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Durability of Low-pH Injection Grout

A Literature Survey

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ABSTRACT

This publication provides an overview of the durability of injection grouts. It is intended for use during planning and construction at the ONKALO underground research facility. The review has been done with respect to the application conditions, materials and service life requirements expressed by Posiva Oy. The publication describes all types of cement-based material durability, with an emphasis on the key issues of shrinkage cracking, leaching and sulphate attack. The second part of the report provides information on how durability expectations have changed with the history of injection grout development. The report gives information specific to low-pH injection grouts containing high amounts of silica fume performance and how their durability is expected to differ from traditional normal cement-based mixtures. The final part of the report provides suggestions for future research needs for ensuring the service life of injection grouts. The key finding from this study is that the low-pH grout material is not expected to have worse durability performance compared to the standard injection grout. Combining high amounts of silica fume with the cement to produce low-pH grout should result in a material having lower permeability and thus greater resistance to leaching and chemical attack. Further laboratory testing is needed to quantitatively verify these findings and to provide inputs for future service life modeling.

Keywords: grouting, grout, injection, low-pH, cement-based, silica fume, durability, ONKALO, tunneling

Matalan pH:n injektointiaineen säilyvyys – Kirjallisuusselvitys

TIIVISTELMÄ

Tässä raportoinnissa esitetään tietoa injektiolaastien säilyvyydestä ja siihen vaikuttavista tekijöistä. Raportointi on tehty käytettäväksi maanalaisen ONKALO-tutkimustilan suunnittelussa ja rakentamisessa. Selvityksessä on otettu huomioon Posiva Oy:n määrittelemät injektiolaastien käyttöolosuhteet, laasteissa käytettävät materiaalit sekä laasteille asetetut käyttöikävaatimukset. Raportoinnissa on esitetty tietoa kaiken tyyppisten sementtipohjaisten materiaalien säilyvyydestä. Erityisesti on esitetty tietoa tässä tapauksessa oleellisten säilyvyystekijöiden, kuten kutistumishalkeilun, liukenemisen (leaching) ja sulfaattien aiheuttaman rasituksen, osalta. Raportoinnin toinen osa sisältää tietoa siitä, miten säilyvyysodotukset ovat muuttuneet samalla, kun injektiolaastit ovat ajan myötä kehittyneet. Raportoinnissa on esitetty nimenomaista tietoa sellaisten alhaisen pH:n injektiolaastien, joissa silikan osuus on suuri, säilyvyydestä. Lisäksi on esitetty, miten näiden silikalaastien säilyvyys oletettavasti poikkeaa traditionaalisten sementtipohjaisten injektiolaastien säilyvyydestä. Raportoinnin viimeisessä osassa on esitetty ehdotukset injektiolaastien riittävän säilyvyyden varmistamiseksi vaadittavista jatkotutkimuksista. Selvityksen oleellinen tulos on se, että matalan pH:n injektiolaastin säilyvyys ei ole tavanomaisen injektiolaastin säilyvyyttä huonompi. Suuren silikamäärän lisääminen sementtipohjaiseen laastiin tuottaa alhaisemman pH:n laastia, jonka läpäisevyys pienenee ja näin ollen myös liukeneminen vähenee ja kemiallinen kestävyys paranee. Tämän asian kvantitatiivinen todentaminen vaatii kuitenkin lisää kokeellista tutkimusta.. Soveltuvia kokeellisen tutkimuksen tuloksia tarvitaan myös lähtötietoina tulevissa käyttöikämalleissa.

Avainsanat: injektointi, laasti, injektiolaasti, alhainen pH, sementtipohjainen, silika, säilyvyys, ONKALO, tunneli

TABLE OF CONTENTS

ABSTRACT

TIIVISTELMÄ

NOTATIONS

The notations used in the report are as follows:

ASR	alkali silica reaction
B	binder (sum of all cementitious materials, such as cement, silica fume, slag, etc.)
C	cement
C_3A	tricalcium aluminate
C_4AF	tetracalcium aluminate ferrate
$Ca(OH)_2$	calcium hydroxide
CH	calcium hydroxide (portlandite)
Cl	chloride
CO_2	carbon dioxide
CSH	calcium silicate hydrate
HCO_3	bicarbonate
K	potassium
Mg	magnesium
Na	sodium
NH_4	ammonium
OPC	ordinary portland cement (white, grey or sulphate resistant)
SF	silica fume
SH	silicate hydrate
Si	silicon
SiO_2	silicon dioxide
SO_4	sulphate
SP	superplasticizer
SR	sulphate resistant
UF16	Ultra Fine 16 (A commercial injection cement produced by Cementa Oy)
W	water
W/B	water-to-binder ratio
W/C	water-to-cement ratio

Notes:
Ratios such as W/C or SF/C are given as weight units of dry materials.

All material mass percentages, for instance of silica fume included in a grout, are given as dry material unless otherwise stated. In the case of Grout Aid (a silica slurry product), “SF” denotes only the dry material content of the Grout Aid.

The term “SP dosage” is given as a percentage, calculated by weight unit of superplasticizer compared to the total binder (cement + silica fume) amount.

In literature, PC (portland cement) is used interchangeably with OPC to mean the same thing.

1 BACKGROUND

Spent fuel from the two nuclear power plants (Loviisa and Olkiluoto) is planned to be disposed of in a geologic repository at the Olkiluoto island, on the southwestern coast of Finland. The construction of the underground rock characterization facility, ONKALO, started in 2004. The ONKALO facility will be used to further characterize bedrock properties and find the most suitable locations for the first deposition tunnels and deposition holes for the spent fuel canisters. Testing and demonstration of repository construction, operation and closure technologies will also be performed in ONKALO. The construction of ONKALO is to be completed by the end of 2014. The total underground volume of ONKALO is approximately 300 000 m^3 with a combined length of tunnels and shafts of approximately 8500 meters. The tunnel is being excavated using a drilling and blasting method, with shaft(s) being excavated in several stages to their final depth of 520 meters (Ahokas 2006).

One of the main requirements of the construction is to provide a water-tight structure, with leaking from the tunnels to not exceed 140 liters per minute. In general, the structure should be kept as water-tight as possible and therefore a very general guideline for practice has been a maximum allowed leakage of 1-2 liters per minute per 100 meters of tunnel length. To meet this leakage requirement, it is necessary to seal all fractures and cracks as well as possible with injection grouts. The goal is that fissures greater than about 50 to 100 μm in width are to be sealed with cement-based injection grouts. Injection grouts are also used to improve the bond of rock bolts used for improving structural bearing capacity. It is necessary for the grout to have a low hydraulic conductivity, good penetrability of very fine fissures and physical and chemical compatibility with the host environment.

Injection grout is typically made as a slurry of cement-based materials and water. The porewater pH of normal injection grout is usually greater than 12.5 due to portlandite. Chemical and mineral admixtures are commonly used in injection grout to aid fresh and hardened material properties, which will be further discussed in Chapters 3 and 4. The main chemical admixture used to aid grout workability at ONKALO is a naphthalene sulphonate based superplasticizer. The main mineral admixture or pozzolan used at ONKALO is silica fume, also known as microsilica. Silica fume is a by-product of the silica and ferro-silicon alloy industry. The particles are spherical, have an amorphous (glassy) structure, a SiO_2 content generally above 90 percent, an average diameter on the order of 0.1 μm and surface areas in the range of 20 to 25 m^2/g (two orders of magnitude finer than normal cement). The benefits and risks of using silica fume will be further discussed in Chapter 4.

Table 1. *Example of grout mixture designs to be used at ONKALO.*

	Standard grout mix 5/5	**Reference grout mix U1**	**P308B**
Water (all water; incl. superplastisizer water and silica slurry water) [kg/m^3]	747	713	791
Ultrafin16 (sulphate resistant microcement) [kg/m^3]	625	879	329
Silica fume (solid content) [kg/m^3]	110	0	226
Mighty 150 (naphthalene sulphonate based superplasticizer) [kg/m^3]	20,7	17,5	22,4
water binder ratio (incl. superplastisizer water and silica slurry water)	1.02	0.81	1.42
Density [kg/m^3]	1521	1629	1384
Shear strength 6h [kPa]	0.66 – 1.58	0.16 – 1.61	0.25 – 3.37
Shear strength 24 h [kPa]	> 245	> 245	94.1 – >245
Comp. strength 1 d [MPa]	1.00 – 2.37	1.20 – 2.83	0.41 – 1.08
Comp. strength 28 d [MPa]	22.2 – 22.6	22.9 – 24.0	13.0 – 17.9
Comp. strength 91 d [MPa]	12.2 – 27.1	20.3	21.4 – 24.4

Note: when giving strength results, testing circumstances (temperature, mixing time, mixer type, cement consignment) have varied

All of the injection grout used at ONKALO will be made with sulphate resistant microcement to improve durability. The microcement is ground finer than standard portland cement to improve the injection ability. An example of an injection grout used in the upper sections is a standard cement-based material (labeled 5/5), with the mix design given in the first column of Table 1 (also see Appendix A). This mixture includes silica fume with the trade name GroutAid, produced by Elkem in Norway (Appendix E). The solids content of the GroutAid is 50%, so the total silica fume solid content of the standard grout (mix 5/5) is 15% and the water-to-binder (water / (cement + silica fume)) ratio is 1.0. For comparison purposes, one example of a reference grout mix (U1) containing no silica fume was also provided (as given in the middle column of Table 1). All of the material amounts given in Table 1 are expressed as kilograms per 1 cubic meter of material, whereas Appendix A gives the mixture amounts to produce approximately 3 liters of material.

As noted in Table 1, the test conditions have varied in attempt to match the actual environmental conditions at ONKALO. The water temperature in the tunnel is 6-7°C, while the air temperature during construction is 5-20°C and the rock temperature is 9-10°C. The rock temperature is expected to have an increase of 1°C per 100 meters depth, so at 400 meters the expected temperature is 12°C (annual temperature 8°C, +4°C). Due to the decay heat from spent fuel elevated temperatures will be induced in the near-field of the rock during the first thousands of year after disposal of spent fuel.

Locally the temperature may rise up to 40°C in the near-field rock (Hellä and Pastina 2006).

As the ONKALO construction proceeds deeper, the plan is to replace the present ordinary high-pH grout by some low-pH injection grout material(s). Low-pH injection grout has been studied since 2002 in a joint project between Posiva, SKB and NUMO (Bodén and Sievänen 2005). Within this project a low-pH grout material was developed at VTT (Kronlöf 2004, Kronlöf 2005) and later on further optimized by Posiva for ONKALO (Sievänen et al. 2006). The low-pH injection grout is beneficial for improving long-term environmental safety by having leachates with sufficiently low pH (≤11). The low-pH grout mixtures are achieved by altering the mixture proportions and ingredients in the grout, mainly through replacement of part of the cement with silica fume. The most promising mixture design for this new type of low-pH grout was established by Kronlöf (2004) and is given in the right column of Table 1 (labeled P308B). There is very little experience or internationally published literature on this type of material.

It should be noted that the water-to-binder ratio (w/b) given in Table 1 is calculated directly as a sum of the amount of cement and silica fume solids by weight. There is a difference in the given w/b ratios from 1.0 for the standard mix and 1.4 for the low-pH mix. Yet in engineering and design practice it is known that silica fume has a reactive and binding capacity stronger than cement. Compared to cement, the efficiency factor, or k-value, of silica fume is usually taken as 2 (prEN206 2000, by50 2004). Therefore, the effective w/b ratio for the low-pH mixture would be 1.0, as calculated by Equation 1. In this equation the amounts of water, cement and silica fume are input, for instance as kg/m^3. The w/b ratio is unit less. Using this equation when comparing the mixtures in Table 1, the standard and low-pH grout mixtures then have the same effective w/b ratio of 1.0. This information is used when comparing their expected strength, permeability and durability performance.

$${}^{w}\!/_{b\,effective} = \frac{water}{(cement + (2 \times silicafume))} \tag{1}$$

The required properties of the low-pH grout are given in Table 2, though these values have sometimes been revised and are still under discussion. The basic properties of the standard cement grout and low-pH grout, such as viscosity, strength and working time, are known from the earlier development tests (Kronlöf 2003, Kronlöf 2004, Kronlöf 2005). Very little information is known about the long-term durability performance of the low-pH grout, though assumptions have been made based on literature and past experiences with low-pH concrete.

The aim of this publication is to provide a summary of the durability knowledge for all types of injection grout and to specifically address how low-pH grouts will perform over the long-term. The service life of the low-pH grout should be at least 100 years to ensure water-tightness of the underground research facilities during the construction and operation period. The next chapter provides information about durability of cementitious materials in general. Chapter 3 reviews the development of injection grouts, while Chapter 4 addresses the performance of silica fume content mixtures and

Chapter 5 provides insight to the expected durability performance of the ONKALO low-pH grouts.

Table 2. *Required properties of low-pH cement-based grouts (Kronlöf 2004, Kronlöf 2005).*

Order of Importance	**Property**	**Requirement**	**Measuring method**
Required Properties	pH	≤ 11	Leaching tests
	Penetration-ability b_{min} Penetration-ability b_{crit}	≤ 80 µm ≤ 120 µm	Penetrability meter at 60 min
Desired Properties	Fluidity	Not set numerically	Marsh cone at 60 min
	Bleed	≤ 10%	Measuring glass at 2 hours
	Workability time	≥ 60 min	Determined by penetration-ability and viscosity
	Shear strength	≥ ~ 2 MPa. Not set numerically	Fall cone at 6 h
	Compressive strength	≥ 4 MPa	Uniaxial compressive strength at 28 d

2 DURABILITY OF CEMENTITIOUS MATERIALS

Durability is the ability of material to resist weathering action, chemical attack, abrasion or any other process of deterioration; that is, durable concrete will retain its original form, quality and serviceability when exposed to its environment. It is known that cement-based materials do not have infinite durability, and that their durability will change with time to affect the ultimate service life of a structure. Therefore, it is critical to understand the material on a case-by-case scenario in order to predict the anticipated service life.

Deterioration of cement-based materials is not attributed to any single cause, but arises from the combined action of a number of potentially destructive agents. Deterioration can be caused by physical or chemical mechanisms. These various types of concrete deterioration are given in Figure 1 (Mehta et al. 1993). Many of these types of deterioration are situation dependent, such as water and environmental exposure. Some types affect the structural integrity, while others affect the chemical stability. These differences are important when considering injection grouts, where the groundwater concerns (such as changing leachant with cracking) may be more significant than the physical properties (such as load capacity). The importance of long-term safety risks and grouting durability risks should be kept separate as two different aspects to consider.

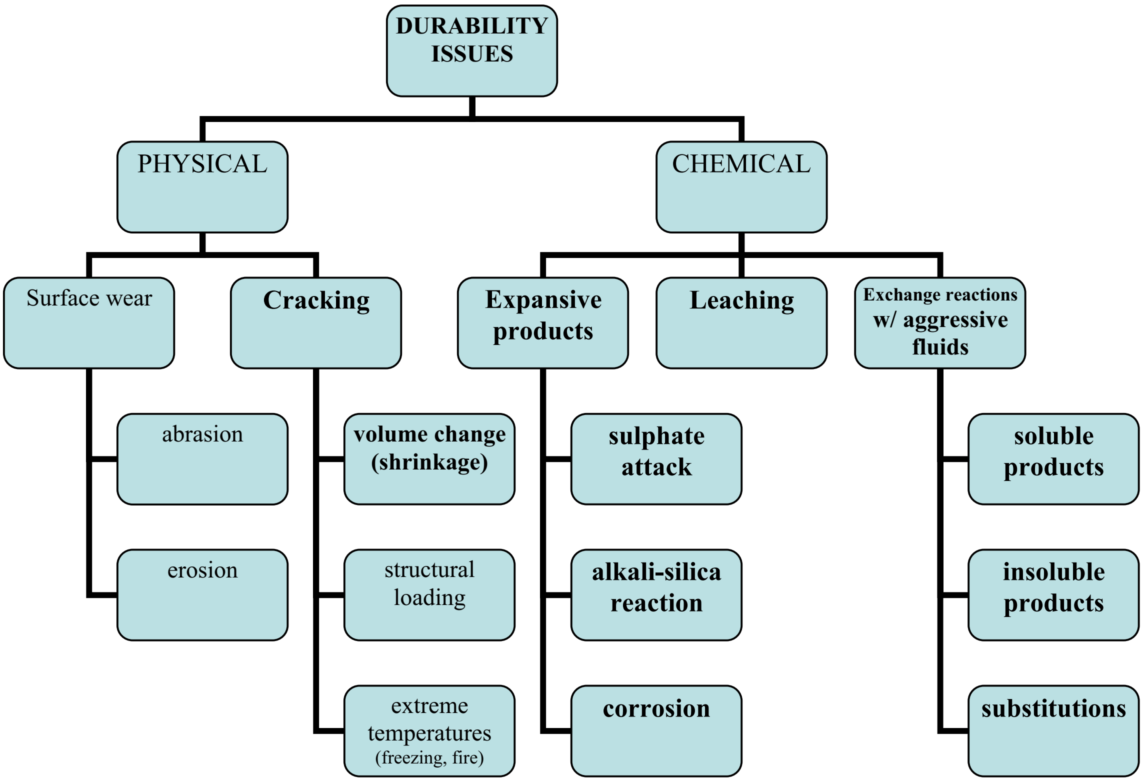


Figure 1. *Types of chemical and physical deterioration of concrete (Mehta et al. 1993).*

The following sub-chapters review all of these types of deterioration, with special attention given to deterioration specifically affecting injection grout durability and highlighted in bold in Figure 1. Since nearly all forms of deterioration are linked to the presence of water, a review of permeability is first presented.

2.1 Permeability

Permeability is defined as the property that governs the rate of flow of a fluid into a porous solid. Permeability of grout is important in limiting the mass transport of corrosive agents (i.e. sulphate and chloride) into the grout and leaching of cement components from the grout. The coefficient of permeability (K) is determined from Darcy's Law, as given in Equation 2.

$$Q = -KA\frac{\Delta h}{L} \qquad (2)$$

Where: Q = total discharge (m^3/sec),
K = coefficient of permeability (m/sec),
A =surface area (m^2).
$\Delta h/L$ = hydraulic head (m/m),
Δh = change in height between two points (m), and
L = distance between points (m).

In hydrated cement paste, the size and continuity of the pores at any point during the hydration process controls the coefficient of permeability. As hydration of the cement paste continues, the capillary porosity in the material decreases, as does the coefficient of permeability. The hydration process of cement-based materials is rarely completed and thus the hydration usually continues over long periods of time. The later formation of new hydration products can lead to further changes in microstructure over tens or even hundreds of years. It is generally known that the durability of hardened cement exposed to aggressive aqueous environments is related to permeability, and thereby, to the pore structure of the hardened cement paste. A lower porosity, or higher coefficient of permeability, will typically result in a more durable material.

Basic relationships have been established in concrete practice regarding the correlation between permeability and porosity, as shown in Figure 2 (Neville 1981).

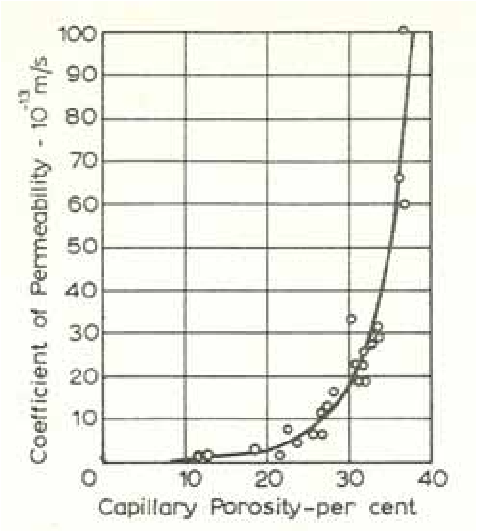


Figure 2. *Relation between permeability and capillary porosity of cement paste (Neville 1981).*

The pore structure and thus permeability of a mixture will also be affected by any material or mix design changes. For instance, reducing the w/b ratio is an effective means of decreasing permeability. However, significant decreases in w/b can result in difficulties with placing and consolidating the cement-based material. These difficulties can be overcome by the use of water reducers or superplasticizer chemicals and the addition of pozzolanic materials. Pozzolans (such as silica fume) may not significantly influence the total porosity, yet they alter the size of the pores so that they decrease the volume of inter-connected pores. By producing smaller and more discontinuous pores, the pozzolan addition can markedly reduce the hydraulic conductivity of cement-based materials, which is beneficial for reducing nearly all durability risks.

2.2 Shrinkage cracking

Shrinkage occurs due to the loss of water from a cement-based material. If there is too much shrinkage, the concrete will crack and the structure's durability can be severely compromised. Shrinkage of concrete takes place in two distinct stages: early and later ages. The early stage is commonly defined as the first day, while the concrete is setting and starting to harden. Later ages, or long term, refers to the concrete at an age of 24 hours and beyond. During this later stage the concrete is demoulded and standardized shrinkage measurements are conducted. The long-term shrinkage is typically the only part that is identified and addressed in literature, as well as being the portion that is accommodated in structural design.

Within each of these two stages of shrinkage there are also various types of linear change, which can be physically measured on a specimen, mainly drying and autogenous. Both of these types can occur during either shrinkage stage. In addition to drying and autogenous shrinkage, the concrete is also subjected to volume reductions due to thermal changes and carbonation reactions. The shrinkage types and stages are mapped in Figure 3.

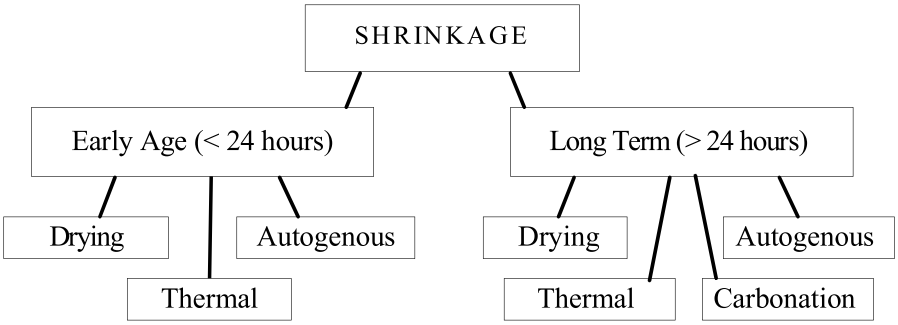


Figure 3. *Diagram of shrinkage stages and types (Holt 2005).*

Drying shrinkage results from a loss of water from the concrete. In the later ages (> 24 hours) it is well understood and can be easily measured by standardized tests of length change. Expected drying shrinkage values are on the order of 0.5 mm/m and are accounted for in design of concrete structures, such as placement of joints in a concrete floor. Early age drying shrinkage (< 24 hours) is also a function of the amount of evaporable water that can be lost from the concrete before the final setting time is reached. It is more difficult to measure but has been addressed by recent research (Holt 2004). All drying shrinkage is dependent on the environment surrounding the concrete, especially the temperature, relative humidity and wind speed. In general, concrete with a high w/c ratio will have higher drying shrinkage because there is more unbound water.

Autogenous shrinkage of cement paste and concrete is defined as the macroscopic volume change occurring with no moisture transferred to the exterior surrounding environment. It is a result of chemical shrinkage affiliated with the hydration of cement particles. Chemical shrinkage is an internal volume reduction while autogenous shrinkage is an external volume change. Chemical shrinkage is the volume reduction resulting from the hydration of cement and water, which consumes less space than the initial products. It occurs immediately after mixing in the early ages. Autogenous shrinkage progresses after the concrete has reached final set and it is attributed to self-desiccation phenomena driven by the chemical shrinkage. Autogenous shrinkage is usually only a concern in high performance concrete (with strengths over > 40 MPa) where there is a low w/c ratio (less than about 0.45). It can be more severe in concrete mixtures that have a very dense paste, without interconnected pores, such as mixtures containing silica fume (Holt 2005).

2.3 Formation of Expansive Products

Sulphate attack typically occurs when the concrete is exposed to water that contains a high concentration of dissolved sulphates. The two most common types of sulphate attack are physical attack, where the sulphate-containing water enters the surface of the concrete, crystallizes, and expands, disrupting the hardened concrete; and chemical attack, where the sulphate salts react with the portland cement paste, causing it to dissolve, soften, and erode (Brainderd 2006).

During sulphate attack, both the calcium hydroxide and the aluminate phases in a cement matrix react with sulphate to form insoluble substances with much greater volumes. To minimize the risk of sulphate attack, it is again beneficial to have a dense concrete with low permeability. It is also possible to alter the chemical composition of the cement paste to make it less susceptible to sulphate reactions. This can be achieved by either using sulphate resistance cement or using pozzolans (such as silica fume or fly ash) as alternative cementitious materials so that there is less portlandite (CH) for the destructive reaction.

Alkali-silica reaction typically occurs when certain silica-containing aggregates react with high-alkali cements to form an expansive gel that causes the concrete to crack. Moisture must be present for the reaction to occur. The cracks typically form in a widespread “map cracking” pattern that is often accompanied by deposits of white or grey gel on the concrete surface or inside air voids. Not all silica-containing aggregates are vulnerable to ASR. To minimize the risk of ASR, either sulphate resistant cement can be used or portland cement can be used in combination with alternative cementitious materials, such as silica fume or low-alkali fly ash, to decrease permeability and reduce the quantity of alkalis in the concrete.

Corrosion is a problem for steel used together with cement-based materials. Corrosion causes deterioration when the rust by-product of the electrochemical process requires much greater volumes of space than the original uncorroded steel. The resulting pressure created inside the concrete will cause cracking and severe deterioration to the structure over time. The most common causes of steel rebar corrosion are exposure to de-icing salt used for roadways and seawater attack. If the concrete and rebar are not protected, the salts will eventually reach the depth of the rebar and cause corrosion (Brainerd 2006). Lowering the pH of a mixture (i.e. by including high amounts of silica fume) can increase the steel corrosion risk, though the pH change must be considered along with potential changes in the permeability. The chloride induced corrosion is usually controlled by concrete diffusion and can be estimated for service life predictions.

Another culprit of reinforcing steel corrosion is “*carbonation*,” where carbon dioxide and moisture in the air enter the concrete and reduce the pH of the concrete. As carbonation advances from the outer surface inward, it eventually can lower the pH at the reinforcement, making the reinforcing steel vulnerable to corrosion. To minimize the risk of corrosion and carbonation, it is beneficial to have low permeability, dense concrete materials. It is also recommended to use stainless steel in situation where corrosion could be a risk. Lowering the pH of a concrete by adding high amounts (> 30%) of silica fume to the mixture would increase the corrosion risk. But adding the silica fume also reduces the permeability of the concrete, thus reducing the corrosion risk because of slower ingress. Both factors are working simultaneously, thus making the overall effect of silica fume on corrosion hard to predict.

2.4 Leaching

Leaching involves the attack of water on the calcium hydroxide and calcium silicate hydrate (CSH) present in hydrated cements. Solid hydrates of cement paste are more persistent at pH above 12-13, but at a lower pH the hydration phases no longer remain stable and thus dissolve. The pore solution of a typical portland cement paste is highly alkaline, so that the leaching process starts by removing alkalis (Na^+ and K^+), followed by dissolution of portlandite (CH) and subsequently by the leaching of calcium from silicates (e.g. CSH). Aluminate phases are also affected (Alonso 2006a).

Leaching is highly dependent on the permeability of the cement-based material. As earlier noted, permeability is affected by many material properties, especially during the formation of the hydration products. For instance, alterations in the curing temperature or humidity of fresh cement paste will affect the size and amount of hydration products. As the degree of hydration proceeds with time, the cement matrix's permeability decreases and thus the water tightness is improved and susceptibility to leaching is reduced.

Leaching may be a slow process; 5 to 10 mm leached depths have been found in concretes submerged for 100 years in standing natural water. This is in part due to the further reaction of unhydrated cement grains during leaching, which leads to a densification of the material and new portlandite being formed from in-situ hydration. The samples were taken from various Swedish concrete and mortar structures, including a water tank, water basins and bridge columns (Lagerblad 2001a).

A variety of test procedures are available to characterize materials with respect to their leaching behavior. Such tests are carried out on a wide variety of materials for regulatory purposes, waste management purposes, environmental impact assessment, and for scientific purposes in several countries (e.g., Netherlands, Germany, France, Switzerland, Canada, USA, Finland, Japan). Test methods have been developed for monolithic, crushed and powdered materials. Leach tests can be classified, e.g., into tests aimed at:

- attaining equilibrium conditions at the end of the leaching experiment,
- dynamic aspects of leaching (e.g. time-dependence),
- accelerated dissolution, or
- understanding the leaching behavior of materials.

Several different procedures are in use but new ones are developed as well. However, a chosen test procedure may have to be altered or combined with other procedures so as to fulfill the aim of the test and to take into account the local environmental conditions and to correspond to them as closely as possible. The distinction between solubility- and kinetically-controlled releases is important for a proper assessment of both the short- and long-term behavior of the material (Vuorinen et al. 2005).

At VTT two leaching methods were used on the test samples prepared by Kronlöf (2004): 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 modeling of diffusion coefficients (Vuorinen et al.2005).

When testing leaching, the results are very dependent on the type of test, for instance a standing or static water test compared to a flowing or dynamic water test, batch tests or diffusion tests etc. The resulting leachant and potential deterioration is also very dependent on the solids-to-water ratio used in the experiment, temperature, water exchange rate, type of water that is used in the test, such as the use of deionized water, sea/saline water, groundwater, or water rich in any potentially aggressive chemical (such as sulphate).

2.5 Exchange reactions with aggressive fluids

Exchange reactions occur when aggressive fluids react with components of the hardened cement paste. These reactions can result in various products, as given here:

- removal of Ca^{2+} ions as *soluble products* (acidic solution forming soluble calcium compounds such as calcium chloride, calcium sulphate, calcium acetate or calcium bicarbonate),
- removal of Ca^{2+} ions as non-expansive *insoluble products* (solutions of oxalic acid and its salts, forming calcium oxalate, as a 'barrier'),
- *substitution reactions* replacing Ca^{2+} in CSH (long-term seawater attack weakening the CSH by substitution of Mg^{2+} for Ca^{2+}).

All of these reactions can lead to deterioration of the cement-based material. The products can be leached out of the material with time, can cause expansion and thus cracking or can lead to strength loss of the cement matrix. Low-pH injection grout may be at less risk for exchange reactions because of the lower amount of CH (easier leaching) and higher amount of CSH. This will be further described in later sections.

Chloride attack is a concern because chloride reacts with the calcium hydroxide in the cement paste to form soluble products, which can be leached away. This results in an eventual loss of all concrete strength. Chlorides can also form salt crystallization products in concrete pores when the material is subjected to wetting and drying cycles (such as in groundwater fluctuations). These deposits can eventually cause cracking and disintegration. Temperature and chloride concentration control the chemical reactions involved in chloride attack. Care should be taken at temperatures above 40°C when the chloride concentrations are above 10,000 mg/L because ettringite can decompose to form Friedel's salt and gypsum (Luna et al. 2006).

Seawater exposure on concrete provides potential for various types of exchange reactions and types of deterioration to occur simultaneously. The main concern with seawater is the presence of magnesium sulphate. Leaching actions remove lime and calcium sulphate while reaction with magnesium sulphate leads to the formation of calcium sulphoaluminate in high temperature, which may cause expansion, rendering the concrete more open for further attack and leaching. The deposition of magnesium hydroxide blocking the pores of the concrete probably tends to slow the action on dense concrete though on more permeable materials it may be without much effect. The presence of chlorides retards the swelling of concrete in sulphate solution (Lea 1970).

2.6 Other durability risks

Surface Wear is the progressive loss of mass from a concrete surface due to abrasion and erosion actions. It is mostly a concern at the exposed surface of a concrete element, such as a roadway or canal lining. As expected, hardened cement paste possesses worse surface wear resistance than concrete containing hard aggregate. To improve surface wear resistance, a minimum water/cement ratio or strength is often specified. Using pozzolans such as silica fume can also aid the surface wear resistance by reducing porosity and bleeding, so the internal and exposed surfaces are more durable, respectively.

Freeze-thaw deterioration occurs when concrete is saturated with moisture while exposed to freezing temperatures. The freezing water within the concrete creates hydraulic pressures within the concrete, causing micro-cracking of the concrete. To resist freeze-thaw deterioration, the hardened concrete must contain an air-void system that consists of small, closely spaced air bubbles, called entrained air. The air-void spacing factor should be on the order of 0.2 mm to protect against frost damage. The voids provide space to relieve the pressure of the freezing water, thereby minimizing stress on the concrete. The process involves using chemical air entraining admixtures to provide about 5% air pores in fairly strong concrete mix (typically over 30 MPa). Freeze-thaw durability is most often a concern with higher w/b ratio mixtures, where there is a higher volume of large pores holding a higher amount of freezable water. Many international guidelines recommend a water/cement ratio less than around 0.50 for durability of concrete exposed to a freezing and thawing environment.

Fire damage is not a primary risk when considering most cement-based materials, as concrete can retain sufficient strength for reasonably long periods at highly elevated temperatures. The factors affecting concrete fire durability include permeability, element size and the rate of temperature rise. The temperature of concrete will not rise until all of the evaporable water in the mixture has been removed. Temperatures on the order of 900°C are required for complete decomposition of the CSH in the cement paste. If the heating rate is high and the cement paste permeability is low, damage can occur in the form of surface spalling due to steam vapor pressure. The spalling can result in exposure of reinforcing steel and loss of strength or bearing capacity. The permeability of the concrete is affected by material selection. For instance, using increased amounts of silica fume often result in lower permeability of the concrete and thus a higher risk of spalling during fire.

3 INJECTION GROUT DEVELOPMENT

3.1 Earlier technology

Grouting technology has been around for hundreds of years to provide a means for improved construction such as sealing cracks in rocks or concrete structures, stabilizing foundations, anchoring bolts, and consolidating or waterproofing fine or fissured soils. Originally grouts were developed using the available basic materials, including very coarse ground cements with a typical specific surface area around 300 m^2/kg. The w/c ratios of early grout mixtures were very high, on the order of 4.0, to allow placing. Over time, technology progressed to include grouts having a lower w/c. The next step in grouting development was the modification of materials. Finer ground, high early-strength cement was utilized to improve workability and placeability. These finer cements typically had a specific surface area of 600 m^2/kg and all particles below 50 μm in diameter. Chemical admixtures became more prevalent in the construction market in the 1980s, including the use of superplasticizers. These organic polymer admixtures alter the viscosity of the grout and reduce the speed of segregation of a grout, thus enhancing its stability. They allow for even lower w/c ratios to be used, typically around 1.0, with sufficient workability and placeability of the grout.

3.2 Current standard grout

Improvements in recent grouting technology have led to the current practices, which are also used at ONKALO for grouting the upper sections of the facility. Very finely-ground microcements are being used to further improve the injection ability to small fissures. These microcements typically have all particles less than 30 μm in diameter and BET specific surface areas around 1500 m^2/kg. Ordinary cement has a maximum particle size of about 100-150 μm in diameter.

As a rule-of-thumb, injection filling is possible for maximum fissures of the size three times the maximum grain size in the grout. For instance, if the maximum grain size in a cement-based material is 150 μm, then the maximum space into which the material can pass is 450 μm. The same holds true for concrete, for instance with a maximum coarse aggregate of 8 mm then the steel reinforcing minimum spacing is 24 mm. Using this rule-of-thumb, the ONKALO grout made from microcements should be able to fill fissures until about 100 μm width. The finer cement also can aid in hydration of the cement paste, creating a different density and durability of the grout.

Special cements, such as *sulphate resistant cements*, are used to improve expected durability performance. Sulphate resistant cement is characterized by a reduced C_3A content in clinker. Since sulphate attack on hydrated portland cement involves mainly the C_3A phase, such a measure significantly increases the ability of the hardened cement paste to resist the corrosive action of sulphates. When cement paste is exposed to SO_4^{2-} from an external source, monosulphate converts back to ettringite and can cause expansion, spalling and disintegration of the material. The effectiveness of altering the C_3A content is demonstrated in Figure 4, showing the expansion for a series of cement pastes.

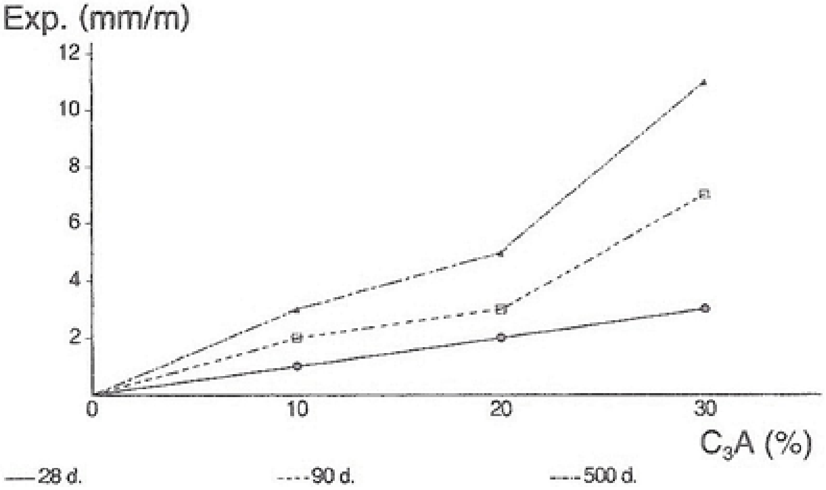


Figure 4. *Effect of C_3A content in portland cement on cement paste expansion ($C_3A+C_4AF=30\%$). (Odler 2000)*

Sulphate resistant cement can be produced by reducing the Al_2O_3 content and/or by increasing the Fe_2O_3 content in the cement raw meal. Thus, sulphate resistant cements are essentially high-iron, low-C_3A cements with an SO_3 content and specific surface area in the same range as ordinary portland cement. It should be noted that even with the modified iron composition, the sulphate resistance of these cements is not absolute. At very high sulphate concentrations, there can still be expansion and deterioration of the cement paste, though more slowly and to a lesser degree. Sulphate resistant cement also does not exhibit any significant resistance to $MgSO_4$ attack, in which a substitution reaction occurs, causing degradation of the CSH phase, rather than an expansion due to ettringite formation, plays the main role (Odler 2000).

In current standard grouts, improvements have been made to the chemical composition of *superplasticizers (SP)*, to provide more variety in selecting products based on job-specific needs. The superplasticizers continue to be updated to control secondary properties such as setting time and viscosity. More information about the effects of superplasticizers on performance is given in the next chapter.

The use of *pozzolan materials* in injection grouts has grown in recent years with the wider introduction of *silica fume* in the 1980s. The physical properties of silica fume were briefly noted in Chapter 1. The initial use of silica fume was motivated by the possibility of producing concrete of a specified strength using less cement. However the high cost of most silica fume has lead to the trend of it being used in lower dosages, usually around 5-10% by weight of cement, to enhance both fresh properties (such as stability and workability), and long-term properties (such as strength and durability). Ultrahigh strength concretes with compressive strengths over 100 MPa often incorporate much higher amounts of silica fume, on the order of 20 to 30%.

Using silica fume can result in a very strong, brittle concrete. Using over 10% can result in a sticky consistency of the fresh concrete. Because of silica fume's very fine particle size and high surface area, there is also an increased water demand in the mix and thus a water reducing admixture or superplasticizer is often used. There is a concern with future availability of silica fume due to the changing demands of the energy market.

3.3 Low-pH grouts

Recent grouting technology has addressed that in certain environments, even higher amounts of silica fume than normally used may be beneficial for improving long-term environmental safety by having leachates with sufficiently low pH (≤11). Support for the development of low-pH injections grouts using high amounts of silica fume was found from studies in other Nordic countries.

Advanced research has been done in Norway (Roald et al. 2002, Tolppanen and Syrjänen2003) on the use of silica fume mixtures where the solids content of silica fume in the injection grout can be very high (> 20%). The work has been partially based on the need for high pressure grouting with up to 10 MPa pressure when tunneling in mountainous areas with a grout that can penetrate fine fissures. With this knowledge and through earlier studies by Posiva Oy, a similar low-pH grout with a high silica fume content is a potential alternative when deciding at ONKALO about the injection material as the construction proceeds deeper.

The development of low-pH grout mixtures was presented by Kronlöf (2004) and the chemical information is partially repeated in Appendix B for background information. The early age and long term performance of silica fume based mixtures is addressed in the next chapter, while specific expectations for low-pH ONKALO injection grouts are addressed in Chapter 6. Some other international research has also been done recently on low-pH injection grouts and presented by Alonso et al. (2006b) and Luna et al. (2006). Yet few of these reports provide quantitative data from long-term durability studies.

4 CHARACTERISTICS OF LOW-PH GROUT RELATED MATERIALS

The low-pH grout at ONKALO has been developed with a primary focus on its early-age performance during mixing and injection. Most of the expected long-term properties were kept in-mind but have not been validated. The first section of this chapter summarizes some of the influences of mixture design on these early-age properties. The next sections give examples from literature about possible long-term performance characteristics of low-pH grout based on the w/b ratio and inclusion of silica fume.

4.1 Early-age properties

4.1.1 Influences of superplasticizer

In order for injection grout to have good penetration, it is important for the material to have a low viscosity. Thus it is sometimes an advantage that the w/c ratios are as high as possible. On the other hand, to maximize the grout density and consequently minimize the porosity, it is beneficial to have a low w/c ratio. The lower w/c ratios with maintained low viscosity can be achieved by the use of superplasticizers, as shown in Figure 5 (Onofrei et al. 1992). At the higher dosage of 1.25% SP the viscosity was low and the shear rate was maintained. For grouts containing microcement, water and a superplasticizer, it has been seen in practice that the lowest w/b ratio that can be used is about 0.40 and the highest possible w/b ratio is about 2.0. At higher water contents, there is a high likelihood that water separation will occur.

There is the risk of organic superplasticizers harmfully dissolving in the presence of water and leaching into the surrounding environment. Yet there is very little, if any, data on the effect of superplasticizers on the long term properties of repository grouts with regard to release of organic materials (by leaching and dissolution) into the environment. The leachant from superplasticizers may enhance the rate at which radionuclides migrate in groundwater. The presence of organic materials from superplasticizers may provide sustenance for microorganisms present in repositories.

It is known that through cement hydration, superplasticizer becomes increasingly immobilized. Yet sorption studies on unset cement grout have shown free superplasticizer in the pore space of the hardened paste, which could be liberated during leaching (Figure 6, Onofrei et al. 1992). The superplasticizer tested was of based on sulphonated naphthalene formaldehyde, Na-SNF. At a 1% superplasticizer dosage, approximately 40% of the superplasticizer remained in the pore fluid after the grout had reached final set. Therefore, care must be taken when selecting the proper superplasticizer to use.

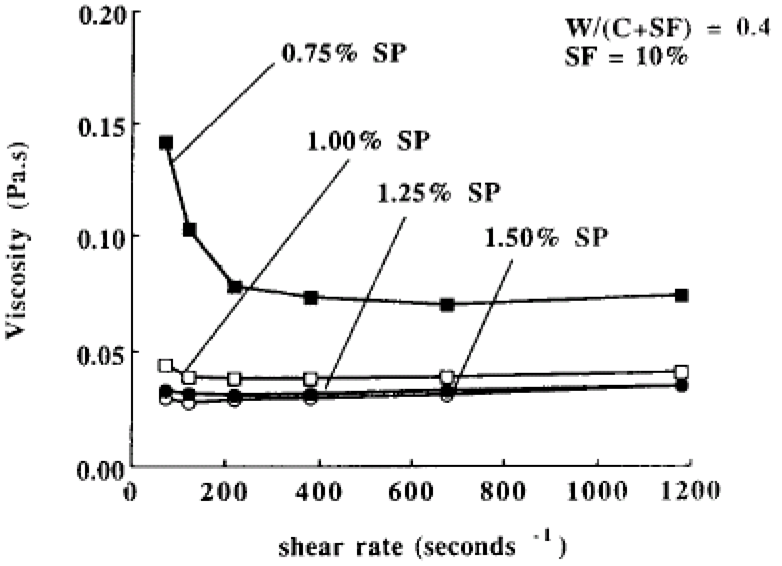


Figure 5. *Viscosity versus shear rate for grout containing various amounts of superplasticizer (SP), with w/b=0.40 and 10% silica fume (Onofrei et al. 1992).*

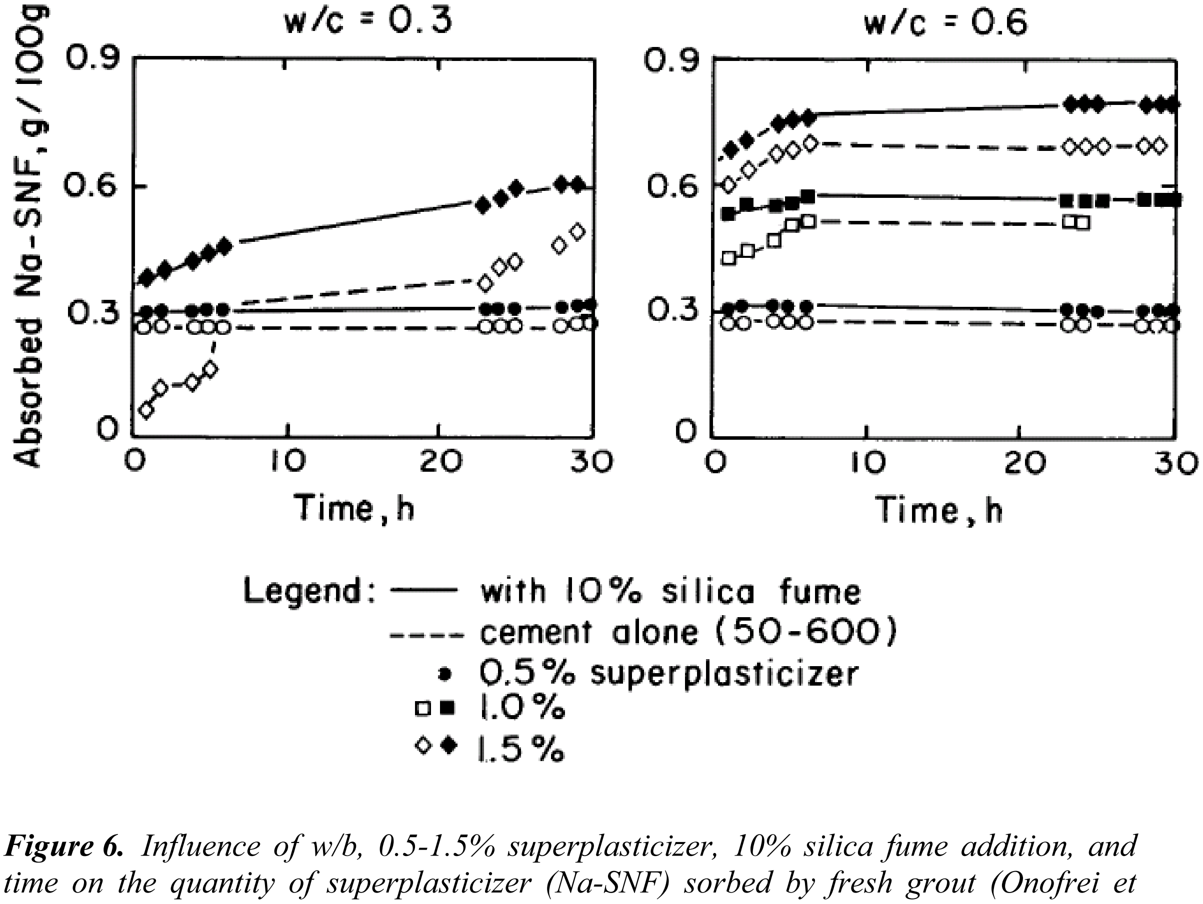


Figure 6. *Influence of w/b, 0.5-1.5% superplasticizer, 10% silica fume addition, and time on the quantity of superplasticizer (Na-SNF) sorbed by fresh grout (Onofrei et al.1992).*

Leaching tests to evaluate superplasticizers by Onofrei et al. (1992) showed that superplasticizers can be leached from grout, however the cumulative fraction of release rates of the superplasticizer into solution were very small (10^{-12} kg/m^2). Her mixtures were similar to those shown in Figure 6, with 10% silica fume, w/b ratios 0.4 to 0.8 and 0.5 to 2.0% superplasticizer. The addition of silica fume to the cement grout increased the quantities of superplasticizer in solution. This led to the conclusion that the adsorbed superplasticizer is only loosely bound to the silica fume and, like any free superplasticizer in the capillary pore space of the grout, is readily leached from the silica fume surfaces. Also, the amount of superplasticizer lost to solution increased at lower w/b ratios, which was attributed to the nonhomogeneous distribution of superplasticizer in the grout.

Studies by Gray (1993) confirm that the use of superplasticizers will increase the total organic load in groundwater. Yet the total increases are likely to be significantly less than the quantities of superplasticizers used in the construction of seals. He concluded that the benefits of material properties and performance gained through the use of superplasticizers would outweigh any adverse effects of increased organic loads.

A main benefit of using superplasticizers together with silica fume in concrete and grouts is that these mixtures exhibit less bleeding and segregation than plain mixtures, as shown in Figure 7 (Onofrei et al. 1992). The superplasticizer and silica fume combination can lead to a more homogeneous mass and improved durability. This was further investigated and reported by Kronlöf (2004, 2005) from the ONKALO grout development.

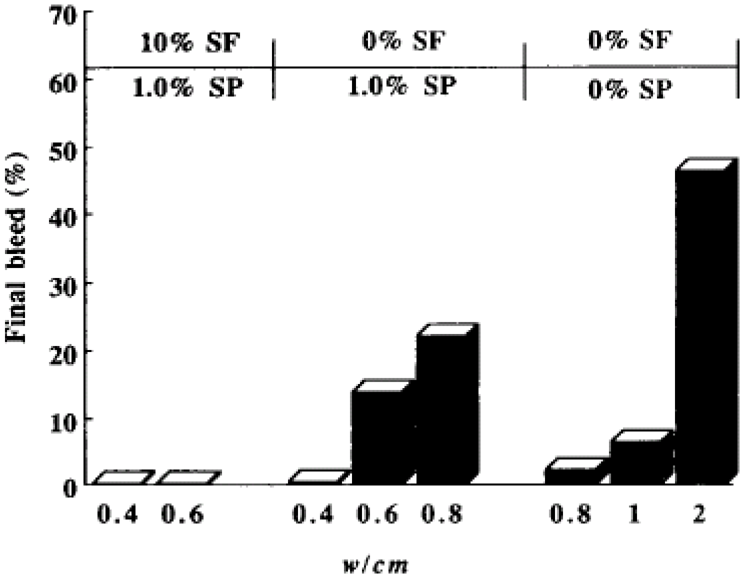


Figure 7. *Bleeding observed for various grout mixtures. 0-10% SF = silica fume, 0-1% SP = superplasticizer, w/cm = w/b ratio 0.4 to 2.0 (Onofrei et al. 1992).*

4.1.2 Positive influences of silica fume

The goal of combining microcement and high amounts of silica fume is to produce a grout with a high water/binder (cement + silica fume) ratio, low water separation and high penetration. Even though using silica fume results in a higher water demand in the grout, the use of a superplasticizer allows for improved viscosity while maintaining a higher w/b ratio. Silica fume manufacturers have shown that it is possible to successfully develop and use injection grouts with a w/b ratio of 6.0 using silica fume and microcement combinations. The higher w/b ratio grouts containing silica fume also have significantly improved penetration compared to microcement grout mixtures (Appendix E).

The most likely explanation for improved penetration of grouts containing silica fume is that the modified grout is much more stable, resulting in minimal bleeding and sedimentation, and thus, no blocking. Since water is not expelled during the injection, the solids do not settle and deposit in cracks or pores close to the borehole, so that a homogenous grout flows into the formation (Jørgensen and Fidjestol 2006).

Hooton and Konecny (1990) conducted a series of tests by grouting fissured granite and then taking core samples to assess the grout behavior. The grout was composed of sulphate resistant cement, superplasticizer, 10% silica fume and had a w/b ratio 0.50 to 3.0. Their research showed that silica fume mixtures resulted in more effective grout penetration and sealing, though fracture openings less than 200 μm wide remained generally ungrouted. Finer fissures (50-100 μm) had unhomogeneous filling, which was attributed to filtering or blocking by the coarser cement particles. This size of fissure opening is to be expected when using portland cement with a normal grain size (~ 100 μm diameter).

Hooton and Konecny (1990) also reported that the silica fume grouts provided a very good bond to the granite, which was verified by scanning electron microscopy. They noted that the silica fume mixtures did not segregate or bleed and more fully coated the fracture surfaces compared to the reference grout. A main conclusion of the report was that adding silica fume would likely enhance resistance to chemical attack and leaching.

4.1.3 Possible negative influences of silica fume

Some risks or problems can occur during the early ages when using high amounts of silica fume. The actual ‘high’ percentage addition limit depends on the other mixture parameters, such as the cement type, w/b ratio and use of admixtures. The main concerns of a high silica fume concrete mixtures are:

- the overall sticky feeling of the mix,
- possibilities of silica fume conglomerates,
- retardation or late setting times.

A mixture that is too sticky would result in viscosity and grouting penetrability problems. Kronlöf (2003) had identified this in her work establishing a low-pH grout material for ONKALO and reported on the risk of gel-blocking. It was found that with fine cements some other mechanism apart from the traditional particle blocking inhibits penetration. This other mechanism was named “gel blocking”. It dominated the penetration-ability of mixes made with fine SR cement Ultrafin 12. The mix composition was modified by increasing the water-to-cement ratio from 1.0 to 3.3 and simultaneously increasing silica-to-cement ratio from 0 to 0.3 (as dry materials). This strongly deteriorated the penetration-ability and increased the yield value by tenfold. The conclusion was that the very fine silica fume reacted during the first hours (the open time) and produced gel like grout, which blocked the sieves of the penetration-ability device. According to the work by Lagerblad partly presented in Lagerblad and Fjellberg (2001b) other fast pozzolans seem to behave similarly.

Another concern with using high amounts of silica fume is the possibility of having silica conglomerates or lumps in the grout. These conglomerates would result from poor distribution of the silica fume particles during mixing. The risks can be eliminated or improved by ensuring good mixing with powerful enough equipment to properly distribute the silica fume. Recent research has shown some concern with the possibility of the silica fume conglomerates reacting with alkali cement to cause alkali-silica reactions (ASR). Such reactions form an expansive gel, which could eventually crack the cement-matrix due to high volume demands. The expansion behavior would not be detrimental within grouted fissures, but could be a problem at exposed grout surfaces within the tunnel or in shotcrete materials. There would also be the risk if the ASR expansion or cracking occurred in load bearing areas where tensile strength is needed, such as in areas of grouting to secure rock bolts. Further information about the risks of silica fume conglomerates causing ASR is reported in Appendix C by Paula Raivio from Contesta Oy.

The last concern noted about a delay of setting time is due to the difference in hydration time of the silica compared to the cement. It may take longer for the matrix to gain strength because of the slower setting. This can be offset by using an accelerating admixture if allowed in the environmental conditions of the concrete. The GroutAid silica fume product (Appendix E) does not include an accelerator and thus the ONKALO grout may also risk later setting times.

4.2 Influence of water-cement ratio on durability

One of the main characteristics used to evaluate cement-based materials is the water-cement (w/c) ratio. Correlations between w/c and numerous other properties have been established for many years. Not all of these correlations are applicable for all material situations because the paste structure can change due to other parameters, such as including admixtures or pozzolans and altering the curing or hydration environment. The information and figures presented here from Neville (1981) unless otherwise cited and are intended to show the general trends accepted in practice for the influence of w/c ratio on durability.

It is generally agreed that increasing the w/c ratio of a mixture will result in a decrease in compressive strength, as shown in Figure 8. This decrease in strength is attributed to the weaker cement paste and also in concrete to the weaker bond between the paste and the aggregate particles.

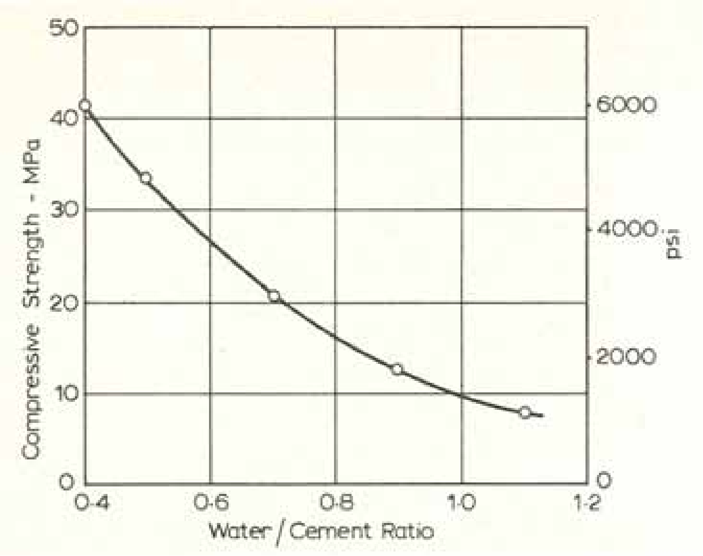


Figure 8. *Relation between strength and water/cement ratio for concrete made with a rapid-hardening portland cement (Neville 1981).*

For the ONKALO injection grouts with an effective w/b ratio of 1.0, the 90 day compressive strength has been about 20 MPa. Therefore, the curve presented in Figure 8 should shift up accordingly by about 10 MPa to predict performance at other w/b ratios. This shift is attributed to the improved cement quality and use of silica fume compared to the data from 1980s and earlier used to generate Figure 8.

Another key correlation established for w/c ratio is the influence on porosity, as shown in Figure 9. For pastes hydrated to the same degree, the permeability is lower the higher the cement content of the paste, i.e. the lower the w/c ratio. Material parameters may also have the same affect as altering the w/c ratio. For instance, at the same w/c ratio, coarser cement tends to produce a paste with a higher porosity than finer cement.

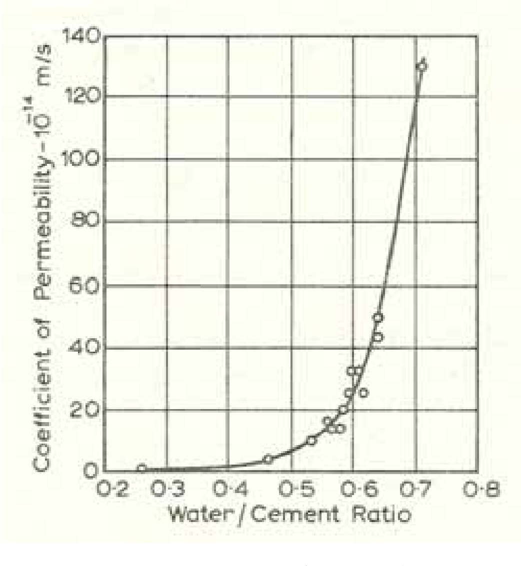


Figure 9. *Relation between permeability and water/cement ratio for mature cement pastes hydrated 93% (Neville 1981).*

The coefficient of permeability of granite rock is about 1.5 x 10^{-10} m/s, which would be equivalent to a mature cement paste having a w/c ratio of 0.71. The coefficient of permeability decreases with time due to the hydration of cement paste. The reduction in the coefficient of permeability is faster the lower the w/c ratio of the paste, and there is little reduction after wet curing for a period of:

7 days when the w/c is 0.45,
28 days when the w/c is 0.60 and
90 days when the w/c ratio is 0.70.

The initial value of hydraulic conductivity can be reduced down to two orders of magnitude in about one year due to continued cement hydration.

Saito and Deguchi (2000) have conducted leaching tests on mortars with w/c ratios 0.32 to 0.60. The sand to solid volume ratio was held constant at 50%, so the resulting sand/cement ratios were from 0.67 to 0.97. Thus the lower w/c ratio mixtures had greater volumes of cement content per unit of mortar volume. As expected, their results showed higher leaching of mixtures with the higher w/c ratios, as seen in Figure 10.

This increase in the amount of leachant also results from the difference in permeability and pore structure of the material with progress of testing. This can be seen in tests by Haga et al. (2005) for leaching tests performed on cement paste samples with w/c of 0.7. Their results on plain paste showed the pore volume became larger with longer leaching periods (Figure 11) and the bulk density became smaller due to the loss of CH. This trend may not always be the same if the paste composition changes, for instance with the use of silica fume.

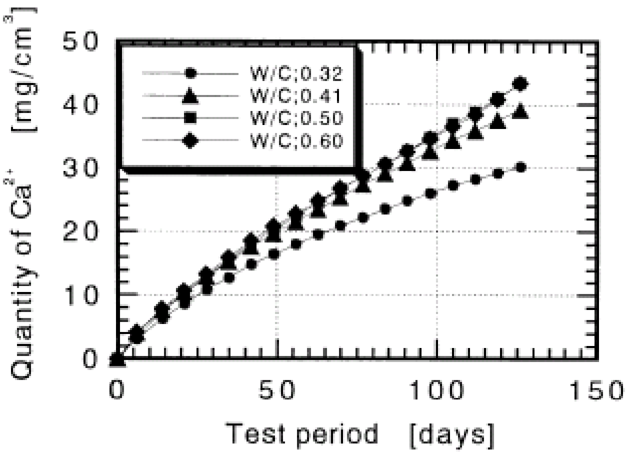


Figure 10. *Cumulative quantity of dissolved Ca^{2+}, for mortar with w/c 0.32 to 0.60 (Saito and Deguchi 2000).*

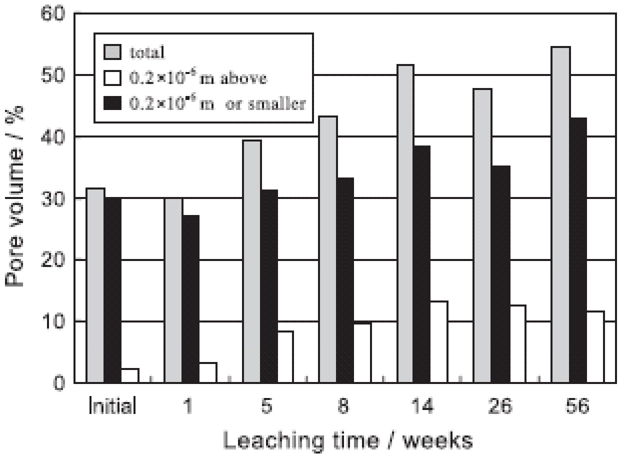


Figure 11. *Leaching time dependency of pore volume for paste with w/c 0.7 (Haga et al. 2005).*

From these examples, it is evident that the w/c ratio plays a role in predicting the durability of a cement-based material. Higher strength, and thus usually greater durability, can be achieved using a mix with a lower w/c ratio where there is a lower permeability and fewer pores. As earlier noted, one of the main methods for achieving even higher strength concretes is to incorporating silica fume and superplasticizer to the mixture, thus maintaining workability while allowing a lower w/b ratio to be used. The influence of including silica fume in cement-based materials is reviewed in the next section.

4.3 Influence of silica fume on durability

The durability of concrete containing silica fume has been widely studied in the past 25 years. These studies are often done on high strength or high performance concrete, where there are various forms of harsh environmental exposures. It is possible to consider the durability of mixtures with medium (10%) to high (>15%) silica fume contents when trying to assess how low-pH (rich silica fume, > 30%) grout will perform. It must be kept in mind that typically silica fume has been used in mixtures with a low w/b ratio and having very high compressive strengths, which is not true for low-pH injection grout.

One of the first constructions with silica fume was done in 1952 in Norway where various concrete samples were placed in a tunnel with water with average pH 5-6 and mean sulphate content of 2.5 g/l. After 30 years of exposure, only the concretes made with either sulphate resistant cement or incorporating 15% silica fume were in satisfactory condition (Maage and Sellevold1987). Many test concretes with w/b 0.18 to 0.42 and up to 50% silica fume were used in 1981 in Norway, which have continued to be monitored until today. The concretes have shown no bad signs of deterioration after 20 years of service (Buhr et al. 2002). These early examples are encouraging when considering long-term longevity of the low-pH grout made from sulphate resistance cement and silica fume.

Adding silica fume to cement-based materials provides a reactive material generating silicate. Silicate reacts readily with available lime and/or portlandite (CH) and forms CSH paste. CH is the most soluble of all the cement hydration products. By removing the CH, silica fume addition creates a hardened grout with improved properties, such as better leach resistance.

The next sections describe the various durability changes seen in cement-based materials when adding silica fume. Again, it should be kept clear that nearly all of these past studies using silica fume have been done on high strength mixtures where the w/b ratio is very low (< 0.5). Due to this fact, the reported silica fume mixtures are not 100% comparable to the ONKALO injection grouts where the effective w/b ratio is 1.0.

4.3.1 Strength

Silica fume is often used to aid production of high strength concrete. Studies have been done to determine the optimal content of silica fume, where the most benefits are achieved without excessive costs for the material. Bhanja and Sengupta (2003) have studies high strength concrete with w/b ratios 0.26 to 0.42 with up to 30% silica fume. Figure 12 shows their results of the relationship between silica fume content and strength at various w/b ratios. They found that silica fume had both physical (microfiller action) and chemical (pozzolanic activity) factors attributing to the strength gain. The optimum silica fume replacement percentage was a function of the w/b of the mixture.

Al-Manaseer and Keil (1992) present similar correlations between silica fume and compressive strength, as shown in Figure 13. Their tests were done on mixtures with w/b ratio of 0.40, using re-ground sulphate resistant cement (Blaine 690 m^2/kg) and up to 25% silica fume. The results showed that the superplasticizer dosage had no apparent impact on the strength, while the silica fume content affected the rate of strength gain and ultimate strength.

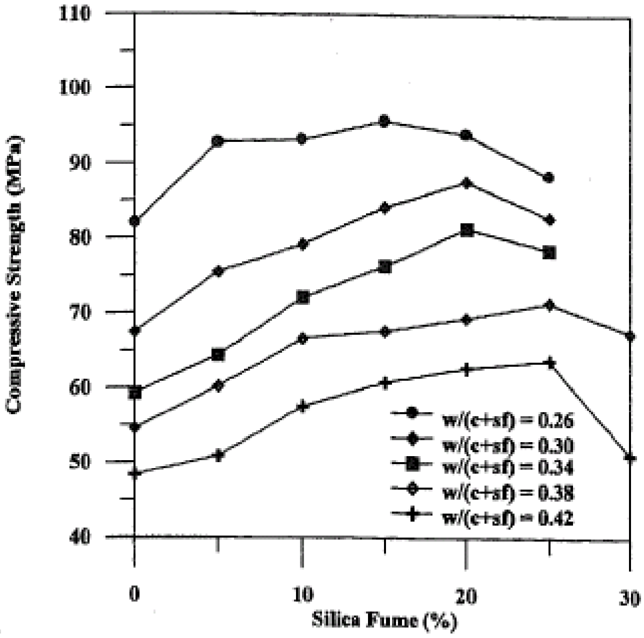


Figure 12. *Relationship between 28-day compressive strength and percentage replacement of silica fume, for w/b 0.26 to 0.42 (Bhanja and Sengupta 2003).*

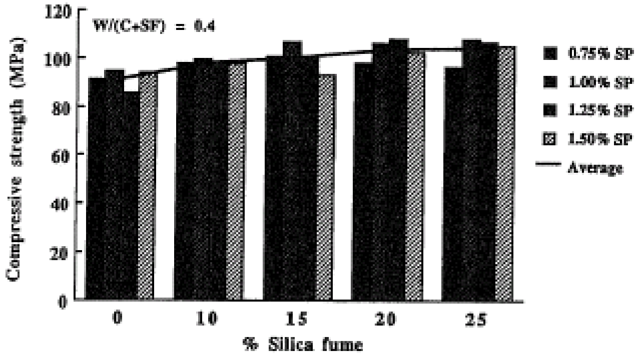


Figure 13. *Compressive strength at 90 days for 0-25% silica fume content, mortar with w/b 0.40 (Al-Manaseer and Keil 1992).*

4.3.2 Porosity

Studies by Cheng-Yi and Feldman (1985) indicate that pozzolans, such as silica fume, do not significantly influence total porosity. They reduce the volume of capillary pores, while increasing the hydrated product porosity and significantly decreasing the volume of inter-connected pores. By producing smaller and more discontinuous pores, the addition of silica fume markedly decreases the permeability, and thus improves durability, of the cement paste.

4.3.3 Permeability and leaching

Permeability and leaching tests have been done on low-pH grouts similar to the ONKALO suggested materials, as reported by Vuorinen et al. (2005). Equilibrium and diffusion tests were done in a glove-box (N_2 atmosphere) with both fresh and saline groundwater solutions. The tests were done on mixtures with different cement types along with varying amounts of blast furnace slag and silica fume (Kronlöf 2004). The silica fume contents were 7% to 46% by solid dry weight of cement, with w/b ratios 1.21 to 2.91, respectively. The test results showed:

- pH was lower in the saline leachate compared to the fresh leachate,
- equilibrium tests had an overall lower amount of leachate than the complete diffusion tests,
- all promising low-pH blast furnace slag mixtures had unfavorable attributes due to sulphides in the slag dissolving in the leachates, and
- mixtures containing silica fume showed promising technical characteristics (i.e. diffusion test: fast depletion of K, Al, SO_4^{2-} and no release of Na, declining trend of Ca concentration).

Onofrei et al. (1991, 1992) reported on grouts used for nuclear waste disposal facilities in the U.S.A. and Canada. Their experience includes mixtures with w/b ratio mixtures of 0.4 to 0.8 using sulphate-resistant cement combined with 10% silica fume and 1% superplasticizer. None of their studies have contra-indicated the use of cement-based grouts containing silica fume and superplasticizer in sealing applications. Some of their key results regarding long-term durability of silica fume grouts are described in the next paragraphs.

Onofrei's static leach tests (1992) showed the release of Ca^{2+} was independent of the silica fume addition. The w/b ratio also did not significantly influence the Ca^{2+} release into solution. The relatively high release of Si^{4+} was not controlled by hydration reactions and was mainly due to dissolution of unreacted materials from the silica fume. Dynamic leach tests showed steadily decreasing leach rates of Ca^{2+}, indicating the presence of a surface layer acting as a protective barrier imposing lower solubilities on the cement constituents. Models were evaluated based on the various leaching tests, but they could not account for the precipitation of portlandite, carbonate and CSH, which tended to clog the pores of the grouts. Overall, it was concluded that existing long-term leaching models which do not allow for precipitation as well as dissolution of solids likely lead to an underestimate of grout longevity.

Gray (1993) reports on similar static and dynamic leaching tests that under low hydraulic gradients, fractures filled with cement grout will progressively tighten due to reaction, alteration and formation of secondary minerals. It is specifically noted that components present in granite can also participate in the cement reaction, suggesting that the interface between the grout and rock will interact chemically, minerals may precipitate and new secondary minerals may be formed. These interactions may further enhance the sealing effects of the grout by clogging of fractures.

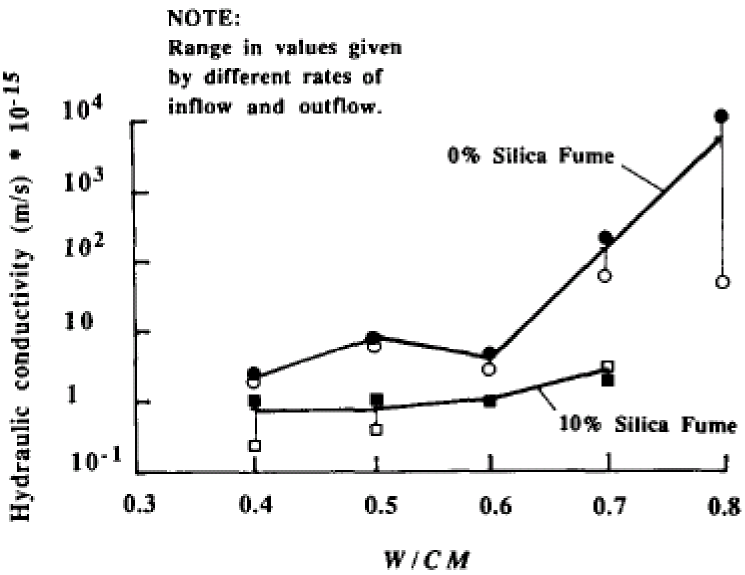


Figure 14. Effect of silica fume and w/b on the hydraulic conductivity of grout (i > 28500 for 0% SF and i > 35000 for 10% SF) (Onofrei et al. 1992).

Onofrei's hydraulic conductivity and permeability tests (1992) with w/b 0.4 to 0.8 showed that adding silica fume decreased the apparent hydraulic conductivity (K) of the grout (Figure 15), which was approximately 10^{-15} m/s and was little influenced by w/b. For comparison, the reference mixtures had higher K values and were influenced by w/b, especially over a w/b of 0.6. It was not noted how even higher w/b ratios would affect these trends. In Figure 15 the hydraulic gradient, i (m/m), is given and the higher i value in the silica fume mixtures indicates the need for greater pressure to achieve flow.

Related research by Onofrei reported by Al-Manaseer et al. (1991) noted that hydraulic conductivity of the high strength silica fume grout was two to three orders of magnitude lower than typically observed for intact granite (10^{-12} m/s). He also addressed that longevity models assume a K of 10^{-12} m/s and predict cement grouts to function hydraulically for hundreds of thousands of years. Therefore, Al-Manaseer concluded that the models for high strength silica fume grouts will tend to underestimate the material longevity.

Both Onofrei et al. (1992) and Al-Manaseer (1991) have concluded from the leaching and permeability tests that the decrease in hydraulic conductivity caused by the decrease in w/b ratio and silica fume additions was a consequence of the decrease in pore size and the decreases in connected capillary pore space. In another report, Onofrei et al. (1991) stated that the changes in porosity during leaching are mainly attributed to the changes in the volume of solids caused by the formation of new hydration products as a result of the increase in the degree of hydration. Their results also confirmed that silica fume grout has the potential to self-heal and maintain its performance for very long time periods.

Gray (2003) has also reported after leaching tests of Onofrei et al. (1992) that the hydraulic conductivity tended to decrease with increasing testing time. The hydraulic conductivity decreased by as much as two orders of magnitude after water had permeated the grout for 230 days. This decrease was attributed to the formation of reaction products during leaching and the ability of the grout to self-healing.

Al-Manaseer et al. (1991) has concluded that conventional models, which suggest that porosity will increase as water flows through and dissolves the cement, may not be valid for bulk performance of grout. This is because his results showed that pore size distribution rather than total porosity should be accounted for when estimating longevity and the long-term performance in durability models.

Permeability tests by Ballivy et al. (1992) were conducted using an environmental permeameter on solid and fractured granite that was injected with grout to simulate in-situ conditions. The injection grout was made from sulphate resistant cement, 10% silica fume, 1% superplasticizer and having a w/b of 0.35. Their tests showed that there was little difference in the permeability of the injected rock compared to the reference sound rock. The concentration of the leachant was assessed after testing. A close relationship was found between the leachate and the permeability.

Leaching tests performed by Alonso et al. (2006a) on high strength concrete found improvements when silica fume was used compared to the reference mixture without silica fume. Their tests included both standing and running water leaching environments, using natural granitic ground water. The concrete mixtures had very low w/b ratios of 0.20 to 0.24, with sulphate resistant cement and 5 to 25 % silica fume. The amount of leached calcium (Ca^{2+}) was measured and used as the indicator of attack. The results showed that mixtures with higher amounts of silica fume performed best in the standing water test, yet lower silica fume content mixtures performed better in the running water test. All silica fume mixtures had much better leaching resistance than the reference (no silica fume) concrete. The diffusion coefficients were on the order of 10^{-14} m^2/s. Their tests again showed the ability of the concrete to self-heal and slow down the leaching process due to the formation of calcite precipitates.

Testing by Johnston and Wilmot (1992) found that over 10% silica fume was needed in grout to significantly increase the retardation capacity of Cs and Sr for a nuclear fuel waste repository. The measured distribution coefficients, Kd, are given in Table 3 and are expressed as mL/g. This parameter, Kd, describes the concentration of the solute in the solid phase divided by the concentration in the solution phase. They also noted again that the porosity values, measured by mercury porosimetry decreased as the w/b ratio decreased, though the silica fume mixtures had varying porosity compared to the reference. Adding 5% extra silica fume (from 10 to 15%) had the same effect of lowering the diffusion coefficient for ^3H_2O as reducing the w/b ratio from 0.35 to 0.25, as seen in Figure 16. Their leaching tests were performed on grouts made from sulphate resistant cement, superplasticizer, up to 15% silica fume and w/b ratios of 0.25 to 0.35. Leaching tests were performed in three different conditions of saline groundwater, granitic groundwater and saturated limewater.

Table 3. *Measured Cs and Sr distribution coefficients (Kd) in grout (Johnston and Wilmot 1992).*

		Distribution Coefficients (mL/g)		Porosity (g/cm^3)
Mix	w/b	Sr	Cs	
Reference	0.35	0.18	0.12	0.181
	0.25	0.10	0.12	0.113
10% SF	0.35	0.10	0.15	0.225
	0.25	0.14	0.20	0.142
15% SF	0.35	0.19	0.25	0.198
	0.25	0.17	0.31	0.130

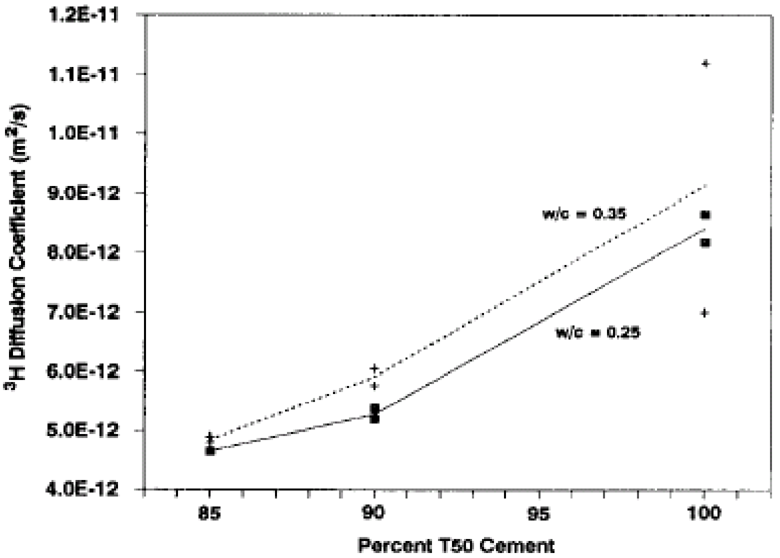


Figure 15. *Effect of 0-15% silica fume and w/b on the measured diffusion coefficients for ^3H_2O in grout (Johnston and Wilmot 1992).*

Leaching studies were done by Palardy et al. (1998) at various temperatures on grout made from sulphate resistant cement, 1% superplasticizer, 15% silica fume and a w/b of 0.30. The results showed that permeability increased along with increasing temperature, in the temperature range of 25°C to 100°C, which was attributed to the change in microstructure and the decrease in the viscosity of permeated water. At the onset of testing there were higher permeabilities due to the thermal expansion of the cement paste, which can cause fractures and cracks. However, the increased conductivity was only for a short period of time, after which it decreased with time. This was attributed to the ability of the material to self-heal with further hydration and the formation of precipitate in the cracks. The testing results and hypotheses were verified by microstructural and chemical characterization of the grout after the leaching tests. Palardy concluded that both leaching and hydraulic conductivity of the grouts decreased with time, as shown in Figure 17.

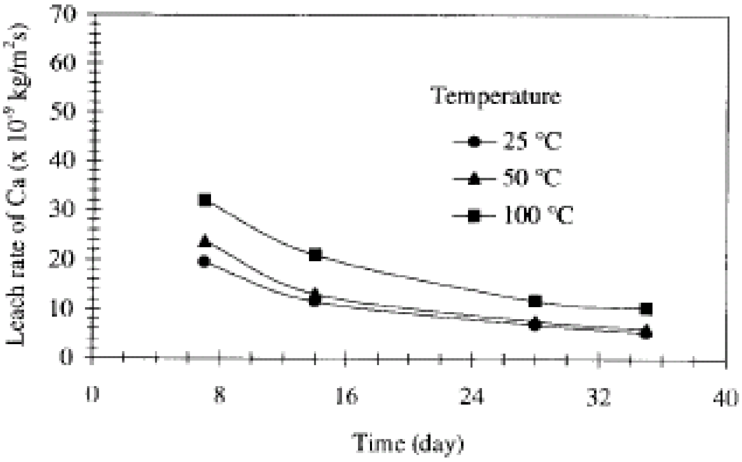


Figure 16. *Effect of leaching time and temperature on the leach rate of calcium for grout with 15% silica fume and w/b of 0.30, tested in deionized water (Palardy et al. 1998).*

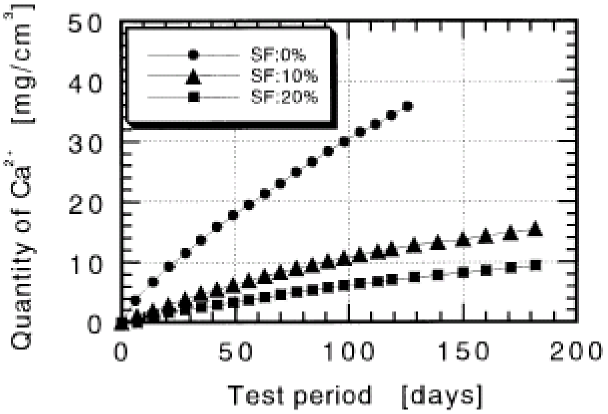


Figure 17. *Cumulative quantity of dissolved Ca^{2+}, for silica fume mortars with w/b 0.41 (Saito and Deguchi 2000).*

Leaching tests were done by Saito and Deguchi (2000) on mortars with 10% and 20% silica fume at a w/b ratio of 0.41. Their results showed smaller quantities of dissolved Ca^{2+} at higher silica fume amounts, as shown in Figure 18. Initially they noted no change in the pore size distribution with the addition of silica fume. The cement hydration structure was investigated before and after the leaching tests. The silica fume mixtures had a pore volume increase by 40-50%, showing that the cement hydration structure became coarser with leaching. Yet the mixtures containing silica fume had better leaching resistance showed less change in performance after the leaching test compared with the reference mixture.

As another example in a very aggressive environment, leaching tests using a 50% concentration solution of ammonium nitrate by Carde et al. (1996) confirmed similar findings. Their tests were done on a reference paste with a w/b of 0.50 or a 30% silica fume paste with w/b of 0.45. Their results showed different amounts of CSH consumption during the test between the mixtures, which is due to the aggressive nature of the concentrate on the cement. The mixture containing silica fume has less cement (and CH) attacked. Therefore the silica fume paste had enough residual strength remaining to provide some mechanical functionality after the test.

Carde and François (1999) have done a lot of work on modeling the loss of strength and porosity after the same leaching test described in the previous paragraph. They have calculated the relative loss of average strength compared to the amount of degradation, as shown in Figure 19. Another model they have developed shows the correlation between the amount of degradation and the increase in porosity, as seen in Figure 20. From these results they have modeled the degradation and concluded that the initial amount of calcium hydroxide is the main parameter governing the decrease of mechanical performance and thus performance.

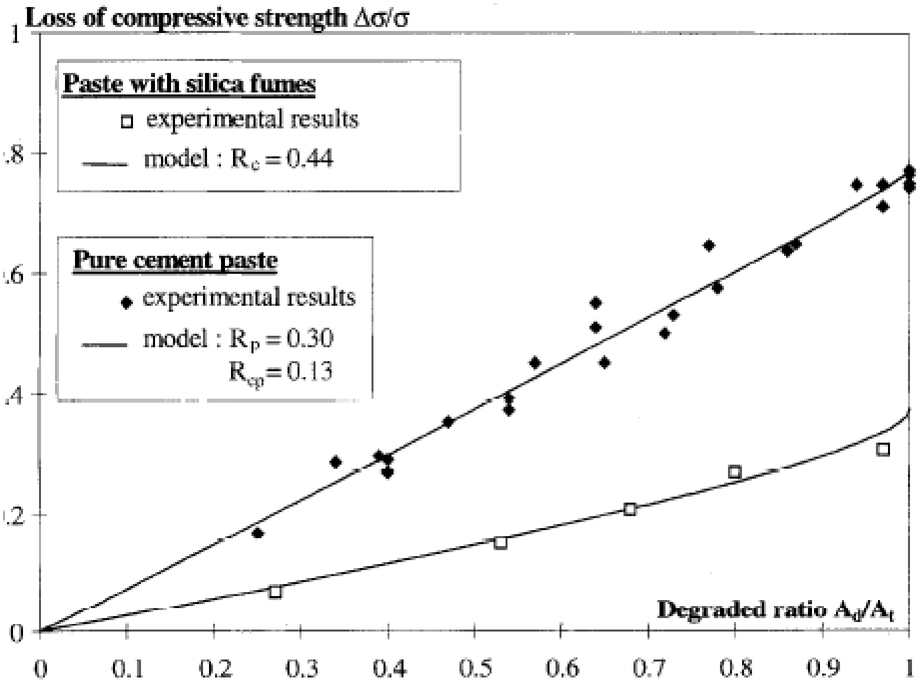


Figure 18. *Relation of strength and degradation for comparison between model and experimental results for 30% silica fume (w/b=0.45) and reference paste (w/c=0.50) mixtures after leaching tests (Carde and François 1999).*

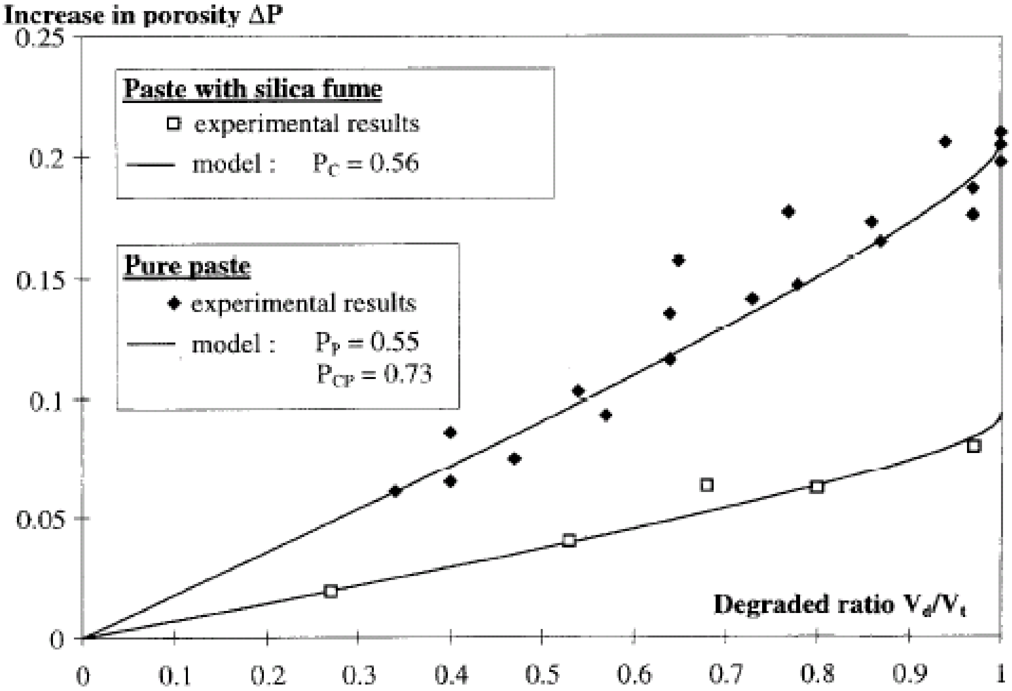
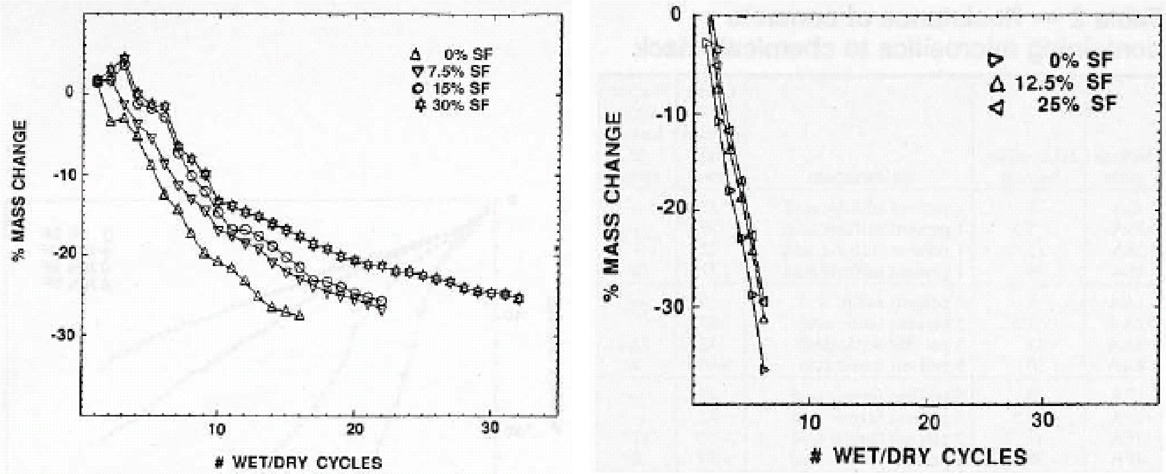


Figure 19. *Relation of porosity and degradation for comparison between model and experimental results for 30% silica fume (w/b=0.45) and reference paste (w/c=0.50) mixtures after leaching tests (Carde and François 1999).*

4.3.4 Chemical resistance

In general, cement-based materials containing silica fume show enhanced chemical resistance compared to portland cement with the same w/b ratio due to the lower permeability and higher CSH content. Many building codes set a limit, such as 10% by weight of cementitious material, for the amount of silica fume that can be incorporated to concrete (by50 2004). These limits are based on the potential long-term durability (steel corrosion) problems that can results from lowering the pH. In the case of low-pH injection grout, steel corrosion is not the main durability risk and the other benefits of higher silica fume contents are considered. The following paragraphs give examples of how silica fume concrete performs in a chloride environment and for various other types of chemical attack.

Durning and Hicks (1991) have studied the benefits of using silica fume for high strength concrete in aggressive environments (low w/b of 0.26 to 0.36 with up to 30% silica fume). They concluded that decreasing the permeability is the most important factor for improving the resistance to any type of chemical attack, for this aspect influences the depth of attack, amount of exposed material, rate of attacking medium replenishment and rate of leaching. It should also be kept in mind that the permeability of the cement matrix changes as the attack proceeds and at sufficient concentrations, all concrete will decompose. During sulphuric acid attack, using 30% silica fume more than doubled the time to 25% mass loss in a 1% solution (Figure 21a), but using silica fume exhibited very little improvement in a 5% solution (Figure 21b). Examples of other acid attacks on concrete with varying silica fume contents are given in Figures 22 to 24. In all cases, as the amount of silica fume was increased, the number of cycles until failure also increased. They noted that at the 30% silica fume dosage, the deterioration of the concrete may have been partially attributed to aggregate durability rather than just the calcium hydroxide deterioration.



(b)

(a)

***Figure 20**. Chemical resistance of concrete in sulphuric acid solution, (a) 1%, (b) 5%. w/b 0.26-0.36, silica fume 0-30% (Durning and Hicks 1991).*

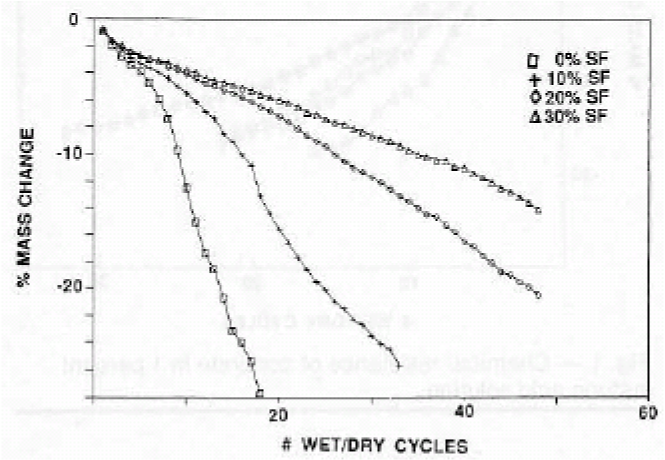


***Figure 21.** Chemical resistance of concrete in 5% formic acid solution. w/b 0.26-0.36, silica fume 0-30% (Durning and Hicks 1991).*

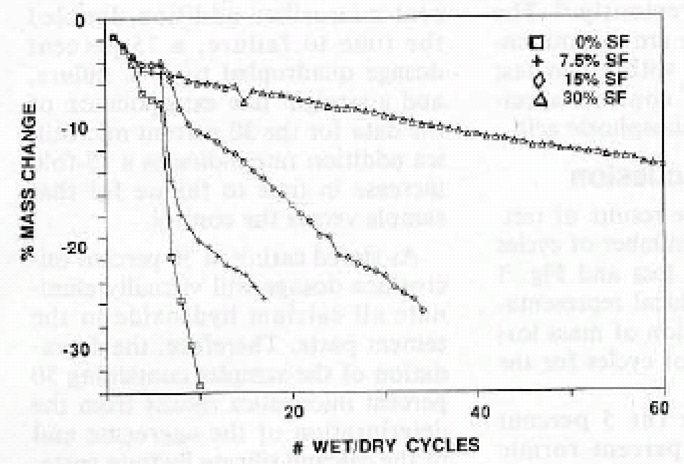


Figure 22. *Chemical resistance of concrete in 5% acetic acid solution. w/b 0.26-0.36, silica fume 0-30% (Durning and Hicks 1991).*

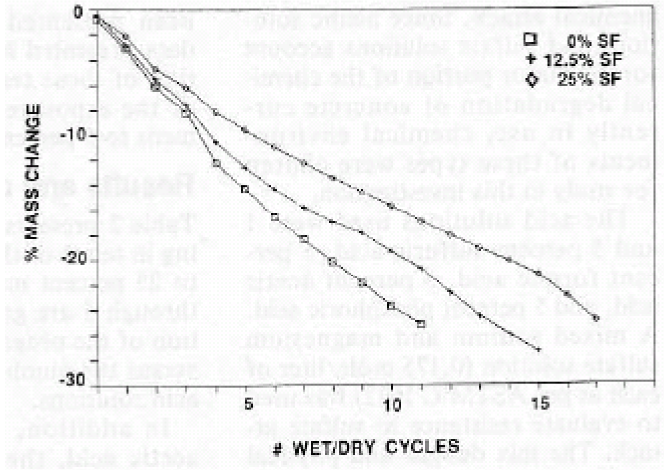


Figure 23. *Chemical resistance of concrete in 5% phosphoric acid solution. w/b 0.26-0.36, silica fume 0-30% (Durning and Hicks 1991).*

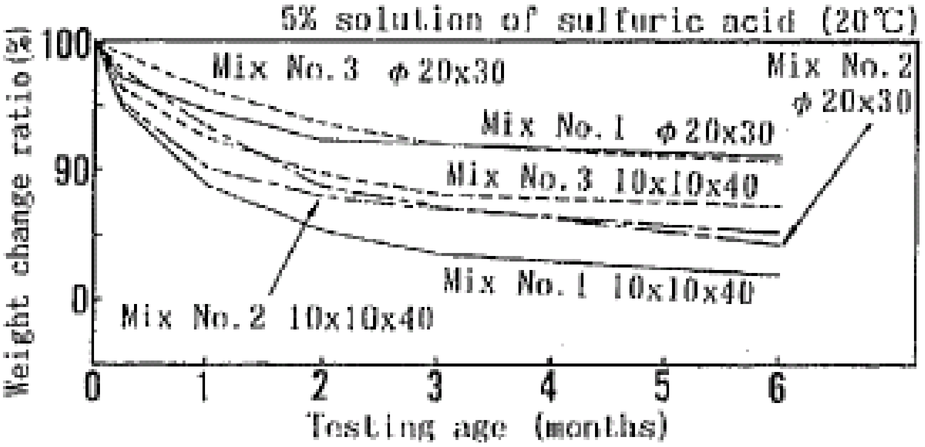


Figure 24. *Results of resistance to sulphuric acid chemical attack test. Concretes mix 1: w/b=0.28 30% SF, Mix 2: w/b=0.25 20% SF, Mix 3 w/c=0.34 0% SF (Maruyama ey al. 1990).*

Maruyama et al. (1990) did a series of durability tests on ultrahigh strength concrete with low w/b ratios of 0.25 and 0.28 containing 20 and 30% silica fume (Mix labels 2 and 1, respectively). Different sized samples were made and cured in 4 different conditions. They found that compared to the reference concrete (Mix 3 w/b 0.34, with no silica fume), mixtures containing silica fume had higher 91 day compressive strength (up to 140 MPa compared to 85 MPa) and exhibited a more brittle, explosive failure. Chemical attack tests were done using four separate reagent solutions: 2% hydrochloric acid, 5% sulphuric acid, 10% sodium sulphate and 10% magnesium sulphate. Only the silica fume mortars exposed to sulphuric acid attack showed any changes in weight after 6 months of exposure (Figure 25).

With regard to chloride ingress, many researchers have done studies on the risk of reinforcement corrosion. They have concluded that the use of silica fume effectively prevents chloride for entering very far into concrete due to the reduced permeability. For instance, using 8% silica fume would require eight times longer for chlorides to reach the threshold level required for corrosion to occur. (Luther 1989) Even though silica reduces the pH and results in less CH in the cement-matrix (which would increase corrosion), there is usually a lower permeability (which would increase corrosion protection). The overall effect on chloride ingress durability of including higher amounts of silica fume is therefore case-dependent on other mix designs and environmental factors. In general, research has concluded that when concrete is placed in harsh marine (seawater) environments, there should not be any significant detrimental changes in long-term properties for silica fume concretes compared to plain mixtures (Maage and Sellewold 1987).

In cement-based materials, the rates of chemical reactions increase rapidly with increasing temperature and so does the detrimental chemical effect of aggressive water. For instance, if the groundwater environment changes from 12°C to 40°C, it would be expected that the rate of chemical reactions increases and thus deterioration proceeds faster. On the other hand, chemical reactions are retarded at low temperatures and may even come to a standstill under extreme conditions. These dependences on temperature are shown in Figure 26 for solubility of sulphates (Biczok 1972).

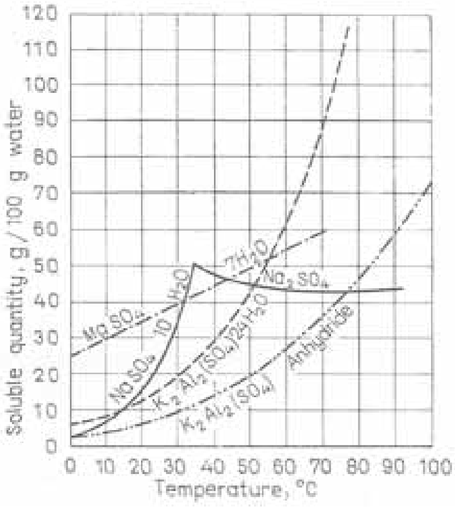


Figure 25. *Solubility of sulphates vs. temperature (Biczok 1972).*

Glasser (1992) has described microbiological attack for radioactive waste repositories and notes that this type of attack appears to be relatively unimportant in normal cement-matrices. Even in repository environments with a lower pH where there are reactions such as carbonation and leaching, the bioactivity is not anticipated to be problematic. He states that this is because the SO_4^{2-} content of cement is normally low, on the order of 2-3%, and there have been no reports of such type of cement deterioration. Glasser continues to discuss how groundwater attack is the most straightforward and potential type of degradation to be encountered.

Neville (1981) also describes the risks of microbiological attack for applications of concrete sewage pipes. "Although domestic sewage by itself is alkaline and does not attack concrete, severe damage of sewers has been observed in many cases, especially at fairly high temperatures, when sulphur compounds becomes reduced by anaerobic bacteria to H_2S. This is not a destructive agent in itself, but it is dissolved in moisture films on the exposed surface of the concrete and undergoes oxidation by aerobic bacteria, finally producing sulphuric acid." Therefore, the microbiological attack is two-fold, requiring both moisture for the first reaction and air exposure for the second oxidation reaction prior to harmful acid attack to the concrete. In the case of injection grouts, there is typically a small surface area to volume ratio, so the exposed oxidation area is low and thus the risk of microbiological attack would be low. The potential risks of microbiological attack related to the interaction between sulphate products and other repository materials, such as copper, are outside the scope of this work.

4.3.5 Shrinkage

Shrinkage of concrete or grout containing silica fume can be greater because of the reduction in bleeding and thus higher susceptibility to early age drying. Extra curing precautions should be taken during the early ages to prevent plastic shrinkage cracking of silica fume mixtures. These precautions include actions that prevent water from being evaporated from the concrete surface, such as applying a liquid-membrane forming curing compound or providing moisture misting/fogging to maintain the relative humidity at 100% in the surrounding area. Curing often proceeds immediately after placement until the material has gained sufficient strength or other required properties, sometimes lasting many days.

Autogenous shrinkage can also be a concern in silica fume mixtures with very low w/b ratios (< 0.45) due to the refined pore structure (Holt 2004). Baroghel-Bouny (1996) has shown a linear correlation between the amount of silica fume and the autogenous shrinkage for silica fume contents to 20% at a w/b of 0.25. Her testing has also established a correlation for autogenous shrinkage related to w/b, which shows expansion rather than shrinkage when the reference (no silica fume) mixture had a w/c ratio over 0.5.

The durability tests by Maruyama et al. (1990) on ultrahigh strength concrete (as reported in Chapter 4.3.3) found no change in either drying shrinkage or carbonation in concretes made with or without up to 30% silica fume (w/b 0.24 to 0.34).

Research has also shown that silica fume concretes show a higher amount of microcracking compared to ordinary portland cement mixtures (Maage and Sellewold 1987), though these cracks do not prove to be detrimental to strength, permeability or durability because of the other microstructural improvements when using silica fume.

For injection grouts, the influence of altering the w/b ratio has a much greater influence than the use of silica fume with regard to drying shrinkage magnitudes and cracking risks.

4.3.6 Carbonation

In addition to the results by Maruyama et al. (1990), as noted in Chapter 4.3.4, other work has found some influence of silica fume on carbonation. Research by Baronio et al. (1990) on normal strength mortars containing 5 to 20% silica fume (w/b = 0.40 to 0.67, sand 2 mm diameter) found that there was about a 35% reduction in carbonation compared to the reference mixture. Similar to other research, they also noted a reduction in workability and permeability in the silica fume mixtures.

4.3.7 Severe temperatures

The addition of silica fume to concrete mixtures either improves or shows equivalent frost resistance when compared to portland cement concrete made with the same materials. The resistance to scaling with freeze-thaw exposure has been varied, with some test results showing improved resistance with increasing silica fume content and other tests showing poor performance for lean mixtures with shorter curing times (Luther 1989).

Tests by Maruyama et al. (1990) on ultrahigh strength concrete (as reported in Chapters 4.3.3 and 4.3.4 with up to 30% silica fume and w/b of 0.25-0.34) also reported on freeze-thaw durability. Freeze-thaw performance, assessed by both internal damage and weight loss up to 300 cycles, was improved with the use of silica fume (Figure 27). It was observed by mercury porosimetry that silica fume mixtures had fewer micropores, which was attributed to their lower w/b ratios and the incorporation of the fine silica fume particles.

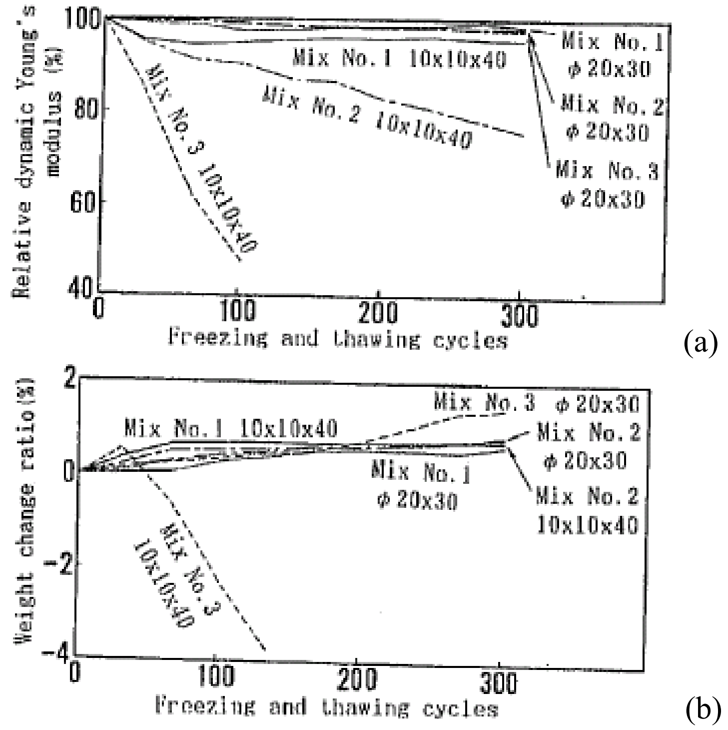


Figure 26. *Results of freezing and thawing test, (a) internal damage by relative dynamic modulus, (b) decrease in weight ratio. Concretes Mix 1: w/b=0.28 30% SF, Mix 2: w/b=0.25 20% SF, Mix 3 w/c=0.34 0% SF (Maruyama et al. 1990).*

Test results from various other researchers have also confirmed that there is no detrimental effect on freeze-thaw resistance when incorporating silica fume to concrete. Silica fume producers report that there is no significant influence on the production and stability of the air void system when using silica fume.

With regard to fire resistance, concrete with a denser microstructure and lower permeability has a higher risk of deterioration at extremely high temperatures due to spalling. Free moisture in the concrete cannot escape as fast in a denser concrete and thus there may be more damage. Therefore, adding silica fume to a mixture would result in a higher risk of deterioration during fire because of the dense and low permeable cement matrix.

4.4 Models of grout degradation

Various models have been developed to estimate the deterioration or service life of grouts. The boundary conditions and input parameters have a wide variety, depending on the scope of the model. A few examples of different types of models are described here.

Vuorinen et al. (2005) have used a thermodynamic model to successfully qualitatively reproduce experimental leaching tests results. Their tests used different cement types along with varying amounts of blast furnace slag and silica fume. Two different Fickian diffusion models were also used to predict the leaching rates and/or diffusion coefficients. Their models and test results showed the mixtures containing silica fume showed promising technical characteristics. Their leaching model results could possibly used as inputs for further modeling of durability and service life.

Carde and François (1999) have modeled the effects of strength and porosity after leaching of cement pastes, as described in Chapter 4.3.3 Figures 19 and 20. Their model has numerically simulated experimental data on degradation of cement and silica fume pastes.

Kamali et al. (2003) have developed a model based on existing experimental data from literature for paste and mortars. The model considering material parameters and environmental conditions to predict deterioration with respect to leaching depth with time for up to 400 years. The model incorporated data showing leaching decreased with increasing silica fume content or with decreasing w/c ratio, more significant dissolution of hydrates at lower pH, and decreased solubility with increasing temperature. The approximate ranges of values used for the simulation were a w/b of 0.25-0.6, silica fume contents 0-32% and temperature 25-85°C.

Schmidt-Döhl et al. (2004) have used a transport reaction model called TRANSREAC to simulate heat and moisture transport for concrete structures. They have simulated acid attack, corrosion depth, and leachant formation (including Mg, Na, Cl, K, Ca, and SO_4). From the data they are able to assess long-term behavior of concrete for thousands of years. The report did not include comparisons between various types of concrete mixtures yet showed model verification.

Maltais et al. (2004) have used models to predict the durability of cement-based materials based on laboratory studies on the influence of w/c ratio, type of cement and type of degradation solution. They used both ordinary and sulphate resistant cement to make paste with w/c ratios of 0.40 and 0.60. Microstructural assessments were done after leaching tests, as well as determining the porosity, diffusion coefficient and resistance to chloride ion penetration. A numeric model called STADIUM was used to predict deterioration compared to microprobe measurements. Results showed good correlation with the model, along with the facts that reducing the w/c ratio reduced leaching and there was a significant influence of cement type on degradation.

2D simulation of grouting and backfilling was done by Luna et al. (2006) using conceptual and numeric models. The numerical models used the code PHAST, composed of a transport code H3T3D and a geochemical code PHREEQC. The simulation was done for 4000 years to evaluation the interaction with backfill material. Their model used hydraulic conductivity, porosity and diffusion coefficients representative of shotcrete and low-pH grout. The results found that the shotcrete layer would have total dissolution of gypsum occurred after 640 years, while for grout it occurred after 600 years. The deposition tunnel would show no effects on the geochemical evolution of the system other than an increase in pH in the vicinity of the shotcrete grout. No performance alterations of the backfill material were expected.

It should be noted for all models that it is very important to establish the proper input parameters and boundary conditions. It is most beneficial if the materials parameters identified through characterization or testing are determined by the modelers. There is often a high degree of uncertainty in the modeled results due to the assumptions made and the changing parameters with time. For instance, this is especially true in the case of modeling leaching results of low-pH grout, where the process of leaching further transforms the material structure, thus complicating the durability predictions. Identifying the ideal model(s) to use for estimating injection grout durability and service life requires its own literature review and investigation of current practice.

5 PERFORMANCE OF ONKALO LOW-PH GROUT

5.1 Specified materials and conditions

A low-pH injection grout will be used at ONKALO in order to improve long-term environmental safety by having leachates with sufficiently low pH (≤11). There is not a long history of experience with this material, so the assumptions about long-term performance are mostly based on similar concrete and cement-based mixtures containing silica fume.

The ingredients for the ONKALO low-pH injection grout are as follows:

- Cement: Ultrafin 16 - sulphate resistant, low alkaline injection microcement, manufactured by Cementa AB in Sweden. Specific surface of 1600 m^2/kg, C_3A content of 2 %, and alkali content of ~ 0.5 %.
- Pozzolan: GroutAid – silica fume-based additive for grouting, produced by Elkem ASA Materials in Norway. Minimum SiO_2 content of 86%, solids content of 50%, specific surface area about 15 000 m^2/kg, 90% of particles < 1 μm diameter, pH of 4.5 to 6.5, and no accelerator additive.
- Chemical admixture: Mighty 150 - naphthalene sulphonate based superplasticizer produced by Degussa (now BASF Construction Chemicals).

As noted in Chapter 1, the effective w/b ratio is 1.0 for both grout mixtures. Even though the actual w/b for the low-pH grout is 1.4, the reaction efficiency of the silica fume gives it a stronger 'weighting factor' than the plain cement. Therefore the mixtures are assumed to behave similarly with respect to their equivalent w/b ratios.

5.2 Current material-based durability expectations

Based on the material selection for the two types of injection grouts, some comments can be given on their expected durability. These conclusions are based on the literature reviewed and presented in Chapters 2, 3 and 4.

The standard reference grout should perform satisfactory for injecting fissures, rock bolts and related areas. It is beneficial to use sulphate resistant cement in both grout types to improve the resistance to chemical attack and leaching. The w/b ratio is within the ranges used in practice.

The addition of silica fume to produce a low-pH grout will provide many beneficial results regarding long-term performance. No published references could be found that would suggest harmful durability results from the use of high amounts (over 15%) of silica fume. When using the high amount of silica fume, an increased amount of superplasticizer is used but this amount is still within acceptable "normal" ranges and should not pose any significant change to the leaching characteristics of the grout. The specific benefits and risks of the low-pH grout compared to the standard (reference) grout are given in the next sub-sections.

Benefits of low-pH grout

The main characteristic difference between the reference and low-pH grout is increasing the silica fume content from 15 to 40% by dry weight. The microstructure of a high silica fume injection grout (low-pH mixture) should be denser than a reference grout at equivalent w/b ratios. Compared to the reference grout mix, the low-pH mixture will probably have the following characteristics:

- less CH in hydrated cement,
- better stability after mixing (fresh state),
- greater homogeneity, due to less bleeding and better fine particle dispersion,
- better penetration into fine fissures,
- better bond to granite bedrock and clay deposits in fissures,
- higher compressive strength,
- possibly higher total porosity, yet with fewer capillary pores and fewer interconnected pores, and
- better potential for self-healing.

All of these properties would lead to generally improved durability performance, including:

- lower permeability,
- lower diffusion coefficient,
- better leaching resistance,
- greater resistance to chemical attack (especially sulphate), and
- better protection against steel reinforcement corrosion.

Risks of low-pH grout

A few of the risks that are associated with the low-pH mixture compared to the reference grout are shrinkage, corrosion, gel-blocking and silica conglomerates leading to alkali-silica reactions (ASR). The gel-blocking and silica conglomerate phenomenon were addressed in Chapter 4.1.2 since they are early-age problems. They are also elaborated on in Appendices B and C. The shrinkage and corrosion risks are addressed in the next paragraphs. Other durability topics presented in Chapter 2, such as freeze-thaw, fire, carbonation and surface wear, are not a main concern for injection grouts due to the application situation.

One durability issue that is potentially worse in the low-pH grout mixture compared to the standard grout is the shrinkage. This is because the total drying shrinkage will likely be higher for the low-pH mixture compared to the standard reference grout due to the higher w/b ratio and higher total water content, increased superplasticizer dosage and longer setting time. Yet drying shrinkage will only be a concern at exposed surfaces, which are in contact with the surrounding environment having a lower humidity and possible wind. The availability of groundwater will likely maintain that the grout inside sealed fissures will not be subjected to water depletion and thus drying. Autogenous shrinkage will not be a concern because of the high w/b ratios (>>0.45). It is expected that the magnitude of any shrinkage is still relatively small compared to the size of the fissures and anticipated maximum allowable aperture size after sealing, and therefore should not be a problem.

As noted for steel corrosion and carbonation, the risk of deterioration is higher when the pH of the concrete is lower, which occurs when using a high amount of silica fume as in the low-pH grout mixtures developed for ONKALO. Yet the benefit of the high silica fume content results in a lower permeability and hydraulic conductivity of the cement paste. Therefore, the silica fume is simultaneously acting to both potentially increase (because of pH) and decrease (because of permeability) the corrosion risk. The total risk level is dependent on other unpredictable factors related to groundwater and grout properties. Overall, it is expected that the corrosion risk of the low-pH grout would be about equivalent to the reference mixture, though further testing to quantify the results would be beneficial. This corrosion risk is a structural application problem when considering steel in the repository, such as rock bolts and shotcrete fibers.

5.3 Alternative grout durability concerns

It is possible after further experience at ONKALO that it will be necessary to change the mix design or material used for the injection grout, both for the reference or low-pH mixtures. The potential changes would likely alter the long-term grout durability. For instance, a lower quality grout may result from changes such as increasing the w/c or w/b ratio, decreasing the amount of silica fume, decreasing the amount of cement, increasing the water amount or incorrectly dosing the superplasticizer. All of these could result in lower strength, higher permeability, greater potential for leaching and a higher risk of chemical attack. Increasing the superplasticizer dosage may also result in a change to the leachant products due to the superplasticizer alone.

5.4 Construction-based durability

During the construction of ONKALO, there may be changes in the construction techniques or the environmental conditions in the tunnels. Some of these changes could also have effects on the grout performance and long-term durability. For instance, the temperatures in the tunnel during construction affect the hardening and hydration process of the injection grout. As the temperature or humidity changes, the rate of hydration and thus the microstructure of the cement paste, is altered. Also if there is a higher rate of evaporation from the fresh grout, then there can be a higher amount of drying shrinkage and greater potential for cracking. Significantly increasing or decreasing the environmental conditions could alter the grout hydration products and microstructure and thus the long-term performance. This could be related to characteristics such as pore size, microcracks and amount of certain hydration products. All of these affect durability issues such as permeability, leaching and cracking.

In addition to environmental conditions during construction, if there are delays in grouting then there is the risk of altered properties of the final injected product. These delays could results from traffic or equipment problems resulting in slower delivery of grout or slower injection placement.

It should also be noted that the grout material is very sensitive and somewhat weak during the early ages (hours and days). Changes in blasting or vibrations during construction and excavation can upset the grouting quality and bond in fissures. This could result in additional pathways for future leaching or deterioration. Care should be taken to protect recently injected grout during high construction activity periods.

5.5 Effect of site conditions

The main concern with the Olkiluoto site conditions regarding injection grout performance is the groundwater composition. The bedrock is a durable granitic-gneissic with typical fracture infillings of calcite and clay minerals. The only bedrock concern to note is that over long periods of time there can be stress changes in the rock, which may alter the water tightness, yet this water tightness would not be grout-material-dependent.

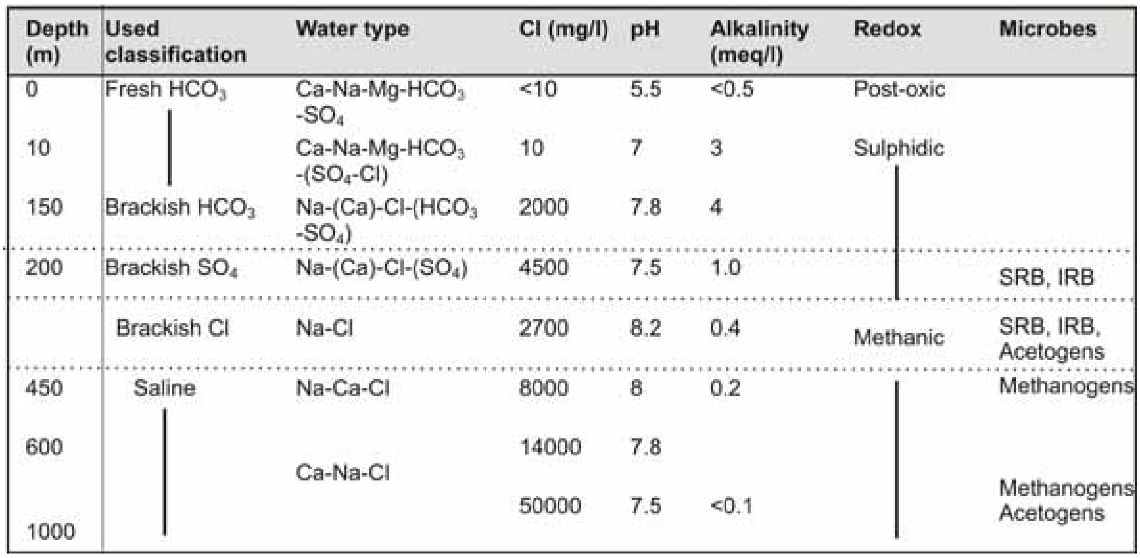
The hydrochemical conditions were given by Posiva Oy (see Appendix A), as shown in Tables 4 and 5.

From Tables 4 and 5, some notes with regard to the injection grout performance can be given.

- The *bicarbonate* (*HCO_3*) content in the fresh groundwater at the upper levels can react with calcium leaching from cement and form carbonates, which precipitate.
- The presence of *sodium (Na)* creates a moderate risk level due to its influence on alkali-silica reactions occurring.
- The presence of *chloride (Cl)* may be a concern because of potential chloride attack forming leachable compounds or expansive reaction products. There is also the risk of corrosion caused by calcium chloride. Steel used in combination with the injection grout, such as in shotcrete fibers or when securing rock bolts, has a risk of deteriorating, causing expansion and thus cracking. The groundwater chloride content is in the thousands range, much higher than standard seawater, and therefore the best types of steel need to be considered for use. Their corrosion potential of the steel for over 100 years service life should be checked.
- The presence of *magnesium (Mg)* may pose a possible moderate risk for grout durability. Mg reacts with CSH and any other Ca present in the cement paste to create insoluble products. The products will be continuously precipitated with groundwater contact. Thus there is a risk of total loss of grout physical properties if prolonged contact.
- The presence *of sulphate* (*SO_4*) is a concern because of its contribution to sulphate attack causing potential expansion and cracking or dissolution, as addressed in Chapter 2. Sulphate reacts with aluminate and calcium components to create degredative expansive products. Durability is usually a concern when the sulphate content is > 200 mg/l. The deterioration risks of the injection grout are lowered by the use of sulphate resistant cement and by incorporating a high amount of silica fume.
- The groundwater *pH, acidity* and *ammonium* (NH_4) contents are acceptable and should not cause any concern for grout performance.

The European and Finnish standards for concrete construction identify aggressive environments by their chemical composition and thus define allowable exposure classes. Each different exposure class can have different concrete requirements. Table 6 (EN206-1 2000; by50 2004) shows the limiting ranges for different exposure classes for chemical attack from natural soil and groundwater.

Table 4. *Hydrochemical constituents at Olkiluoto (Luukkonen et al. 2005).*



Depth (m)	Used classification	Water type	Cl (mg/l)	pH	Alkalinity (meq/l)	Redox	Microbes
0	Fresh HCO_3	Ca-Na-Mg-HCO_3 -SO_4	<10	5.5	<0.5	Post-oxic	
10		Ca-Na-Mg-HCO_3 -(SO_4-Cl)	10	7	3	Sulphidic	
150	Brackish HCO_3	Na-(Ca)-Cl-(HCO_3 -SO_4)	2000	7.8	4		
200	Brackish SO_4	Na-(Ca)-Cl-(SO_4)	4500	7.5	1.0		SRB, IRB
	Brackish Cl	Na-Cl	2700	8.2	0.4	Methanic	SRB, IRB, Acetogens
450	Saline	Na-Ca-Cl	8000	8	0.2		Methanogens
600		Ca-Na-Cl	14000	7.8			
			50000	7.5	<0.1		Methanogens Acetogens
1000							

Table 5. *Groundwater composition (measured mean values) at Olkiluoto, given at various depths (Appendix A).*

Depth / Parameter	0-100 m	-100-200 m	-200-300 m	-300-400m	-400-600m
pH	7,0 (5,0)	7,7 (7,1)	7,8 (7,2)	7,6(7,0)	7,8(7,1)
Acidity, meq/l	0,4 (1,4)	<0,2	<0,2	<0,2	<0,2
Cl, mg/l	210 (3400)	2500 (4600)	2800 (4600)	4000(5600)	8600(22000)
Mg, mg/l	19 (180)	110(260)	65 (190)	55(160)	50(90)
SO_4, mg/l	63 (370)	310 (540)	200(520)	130(470)	25(140)*
NH_4, mg/l	0,3(1,2)	0,4 (2,1)	0,1 (0,7)	0,2(0,9)	<0,05
() the values given in the brackets are max.values except for pH a min.value is given * Sulphate level in saline water is very low, the probable range is closer to 0-40 mg/l					

Table 6. *Limiting values for exposure classes for chemical attack from natural soil and ground water (prEn206-1 2000).*

Chemical characteristic	Reference test method	XA1	XA2	XA3
Ground water				
SO_4^{2-}, mg/l	EN 196-2	≥ 200 and ≤ 600	> 600 and ≤ 3000	> 3000 and ≤ 6000
pH	ISO 4316	≥ 5.5 and ≤ 6.5	≥ 4.5 and < 5.5	≥ 4.0 and < 4.5
CO_2 mg/l aggressive	prEN 13577:1999	≥ 15 and ≤ 40	> 40 and ≤ 100	> 100 up to saturation
NH_4^+ mg/l	ISO 7150-1 or ISO 7150-2	≥ 15 and ≤ 30	> 30 and ≤ 60	> 60 and ≤ 100
Mg^{2+} mg/l	ISO 7980	≥ 300 and ≤ 1000	> 1000 and ≤ 3000	> 3000 up to saturation
Soil				
SO_4^{2-} mg/kg total	EN 196-2	≥ 2000 and ≤ 3000	> 3000 and $\leq 12\,000$	$> 12\,000$ and $\leq 24\,000$
Acidity ml/kg	DIN 4030-2	> 20° Baumann Gully	not encountered in practice	

The concrete requirements to meet these XA (chemical attack) exposure classes are also defined in the EN and Finnish standards, though the Finnish requirements are stricter. The design of concrete for chemical attack environments is given in Table 7 (by50 2004). The strength class (K) should be calculated using the k factor equations for incorporating silica fume with sulphate resistant cement, as defined in the Finnish standard (by50 2004).

In addition to Table 7, the by50 standard also has cement requirements based on the exposure classes. Concrete exposed to class XA1 can be made from a variety of CEM I types and can include up to 11% silica fume. Concrete exposed to XA2 should be made from sulphate resistant cement and can include silica fume, while concrete exposed to XA3 should be evaluated on a case-by-case basis by experts to determine suitable materials.

Table 7. *Finnish limiting values for composition and properties of concrete in aggressive chemical environments for 100 year design life (by50 2004).*

	Aggressive chemical environments		
	XA1	XA2	XA3
Maximum w/c	0.50	0.45	0.40
Minimum strength class	K40	K45	K50
Minimum cement content (kg/m^3)	300	320	330

It must be kept in mind that Tables 6 and 7 are designed for concrete mixtures, not injection grout with much higher w/c ratios and no aggregates. The aggregates work in a positive way to provide strength and durability, but also in a negative way because of the weak interfacial transition zone where the paste bonds to the aggregate.

The only way to ensure the long-term performance and a service life of over 100 years for the injection grout is to conduct accelerated durability tests (addressed in Chapter 7). The results from accelerated tests can then be combined to model performance and predict service life. There are many existing models that address different aspects of cement-based material durability, as described by Leivo et al. (1997). Often the models use input data taken from past work on cement-based materials with much different w/b ratios and compositions (specifically without high silica fume contents). Therefore more work is needed in this area.

For all deterioration types, the expected durability is highly dependent on the groundwater contact, type of groundwater, rate of water flow and grout contact area. Permeability of the grout is the main parameter to address when trying to improve the long-term durability. If there is a denser grout structure with low permeability, there will be a slower groundwater flow through grout and thus longer time until harmful deterioration.

6 FUTURE RESEARCH NEEDS

There is a good basis of knowledge about the fresh mixture properties of the reference and low-pH injection grouts to be used at ONKALO. The mixtures have been developed with confidence regarding material compatibility, strength development, workability, viscosity, bleeding and setting time. There is a lack of information on the long-term performance of these materials, especially with regard to durability and ensuring a watertight repository structure for over 100 years.

The following topics are suggestions for future research needs to improve the confidence in using the low-pH injection grout material. In all cases it is best to test both the standard (reference) grout as well as the low-pH grout. The samples should always be well-cured before testing to ensure adequate reaction of the silica fume and hydration of the cement. Potential test methods to use for some of these tests are given in Appendix D.

- Permeability: The permeability and hydraulic conductivity should be measured and compared to the granitic-gneissis bedrock to assess the flow rate through grouted fissures. The tests can be done with either a constant or falling head, with and without pressure. These measurements are needed when using the leaching test results with long-term service life and deterioration models.
- Leaching: The grout should be tested in conditions of both standing and flowing water to assess how the grout deteriorates through leaching processes, and test set up should consider modeling needs. Proper solid-water ratios, water types, temperature, CO_2-controlled conditions, etc. should be used. It is important to look at both the leachant composition and quantity, as well as to assess the grout both before and after testing. The grout investigations provide an indication of how performance will change with time and is needed for service-life modeling.
- Chemical resistance: The affect of various chemicals present in the groundwater on the grout durability can be tested. These accelerated chemical tests may use methods similar to the leaching tests, with pre- and post-testing analysis of the grout properties. Special attention should be given to the impact of sulphate, magnesium and chloride on the grout longevity.
- Pore structure: The pore structure of the grouts should be measured to assess the difference porosity with time and grout composition. This includes characterizing the total porosity as well as the sizes of capillary and micropores. It can also be tested after leaching or chemical resistance tests to assess variations with time and hydration products. The pore structure can be assessed by methods such as mercury intrusion or by capillary water uptake tests.
- Strength: The compressive strength of grout should be measured after exposure to leaching or chemical attack tests to assess the change in performance. Pre-testing strength measurements should be taken for reference. The sample size for strength testing can play a role in selection the testing boundary conditions for the exposure tests.
- Microstructure and chemical characterization: The tendency for the grouts to have different properties after leaching or chemical attack tests should be

verified by Microstructural and chemical assessment. These assessments could include tools such as thin-section analysis with fluorescent and polarized light, X-ray diffraction, thermogravimetry, scanning electron microscopy and optical microscopy. It would be possible to see the grout's potential ability for self-healing and the formation of additional hydrated precipitants.

- Shrinkage: Since the injection grout materials have a high w/b ratio, they have excess free water after hardening which can be lost in a drying environment. It would be beneficial to have long-term drying shrinkage tests (180+ days) conducted to assess the risk of cracking. The samples should be adequately cured prior to the onset of drying to allow for sufficient hydration and silica fume reaction.
- Corrosion: Due to the high chloride content in the groundwater, the potential for steel (shotcrete fiber and rock bolt) corrosion should be assessed. The chloride diffusivity in concrete can be measured to predict the service life of reinforced structures. The CTH method (NT BUILD 493) is the most rapid and uses non-steady state migration. Measurements of actual steel corrosion can also be performed.

All of the proposed studies would provide quantitative and qualitative results to verify the long-term performance of the low-pH grout compared to the reference grouts. They would also provide beneficial information about the effects of the very high additions of silica fume on long-term durability. From the results it should be possible to create models of deterioration, which could be used to make service life predictions on the longevity of injection grout materials.

Further work could also be done to establish what types of models to use or create for predicting the service-life of injection grouts in spent fuel repositories. Some comprehensive deterioration models exist based on porosity and leaching tests, yet these often include a lot of speculative inputs. It is important to review the model development plans to ensure the proper input parameters can be identified and quantified. Review of modeling techniques would be beneficial before proceeding too far with laboratory investigations.

7 SUMMARY

Construction at ONKALO is planned to include both normal cement-based injection grout and a low-pH grout containing 40% silica fume. The grouts are made from the same type of sulphate resistant cement and have equivalent water-binder (w/b) ratios of 1.0. This study has investigated the expected performance of both types of grouting material, with special attention given to durability issues such as leaching, chemical attack and shrinkage.

Most of the existing durability literature is for concrete and related cement-based materials with a lower w/b ratio than what is used at ONKALO. There are also very few examples on performance of mixtures containing such high amounts of silica fume. Reporting on low-pH grouts has mainly focused on fresh properties such as viscosity and strength development, rather than long-term performance. Therefore, from the literature review it has only been possible to speculate on the long-term durability performance of low-pH grouts.

It is well documented that to achieve the most durable grout, it is beneficial to have a dense microstructure so the hydrated cement-matrix has the lowest possible water permeability. The denser microstructure is often achieved by lowering the w/b ratio, using superplasticizer and incorporating pozzolans, such as silica fume. The lower permeability will result in better resistance to leaching, chemical attack and corrosion. In this regard, it is expected that the low-pH mixture will perform the same or better than the reference grout.

Many research studies have confirmed that during a leaching test, the physical and chemical properties of the material change with time. The porosity and leaching potential may increase with time due to removal of hydration products but these properties can also decrease due to additional hydration, blocking of pores, and formation of barriers on particle surfaces. Grout containing silica fume have also shown the ability to self-heal, which would also reduce the leaching potential.

Other durability issues that may pose a minor concern for the low-pH material include shrinkage cracking, gel-blocking and ASR formation from silica conglomerates. Care should be taken during construction to protect recently grouted areas to ensure sufficient strength and hydration of the grout. Excessive changes in temperature, humidity or wind should be limited so as to limit drying shrinkage of exposed grout surfaces.

The main environmental concern in the repository is the composition of the groundwater, with respect to potential sulphate, magnesium and chloride attack on the grouts. The risks are reduced by the use of sulphate resistant cement and the high amount of silica fume, which results in a lower amount of calcium hydroxide being formed. Further assessments can be done regarding the degradation potential and duration after material parameters of the grout are quantified.

The only way to assess if the low-pH injection grout will perform better than the standard reference grout regarding long-term durability is through laboratory assessment of the material parameters. Tests should be done to quantify grout properties such as porosity, permeability or hydraulic conductivity, and shrinkage. Tests of the grout- groundwater interaction should be investigated through leaching and chemical attack tests. In addition to studying the resulting leachant, the material properties such as strength and microstructural investigations should be evaluated both before and after these leaching or chemical attack tests.

From the laboratory studies it would be possible to apply or develop models of grout longevity. Some models exist, but it is important that the proper boundary conditions and input parameters are measured and used prior to modeling. From the models it is possible to make predictions on the expected service life of the injection grouts.

From the reviewed literature, it appears that both the reference and low-pH grouts would have satisfactory performance with regard to durability though this should be verified through testing and modeling.

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APPENDIX A: BASIC INFORMATION FOR DURABILITY RISKS OF INJECTION GROUTS

Provided by Ursula Sievänen and Margit Snellman, Saanio & Riekkola Oy, 2006.

Examples of grout mixes:

	Standard grout mix 5/5	**Standard grout mix U1**	**P308B**
Water	1785 g	2133 g	1655 g
Ultrafin16 (sulphate resistant microcement)	1785 g	2667 g	988 g
GroutAid (liquous microsilica, 50% solids)	630 g	-	1358 g
Mighty 150 (naphthalene sulphonate based superplasticizer, 42% solids)	59 g	53 g	67 g
W/C	1,0	0,8	1.4
Density, kg/m^3	1521	1629	1384
Shear strength 6h	0,66 – 1,58	0,16 – 1,61	0,25 – 3,37
Shear strength 24 h	> 245	> 245	94,1 - > 245
Compressive strength 1 d	1,00 – 2,37	1,20 – 2,83	0,41 – 1,08
Compressive strength 28 d	22,2 – 22,6	22,9 – 24,0	13,00 – 17,90
Compressive strength 91 d	12,2 – 27,1	20,3	21,4 – 24,4

Note: when giving strength results, testing circumstances (temperature, mixing time, mixer type, cement consignment) have varied

Other information on circumstances

Max allowable aperture size after sealing: not possible to determine exactly; magnitude < 50 – 100 μm – the closer to 0 the better (very rough, trendsetting figures).

Leakage from sealed fractures target is < 0-0,1 l/min/fracture (very rough, a trendsetting figure) or 1-2 l/min/100 tunnel-m.

Properties of hardened grout to meet above requirements:

- compressive strength: several MPa
- homogenous enough?
- durable enough to keep the bedrock tight for > 100 years
- Low shrinkage? Not measured
- Stay “tight” (or tight enough) for over 100 years
- Permeability - not measured

Conditions in the tunnel:

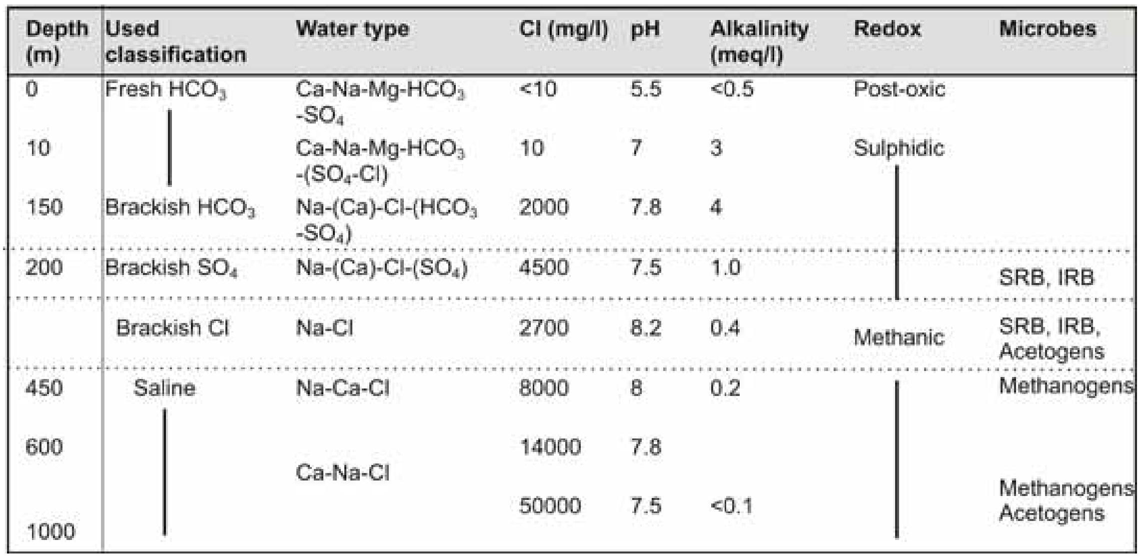
- Relative humidity 50-100% (during construction) and 60-80% in completed tunnel
- Temperature 5-20°C (during construction) and 15-24°C in completed tunnel

- Wind speed 1-2 m/s in completed tunnel. Varying during construction
- Temperature in rock 7-12°C (in deep parts, in the long term rises to even 40°C) and in groundwater 7-12°C.

Bedrock mineral composition: granitic-gneissic bedrock, typical fracture infillings calcite dominating, clay minerals (illite, kaolinite), chlorite, pyrite.

Groundwater chemical composition:

A vertical variation of main hydrochemical constituents at Olkiluoto is shown in the Figure below (Posiva Working Report 2005-72[1]).



Depth (m)	Used classification	Water type	Cl (mg/l)	pH	Alkalinity (meq/l)	Redox	Microbes
0	Fresh HCO_3	Ca-Na-Mg-HCO_3 -SO_4	<10	5.5	<0.5	Post-oxic	
10		Ca-Na-Mg-HCO_3 -(SO_4-Cl)	10	7	3	Sulphidic	
150	Brackish HCO_3	Na-(Ca)-Cl-(HCO_3 -SO_4)	2000	7.8	4		
200	Brackish SO_4	Na-(Ca)-Cl-(SO_4)	4500	7.5	1.0		SRB, IRB
	Brackish Cl	Na-Cl	2700	8.2	0.4	Methanic	SRB, IRB, Acetogens
450	Saline	Na-Ca-Cl	8000	8	0.2		Methanogens
600		Ca-Na-Cl	14000	7.8			
			50000	7.5	<0.1		Methanogens Acetogens
1000							

The specific parameters of interest (mean values given), which may affect the long-term durability of cement, are listed in the Table (compiled from the representative data in the file *uusiOIVA_12092006.xls*).

Depth / Parameter	0-100 m	-100-200 m	-200-300 m	-300-400m	-400-600m
pH	7,0 (5,0)	7,7 (7,1)	7,8 (7,2)	7,6(7,0)	7,8(7,1)
Acidity, meq/l	0,4 (1,4)	<0,2	<0,2	<0,2	<0,2
Cl, mg/l	210 (3400)	2500 (4600)	2800 (4600)	4000(5600)	8600(22000)
Mg, mg/l	19 (180)	110(260)	65 (190)	55(160)	50(90)
SO4, mg/l	63 (370)	310 (540)	200(520)	130(470)	25(140)*
NH4, mg/l	0,3(1,2)	0,4 (2,1)	0,1 (0,7)	0,2(0,9)	<0,05
() the values given in the brackests are max.values except for pH a min.value is given * Sulphate level in saline water is very low, the probable range is closer to 0-40 mg/l .					

Leaching of grout materials information obtainable in Posiva working reports e.g. 2004-46, 2004-25 and 2006-45. Change in grout properties due to leaching: not known.

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[1] Luukkonen, A., Pitkänen, P. & Partamies, S. 2005. Evaluation of Olkiluoto hydrogeochemical data in 3-D - Extended with recent geochemical interpretation results. Posiva Oy, Olkiluoto, Working Report 2005-72.

APPENDIX B: ESTABLISHING LOW-PH GROUT (KRONLÖF 2004)

Excerpt from:
Kronlöf, Anna. 2004. Injection Grout for Deep Repositories – Low pH Cementitious Grout for Large Fractures: Testing technical performance of materials. VTT Building and Transport, Posiva working report 2004-45, 171 p.

According to the work by Lagerblad partly presented in Lagerblad (2001b), the use of silica fume was found to be an efficient component for lowering the pH of grout leachate. One of the reaction mechanisms of silica fume is the silicate reaction with $Ca(OH)_2$, which forms 20% of pure portland cement's hydration products. Because the equilibrium pH of calcium hydroxide with water is as high as 12.5, it is clear the all $Ca(OH)_2$ needs to be consumed in the reaction in order to lower the pH to 11 or lower.

Silica fume is a very reactive pozzolan. The reaction is fast enough to bind $Ca(OH)_2$ into CSH to a large extent as it forms. Yet, it is likely that a part of the silica fume particles react slowly and remain un-reacted over long periods (years) of time.

It is possible to use also less reactive pozzolans such as blast furnace slag, glass or quartz. Those would first allow $Ca(OH)_2$ precipitation. The $Ca(OH)_2$ crystals would be in contact with pore solution, which would be seen as high pH until the pozzolanic reaction proceeds.

A complete reaction of $Ca(OH)_2$ and silica into CSH does not produce a product with a sufficiently low pH. This is because also CSH with a high Ca/Si -ratio (1.8) yields high pH (Stronach 1997). To reach the pH of 11.03 or lower, the total Si content composed of all Si sources such as pozzolans, OPC or blast furnace slag, needs to be high enough to produce CSH with the Ca/Si ratio of 1.1 or lower.

As the pozzolanic reactions proceeds the Ca/Si ratio of the CSH decreases which in turn decreases the pH. Therefore the pH does not depend solely on chemical composition (elements) or material combination, but on the composition of reaction products formed, which depends largely on reaction rate and time.

The CSH-reactions takes several months, possible years to be completed. The reaction rate depends on the fineness and chemical composition and content of vitreous material for instance in the case of slag.

The amount of silica fume needed for pH < 11 depends on the cement composition. According to the work by Lagerblad partly presented in Lagerblad (2001b) approx. 30 w-% silica fume was needed with Aalborg White Cement (SF 30 w%, OPC 70 w%, SF/OPC = 0.43). According to his estimation this would give a CaO/SiO_2 ratio of the CSH product lower than 1 and consequently pH below 11. Calculations have shown that slightly too low SF/OPC ratios were used both by Lagerblad as well as in Kronlöf's (2004) preliminary experiments to yield the CaO/SiO_2 ratio of 1.

According to Cau Dit Coumes et al. (2004) the total SiO_2 content showed good correlation with the equilibrium pH regardless of the composition. The total SiO_2

content (originating from all sources such as cement, silica fume, slag, etc.) needed to yield the pH 11 or less is 55% or more. The reason for this behavior is not known. This leads to a higher demand for SF than earlier identified. According to the "55w% requirement" the minimum SF/OPC would be as high as 0.75 and 0.80 for the white cement used by Lagerblad and UF16 used in Kronlöf's (2004) work, respectively.

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Stronach, S. A. & Glasser, F.P. 1997. Modelling the Impact of Abundant Geochemical Components on the phase Stability and Solubility of the $CaO\text{-}SiO_2\text{-}H_2O$ System at 25°C: Na^+, K^+, SO_4^{2-}, Cl^-, and CO_3^{2-}. Advances in Cement Research, 9-36, 167-181.

APPENDIX C: ALKALI SILICA REACTION CAUSED BY SILICA GRANULES

By Paula Raivio, Contesta Oy, November 2006

Alkali silica reaction (ASR) in concrete is caused by a reaction between the hydroxyl ions in the alkaline cement pore solution in the concrete and reactive forms of silica in the aggregate. A gel is produced, which increases in volume by taking up water and so exerts an expansive pressure, resulting in failure of the concrete. The conditions required for ASR to occur are: 1. sufficiently high alkali content of the cement (or alkali from other sources), 2. reactive aggregate, such as chert and 3. water. ASR will not occur if there is no available water in the concrete, since alkali-silica gel formation requires water. The use of pozzolans in the concrete mix as a partial cement replacement can reduce the likelihood of ASR occurring as they reduce the alkalinity of the pore fluid (Alkali 2006).

Silica fume in concrete acts both as a microfiller and a very active pozzolan. Microsilica accelerates cement hydration during the first hours, possibly as an effect of the increased number of nucleation sites. Later the silica fume reacts with hydroxides. Like other pozzolans it depresses alkali-silica reactions (Lagerblad 1993).

During approximately the last 15 years it has been recognized that silica fume often forms more or less poorly dispersed granules (agglomerates) in concrete that sometimes may react harmfully and cause swelling and cracking in concrete. Silica granules contain a large number, at least hundreds, of single silica particles attached or fused to each other. This is more common of dry densified silica fume products compared to silica slurry products. Granules of the dry silica product may range in size from 10 μm up to several mm. These granules may be difficult to disperse with conventional mixing of concrete and many of them may remain intact in hardened concrete (Diamond 2004).

Diamond et al. (2004) divided such silica granules into two types: 1. granules generating low-calcium calcium-silicate-hydrate gel as reaction products and 2. granules generating alkali silica reaction with even lower calcium and substantial alkalis in the reaction products. The former are generally smaller, considered to be "quiescent" and not to cause significant cracking of concrete. The latter type usually shows local evidence of volume instability. The two types often appear within the same concrete. Local ASR-type behavior of individual granules does not necessarily imply sufficient ASR to produce distress in concrete.

It is known that by mixing some silica fume to concrete, the ASR caused by aggregate may be prevented or at least retarded. On the other hand, ASR caused by silica fume granules in concrete is rarely known and only a handful of articles have been published on such phenomena. However, it has been observed also in a concrete structure in Finland that ASR of silica granules had damaged a concrete structure (swimming pool) that was subjected to constant inflow of chlorine water about 35 years (Raivio 2007a).

According to Helmuth (1993), external salt solutions from seawater or NaCl deicing salt provide unlimited amounts of alkali to exposed hardened mortar or concrete. Their pore solution concentrations can become very high, up to saturation with salt. NaCl has been shown to accelerate ASR, especially in tests at elevated temperatures. High C_3A content

Portland cements have higher chloride binding capacity by formation of Friedel's salt ($C_3A.CaCl_2.H_{10}$). The overall reaction with NaCl to form Friedel's salt dissolves calcium hydroxide and tends to increase alkalinity. It has been considered that the specific chemical agent initiating ASR and most responsible for the effects is the OH^- ion. Alkali merely balances the resulting excess negative charge, but alkali ion is also incorporated into the gel. But, it has also been presented (Chatterji 1987) that alkali salts are the actual attacking components in the ASR. The reactions take place in systems of calcium hydroxide, sodium chloride salt, reactive silica and water.

The even distribution and break-down of silica granules was a significant issue in the concrete durability experimental study by Lagerblad & Utkin (1993). Silica granules were deliberately created in poorly mixed concrete samples. They found that silica granules in concrete sometimes developed ASR and the concrete disintegrated rapidly both in an accelerated alkali-silica reaction test (NT Build 1985) and a freeze-thaw test. Both tests use sodium chloride as an accelerating agent. If the prisms expand more than 0.7 mm/m in 20 weeks with Slite Std. cement (about 1.2 % Na_2O-equivalent by weight) in an accelerated test (NT Build 1985), the concrete mix is considered reactive. In another test (NT Build 1985) a low alkali cement (Degerhamn Std. Portland with about 0.5 Na_2O-eq.) with a higher water/binder ratio of 0.57 also expanded, which indicates that permeability is an important factor (Lagerblad 1993).

To prevent the reaction it was essential that the concrete was well mixed and silica granules smashed (Lagerblad 1993).The break-down of silica granules was best achieved by mechanically crushing the granules with the help of aggregate sized about double (like 0.6/2.5 mm) that of the maximum silica granules and by dry mixing silica first with aggregate before adding cement and water. The detrimental influence of cement is probably due to the fact that paste hinders the crushing impact. Superplasticizers may help the break-down of silica granules but are not necessary (Lagerblad 1993).

In most cases the cracking caused by silica granules has been of minor importance as it occurs only locally close to the silica granules. If the size of the silica granules is bigger, more cracking may be observed and sometimes reach also larger volume (Diamond 2004, Raivio 2007a). According to Lagerblad & Utkin (1993), the formation of alkali silica gel from silica granules occurs already before the concrete has hardened properly. Thus, to expand and induce cracking the gel has to be enriched in alkalis. The alkalis may intrude the concrete from seawater or de-icing salts. There is some evidence that also mere chlorine may take part in the reaction and cause harmful reaction of silica granules (Raivio 2007a).

Potential ASR behavior of low-pH grout planned for ONKALO

The low-pH grout contains approximately 60 w-% cement and 40 w-% silica fume as dry materials. Silica is added as aqueous suspension to the mass after two minutes mixing of water and cement, superplasticizer is added just before silica and mixed for further three minutes. The mass changes to somewhat gelatinous at the latter half of the mixing due to reacting silica. In laboratory it has been observed many times that plenty of small silica granules sized about 0.1 mm diameter remain in the mass even when the mass has been mixed with the most efficient mixers (Raivio 2007b).

The accelerated ASR test (NT Build 1985) resembles somewhat the conditions in ONKALO at least if the total service life of the low-pH cement grouts are considered. In the test, the prisms are immersed in saturated NaCl salt solution at 50 °C for several weeks and changes in prism dimensions are recorded weekly. In ONKALO the alkalis (sodium) and chloride come from the saline ground water and the temperatures are expected to rise up to 50 °C in the future as the spent nuclear fuel capsules are placed in the deep repository.

Because of the unusually high amount of silica in the low-pH grout mix, observed silica granules in it and the resemblance of the ONKALO future environment to the ASR test method NT Build 295 (1985), also the low-pH mix needs to be tested for potential ASR risk. The Ultrafin 16 cement used is sulphate resistant and has a low alkali cement with a low C_3A content (≤0.6 % Na_2O-eq., 2 % C_3A (Cementa 2005)). The cement composition itself is not liable to react with silica granules and to give rise to ASR. Besides, lack of calcium hydroxide that is consumed in the reaction of cement and silica results in low-pH (i.e. low OH^- ion concentration) of the mix and should also prevent the possibility to ASR.

It appears that the low-pH grout mix should not possess AS reactivity even if unbroken silica granules are present in the mass. However, the reactions are complicated and experimental tests are needed to estimate the risk of potential ASR caused by saline waters. Microscopy can be used to see the possible defects and/or reaction products if formed during the accelerated ASR test. If any signs of AS reactivity of the low-pH mix are seen, it would be advisable to try to relate the test results to the long-term performance and resistance to saline water inflow of the low-pH grout mix and to consider whether it persists for the approximately 100 years service life in ONKALO.

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APPENDIX D: TEST METHODS

The following table provides suggested test methods that could be used for evaluation of injection grout properties.

Test type	**Test standard number (& year)**	**Test title or reference**
Permeability / hydraulic conductivity	CEN ISO/TS 17892-11 (2004)	Geotechnical investigation and testing. Laboratory testing of soil. Part 11: Determination of permeability by constant and falling head
	ASTM D 5084 (2003)	Standard test methods for measurement of hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter
	Cembureau permeability test	J.J. Kollek. 1989. The determination of the permeability of concrete to oxygen by the Cembureau method – a recommendation. Materials and Structures, 22, 225-230.
Pore structure / air voids	ISO 15901-1 and 15901-2 (2005)	Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption -- Part 1: Mercury porosimetry, Part 2: Analysis of mesopores and macropores by gas adsorption
	DIN 66133 (1993)	Determination of pore volume distribution and specific surface area of solids by mercury intrusion
	SFS-EN 13057 (2002)	Products and systems for the protection and repair of concrete structures. Test methods. Determination of resistance of capillary absorption (as defined in prEN 1504-31)
	Water porosity test	*Very common. Used for instance in:* Carde, C. & François, R. 1997. Effect of the leaching of calcium hydroxide from cement paste on mechanical and physical properties. Cement and Concrete Research**,** 27-4, 539-550.
	EN 480-11 (1998)	Admixtures for concrete, mortar and grout – test methods – part 11: Determination of air void characteristics in hardened concrete
	NT BUILD 381 (1991)	Concrete, hardened: air void structure and air content
	ASTM C457 (2006)	Standard test method for microscopical determination of parameters of the air-void system in hardened concrete
Leaching	Static leach test	Onofrei, M., Gray, M.N. & Roe, L. 1991. Cement based grouts – Longevity: laboratory studies of leaching behaviour. Stripa Project TR 91-33, SKB, Stockholm, 95 p.

Test type	Test standard number (& year)	Test title or reference
	Pulsed (dynamic) leach test	(same as 'static leach test' reference)
	Electrochemical acceleration leaching method	H. Saito, & Nakane, S. 1999. Comparison between diffusion test and electrochemical acceleration test for leaching degradation of cement hydration products. ACI Materials Journal, 96-2, 208-211.
	-	Leaching methods for conditioned radioactive waste: Review of leaching methods within the Working Group on 'Destructive Analyses' of the European Network of Testing Facilities for the Quality Checking of Radioactive Waste Packages. Report WG-B-02, April 2004.
Chemical attack	ASTM C 452 (2002)	Standard test method for potential expansion of portland-cement mortars exposed to sulfate
	ASTM C 1012 (2004)	Standard test method for length change of hydraulic-cement mortars exposed to a sulfate solution
	NT Build 295 (1985)	Sand: Alkali-silica reactivity accelerated test.
	Wittekindt method for measuring sulphate attack	W. Wittekindt. 1960. Sulfatbeständige Zemente und ihre Prüfung. *Zement-Kalk-Gips,* 13-2, 565–572.
Shrinkage	RILEM CPC 9 (1994)	Measurements of shrinkage and swelling of concrete
	ASTM C157 (2003)	Standard test method for length change of hardened hydraulic-cement, mortar and concrete
	NT BUILD 366 (1991)	Concrete, repair materials and protective coating: shrinkage and swelling
Corrosion	NT BUILD 355 (1997)	Concrete, mortar and cement-based repair materials: Chloride diffusion coefficient from migration cell experiments
	NT BUILD 443 (1999)	Concrete, hardened: Accelerated chloride penetration
	NT BUILD 492 (1999)	Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-stat migration experiments

APPENDIX E: GROUTAID PRODUCT INFORMATION SHEET

GroutAid: Microsilica Additive for Improving Cement Injection Grouts, 2006. Product Information Data Sheet P-2-1, Elkem ASA, Norway.
At: http://www.multigrout.elkem.com/

MultiGrout
The problem solver

Product Information
Data sheet P-2-1

GroutAid®

Microsilica Additive for Improving Cement Injection Grouts

Introduction

GroutAid®, a silica fume (microsilica) -based additive for use in combination with microcement and other cement-based grouts, has been developed by Elkem Materials of Norway during the last decade.

The use of GroutAid will increase the efficiency of injection grouting by improving both the plastic and hardened properties of the grout, enabling injection into soils and cracks in rock and concrete.

This improved permeation capability of cement-based grouts further reduces the need to use chemical grouts with the subsequent advantages of cost reduction and environmental safety.

The advantages of using microsilica in cement-based systems are well known from concrete technology. The microscopic particle size and pozzolanic reactivity of microsilica act to reduce bleeding and segregation, develop stronger and less permeable concrete, and increase durability and resistance to chemical attack. These same properties are also important for injection grouts.

GroutAid - ready for action !

GroutAid® improves the properties of the injection grout and the injected formation :

Stability
Penetration
Strength
Permeability
Durability
Environment
Economy

GroutAid® properties

GroutAid is an aqueous suspension of microsilica.

Chemical composition

SiO_2	86% min.
Carbon	2.5% max.
LOI (Loss on Ignition)	3.0% max.
Alkali oxides	2.0% max.

Physical properties

Bulk density	1350-1410 kg/m³
Solids content	50% ± 2%
Surface area dry (BET)	15 m²/g min.
Viscosity	100 cP max.
Coarse particles (+45µm)	1.0% max.
pH	4.5 – 6.5
Color	gray

Packaging

GroutAid is packaged in 1000 liter containers or bulk.

Elkem

Particle Size

The microsilica used in GroutAid production has been carefully selected and quality-controlled so that the coarse particles content is extremely low, ensuring complete compatibility with the finest of microcements. GroutAid particles are extremely fine (Fig.1) having more than 90% less than 1µm.

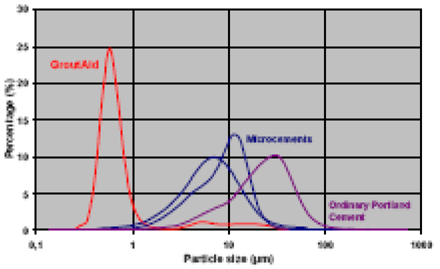


Figure 1. Particle size distribution of GroutAid compared to typical microcements and ordinary Portland cement.

Stability

A stable, non-segregating grout is extremely beneficial for successful injection. Stable grouts will ensure that cracks and voids will be more thoroughly filled, which can lead to reduced need for injection. The important parameters to determine the stability of an injection grout are bleeding and fluid loss.

The addition of GroutAid means the addition of a great number of extremely fine particles of very high specific surface area. This very high surface area and corresponding internal attraction forces, keep the cement and microsilica particles suspended without settling within the water, even at high water/powder ratios.

Pure cement grouts are stable only up to water/powder ratios of approximately 1.0. However, stable grouts with water/powder ratios as high as 6.0 can be made by replacing a proportion of the cement with GroutAid (Fig. 2).

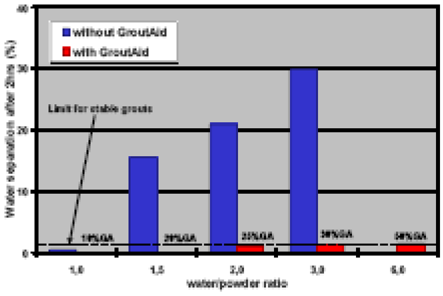


Figure 2. Stabilizing effect of GroutAid

Penetration

The extremely fine particles of GroutAid fill the voids between the cement particles (Fig.3) and produce an injection grout with minimal bleeding and segregation.

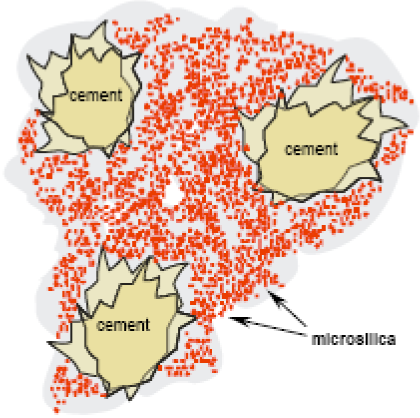


Figure 3 Ultrafine microsilica particles fill the voids between the cement grains.

Since the water is not forced from the grout under the pressure of injection, the solids remain in suspension and are not deposited in cracks or pores close to the borehole. The homogeneous grout flows into the formation.

At the same dry solids content, a grout based on GroutAid and cement will have improved penetrability compared to a pure cement-based grout (Fig. 4).

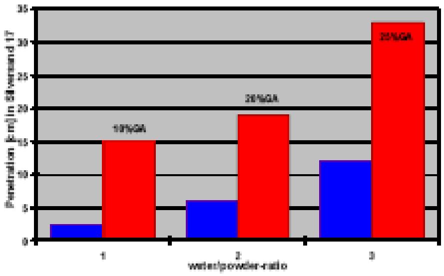


Figure 4. Penetration into Silversand 17 for injection grouts with varying water/powder ratios, with and without GroutAid

Strength

The microsilica particles in GroutAid react with the calcium hydroxide that forms during the hydration of the cement. This creates an increased amount of binder, improving strength and durability. In addition, the ultrafine microsilica particles also provide an increased concentration of particles (Fig. 3) in an injection grout and improve the interface strength between the grout and the sand particles or rock. (Fig.5 and Fig.6). Even at very high water/powder ratios, acceptable strength of the injected formation can be achieved.

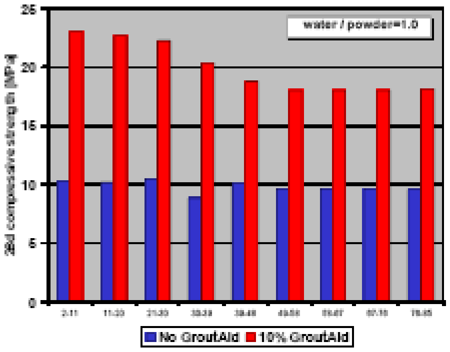


Figure 5. Compressive strength of injected sand at various depths, grouts with water/powder ratio 1.0, with and without GroutAid.

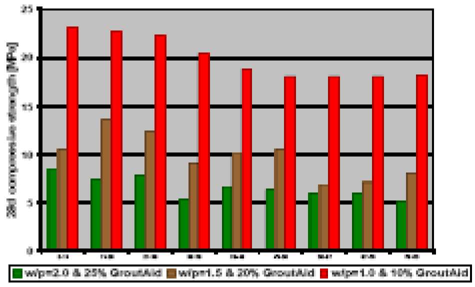


Figure 6. Compressive strength variation of injected sand with injection grouts of various water/powder ratios and varying % of GroutAid

Permeability

The addition of GroutAid to a cement-based injection grout will, at the same water/powder ratio, reduce the permeability of the injected formation. The reasons for this are improved filling of cracks and voids, and the improved interface between grout and sand particles or rock. Also the hardened grout has a lower permeability than the pure cement-based grout due to improved pore structure.

Durability

Most forms of chemical attack on a cement-based injection grout are typified by leaching of calcium hydroxide or by ingress of harmful substances.

Since microsilica reacts with and binds the more easily soluble calcium hydroxide, the use of GroutAid will reduce the permeability and the ingress of harmful substances.

As a consequence, injection work with grouts based on cement and GroutAid will show more resistance to chemical attack and thus have improved durability over work performed with pure cement-based grouts.

Environment

GroutAid is a non-toxic, mineral based product.

Injection grouts based on cement and GroutAid have a positive impact on the environment through:

Reducing the need for potentially harmful chemical grouts.

Reducing permeability that will contribute to a decreased risk of leaching of harmful substances through soils – such as in landfills.

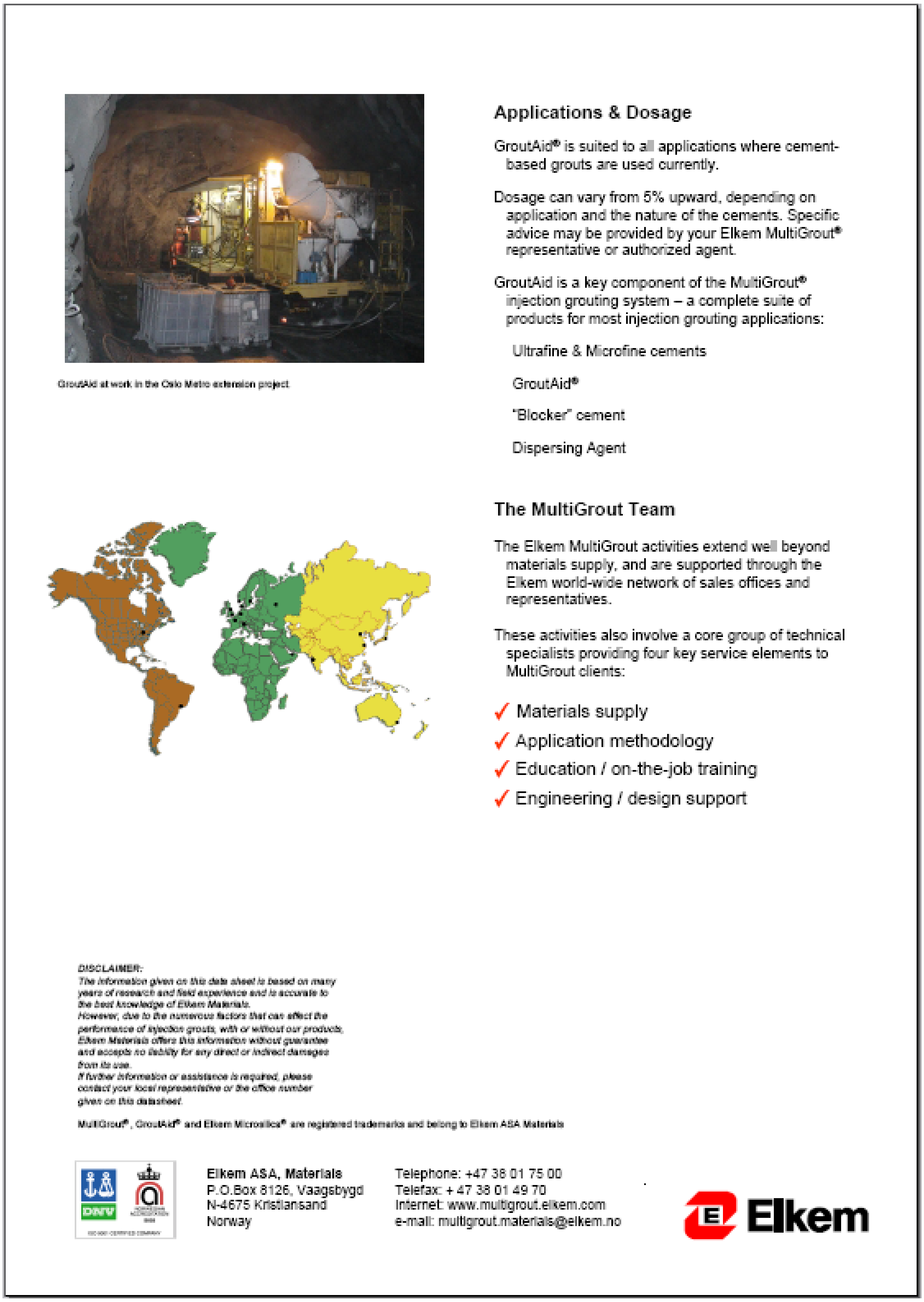
Economy

GroutAid will provide a more cost-effective injection because:

Improved penetration implies that cement-based injection can be performed in finer soils and cracks than was possible before, and may reduce the use of expensive chemical grouts.

Improved penetration implies that the number of injection holes drilled can be reduced, or alternatively, that the total requirement for injection can be reduced.

Material cost can be reduced since the "dry content" is reduced.



GroutAid at work in the Oslo Metro extension project

Applications & Dosage

GroutAid® is suited to all applications where cement-based grouts are used currently.

Dosage can vary from 5% upward, depending on application and the nature of the cements. Specific advice may be provided by your Elkem MultiGrout® representative or authorized agent.

GroutAid is a key component of the MultiGrout® injection grouting system – a complete suite of products for most injection grouting applications:

Ultrafine & Microfine cements

GroutAid®

"Blocker" cement

Dispersing Agent

The MultiGrout Team

The Elkem MultiGrout activities extend well beyond materials supply, and are supported through the Elkem world-wide network of sales offices and representatives.

These activities also involve a core group of technical specialists providing four key service elements to MultiGrout clients:

- ✓ Materials supply
- ✓ Application methodology
- ✓ Education / on-the-job training
- ✓ Engineering / design support

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