for the silica sol and red for the epoxy. /Funehag, 2004a/.*

The microscopy analyses showed that the gel was detected in the investigated fracture in at least three places of the specimen. When drilling a rock core it looses its constriction, allowing the fractures to expand. This can possibly explain why the epoxy glue has also penetrated the fracture during preparation of the specimen. The width of the gel can give a hint of the natural width of the fracture. Since silica sol is sensitive for drying shrinkage there is also a possibility that the width of the gel, when fully moisturized after grouting, was larger than the measured widths. During preparation of the specimen there were a number of processes that could make the silica sol flush away or for instance dry out during vacuum. The analyses of the cross sections of the macro specimen showed that gel was found as a more complete fracture filling towards the depth of the fracture, which would imply that the methods of preparing the macro specimen degraded the gel.

Hydraulic tests after grouting

The visual observations and microscope investigations show if grout penetration has reached as far as expected, whereas hydraulic tests gives additional, more direct information about the effect of grouting. The method and evaluation was the same as used in the hydraulic tests before grouting.

The median values of the transmissivity before grouting were 1.5×10^{-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 4.8×10^{-9} m^2/s representing the transmissivity of the affected boreholes D, E and F. This implies a sealing efficiency of approximately 70%.

4.3 Literature survey on periclase

A number of databases have been searched. In general, the results of the searching were poor. Most results from the searches were from other areas than rock grouting where periclase is used. Most results were connected to 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).

Practical experience with Thermax in grouting and accompanying comments about the utility was found in /Norwegian Public Roads Administration, 2003/. The result was noted to be worse and more expensive than common injection practice. Moreover, the time of injection more than doubled compared to the standard practice. Although the appraisal of Thermax in this case is negative, one should be aware of that the entrepreneur who injected the Thermax did it for the first time in this project.

In a Finnish literature study /Tolppanen and Syrjänen, 2003/ periclase is mentioned to act as snail dynamite when used as an additive in conventional Portland cement injection grout.

The question whether MgO/Thermax should be regarded as hazard to health or not diverts. The producer /Elkem, 2002/ declares that Thermax is not “a hazard to health, safety or environment”. A similar conclusion is stated in /Swedish National Road Administration, 2000/ (translated from Swedish) “the constituents are exclusively inorganic alkaline earth metals and are considered harmless to the environment” while /Whittaker et al. 1998/ says that “the component listed below is identified as a hazardous chemical under the criteria of the OSHA-hazard communication standard (29 CFR 1910.1200)”.

Thermax is intended as a temporary water blocker. Shortly after, a permanent injection with cement-based grout should be done.

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 loosing the equipment.

Grouting tests with Thermax have been carried out in a road tunnel in Stockholm. The delivered Thermax (from Canada) was coarse and contaminated with impurities. The impurities might have been an isolated case. The grain size, d_{95}, was probably 35.9 μm and the specific surface 32.4 m^2/gram. The penetrability was poor, no penetration in a 100 μm filter in a penetrability meter was observed.

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. The quick set time of magnesium oxide also means a risk of losing the equipment.

4.4 Main findings on testing of silica sol

Using the measurements of the compressive strength, flexural strength (gives a value of the tensile strength) and the shear stress, it is possible to investigate if silica sol can be described reasonably well with the Mohr-Coulomb failure criterion. /Axelsson, 2004/ found that, despite some measuring uncertainties, there is a tendency that the friction angle is increasing with time, Figure 4-23.

As described earlier, water is released during the hardening process of silica sol. The most probable process for the water to excude is by diffusion. In the environmental technology it has been showed that if leakage of a substance through diffusion is plotted against time in a log-log diagram the slope of the line is approximately 1:2. The drying shrinkage is plotted together with a 1:2 line in Figure 4-24.

The drying shrinkage seems to initially have a relatively slow development but after some time (less than approximately one week) the shrinkage accelerates. The exact time for this increase is difficult to estimate but it can be concluded that it happened before the first measuring was done after one week (170 hours). Later the shrinkage more or less starts to follow a declination of 1:2. This can be related to the diffusion of water from the silica sol. In the environments that were used in this laboratory study it seems like the diffusion process starts after 1,000–2,000 hours (6–12 weeks). Earlier time for specimen stored in low humidity and longer time for specimens stored at higher humidity.

At the beginning the increase of strength for silica sol is slow but steady, see Figure 4-25. After a week, the compressive strength is around 5 kPa, irrespective of the storage environment. Then it grows steadily but after some time, depending on the humidity, the rate of increase in strength increases. The timing of the rapid increase depends on the humidity. For the specimens stored at a humidity of 75% relative humidity (RH) the increase appears after 1,000 hours and for the specimens stored at 95% RH the increase becomes obvious after 2,000 hours. For the specimens stored at 100% RH this rapid increase did not appear during the first six months.

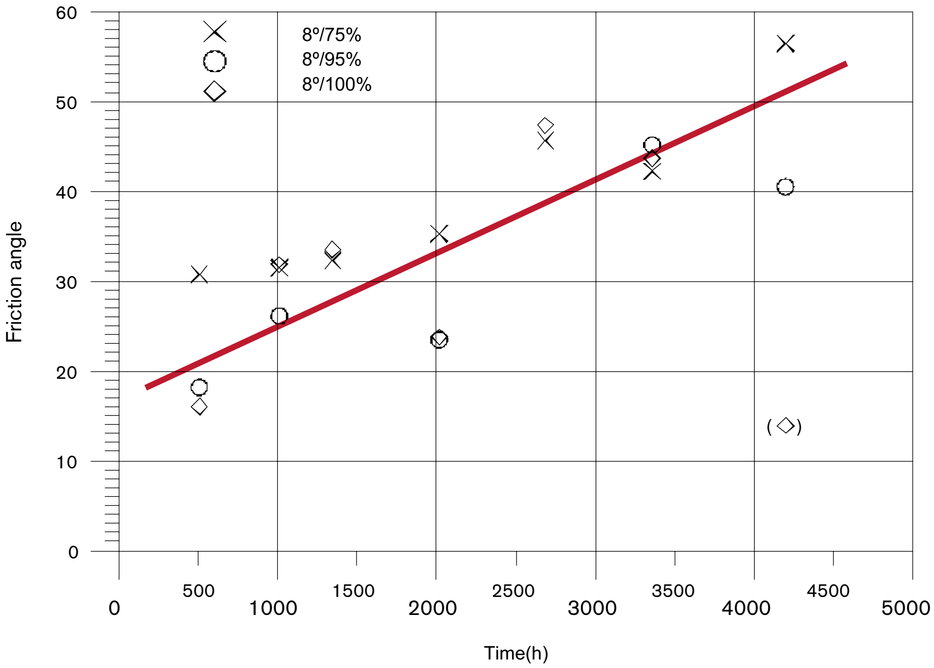

Figure 4-23. Development of the friction angle over time. In the legend the first number denotes the temperature and the second number denotes the humidity that the specimen has been stored in. An estimation of the value of the friction angle versus time is shown with the drawn line. The last value of 8°C and 100% humidity has been put in brackets due to the fact that a higher flexural strength than compressive strength was measured. /Axelsson, 2004/.

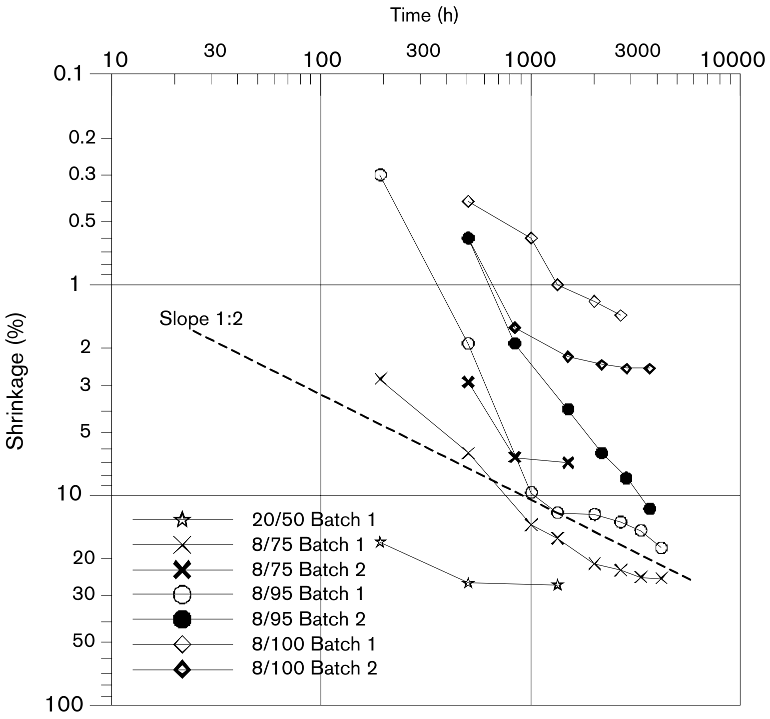

***Figure 4-24.** The drying shrinkage plotted with a dashed line of a slope 1:2. A diffusion process, as the water release during hardening of silica sol, should give a line with a slope of 1:2. /Axelsson, 2004/.*

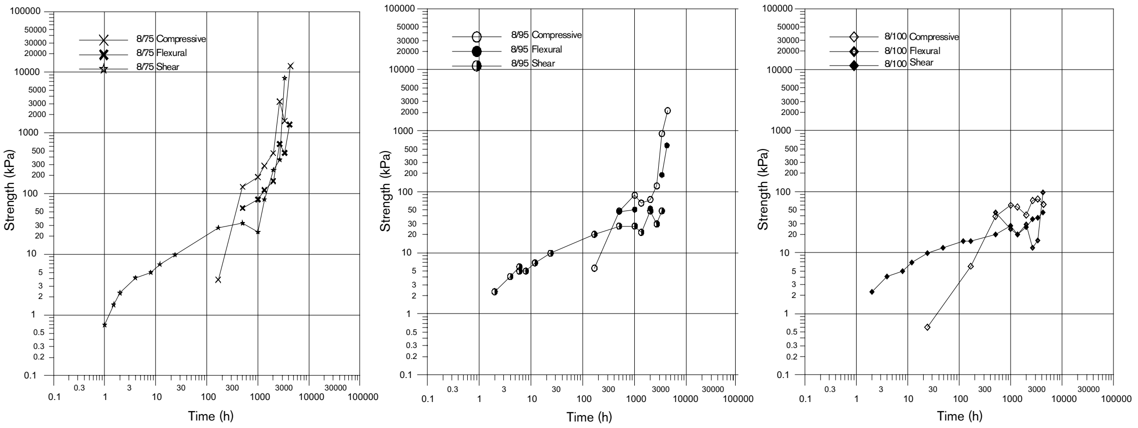

Figure 4-25. The results from the compressive, flexural and shear strength plotted for each storage environment. To the left is the results for the specimens stored at 8°C and 75% RH, in the middle is the results from the specimens stored at 8°C and 95% RH and to the right is the result from the 8°C and 100% RH. /Axelsson, 2004/.

Initially the failure of silica sol appears to be ductile but when the strength increases the failure becomes brittle. This is particularly obvious when studying the failure modes after 12 weeks for the specimens stored at 75% RH and 100% RH, see Figure 4-7. During the failure mode that appeared more ductile, silica sol appeared to have a residual strength due to that the parts started to stick together once again. This can be explained by the applied force in the compressive strength measurement that consisted of two plates that were pressed against each other. At the last measurement, after six months, the specimen stored at 8°C and 75% RH showed an extremely brittle failure. Small pieces spread all over the testing room and safety glasses had to be worn.

As a comparison of the shrinkage, measurements were also done on the shrinkage of a grouting cement (Injektering 30) at a water/cement ratio of 1.0. The result showed that the cement shrunk between 0.5–2% depending on the environment. Notable was that the prism stored in 20°C and 50% humidity shrank around 2%, and cracks appeared in the prisms.

The drying-out test, where a grouted rock core had water on one side and air on the other side, showed a decreasing flow over time, which was interesting and not anticipated. 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.

When silica sol dries out in room climate, it becomes white in colour and very brittle. When it is re-moistured a sparkling sound is heard and it becomes transparent and glass like. The fact that silica sol still seems "thirsty" is a sign that it has not completely formed Si-O-Si bindings but to some extent it may have started to form these bindings. When these bindings have completely formed, silica sol has almost no surface attraction and can almost be considered as sand without any water take.

The measurement of the drying shrinkage was done by a slide-calliper. This is a simple method that does not have the accuracy of a length comparator. There was in most cases shrinkage of several percents up to 25% and the relative error would be small. Also the method of a length comparator has the limit of measuring shrinkage up to a couple of percents. There was no determined time when the moulded prisms were released from the forms and since the shrinkage is dependent on the exposed surface, this could influence the initial shrinkage.

The measuring of the flexural strength implied some problems in the beginning when the initial strength of the silica sol prisms was too low to fasten the prisms in the apparatus. In almost the whole measuring series the values of the flexural strength was in the lowest range of the measuring interval for the apparatus. This implies that the measuring had a higher inaccuracy than would be the case if the whole measuring range were used.

The measuring of the shear strength was done with fall-cone. The fall-cone is a semi-empirical method that is developed to determine shear strength in clay. When testing silica sol there are some aspects that have to be considered when analysing the results. In the beginning the silica sol almost behaved flexible and the fall cone bounced at the surface and the read-off accuracy was lowered. Then followed a stage were silica sol behaved more like clay and the method seemed reliable. But when silica sol had reached some strength it became more brittle and the test method seemed less adjusted for this kind of material. In order to get more precise measurement of the shear strength, a shear box could be used. But it is important to have some idea of the material parameters before starting to use a more complex measuring device and the results can be used as a characterisation for a better use of other methods.

A simple theoretical reflection regarding the shear strength indicates that the requirement on grout to withstand erosion from water is much lower than the obtained strength of silica sol. If silica sol is pumped until it has gelled this should imply that enough shear strength in silica sol is obtained to withstand the erosion from water. A more extensive investigation is going on at Chalmers University of Technology to gain a better understanding on what demands the grout has to fulfil.

The field-tests at the Äspö HRL aimed at investigating the transmissivity and penetration of silica sol (a Newtonian fluid) in a small fracture, aperture 40–50 µm. The fracture has earlier been grouted with cement (a Bingham fluid), resulting in a very limited penetration. The methods for predicting/estimating the grout penetration were hydraulic tests, visual observation of the cores and microscopy analyses.

The visual observation showed that five of total six cores had traces of silica sol. All cores were drilled within the predicted penetration length. One core did not show any traces of grout even though cores further away did. The use optical brightener is not the best tracer because particles may cause some clogging. Other tracers, e.g. Uranine, should be considered in future research, but laboratory work needs to be carried out to see that it does not affect the properties of the grout.

5 Conclusions

The definition of low-pH grout is pH ≤ 11 in the leachate. A short-term pH in the pore water exceeding 11 due to initial leaching can be accepted, but the long-term equilibrium pH should be ≤ 11.

The requirements on grout properties can be contradictory. Therefore it is important to consider bedrock and fracture characteristics (aperture, hydraulic pressure etc), groundwater composition (aggressive components, e.g. sulphate) and possible grouting designs including the proper grouting material in order to make the right priorities between different parameters.

The original requirements on cementitious grout were set based on partly theoretical understanding and partly empirical experience, as different parameters are differently well founded and understood. This is also valid for the updated requirements that were set.

This project concentrated on the technical development of properties for the low-pH grouts. Long term safety and environmental aspects and durability of materials were preliminarily considered. Continued evaluations have to be carried out.

Five cementitious and two non-cementitious systems were initially included in the study. During the course of the study three of the cementitious systems were ruled out due to unavailability or sulphide leaching. Of the non-cementitious system one candidate material was ruled out due to the fact of not being used in grouting, and identified risks associated with the use of it.

The basic mechanical properties of silica sol were investigated. No requirements were set on this grout, except that it should be possible to grout fractures smaller than 100 μm and that the leachant pH should be below 11.

5.1 Cementitious systems

5.1.1 Evaluation of pH on tested cementitious systems

There is no standardised method for pH-measurements that can be applied to the cement leaching process. Different methods of measuring pH will give different results. This is a key issue under discussion. Factors influencing the pH result are e.g. sample status (size, solid or crushed), ionic strength of the leach solution, and protection against CO_2, amount and change of leach solution. The buffering capacity of bedrock and fracture fillings on the pH was not evaluated.

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 modelling of diffusion coefficients. The samples were first subjected to equilibrium testing, and if the progress of the pH was favourable, also to diffusion testing. The testing was performed in CO_2-free atmosphere in glove boxes. Due to ionic strength effect leaching of samples cured at 20°C in fresh water (ALL-MR) gave the upper limit for pH, thus leaching tests in saline water were cut out.

The laboratory tests on the systems showed that alkali content in a mix does not directly influence the measured pH in the leachates. For the OPC+SF, WCE+SF and slag based mixes in order to achieve pH ≤ 11, the minimum content of SiO_2 in mixes should be close to or above 50 weight-% of total binder materials or Ca/Si molar ratio should be close to or less than 0.80. CaO + MgO content of the product is also an important pH-factor.

5.1.2 Evaluation of technical properties on tested cementitious systems

The most promising system consists of ordinary Portland cement and silica fume, OPC+SF, based on laboratory experiments and preliminary short term field testing. It is believed that this system can be further developed. The grouting related properties of OPC+SF mixes were modified with high alumina cement (HAC) and gypsum (G) (called ETTA acceleration). Some modifications were made with superplasticiser (SP) and ETTA. System without ETTA is simpler in practical work. Further modifications are possible, including SP and/or other types of SF. The used OPC was UF16 ground by Cementa and SF in dispersion was GroutAid by Elkem.

In order to gain 28-day uniaxial compressive strength above 7 MPa, the W/DM-ratio needs to be below 1.6.

Most probably SP is needed in order to gain required grout properties. This may, however, influence the long-term safety, and need to be further evaluated for the specific grout and SP used. A system with SP was used in pilot field test 2, giving promising results and it could technically be considered for repository grouting.

The use of SF makes the practical properties of injection grout more sensitive to variations in temperature than without.

With regard to the environmental aspects, there are no special reasons to judge any of the components of OPC+SF system to be unacceptable for grouting (superplasticiser excluded). Interaction with near-field rock and fracture fillings due to leaching and degradation of cement need to be taken into account, some changes in the porosity of fractures is expected due to secondary minerals formed. The long-term durability and phase changes occurring in the new developed low-pH products are not known yet and need to be evaluated. Basically the product consists to a large part of silica, which also is present in crystalline bedrock. However, the quartz in rock minerals is not in a soluble form. The constituent materials include or may include components, such as organics, phosphates, nitrogen compounds or heavy metals. These compounds have to be taken into account when designing the use of them in deep repositories. In addition to the cautions regarding environmental aspects and the long-term safety concerns, the occupational safety questions need to be taken into account.

The planned small scale field-test in Finland was postponed as pilot test 2 showed that more optimisation work should be carried out.

In addition to OPC-cement, Egyptian low-alkali white cement was tested in the laboratory. It was expected that white cement with its low alkali content automatically should give a lower pH, but this was not found. Egyptian low alkali white cement (WCE) was introduced and two mixes were tested for pH. The alkali content of the cement was found not to be the only pH-determining factor.

With respect to technical aspects, no obvious advantages, neither disadvantages, with white cement were found and thus the testing of white cement was stopped at an early stage. The practical grouting properties were not better, when compared to other cements. However, according to the leaching tests, an advantage as compared to the other OPC based cements was less leaching of alkalis (K), sulphate and silica.

5.1.3 Cementitious systems not further developed

Slag and super sulphate cement (SSC)

A slag system is a system activated with OPC only. Super sulphate cement (SCC) denotes a binder system, which is based on slag and activated with gypsum and OPC.

System with slag did not show any advantages compared to SSC-system. Slag system was ruled out also due to high leaching of sulphide, H_2S, which is detrimental to the copper canister. It is also detrimental to the corrosion of any metals such as rock bolts etc.

SSC system showed promising behaviour with regard to grouting related properties as well as leaching behaviour. However, the system was ruled out due to high leaching of sulphide, H_2S.

LAC

Despite the small grain size, LAC was found to be less suitable for grouting purposes. Its ability to penetrate fractures is most likely blocked because gelling of the small particles. Penetrability of LAC fine and LAC fine+coarse has been tested, but not for LAC coarse only. The pH requirement was fulfilled but the material needs modification to improve the grouting properties.

Fly ash

Fly ash system was never tested, but it was ruled out at an early stage due to expected problems concerning the availability and stability of the raw material properties as well as expected difficulties with the setting time of the mixes.

5.2 Non-cementitious grouts

5.2.1 Silica sol

The project has not carried out any pH measurements on silica sol leachates, but the manufacturer states that pH is 9.5–10. Silica sol is colloidal silica in a stable dispersion of discrete non-porous particles of amorphous silicon dioxide, SiO_2 with 5–100 nm particle diameter. The particles in the tested product Eka® Gel EXP36 have a diameter of 14 nm. Adding a salt, sodium chloride and calcium chloride, makes the silica sol particles aggregate and form a gel.

Rock grouting with silica sol is a new application, but some successful minor rock grouting tests had been performed in Sweden at the start of the project. Silica sol has been used for soil grouting in e.g. Japan, where durability, penetration properties and controlling of gel time have been identified as key issues. More than 11 years of permeability tests on grouted sand columns indicate that silica sol is a durable grout /Yonekura, 1996/.

Silica sol is ductile at the beginning of the hardening process and gets more and more brittle as strength increases. This strength increase continues over a long time. In the laboratory tests it was found that the strength increase and shrinkage are highly depending on ambient temperature and humidity. A high temperature and/or low humidity make the strength development faster. Silica sol also has a tendency to shrink in low humidities. The shrinkage, after six months in 8°C and 75% relative humidity, can be as large as 25%.

The results of the tests that were carried out to imitate drying out of silica sol in a fracture are not fully understood. After breakthrough of water, the leakage decreases over time.

Change of humidity in a tunnel and fracture is likely to occur. In order to gain a better knowledge of climatic influences on silica sol behaviour it would be favourable to further investigate strength development and drying shrinkage followed by wetting again, at different humidities and temperatures.

Colloidal silica seems to be a feasible material to seal very small fractures (< 0.05 mm). The gel is sufficiently stable to prevent water flow through the sealed fractures. This can be concluded after other studies carried out during 2–3 years, a time put in relation to the time the tunnel in question is to be open. No chemicals are foreseen released in concentrations that would be harmful to the environment.

Colloid formation has been found small in laboratory tests, less than 1 ppm, and is likely to be suppressed by the high enough content of ions (Ca, Na) in the groundwater.

The long-term stability of silica sol gel has not been demonstrated. The anticipated salt amounts originating from the accelerator are not expected to cause any problem as groundwaters at repository level also have substantial salt concentrations.

The studies presented in this report have given a better understanding of the gel behaviour, but those studies need to be complemented.

The minor field-test carried out in a drained rock pillar at Äspö HRL showed that it is possible to grout, calculate and predict grout spread in fractures that could not be grouted with cement.

5.2.2 Periclase

The indication from the literature search carried out and discussions with experts that have some experience from its use was that periclase, MgO, couldn't be recommended for further studies. It is also difficult to steer the setting time.

5.3 Concluding remarks

Cementitious system based on OPC+SF would probably need modification with superplasticiser to grout fractures down to 100 μm. Any use of SP needs further evaluation. Thus, this system is not yet proven to be acceptable from an environmental and long-term safety point of view. Also the long-term durability of the low-pH cementitious material and the long-term phase changes/degradation and leaching of the grout is not yet known and need to be evaluated.

Silica sol is acceptable from an environmental and long-term safety point of view. The long-term stability of the product needs to be evaluated. However, it is favourable to gain a better understanding of the durability and the mechanical properties to be able to make a proper grouting design before it is recommended for repository grouting.

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