CHALMERS

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PREFACE

This report is part of the project "Low-pH Grouts" financed by SKB, Swedish Nuclear Fuel and Waste Management Co. It is part of SKB's work to develop low-pH injection grouts suitable for construction of a final repository for spent nuclear fuel. The aim of the sub-project "Silica Sol for Rock Grouting – Tests on Mechanical Properties" is to gain a better knowledge of the behaviour of silica sol and the climatic influences on its behaviour. This is a prerequisite for assessing field of application and grouting design.

The laboratory work has been carried out at Chalmers University of Technology during 2005 and 2006. The tests have been carried out by Christian Butron under the supervision of Magnus Axelsson. Project leader at Chalmers, responsible for the test program and its execution has been Professor Gunnar Gustafson. The testing equipment has been prepared by laboratory technicians Peter Hedborg and Aaro Pirhonen. External reviewing of the continuing work has been done by Rolf Larsson, SGI. James Crawford, Kemakta Konsult AB reviewed the diffusivity parts of the report; both reviewers gave valuable advice which we are thankful for. SKB project leader has been Ann Emmelin.

SUMMARY

Silica sol is a gelling liquid that has gained increased interest as a grouting agent in hard rock during recent years. In order to create a foundation for determining if silica sol is a proper material for grouting in hard rock, series of experimental studies have been performed. The studies aimed at gaining knowledge of the mechanical properties of silica sol. The following table gives an overview of the conducted tests, the parameters assessed and studied, the storage environments, and the total number of tests.

Test conducted	**Parameters assessed**	**Storage environments**	**Number of specimens tested**
Unconfined compression	Shear strength and strain	• Immersed in water at 8°C • Immersed in water at 60°C, • 20°C and 100% r.h., • 20°C and 75% r.h., • pH11, and • TDS 35g/L,	45
Fall-cone test	Shear strength	• Immersed in water at 8°C • Immersed in water at 60°C, • 20°C and 100% r.h., • 20°C and 75% r.h., • pH11, and • TDS 35g/L,	70
Unconsolidated undrained triaxial	Shear strength and strain	• Immersed in water at 8°C • pH11, and • TDS 35g/L,	20
Consolidated undrained triaxial	Shear strength and strain	• Immersed in water at 8°C	5
CRS oedometer	Consolidation pressures and hydraulic conductivity	• Immersed in water at 8°C	9
Continuous water loss	Water loss rate	• 8°C and 100% r.h., • 8°C and 95% r.h., and • 8°C and 75% r.h.	3
Water loss with varied humidity	Water loss rate	• 8°C and 95% r.h., and • 8°C and 75% r.h.	5
Drying-out between transparent plates	Diffusion and shrinkage rate	• 20°C to 22°C and around 20% r.h.,	4
Diffusion of chlorides from silica sol	Rate of chloride concentration, diffusion rate	• Immersed in water at 8°C, and • Immersed in water at 40°C	8

The results show that the strength of silica sol increases during ageing in all tested environments. The rate is, depending on the storage environment, high at lower humidity and high temperature. In the contact zone between free water and silica sol a layer is formed that has lower shear strength, initially around 2 kPa. This layer is about 2 mm thick and is formed

due to the interaction between silica sol and water. However, if this initial layer is scraped off, a new such layer will not be formed.

Silica sol used below the groundwater will generally behave as a ductile material with elastic-plastic deformations and is able to withstand loading and unloading cycles at fairly large deformations. The behaviour will change from ductile to brittle if there are no external confining stresses. Silica sol is not considered very vulnerable to blasting vibrations under the groundwater. The tests also indicate that silica sol is stable in a surrounding environment with a pH-value up to 11 and in a surrounding of a solution with 35 g/l of dissolved solids (Cl, Na and Ca) although its behaviour appears to become more brittle in these conditions.

The measurements of the release of chlorides from silica sol indicate that this is a relatively fast process. In a fracture with flowing water around the grouted surface, the chlorides will be released within a time frame of a month.

The tests confirm previous findings that silica sol will shrink at lower humidities in the surrounding environments. It seems that the shrinkage is directly linked to the release of water from silica sol. Most of the shrinkage occurs due to diffusion and evaporation of the bulk water that is not bound to the silica sol particles. The last part of the water loss seems to be related to a process that is slower than diffusion.

The tests have shown that there are two different processes acting on silica sol in a fracture; the diffusion of water from the “groundwater” side and the shrinkage of silica sol from the “tunnel” side. The results show that the shrinkage will stop as it meets the diffusing front of water through silica sol. In a fracture with an aperture of tenths to hundred micrometers, this implies that the shrinkage rate will be much lower than the diffusion rate of water through silica sol. This implies that water will be available in silica sol already after a short shrinkage distance, stopping further shrinkage. The result of this is that a complete breakthrough related to shrinkage is very unlikely in a fracture with groundwater on one side.

Summary regarding the mechanical properties for silica sol in the use as a grouting agent:

- The strength of silica sol is in the magnitude of kPa, after one day, in all the tested environments and the strength is increasing with time. Compared to other common used grouting agents, this implies that it has a high initial strength and hence good resistance against erosion from groundwater.
- Immersed in water, the strength in the outer surface of silica sol will not increase with time and it remains at a couple of kPa. However, this layer is due to early interactions between silica sol and water and it will not appear if an older silica sol comes in contact with water.
- Silica sol will not be sensitive to blasting deformations since it initially behaves ductile with large plastic deformation before failure occurs.
- The ductile behaviour will remain as long as silica sol is immersed in water, at least during the test period of three months.
- Exposed to air (lower humidity than immersed in water) silica sol will change failure mode from ductile to brittle. The time depends on the surrounding environment.
- Surrounded by water, silica sol does not exhibit any shrinkage.
- Exposed to air (lower humidity than immersed in water) silica sol will shrink since it contains around 68% of water. The shrinkage rate depends on the surrounding humidity and temperature.

- Exposed to a non-normal environment (TDS and pH11) silica sol will not be destroyed and the strength increase will be similar to silica sol surrounded by water. However, the failure mode will differ in these environments.
- Silica sol is a low-permeable material; the hydraulic conductivity is around $1\cdot10^{-10}$ to $1\cdot10^{-11}$ m/s.
- Grouting with silica sol in a fracture around a tunnel will mean that silica sol will shrink to some extent since one face will be in contact with air (characterised by the humidity and temperature in the tunnel). However, assuming that silica sol is in contact with groundwater on the other side, water will diffuse through silica sol and as it comes in contact with the dried-out part of silica sol, the shrinkage will stop. Considering the area that is affected in a rock fracture with an aperture of tenths to hundreds of micrometers, the shrinkage will not proceed far into silica sol before it will come in contact with water and the shrinkage will stop.
- The release of chlorides from the accelerator is a rather fast process and after a couple of months, most of the chloride will have been released. However, the rate is depending on the water transport rate around the grouted zone.

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1. INTRODUCTION

Silica sol is a gelling liquid with increased use as a grouting agent during recent years. The main reason for starting to use silica sol has been its ability to penetrate and seal narrow fractures but it has also gained interest for having a lower pH-value than ordinary grouting cement. The latter issue is of special interest around a nuclear waste repository, where the high pH of cement is an undesired property. This report is a development of the work presented in reports by Axelsson (2004) and Butron (2005). The previous reports aimed at characterising the mechanical properties of silica sol and were introductory studies. By proceeding from the findings in these reports, an extensive laboratory investigation programme was developed. The programme aimed at increasing the knowledge of the behaviour of silica sol in different surroundings and also to increase the understanding of the hardening process for silica sol. The final outcome of this study combined with field studies presented by Funehag (2005), will be to describe the behaviour and functionality of silica sol as a grout in hard rock.

Since grouting in hard rock is usually conducted below the groundwater table, it is important to increase the knowledge of the behaviour of silica sol immersed in water. This includes material characteristics such as strength development and shrinkage. It has been shown in the previous reports that silica sol can shrink at lower humidity in the surrounding environment. To further examine this, more frequent shrinkage measurements were performed but also shrinkage tests in simulated fractures. This should also increase the understanding of the practical meaning of shrinkage in a rock fracture. It is also important to examine the effect of a varied humidity in the surrounding environment and how it will affect the behaviour of silica sol.

In the reports by Axelsson (2004) and Butron (2005), the main focuses were to determine how silica sol could be characterised for common grouting environments in shallow hard rock i.e. a temperature of 8 ºC and humidity between 75-100%. However, these introductory tests were not investigating the behaviour of silica sol stored in different environments with different temperatures, ions concentrations or pH. In order to investigate how more extreme environments will affect the strength development and the shrinkage of silica sol, it has been important to perform introductory studies to characterise the behaviour.

A detailed study on the response in silica sol as it is affected by external forces has been performed. The previous studies only considered the total stresses but no evaluation of the effective stresses was made. The effect of effective stresses and consolidation in the material are important issues in characterising the mechanical behaviour of a porous material such as silica sol.

To start the gelling of silica sol some kind of accelerator is added, which is generally a saline solution containing chlorides. As the saline solution is added as a catalyst, the chloride ions will not stay in the silica gel with time. As long as there is a concentration difference, the chlorides will diffuse out from silica sol and into the surrounding groundwater. Concern has been raised that this leakage of chlorides can affect installations made of concrete in the surroundings. It was therefore important to investigate the migration rate of chlorides from silica sol as well as the total amount to assess the potential risk.

In order to develop the knowledge of the concerns stated above, the following tests were conducted in this laboratory study:

- Mechanical tests on silica sol immersed in water during ageing,
- Continuous water loss tests of silica sol,
- Mechanical tests on silica sol stored in different environments (temperatures, pH and ion concentration),
- Mechanical tests on silica sol – CRS oedometer and CU triaxial tests,
- Drying-out tests on silica sol injected between transparent plates,
- Water loss test of silica sol with varied humidity, and
- Diffusion of chloride from silica sol.

2. MATERIALS

2.1. Silica sol

Colloidal silica is obtained from raw glass material with high silica content. The raw glass is heated and diluted with water to form sodium silicate. This solution is then diluted in a mix of water, acid and caustic. The sodium ions are excluded with an ion exchanger, and the solution is processed in a reactor to get the desired size and concentration of the particles (Axelsson and Nilsson, 2002). Colloidal silica is insoluble in water and has hydroxylated surfaces and large specific surface area.

Silica sol is a refined product of colloidal silica where the particle size has been narrowed down to a range of 5 to 100 nm. (Björnström, 2005). It is odourless, tasteless and non-toxic. Its chemical molecular formula is $SiO_2 + H_2O$. It can be used as a cohesive agent, catalyst carrier and for coating in paper and textile industry.

The silica sol used in this study was manufactured by Eka Chemicals AB, with the name “Eka Gel EXP 36”. The silica sol was mixed with a saline solution ($CaCl_2$) to aggregate the particles, which hardened as a gel. This mix is called “silica sol”. A safety data sheet for silica sol is found in Appendix A.

2.2. Riboflavin-5-Phosphate 95%

Riboflavin-5 is an inert material that is soluble in water. In this study it has been mixed with water and used as a tracer in order to detect flow paths through silica sol. Its main function is to give a yellow colour to the water to make it visible. Pretests showed that this tracer had no effect on the gelling time or the strength development, and therefore no effects on the other tests are expected.

2.3. Milli-q water

The water used for the immersion of silica sol specimens was treated in order to obtain accurate measurements of the chlorides concentration. The water was first deionised and then fed through a special ion exchange cartridge, which increased its purity to a milli-q gradient of A10. This milli-q system includes a high-precision resistivity meter to measure trace ionic contaminants. It is designed with a built-in Total Organic Carbon (TOC) monitor, for in-line measurement of TOC levels in ultra-pure water. A three-step purification process and periodic recirculation of water ensure delivery of high-purity water immediately upon demand (Millipore, 2006). Also a photo-oxidation process is used in Milli-Q Gradient, which can effectively carry out the destruction of organic molecules. When irradiated by UV at 254 and 185 nm, the adequate energy required to break down DNA is generated and is therefore highly effective in killing bacteria that might have survived the osmotic pressure of ultra-pure water. The purity of the water is important for the tests concerning chloride concentrations and this treated water will be called “milli-q water”.

3. METHODS

The methodology used in this study initially comprised mixing, moulding and storage of silica sol specimens. The mixing was a common procedure for all the tests but the moulding and storage varied depending on the test methodology. The test methods used are not standardised but are largely related to standardised methods used for clay and fresh concrete.

3.1. Mixing and moulding

The mixing and moulding procedures for silica sol specimens were similar to those used by Axelsson (2004) and Butron (2005). Silica sol (Eka Gel EXP 36) was mixed with $CaCl_2$ in a ratio of 8:1 in weight. The mixing was done in the GeoLaboratory of Chalmers University of Technology. In order to prevent an instant gelling, the solution was stirred during the mixing and the ambient temperature was 20°C.

After mixing, the moulding was conducted. Mainly three kinds of plastic moulds were used depending on the test to be performed, all with an inner diameter of 50 mm and heights of 100 mm, 50 mm and 20 mm; see Figure 1. At the bottom of the moulds a plastic film was placed in order to keep the silica sol in place before gelling. The moulding procedure was done before gelling (approximately 1 hour). All moulds were specifically manufactured for this project.

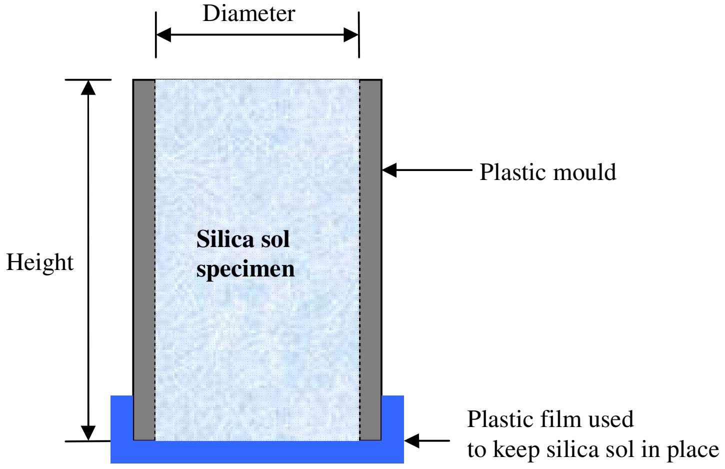


Figure 1. *Schematic view of moulds used in this study for triaxial tests (100 mm height), unconfined compression tests (100 mm height), constant rate of strain oedometer tests (20 mm height), and fall-cone tests (50 mm height). The diameter was 50 mm in all tests.*

After moulding, the specimens were placed in their respective environment box. Each box had a specific ambient temperature, relative humidity and pH depending on the test. Different saline solutions were placed inside the boxes to generate their respective environments. A more detailed description of the storage conditions is given in Chapter 3.2.

For the drying out test between transparent plates, the specimens were moulded directly between the plates in the test equipment. The plates were made of Plexiglas. The mould consisted basically of a rectangular tube with open end surfaces, see Figure 2. The further test methodology is described in Chapter 3.4. A plastic film was placed at one end of the mould, which was kept vertically during gelling in order to keep the silica sol in place before gelling and to leave place for the tracer fluid. The moulding procedure was done before gelling (approx. 1 hour). After moulding the specimens were placed, horizontally as in Figure 2, in a room at 22°C.

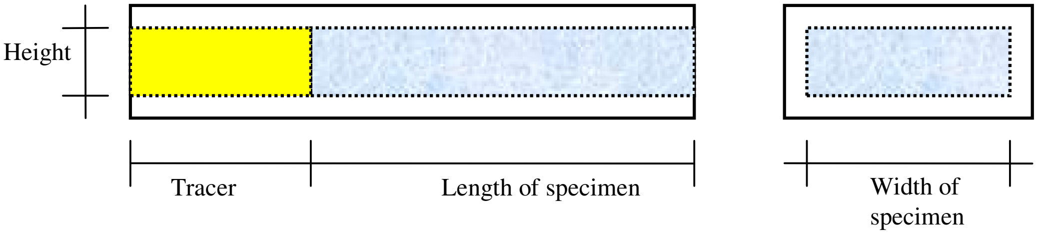


Figure 2. *Schematic view of a transparent plate mould and specimen.*

3.2. Mechanical tests

The mechanical behaviour was investigated by means of fall-cone, unconfined compression, unconsolidated undrained triaxial, consolidated undrained triaxial and constant rate of strain oedometer tests. Six climate boxes were used for these tests. Silica sol specimens were placed inside each box and respectively:

- Entirely immersed in water at a constant temperature of 8°C, further called immersed,
- Partially filled with water to give an inner environment close to 100% relative humidity and kept in a room at approximately 20°C, further called 20°C and 100% r.h, (note that a humidity called 100% r.h. does not mean immersed),
- Partially filled with a saline solution of NaCl to give an inner environment of approximately 75% relative humidity and kept in a room at approximately 20°C, further called 20°C and 75% r.h,
- Entirely immersed in water at a constant temperature of 60°C, further called 60°C immersed,
- Entirely immersed in 180 g of NaCl, 165 g of $CaCl_2$ and 10 l of H_2O (deionised), at a constant temperature of 8°C, to give a solution with 35 g/l of Cl, Na, and Ca ions, further called TDS, and
- Entirely immersed in 500 ml of $NaHCO_3$ at 0.05 molar and 227 ml of NaOH at 0.1 molar, at a constant temperature of 8°C, to give a solution with a pH of 11, further called pH11.

In Figure 3, a climate box with silica sol specimens immersed in a solution with a pH of 11 is shown as an example. The strength development was studied during the first three months of hardening. The measuring intervals are specified in Chapter 4.

Figure 3. *Climate box with silica sol specimens inside their moulds fully immersed in a solution with pH 11.*

3.2.1. Unconfined compression test

35 unconfined compression tests were performed according to the measuring schedule. In theory, the shear strength value observed from an unconfined compression test and an unconsolidated undrained triaxial test on a fully saturated specimen should be approximately the same. This was also shown by Butron (2005) in previously performed tests on silica sol. The procedure for the unconfined compression tests was based on the ASTM D1266-91 standard. The moulded specimen of silica sol was placed between two plates, see Figure 4. The compression rate was 1 mm/min, and the confining pressure in this test was zero. In order to ensure that the test is measuring the strength of the homogeneous silica sol without any disturbance caused by the water and silica interaction at the ends of the specimen, a trimming procedure was conducted. This entailed that the top 1 cm of silica sol that was in contact with water or a salt solution during storage was cut off before the test.

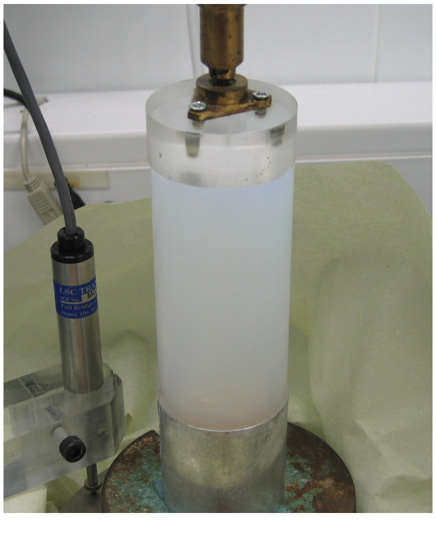


Figure 4. *Silica sol specimen ready to be tested in an unconfined compression test apparatus.*

3.2.2. Fall-cone test

The recommendations from the European committee ETC5 were used as a base procedure for this test to measure the shear strength of the specimen. This test is easy to conduct and has a low cost, but its application to silica sol is limited. Pre-tests have shown that cones with apex angles of 60° can not be used and tests with 30° cones have shown to give unreasonably high values at undrained shear strengths of approximately 40 kPa and more. The test starts by placing a cone with its apex right on top of the silica sol specimen (just touching the silica sol surface). The cone, with an angle of 30 degrees, is released causing an intrusion; this penetration is read off to the nearest 1/10 of a millimetre. Two readings were done in each face for corroboration. A total of 70 fall-cone tests were conducted during the same period of three months as the unconfined compression tests.

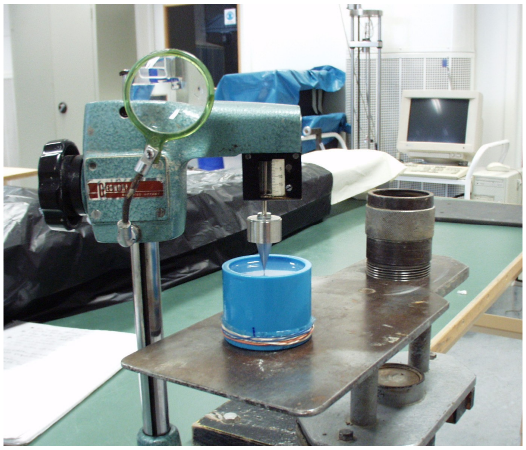


Figure 5. *Silica sol specimen ready to be tested with a fall-cone apparatus.*

3.2.3. Unconsolidated undrained triaxial test

The standard ASTM D2850-87 was used as a base procedure for the unconsolidated undrained triaxial tests. A moulded specimen of silica sol was encased by a thin rubber membrane and fixed inside a triaxial cell. The cell was filled with water in order to give the specimen the desired confining pressure. At each testing occasion, different confining pressures were used in order to observe a possible variation in the shear response. A piston transferred the axial load to the specimen at a specified compression rate. The combined axial and confining pressures caused shear failure in the specimen either by excessive stress or excessive deformation. Butrón (2005) found that the shear rate has an important effect on the patterns of the shear stress, effective axial stress, peak shear stress and axial strain in silica sol. Following this finding, all silica sol specimens in the present investigation were tested at a compression rate of 1.0 mm/min.

It was shown by Butrón (2005) that an unconsolidated undrained triaxial test gives similar shear strength as unconfined compression tests on silica sol. Therefore triaxial tests were mainly conducted as reference tests to be compared with the unconfined compression test results. Figure 6 shows a silica sol specimen encased by a rubber membrane and placed in a triaxial apparatus.

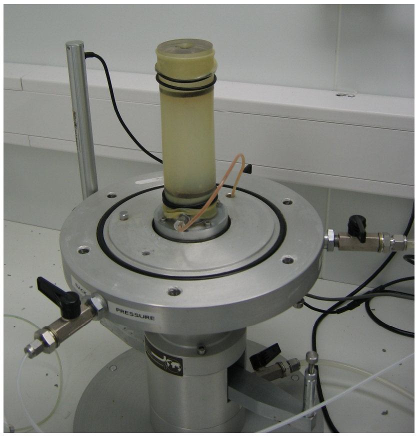


Figure 6. *Silica sol specimen ready to be tested in a triaxial apparatus.*

3.2.4. Consolidated undrained triaxial test

It was shown by Butron (2005) that an unconsolidated undrained triaxial test was the most reliable of the fairly fast and simple methods to measure the shear strength of silica sol. However, to fully understand the behaviour it is also important to observe the behaviour in consolidated undrained triaxial tests (at slower shear rates) and to measure the consolidation strains and pore pressure development during the test. This makes it possible to estimate the influence of effective stresses and not just total stresses as in an unconsolidated undrained triaxial test.

The standard ASTM D4767-04 was used as a base procedure for the consolidated undrained triaxial tests. The methodology is largely similar to the unconsolidated undrained test. However, the specimens were consolidated for about one week until the specimen volume, back pressure and pore pressure were stable. After the consolidation period, the silica sol specimens were sheared under undrained conditions at a compression rate of 0.01 mm/min. A total of 5 consolidated undrained triaxial tests were conducted during the two months testing period.

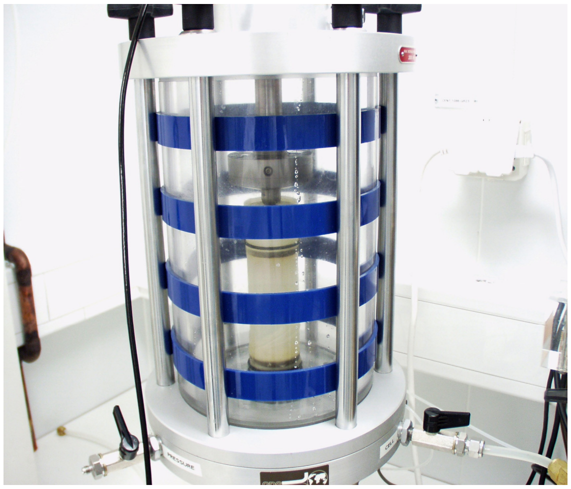


Figure 7. *Silica sol specimen ready to be tested in a triaxial apparatus.*

3.2.5. Constant rate of strain oedometer test

The standard ASTM D 5084 was used as a base procedure for the constant rate of strain (CRS oedometer) tests. A moulded specimen of silica sol was encased in a teflon ring which in turn is fixed inside a metal ring with two porous stones at the end surfaces, one at the bottom and the other at the top of the specimen. At the undrained bottom, a pressure transducer is measuring the pore pressure generated during the test. A piston transferred the axial load to the specimen at a specified compression rate of 0.002 mm/min. The CRS oedometer is immersed in water during the test and the specimens have 50 mm diameter and a height of 20 mm, see Figure 8. The test is important in order to study the consolidation behaviour of the material and also to determine a possible preconsolidation pressure to be used as a starting point in a subsequent consolidated undrained triaxial test. During the test, the permeability of the silica sol specimen was also determined. After the test, the dry weight of the specimen was measured and the void ratio and its change during the test was evaluated.

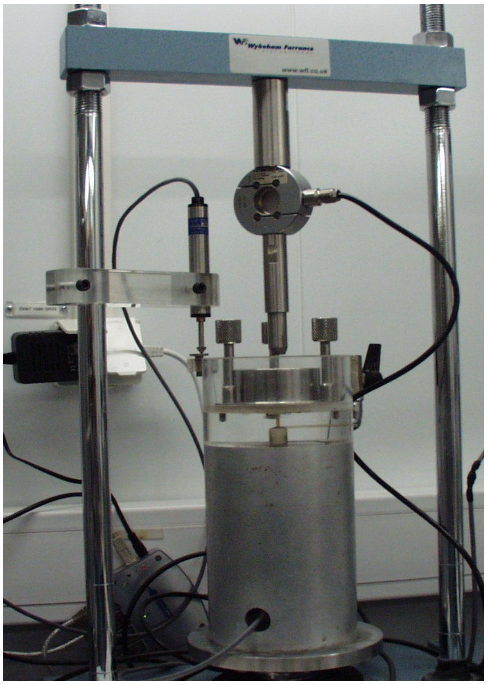


Figure 8. *Silica sol specimen ready to be tested in a CRS apparatus.*

3.3. Water loss measurements

According to Axelsson (2004) silica sol particles during the hardening process start to share hydrogen bindings, form chains and capture water. Afterwards, as hypothesized by Butrón (2005), all the weight loss of silica sol samples over time is due to the loss of water; this water is released by two main factors, evaporation and diffusion, at different stages depending on three conditions:

- The amount of surface exposed to a certain environment,
- Water movements under hydrodynamic pressure forces, and
- The environment conditions; temperature and relative humidity.

These chemical and physical interactions are important in order to understand the shrinkage behaviour of silica sol during ageing. The processes govern the water loss with time in silica sol and thereby the shrinkage. However, there will still remain water that is chemically bound to the silica sol particles that is kept or only slowly released. This has also been indicated in studies performed by Bjömström (2005).

The loss of water in relation to the total weight of the specimen can be written as:

$$S = \frac{W_2 - W_3}{W_2 - W_1} \cdot 100 \qquad (1)$$

Where:

S is the water loss per total weight in (%),
W_1 is the weight of the mould,
W_2 is the weight of the mould + silica sol weighted directly after mixing, and
W_3 is the weight of the mould + drying silica sol (measured weight after different time intervals).

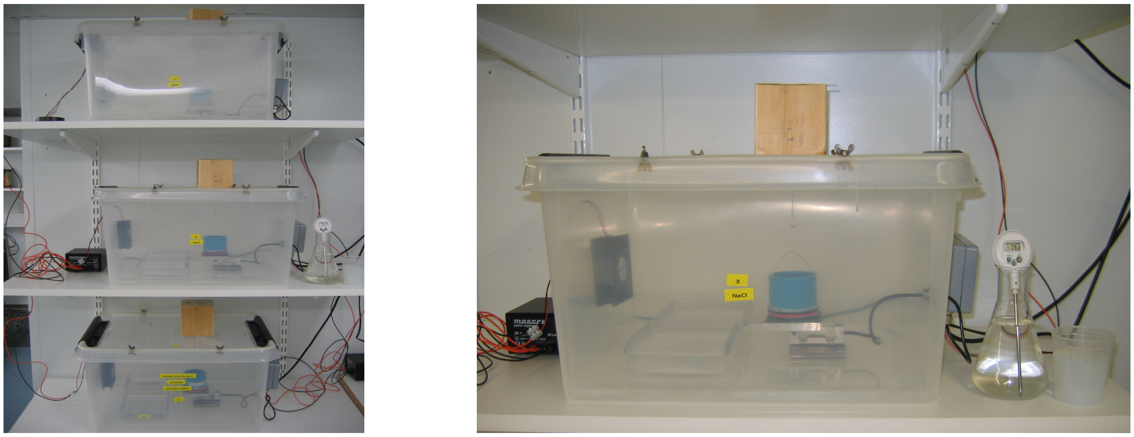
S is the percentage of water loss, by evaporation or diffusion of water, in a given silica sol mass at a certain time during ageing of the silica sol. The determination of this parameter has no standardised test procedure but is of great importance in order to understand the shrinkage behaviour of silica sol.

3.3.1. Continuous water loss measurement test

The tests in this part covered the continuous loss of water (weight) with time at different environmental conditions. As stated previously, the hypothesis is that the loss in weight is due solely to the loss of water. Three climate boxes were used for these tests. The boxes were respectively:

- Partially filled with a saline solution of $BaCl_2$ to give an internal environment of approximately 95% relative humidity and kept in a room at approximately 8°C, further called 8°C and 95% r.h,
- Partially filled with a saline solution of NaCl to give an internal environment of approximately 75% relative humidity and kept in a room at approximately 8°C, further called 8°C and 75% r.h, and
- Partially filled with water to give an internal environment close to 100% relative humidity and kept in a room at approximately 8°C, further called 8°C and 100% r.h,

Figure 9 shows the climate boxes used for the tests. In each box there was a load cell, “scale”, which was recording the weight of mould and specimen at time intervals of 2 min. The measurements had to be interrupted at certain times to check possible changes in the zero values and to ascertain that the transducers were working properly. The check of the zero value was done without opening the box at any time, thereby avoiding any disturbance of the internal environment. Each measurement-period had an average duration of 72 hours before checking and resetting the zero values, which took one to two hours, and starting the measurements again. To ensure a constant humidity inside each box, a fan was used for the recirculation of the air. The boxes were placed in a climate room with a constant temperature of 8°C.



(a) (b)

Figure 9. *Climate boxes used for the continuous water loss measurement test: (a) the three boxes with different environments; (b) a close view of one of the boxes with a silica sol specimen inside*

The silica sol moulds were placed on the scales and the boxes were sealed in order to keep a stable internal environment. The scales were connected to a computer, which was recording the weight of the specimen with time. The stored data was processed using the programs Microsoft Excel and Grapher.

3.3.2. Water loss measurement at varied humidity

The tests in this part covered the weight (water) loss with time at changing environmental conditions; meaning that samples were moved from one box to another box during the tests. Two climate boxes were used for these tests. The boxes were respectively:

- Partially filled with a saline solution of NaCl to give an internal environment of approximately 75% relative humidity and kept in a room at approximately 8°C, further called 8°C and 75% r.h, and
- Partially filled with water to give an internal environment close to 100% relative humidity and kept in a room at approximately 8°C, further called 8°C and 100% r.h.

Figure 10 shows the climate boxes used for this type of test. In each box there is a load cell, “scale”, which was recording the weight of the silica sol specimen at a time interval of 2 min. To ensure a constant humidity inside each box, a fan was used for recirculation of the air. The boxes were placed in an acclimatised room with a constant temperature of 8°C.

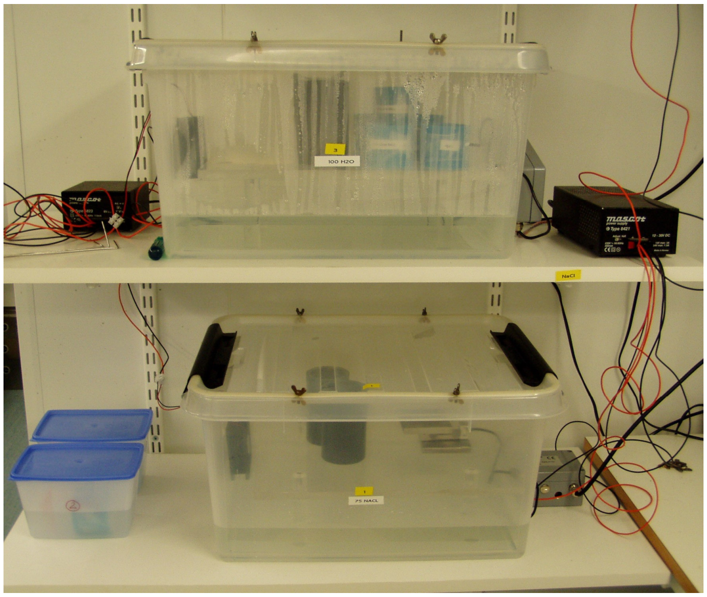
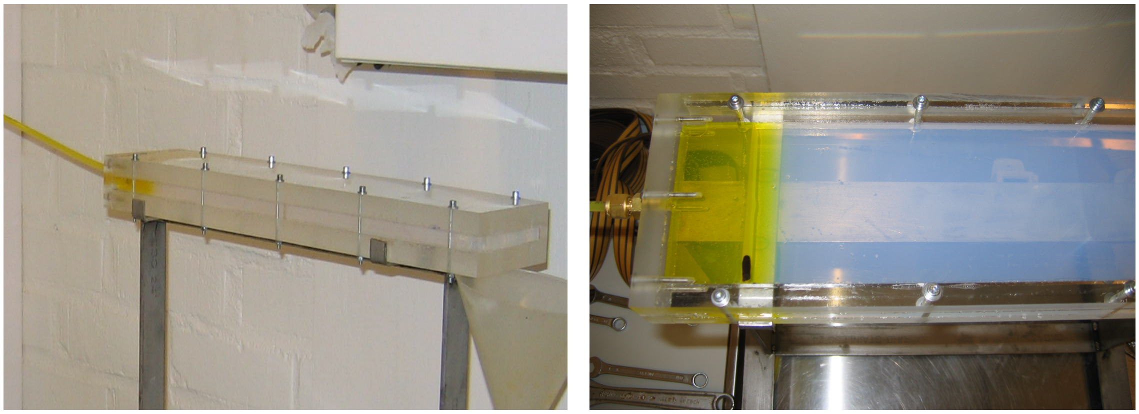


Figure 10. *Climate boxes used for the shrinkage test with varied humidity, scale and silica sol specimens inside*

First all silica sol moulds were placed inside the box with 75% relative humidity. Then the specimens were allowed to lose around 2%, 4%, 8%, 10%, and 14% of weight respectively before they were moved to a box with approximately 100% relative humidity. After the specimens had lost another 2% in weight, they were moved back to the first box with 75% relative humidity. The stored data was processed using the programs Microsoft Excel and Grapher.

3.4. Drying-out test between transparent plates

The drying-out of silica sol was studied through two plates of Plexiglas with silica sol grouted between them. This test was set up in order to understand the shrinkage behaviour of the silica sol and the water transport process in silica sol. In order to simulate a real grouting environment the specimens were subjected to water pressure using a pressurised tank at one side and exposed to air at the other side. Silica sol was grouted between the plates and after a couple of hours, when the strength of the silica sol had increased, the water pressure was applied. The water pressure was increased step wise and held constant between the steps. The specimens and test equipment were kept in a closed room and the humidity was measured during the experiment. The specimens were placed horizontally to ensure that the silica sol would stay between the plates and not be affected by gravitational force, see Figure 11. The tests were designed to show the interaction between air and silica sol as well as the interaction between water and silica sol. Measurements and observations at both sides of the specimens provided an estimate of the shrinkage and the water transport processes. In case that a breakthrough occurred, the tracer was used to localise the flow path through the silica sol and to measure the flow.



(a) (b)

Figure 11. *Set up for drying-out between transparent plate test: (a) full view; (b) view from above where the yellow part is the tracer (water) and the blue is silica sol.*

The specimen dimensions in the different tests are shown in Table 1. The tests covered the drying-out and water transport during time. The test environment was approximately 22°C and 20% relative humidity.

Table 1. *Grouted specimen dimensions in the transparent plates tests*

Test number	Grouted length (cm)	Grouted height (cm)	Grouted width (cm)	Initial water pressure (kPa)
1	45	1	10	5
2	20	2	10	5
3	10	1	10	5
4	10	1	10	8
5	20	2	10	12

3.5. Diffusion of chlorides from silica sol

The test method of measuring the diffusion is not standardised but is important to understand the transport and migration of chlorides from silica sol to the groundwater. The environments used to study this process were:

- 8°C and the specimen immersed in water,
- 20°C and the specimen immersed in water, and
- 40°C and the specimen immersed in water.

Figure 12 shows the climate boxes used for the tests. In each box there was a silica sol specimen immersed in “milli-q” water. The boxes were placed in rooms with a constant temperature of 8°C or 20°C and in a water bath at 40°C respectively. The volume of water in each box was one litre. In order to decrease the risk that the surrounding air should affect the test results, all boxes were kept closed and stored in special acclimatized rooms. However, the boxes were open during the measurements and then absorption of atmospheric CO_2 and reaction with Ca^{2+} could be expected; in order to avoid this, measurements were restricted to Cl^{1-} concentrations.

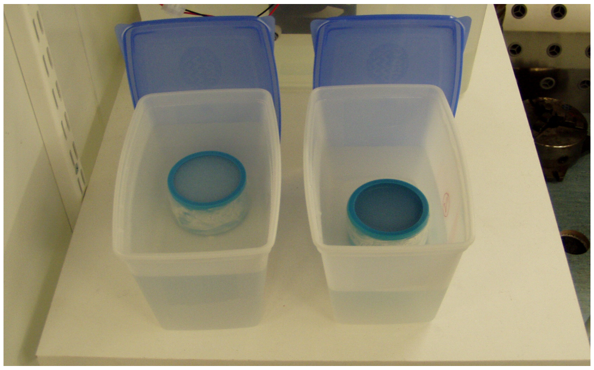


Figure 12. *Climate boxes used for the diffusion of chlorides from silica gel test. Silica sol specimens inside their boxes in a room with 8*°C.

Two types of test were conducted; test 1 where the specimens had one and two surfaces exposed to water at 20°C and test 2 in which the specimens had only one surface exposed to water at 8°C and 40°C. The chloride ratio was measured at intervals during time. In the latter tests, the specimens were either moved to a new box after a certain concentration had been reached in the surrounding water or kept in the same box without changing the water. By moving the specimens to a fresh bath, the concentration difference was kept fairly stable between the silica sol and the surrounding water. For comparison, the remaining specimens were tested at the same time without moving them. The chloride concentration was measured by the ion selective method. This method uses a simple potentiometer sensor to measure the activity of chloride ions in the solution, which is directly proportional to the concentration. Figure 13 shows the equipment used. The accuracy of the method was ±5 mg/L. Each time a measurement was done, the equipment was recalibrated at about 20°C. The equipment for this was located in the water-chemistry laboratory at the Department of Civil and Environmental Engineering at Chalmers University of Technology and the room temperature there fluctuates between 18°C to 22°C. Due to this, a temperature drift effect is expected on the measurements at 8°C and 40°C. It is also important to take into account that silica sol by itself has chlorides in a range of a couple of hundreds of ppm. More precisely it corresponds to a maximum of 50 mg in the specimens tested, (Bo Larsson – Eka Chemicals, personal communication).

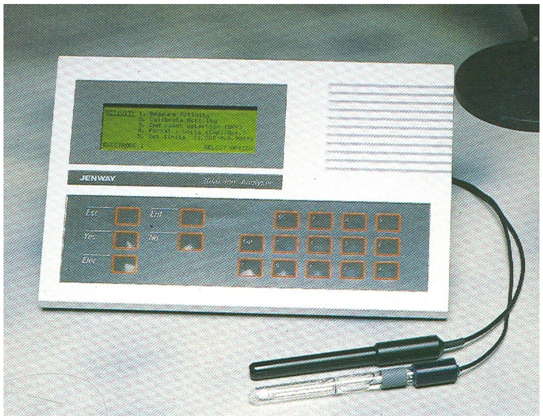


Figure 13. *The ion selective apparatus used for the diffusion of chlorides from silica sol tests.*

Diffusion is defined as the net transport due to random motion, of both ionic and molecular species dissolved in water, from areas of higher concentration to areas of lower concentration, e.g. Fetter (2001). Mass transport of chlorides through silica sol by diffusion is illustrated in Figure 14. Consider a silica sol specimen where chloride ions have motion in the X direction only. The open surface of the mould separates two regions of different concentration, $C_s > C_w$. The motion of each chloride ion is a random walk. In each time interval, t, each particle will move a distance into the milli-q water, until the concentrations reach an equilibrium.

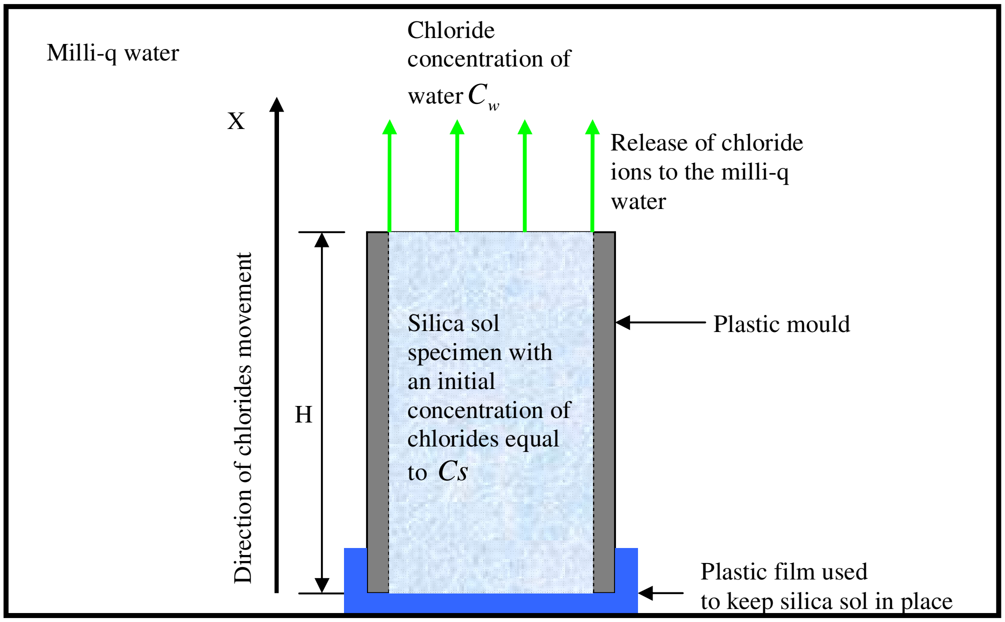


Figure 14. *Representation of a diffusion process. Chloride release from an area of higher concentration to an area of lower concentration.*

For one dimensional diffusion to or from a piece of height H = 2*l*, Crank (1956) gives an equation for fractional uptake, as a function of time where diffusion occurs from both surfaces simultaneously. For diffusion from one surface only, the same equation can be used, although with H = *l,* see Equation 2. A complete derivation of the expression is presented in Appendix J.

$$\frac{C_w}{C_w^{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[- \frac{D \ (2n+1)^2 \pi^2 t}{4l^2} \right] \qquad (2)$$

Where:

C_w is the concentration of chlorides in the water,

C_w^{∞} is the final concentration of chlorides in the water,

D is the coefficient of diffusion,

t is the time that takes by diffusion to go from the initial concentration to the final one,

n is the number of interaction and just positive values greater than zero, and

l is the height of the sample " H"

4. RESULTS

4.1. Mechanical tests

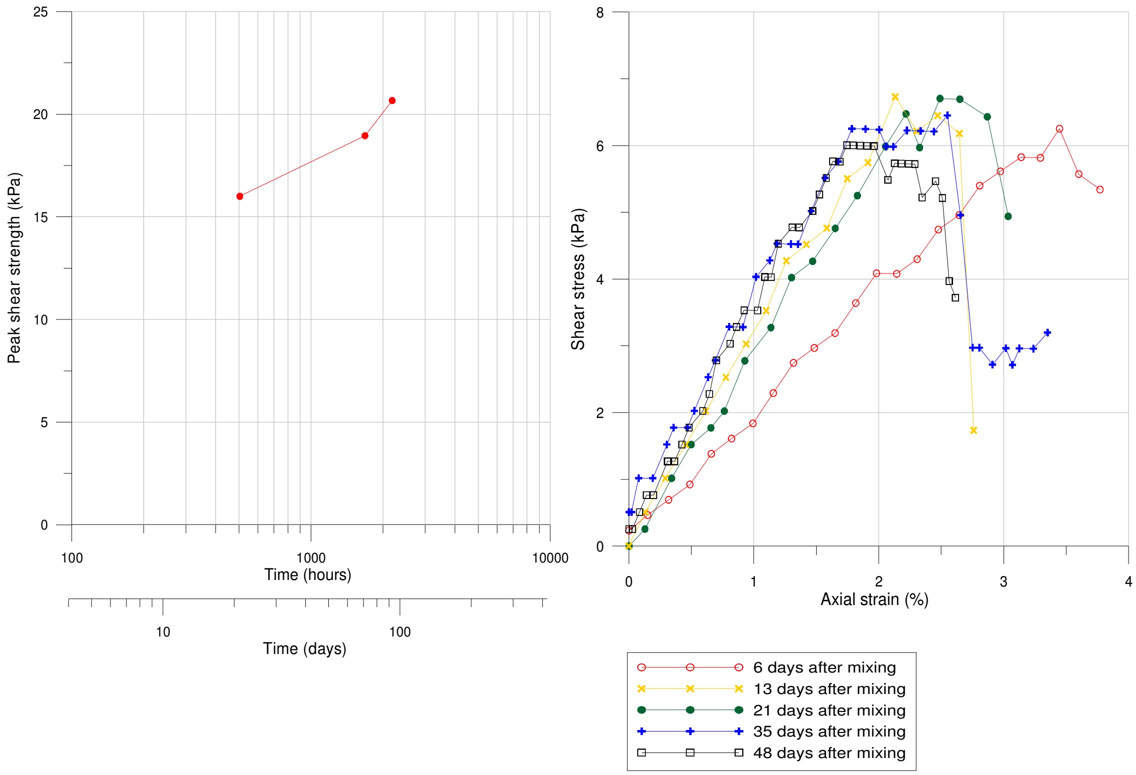
Unconfined compression tests, fall-cone tests, unconsolidated undrained triaxial tests, consolidated undrained triaxial tests and CRS oedometer tests were conducted on silica sol specimens immersed in water or kept in different environments. The results show the influence of age on the strength of silica sol under these conditions and in comparison among them the influence of each storage environment. They also show the influence of age on the consolidation behaviour and the influence of age and consolidation on the strength of silica sol. Most of test results are presented as peak shear strength versus ageing time and these are presented below. Detailed results of the unconfined compression tests are shown in Appendix B, fall-cone tests in Appendix C, unconsolidated undrained triaxial tests in Appendix D and the consolidated undrained triaxial tests in Appendix E.

4.1.1. Unconfined compression tests on silica sol specimens immersed in water

Following the methodology described in Chapter 3.2.1; the specimens were tested under no confining pressure. In Figure 15, the resulting failure mode in a test performed 6 days after mixing is shown. This was an entirely vertical failure, which is a characteristic behaviour of fully saturated materials under low or none confining pressures.

Figure 15. *Vertical failure plane in a silica sol specimen tested 6 days after mixing.*

In Figure 16a, the peak shear stresses, evaluated as half of the maximum compressive stress, after 21, 70 and 90 days are presented. The peak shear stress increases with time from about 16 kPa after 21 days up to around 21 kPa after 90 days. These results show similar values to the results obtained in unconsolidated undrained triaxial tests. Note that these specimens were trimmed before testing them. Figure 16b shows the results of the rest of the tests conducted without trimming. The results show similar shear strength and failure mode independent of the time of testing. The reasons for this are discussed in Chapter 5.



(a)

Figure 16. *Unconfined compression test results for: (a) trimmed specimens, figure shows the peak shear stress plotted against time; (b) un-trimmed specimens, figure shows shear stresses plotted against axial strain. All specimens were kept immersed in water.*

4.1.2. Unconfined compression tests on silica sol specimens kept in different environments

The peak shear stresses measured after 1, 7, 14, 22, 35, 48, 67 and 91 days for the different test environments are presented in Figure 17. The results show trends of a continuously increasing strength with time; however the rate of the increase varies depending on the storage environment. Thus, during a period of 90 days in a storage environment of:

- 20°C and 100% r.h. the strength increased up to 60 kPa,
- 60°C immersed the strength increased up to 34 kPa,
- TDS 35g/l the strength increased up to 23 kPa,
- pH11 the strength increased up to 24 kPa, and
- 20°C and 75% r.h. the strength increased up to over 300 kPa after 35 days.

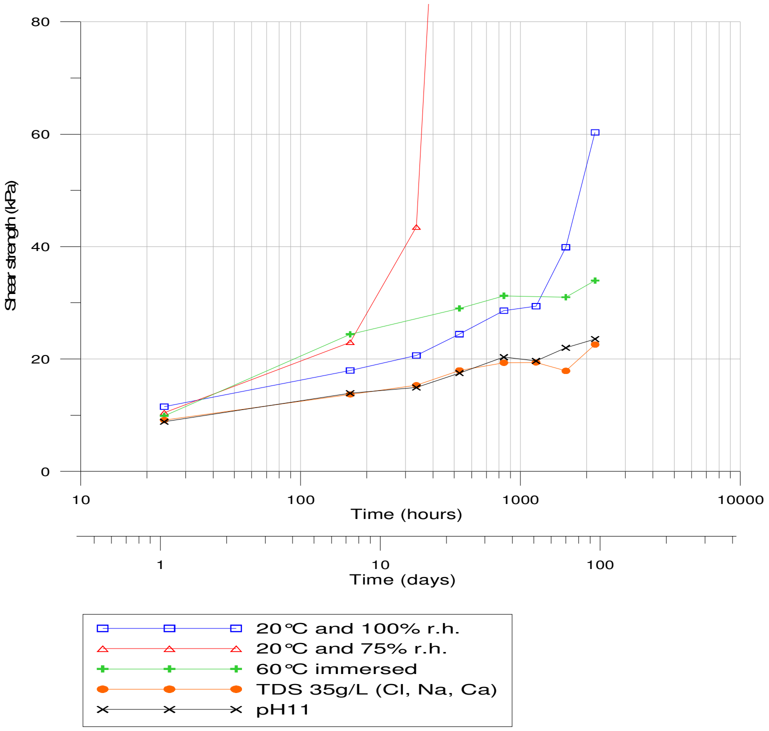


Figure 17. *Unconfined compression test results for all test environments.*

4.1.3. Fall-cone tests on silica sol specimens immersed in water

During the period of 90 days a total of eight fall-cone tests were conducted on specimens immersed in water. The results showed a trend of increasing strength from 5 kPa after 1 day to about 18 kPa after three months, see Figure 18. These measurements were done on the surface that was not in contact with water during storage.

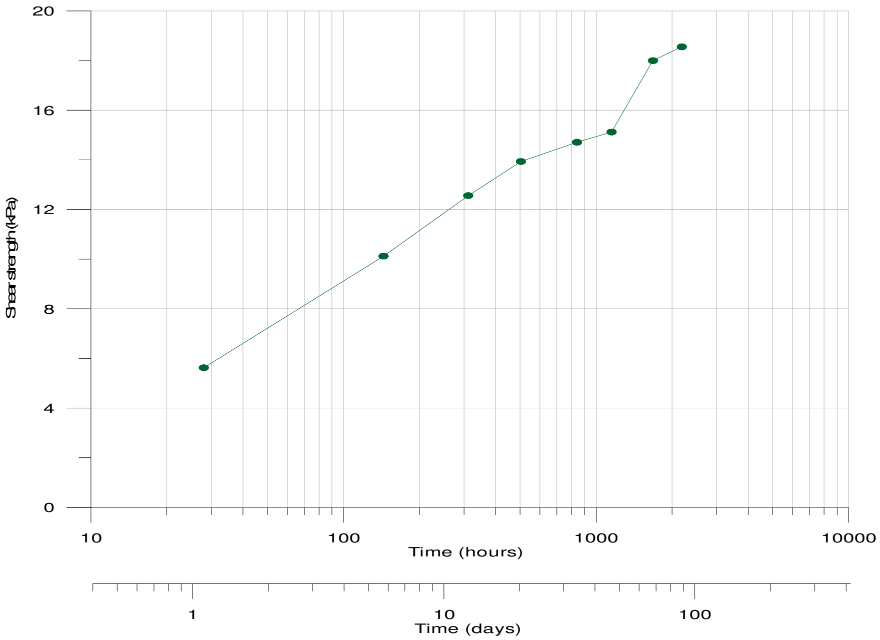
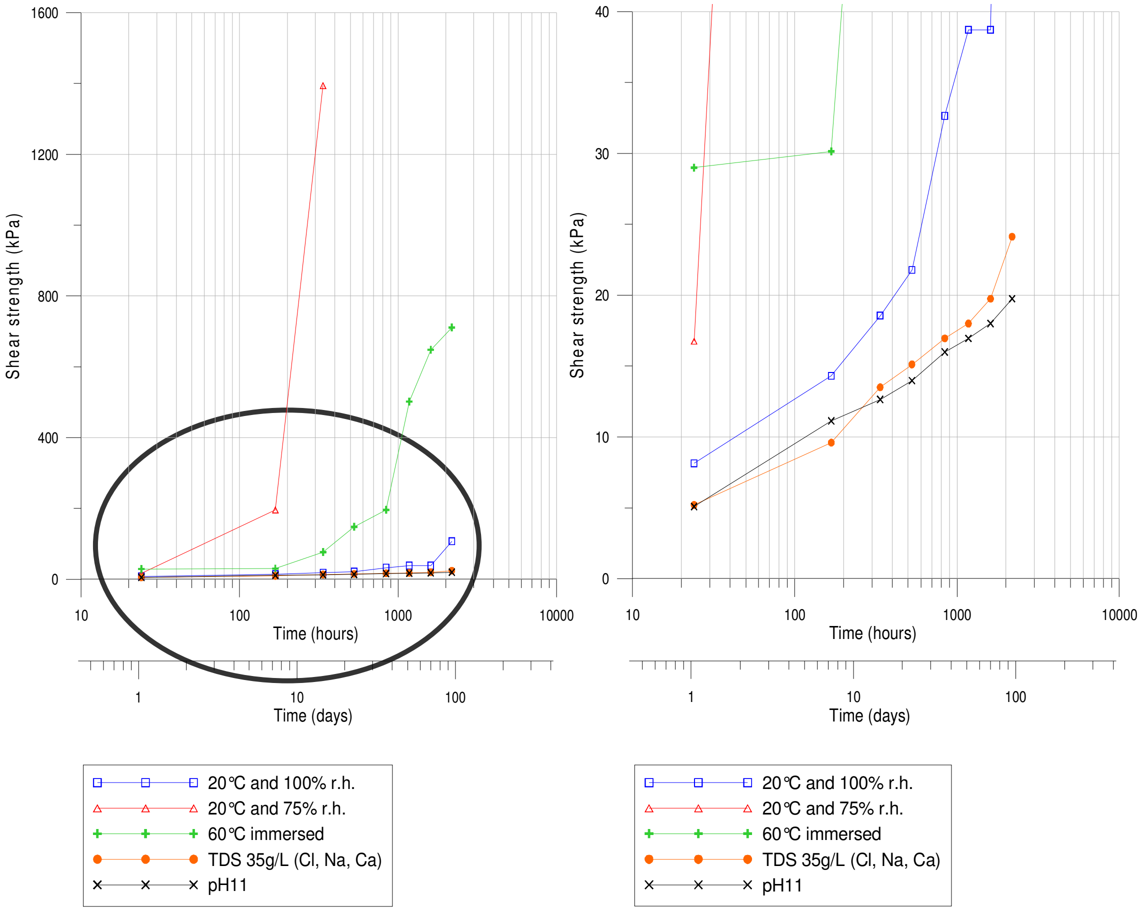


Figure 18. *Results from fall-cone tests on the closed ends of the specimens.*

4.1.4. Fall-cone tests on silica sol specimens kept in different environments

During the period of 90 days a total of 70 fall-cone tests were conducted. The tests were performed on two surfaces for each sample. The results show a trend of increasing strength for all the specimens tested during the three months; see Figure 19. The plotted results represent the measurements done at the surface that was not in direct contact with air, water or environment solution used during storage. This implies that these results can be regarded as the most representative shear strength values for the bulk of the homogeneous silica sol. Results from measurements done on the open surface will be discussed in Chapter 5.



(a) (b)

Figure 19. *Results from fall-cone tests on silica sol specimens: (a) all values; (b) magnified shear strength scale for easy viewing.*

4.1.5. Unconsolidated undrained triaxial tests on silica sol specimens immersed in water

The results showed a trend of a continuously increasing strength with time where the peak shear stress increased from 12 kPa after one day up to almost 20 kPa after 90 days, see Figure 20. The figure shows the average values from the two tests with different radial stresses performed at each testing occasion.

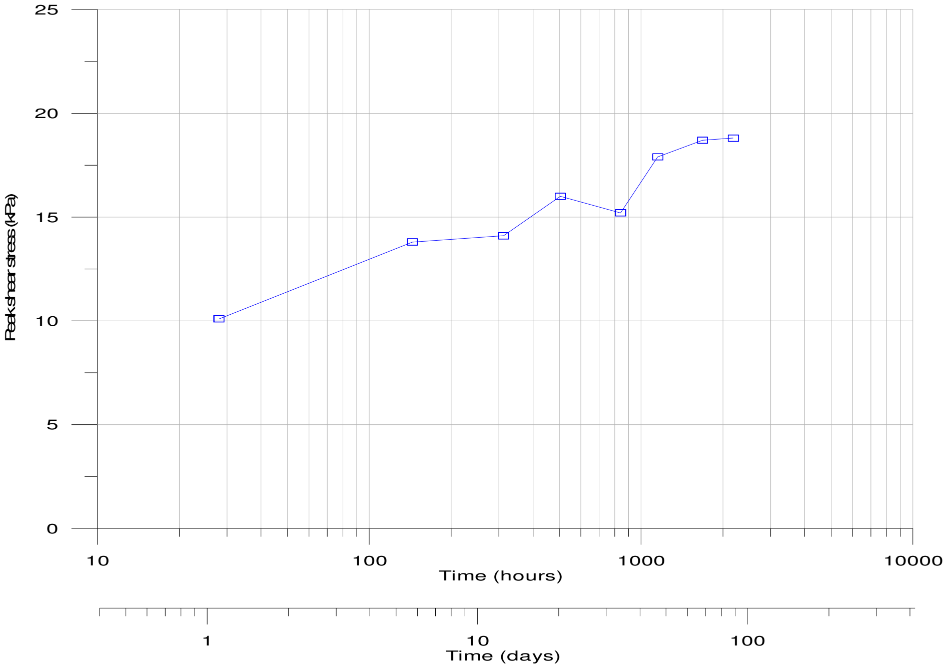


Figure 20. *Average peak shear stress from the unconsolidated undrained triaxial tests.*

4.1.6. Unconsolidated undrained triaxial tests on silica sol specimens kept in different environments

In Figure 21, the result of four peak shear stresses of specimens stored at pH11 and in TDS measured after 1, 35 and 67 days are presented. These results show similar values as the results obtained in the unconfined compression tests and the tests were done in order to corroborate the results.

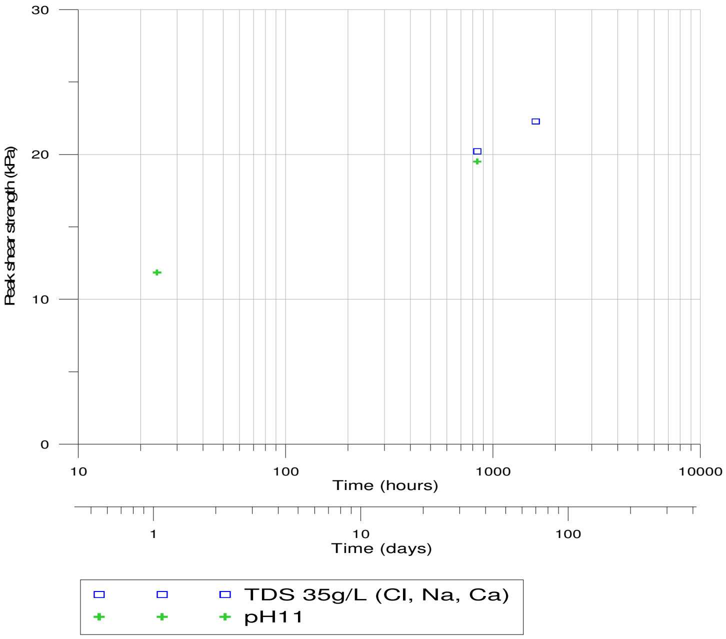
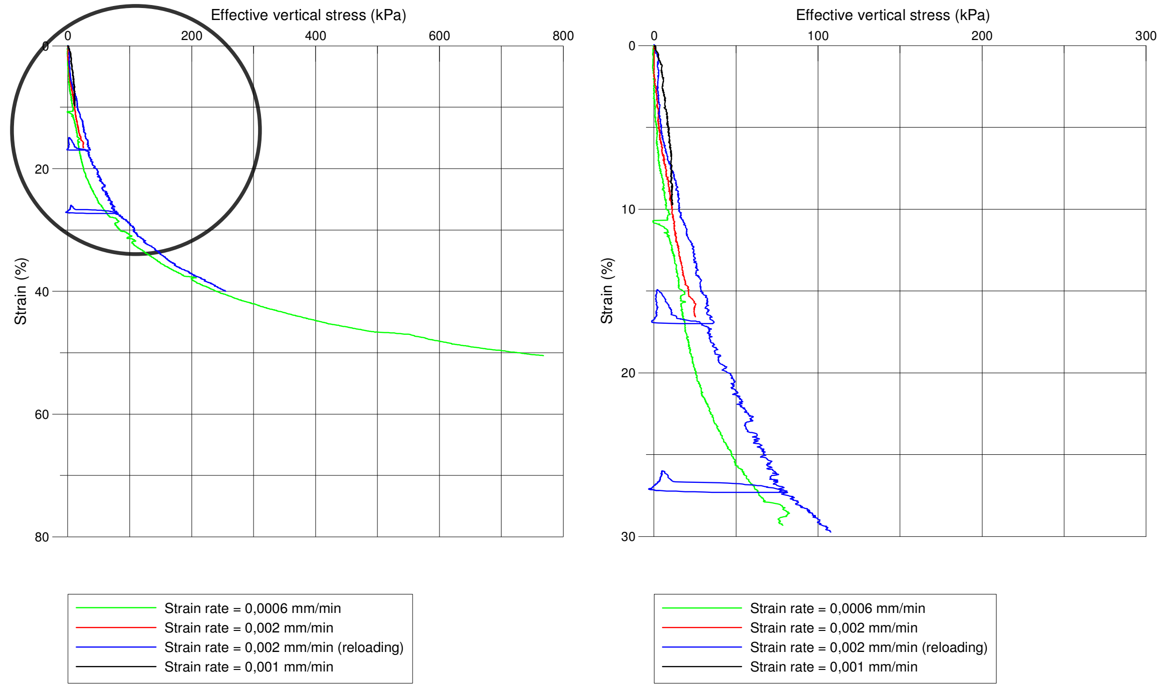


Figure 21. *Peak shear stress from the unconsolidated undrained triaxial tests.*

4.1.7. Effect of compression rate in CRS tests on silica sol specimens immersed in water

As stated in the methodology, it is prudent to verify the influence of the loading rate on the measured stresses. In order to calculate a proper loading rate, a series of CRS oedometer tests with different rates of strain was conducted one day after mixing.

Figure 22 shows the results of this test series on silica sol at different strain rates. Three different strain rates were used; 0.0006 mm/min, 0.001 mm/min and 0.002 mm/min. The response in load and pore pressure against strain was recorded and the effective stress evaluated. A certain decrease in effective stress with decreasing strain rate could be observed. This is typical for similar types of material as clays; see e.g. Sällfors (1975). As a result, a testing rate of 0.002 mm/min was selected for the tests.



(a) (b)

Figure 22. *CRS test results obtained at three different strain rates. (a) all values; (b) magnified strain scale for easy viewing.*

The results also show an approximate value or rather a range for the hydraulic conductivity of the silica sol specimens tested, which is typically less than $1 \cdot 10^{-10}$ m/s. Figure 23 shows the hydraulic conductivity of silica sol measured at different strain rates. All the tests show a similar pattern for the hydraulic conductivity plotted against strain. The results also show that even when a strain of 50% is reached, the patterns still follow a continuous relation. The peaks in the curves are due to the unloading-reloading processes in some of the tests.

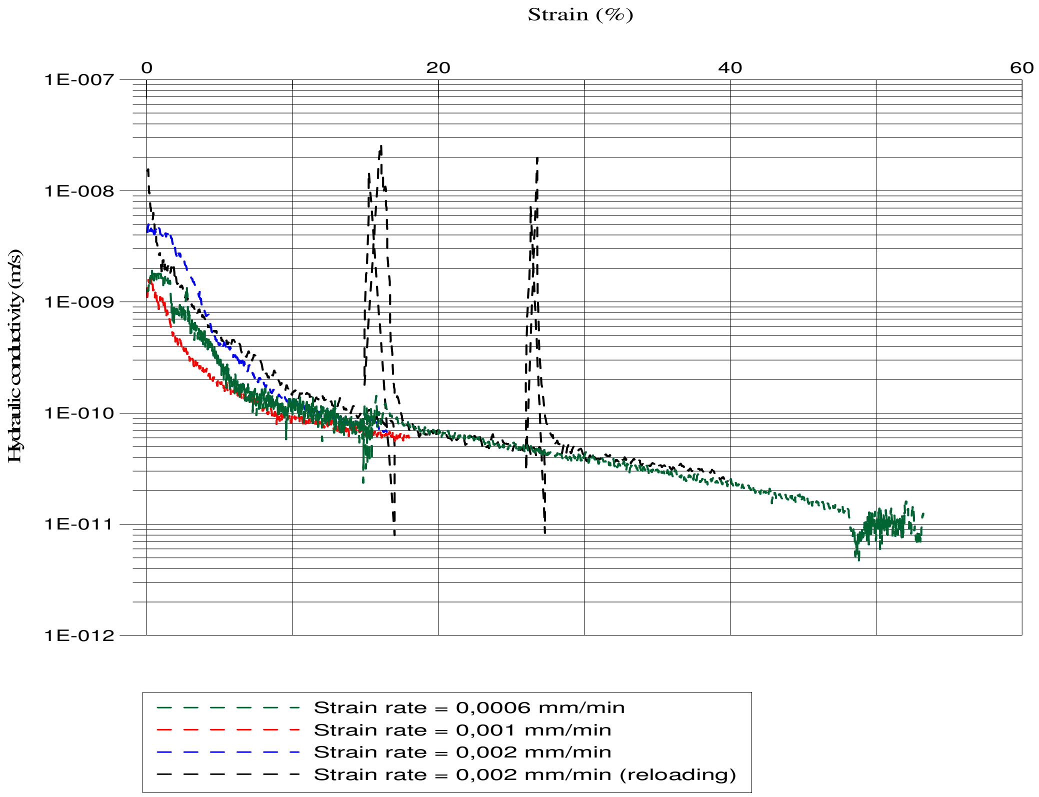


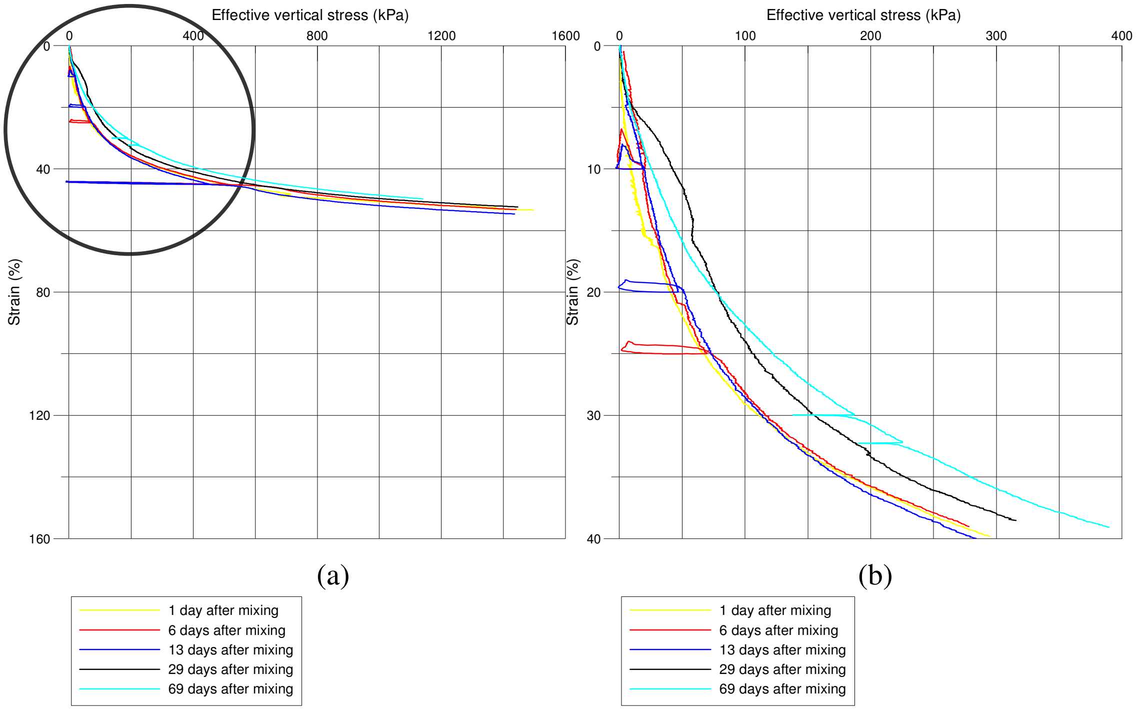
Figure 23. *Hydraulic conductivity obtained from CRS oedometer tests at three different strain rates.*

4.1.8. CRS oedometer tests on silica sol specimens immersed in water

The influence of the strain rate in the CRS test was studied before beginning the main test series. Earlier studies showed that the rate of strain has a great influence on the patterns of the shear stress, effective axial stress, peak shear stress and axial strain when testing silica sol in an unconsolidated undrained triaxial test. Hence, it was considered important to determine a proper rate. The results showed moderate and expected differences and a strain rate of 0.002 mm/min was chosen based on the ASTM D 5084 standard.

During the testing period of two months, five CRS tests were conducted. Effective vertical stress-strain relations were measured after 1, 6, 13, 29 and 64 days, see Figure 24a. The results show some scatter but a general trend is that for a longer hardening time a higher pressure is needed to compress the silica sol specimen.

At first loading, the results do not show a typical S-shaped curve, as for natural clay, from which a preconsolidation pressure can be obtained. Figure 24b shows a magnification of the first 400 kPa of effective vertical stress and it is obvious that the consolidation process does not follow a typical clay behaviour. Figure 24 also shows two test results with unloading-reloading cycles. In both cases the patterns are similar. It shows that silica sol swells to some extent at unloading and that it at reloading exhibits a preconsolidation pressure corresponding to the previous maximum effective stress, i.e. exhibits the same behaviour as clay.



(a) (b)

Figure 24. *CRS test results obtained during the two months testing period. (a) all values; (b) magnified strain scale for easy viewing.*

The hydraulic conductivity obtained from the CRS tests is shown in Figure 25. The results are mainly uniform and similar to each other. This can be expected since the hydraulic conductivity is mainly a function of the pore sizes and porosity in the specimen and no effect of the strain rate was observed in previous tests. The typical range of the hydraulic conductivity can be observed to be going from $1{\cdot}10^{-10}$ to $1{\cdot}10^{-11}$ m/s.

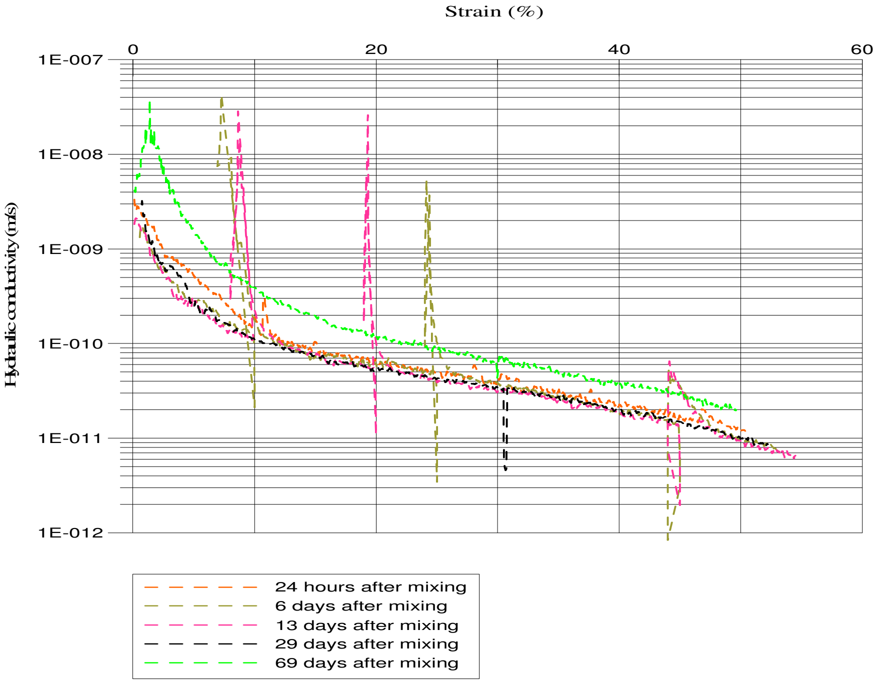


Figure 25. *Hydraulic conductivity from the CRS tests.*

4.1.9. Consolidated undrained triaxial tests on silica sol specimens immersed in water

In Figure 26, the results of five consolidated undrained triaxial tests performed after 1, 6, 13, 29 and 64 days of hardening are presented. Because of the material characteristics of silica sol, no preconsolidation pressures were obtained from the previous CRS tests. Thus, the effective consolidation stresses assumed for the different tests were chosen to be around 10 kPa for the radial stress and around 20 kPa for the axial stress. This resulted in axial compressions of the specimens during consolidation varying between 2 and 13% with the largest values for the specimens with relatively short hardening times.

The tests conducted after 1, 6, and 13 days did not show any failure although the specimens were compressed 13-18% further after the consolidation. In tests performed 29 days and 64 days after mixing failure occurred, and the peak shear stresses were 27 kPa and 33 kPa respectively. The failure in these tests occurred after 10-17% undrained axial compression after the consolidation. Each test took more than one week to be concluded due the consolidation process. The influence of this will be discussed in the next chapter.

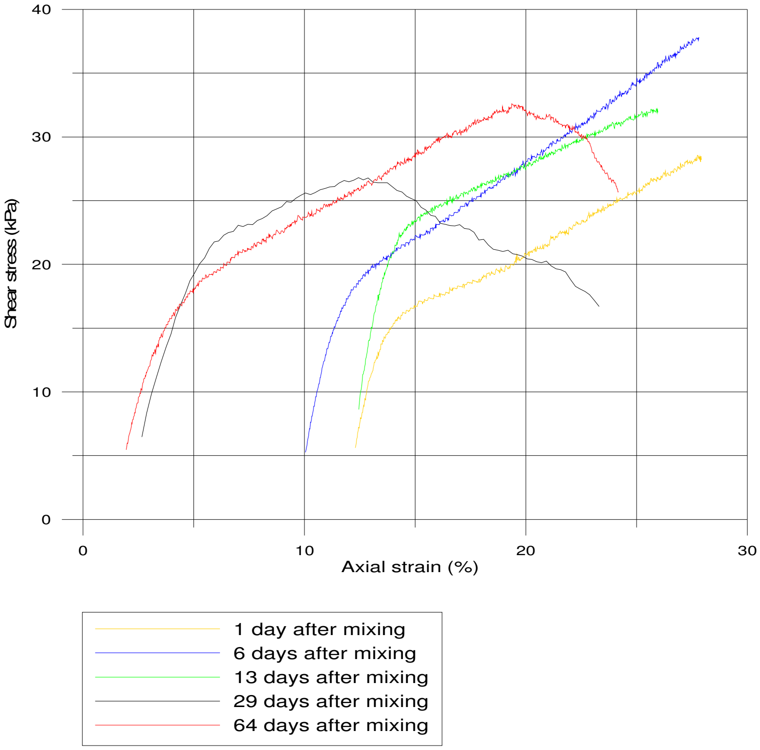


Figure 26. *Results from consolidated undrained triaxial tests.*

4.2. Continuous water loss measurement tests

The changes in weight of silica sol specimens kept in three different environments were measured continuously during three months, and the results of the continuous water loss measurements are presented in Figure 27. The results show a trend of a continuous release of water for all the specimens. The loss of water was faster when the specimen was kept in a lower relative humidity.

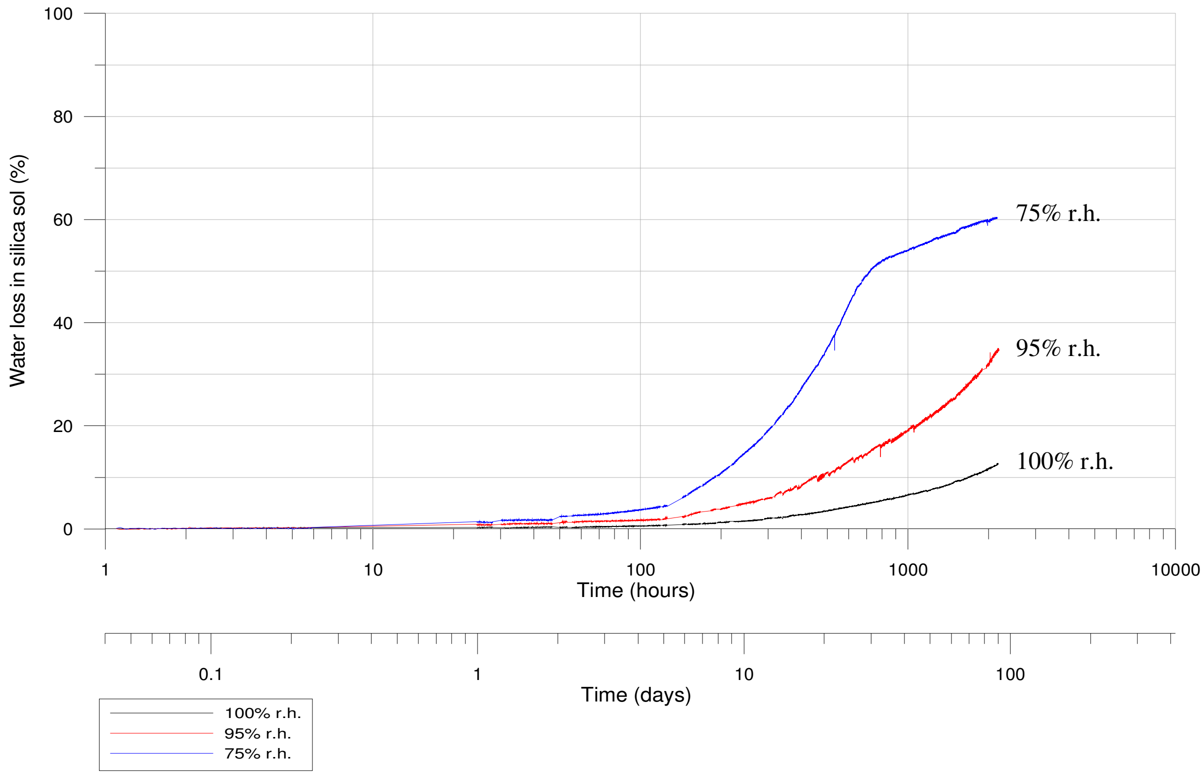


Figure 27. *Continuous water loss measurements of silica sol during three months. Three different environments with a constant temperature of 8°C.*

The water loss thus depends on the environment. The specimen stored at 8°C temperature and 75% relative humidity shows a bend in the weight loss-time curve after one month when it had lost about 50% of its weight and the rate of water release then started to slow down. Three months after mixing, the specimens had lost 14%, 35% and 60% of their weight in environments with 100%, 95% and 75% relative humidity respectively. Additional tests with drying of specimens in an oven at 105°C for two days showed that the total amount of free water in a fresh silica sol specimen is 68% of the total weight. A comparison with previous results presented by Butron (2005) shows a good correlation for specimens kept at 8°C and 95% relative humidity validating the repeatability of the methodology.

4.3. Water loss measurement with varied humidity

Five tests were performed and the weight of the specimens was measured continuously during three months. The results in terms of water (weight) loss at varied humidity are presented in Figure 28. All the results show a similar trend for the weight loss due to release of water before and after moving the specimens between the environment boxes. The loss of weight was faster when the specimens were kept in the box with 75% relative humidity, slower when they were moved to the box with 100% relative humidity and faster again when they were moved back to the box with 75% relative humidity.

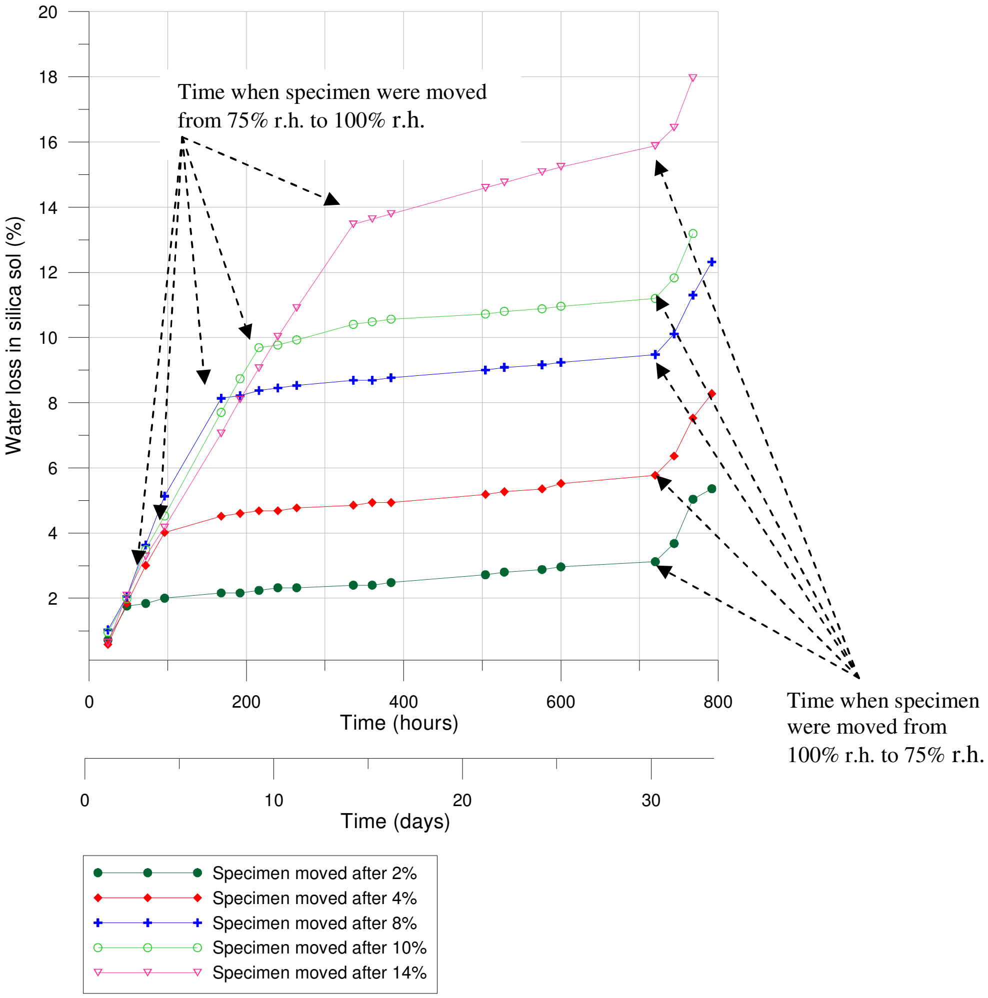


Figure 28. *Water loss test results. Results from the five different tests with specimens moved from 75% to 100% relative humidity after weight losses of 2%, 4%, 8%, 10%, and 14% respectively.*

As shown earlier, the water loss rate depends on the environment. All the specimens showed a change in weight loss rate when being moved from 75% to 100% relative humidity, and another one when being moved back again to 75% relative humidity. Detailed results can be seen in Appendix F.

4.4. Drying-out tests between transparent plates

Four tests were conducted during three months. Three of these tests did not present a water breakthrough and were used to evaluate the shrinkage of silica sol and mass transport processes of water into silica sol. The last test was induced to present a water breakthrough by increasing the water pressure to evaluate the flow and flow path obtained through silica sol in such conditions.

The results for the three first drying-out test are presented in Figure 29. The results are presented as length of water penetration in the specimen by means of appraising the front of the tracer movement in centimetres (water-contact face), and shrinkage by the shrinkage front movement through the silica sol specimen (air-contact face). Figure 30, shows test number 3 where the length of shrinkage (air-contact face) and tracer penetration (water-contact face) in silica can be clearly observed. The results show a trend of increasing tracer penetration in the specimen in all three tests. The shrinkage of the silica sol specimen represented by the air-contact face movement shows a rapid stage followed by a slower movement of the front until not much change in the zone affected by the shrinkage is observed with further time. Tests 1 and 3 were similar in height and they show similar results on both sides. Test 2 had double height, therefore double cross-section area, resulting in a larger shrinkage ratio and less tracer penetration, but with the same trend as the other two tests. All the tests can be studied in Appendix G. The final pressures in the three first tests were:

- Test 1 final pressure = 110 kPa, and a gradient = 25 m/m
- Test 2 final pressure = 40 kPa, and a gradient = 20 m/m
- Test 3 final pressure = 50 kPa, and a gradient = 50 m/m

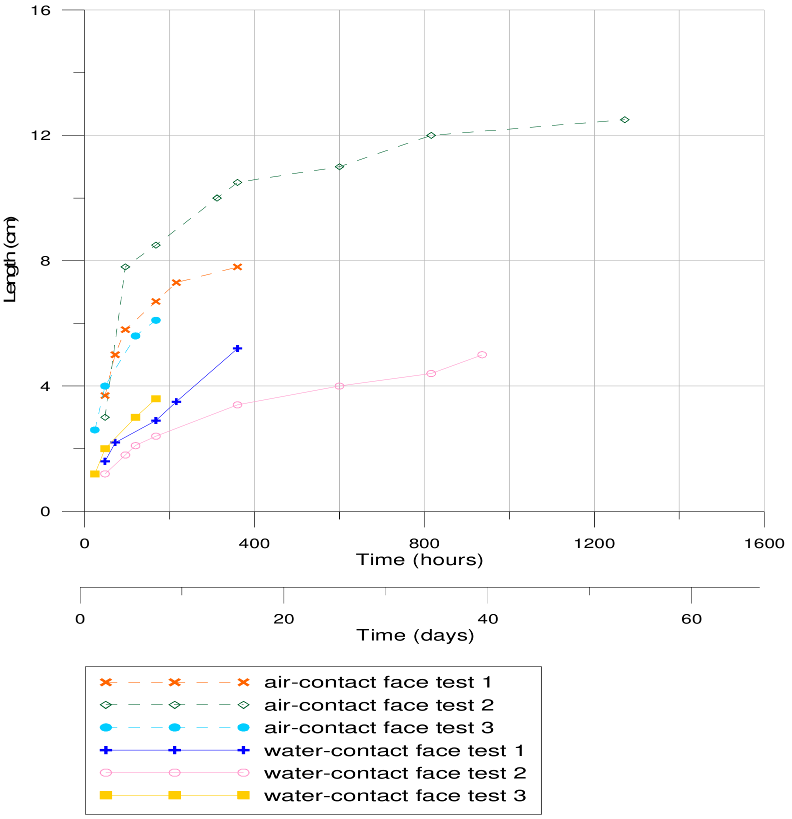


Figure 29. *Results from drying-out tests on silica sol during three months; three first tests.*

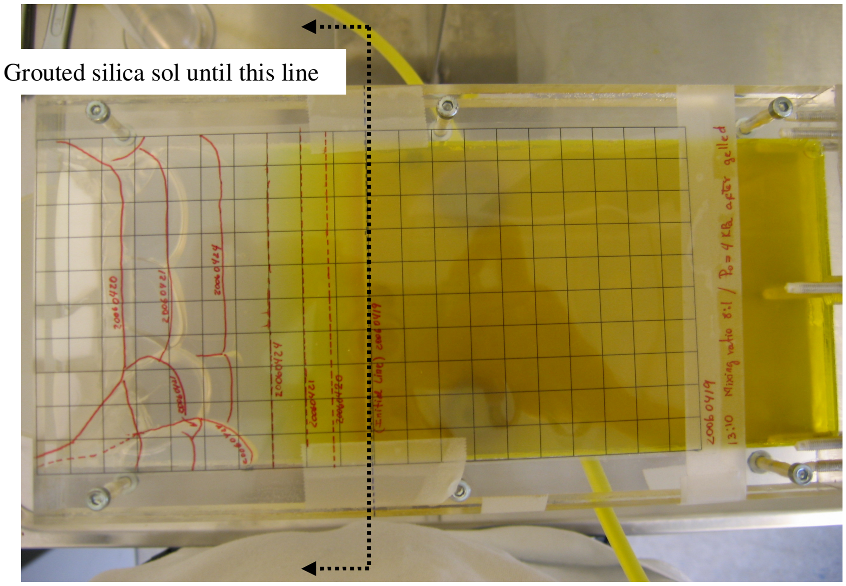


***Figure 30.** Drying-out of silica sol sample.*

The last test was used to evaluate the flow and flow path of water through silica sol once a breakthrough had occurred. This breakthrough occurred due to a higher water pressure than in the other tests being applied just after gelling (gradient larger than 0.8 m/m). Figure 31 shows the volume of the flow obtained in a measuring vessel were a larger flow is obtained at the beginning of the test followed by a decrease of the amount of water obtained until it finally stops after two to three days; the pressure was continuously increased and the gradient reached was 20 m/m.

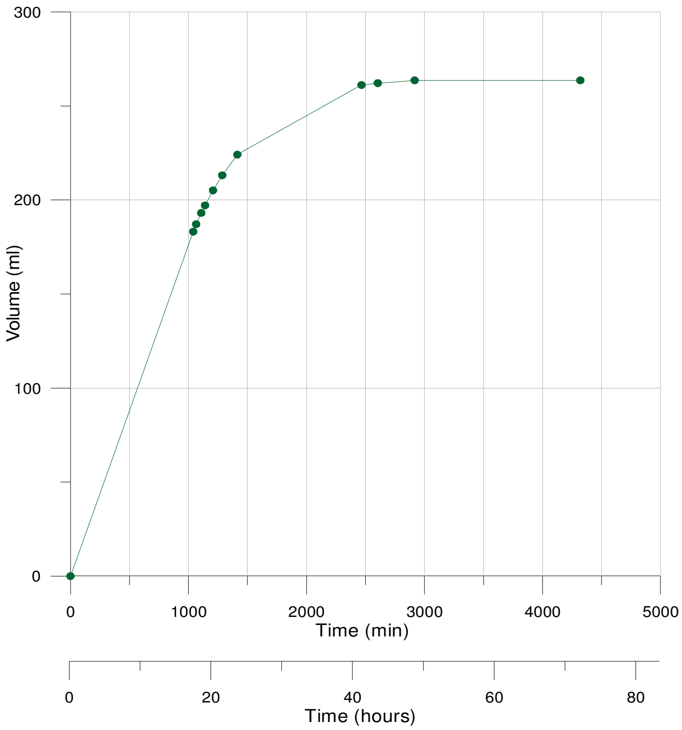


***Figure 31.** Results from drying-out tests on silica sol during three months; accumulated flow in breakthrough test.*

4.5. Diffusion of chlorides from silica sol

Two test series with four specimens in each were performed. The results for the release of chlorides from silica sol with one and two exposed surfaces are presented in Figure 32. The tests showed similar results and the concentrations of chloride ions obtained after 10 days were in average 280 mg/l for two exposed surfaces and 210 mg/l for one exposed surface. The results also showed a faster release of chlorides in the beginning, which slowed down and almost stopped after 8 days for two contact surfaces. However, the increase continued for at least 10 days when just one surface was in contact with water. Important to note is that the total concentration of chlorides, calculated in Appendix I, is 270-290 mg/l, which is close to the values obtained in silica sol mixture with two open surfaces showing an almost total release of chlorides 10 days after mixing, see Figure 32. In the same figure can be seen that for one exposed surface, around 70% of the chloride ions had been released 10 days after mixing.

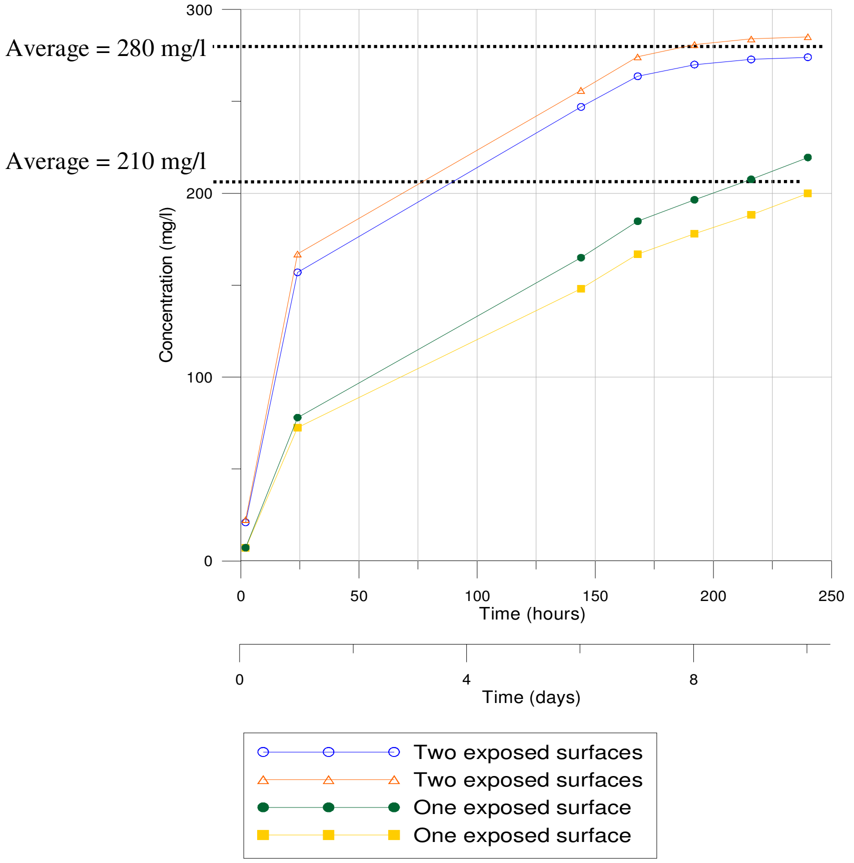


Figure 32. *Release of chlorides from silica sol samples. Two different tests with one or two exposed surfaces.*

Figure 33 shows the results of the concentration plotted against the square root of the time. The release of chloride results show a linear trend for tests with one exposed surface which is an indication of diffusivity, indicating that the chloride release from silica sol follows a diffusion matrix as described by Higuchi (1963). Using an equation developed by Crank (1956) the diffusion coefficient can be evaluated, see Appendix J. The calculated diffusion coefficient for silica sol is approximately $1 \cdot 10^{-9}$ m^2/s.

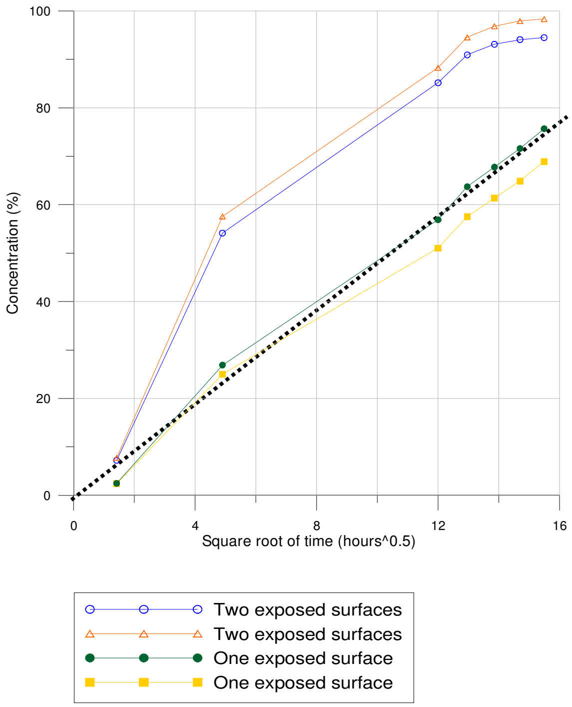


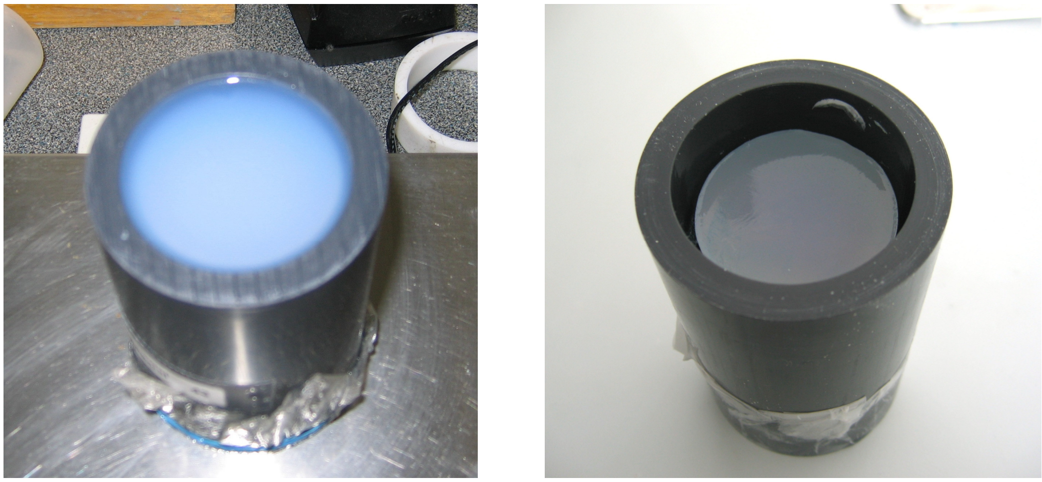
Figure 33. *Release of chlorides from silica sol samples stored at 20 °C and immersed in Milli-q water. The vertical axis represents the concentration percentage and the horizontal axis the square root of time.*

5. DISCUSSION

5.1. Laboratory tests

5.1.1. Mechanical tests

The results from the mechanical tests show that the shear strength increases with time whereas the strain at failure tends to decrease. This supports previous findings that the strength of silica sol increases as the specimen shrinks. However, silica sol specimens kept immersed in water do not show any shrinkage. Figure 34 shows a comparison between a sample stored immersed in water during 90 days and one kept in an environment with 75% relative humidity and 20 ºC during 30 days.



(a) (b)

Figure 34. *Silica sol specimens: (a) immersed in water during 3 months without any shrinkage; (b) stored at 20ºC and 75% r.h. during 1 month with considerable shrinkage.*

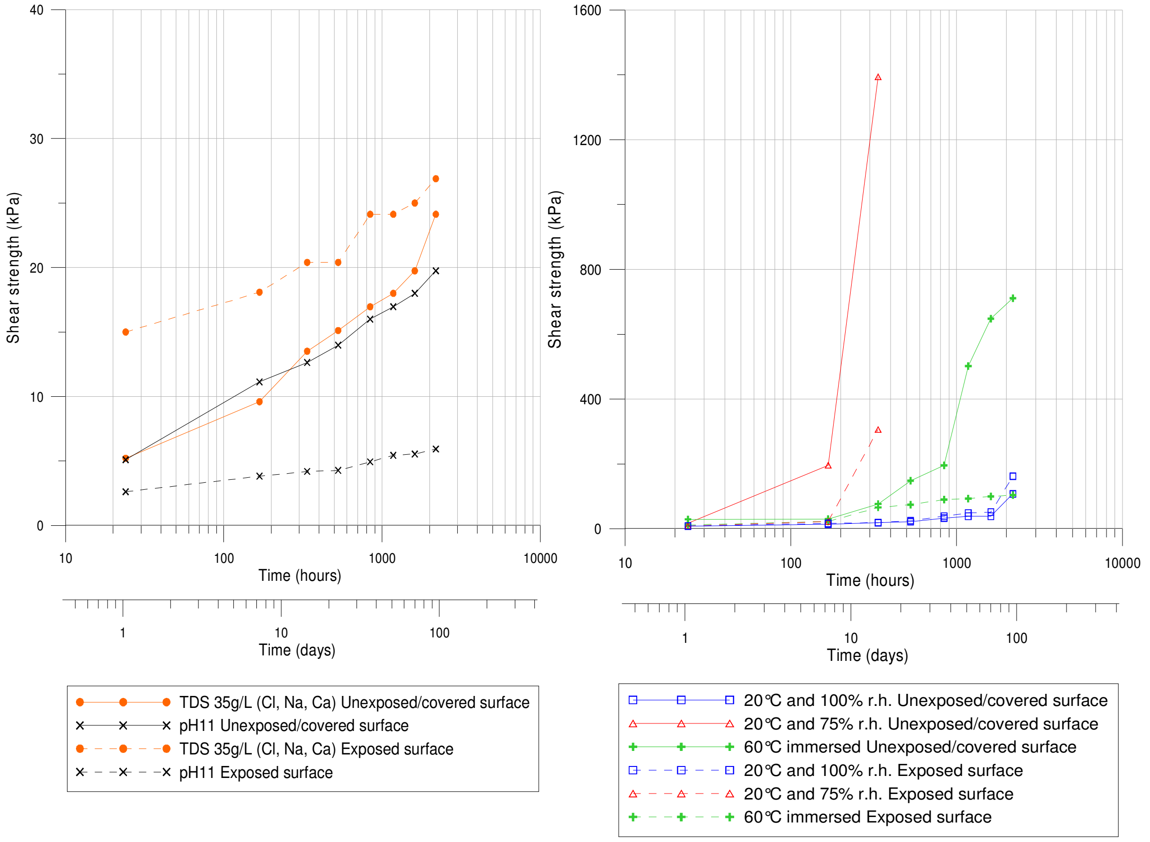
Following the methodology described in chapter 3.2.2, both the outer and the inner end surfaces on each silica sol specimen were tested at the same time with the fall-cone method. Differences in the shear strength were obvious from the beginning of the measurements and increased with time depending on the storage environment. The closed surface, used as a base, was covered with a plastic film and had no direct contact with the surroundings.

For samples kept in environments other than immersed in water at 8°C, different trends were found, see Figure 35. Keeping in mind that all values above 40 kPa are probably somewhat too high for measuring with the fall-cone test, it can be noticed that:

- 20°C and 100% r.h., while the shear strength of the surface in contact with air increased to over 160 kPa after 91 days, the surface covered with the plastic film increased only to around 110 kPa,
- 20°C and 75% r.h., while the shear strength of the surface in contact with air increased to over 1300 kPa after 14 days, the surface covered with the plastic film increased to approximately 300 kPa,

- 60°C immersed, while the shear strength of the surface in contact with water increased to around 103 kPa after 91 days, the surface covered with the plastic film increased to over 700 kPa,
- pH11, while the shear strength of the surface in contact with the solution only increased to 6 kPa after 91 days, the surface covered with the plastic film increased to 20 kPa, and
- TDS 35g/L, while the shear strength of the surface in contact with the solution increased to 27 kPa after 91 days, the surface covered with the plastic film increased to 24 kPa.

Contact with air or lower humidity implies a faster growth in strength. Direct contact with water as well as direct contact with high pH implies a slower increase. It can also be noticed that a direct contact with ion solution appears to imply a faster initial increase in the strength, which evens out through the specimen with time.



(a) (b)

Figure 35. *Comparison between results off all-cone test on the unexposed and exposed surfaces in different scales: (a) TDS and pH11 environments; (b) the other environments.*

In the tests on specimens kept at 8°C and immersed in water, the results showed that the shear strength at the surface in contact with water just increased up to 5 kPa after 90 days while the corresponding strength at the surface covered with the plastic film increased up to 18 kPa, as shown in Figure 36. This also implies that the strength development was different and independent at the open surface compared to the covered surface.

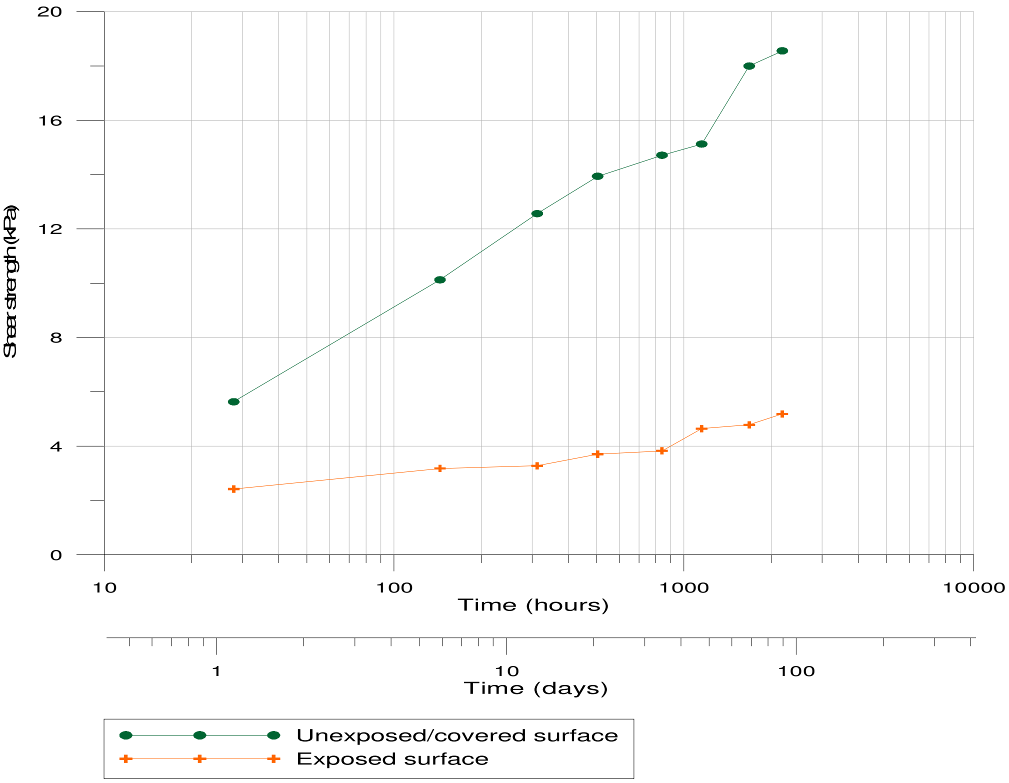


Figure 36. *Comparison of fall-cone test results at the end surfaces unexposed and exposed to water respectively.*

A "muddy" face was observed at the surface that was in direct contact with water. This layer had a lower strength due to the interaction between silica sol and water, and extended approximately 2 mm into the specimen, see Figure 37. No reduction of the strength was measured deeper into the silica sol specimens, and no shrinkage of these specimens was observed during the testing period. However, at the surface that was in direct contact with a TDS solution, a "muddy" face was not observed. Instead an expansion of the specimen was observed at this surface and no overall shrinkage occurred. The interaction of silica sol and this salt solution yields a high shear strength compared to the other surface, possibly due to the incorporation of salt ions in this part of the gel. The Cl^{1-} added to the initial concentration of silica sol could have started a process of incorporating Cl^{1-} ions into silica sol instead of releasing them to the surrounding solution. It is also important to note that a pH11 did not destroy the silica sol, even though the shear strength was lower.

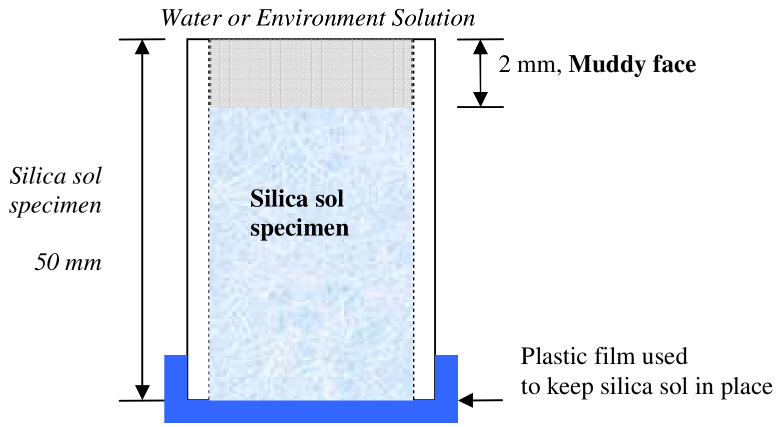


Figure 37. *Silica sol specimen immersed in water with the low strength face in the contact zone with air, water or environment solution. Observe that the figure is not in scale.*

At the surfaces that were in direct contact with air this "muddy" face was not observed. The surface had then a higher strength due to the interaction of silica sol and air, see Figure 35b. The interaction of silica sol and air yields higher shear strength because of the resulting partial drying of the silica sol. In Figure 38, the results from unconfined compression test conducted on silica sol specimens stored in water without trimming afterwards show similar shear strength independent of elapsed time, which is totally different from the values of shear strength obtained with trimmed specimens. These tests show that silica sol specimens immersed in water during storage should be trimmed before testing them to measure the actual strength within the silica sol since the muddy face has no implication in grouting applications, as is explained in Chapter 5.2. The results from untrimmed specimens are similar to the results obtained with fall-cone tests conducted in the muddy face.

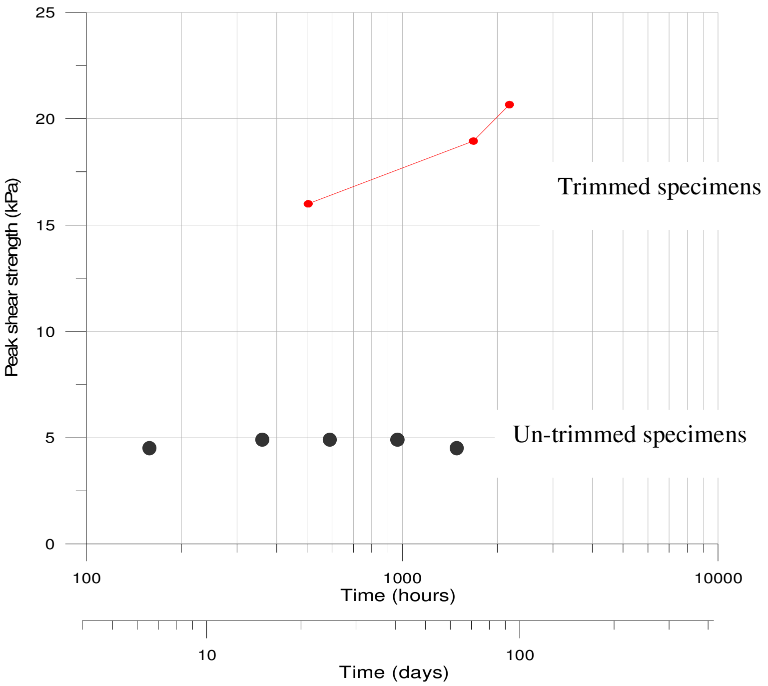


Figure 38. *Comparison of unconfined compression test results from silica sol specimens measured during ageing; trimmed and without trimming.*

Moreover, in the tests with the lowest confining radial pressures there was often a part in the triaxial tests where there was an increase in the strain without any increase in the shear stress at around 8-14 kPa. This can be seen in Appendix D. The ends of the specimens in the triaxial tests were not trimmed and this threshold stress can be compared to the failure stress in the unconfined compression tests on untrimmed specimens. The failure stresses in the latter tests are generally somewhat lower than the threshold stresses, but these tests are totally unconfined. Because of the confining stresses, this first yield in the softer zone did not lead to complete failure in the triaxial tests. Instead, after a certain extra deformation, the shear stress started to rise again until full strength of the silica sol was mobilised. At higher confining pressures, this process is generally not observed due to the specimens being even more constrained.

Measurements of the shear strength of silica sol shows that the strength increases during time for samples kept immersed in water, see Figure 39. A comparison of the results shows the same general behaviour during ageing, which confirms the findings and indicates a good correlation of the various tests.

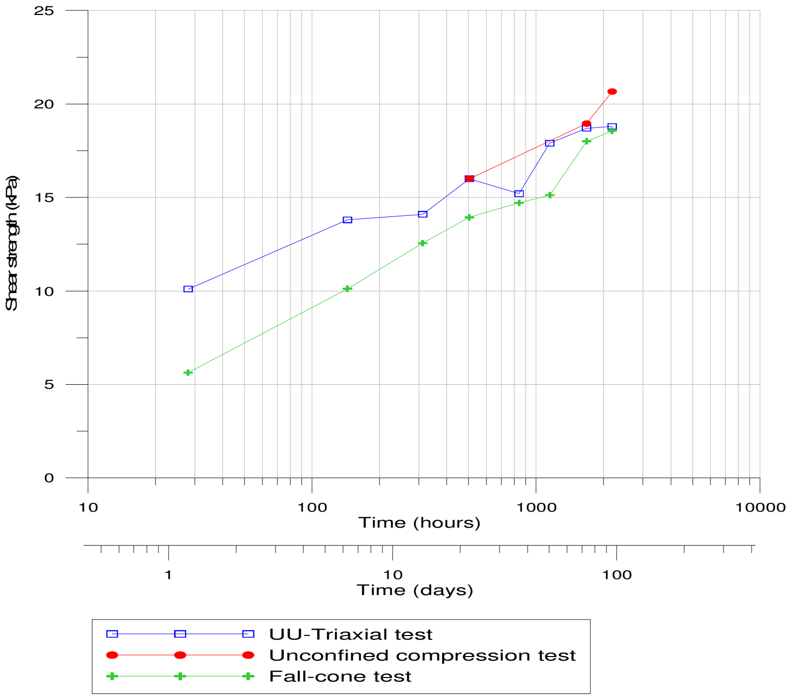
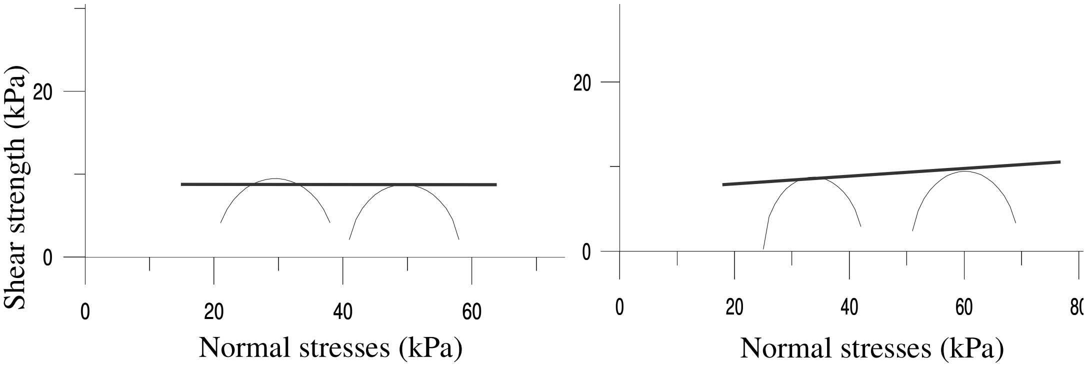


Figure 39. *Comparison of shear strength-time curves for silica sol specimens measured with fall-cone, unconsolidated undrained triaxial and unconfined compression tests. All specimens have been stored immersed in water.*

The specimens tested in unconsolidated undrained triaxial tests were sheared to failure under different confining conditions (radial pressure, σ_3). Slow increase in peak shear strength related to the confining pressure was observed during the first 91 days after mixing, see appendix D. A Mohr-Coulomb presentation is shown in Figure 40 for the samples tested 70 and 91 days after mixing as examples. Due to the natural spread in test results, the failure lines fluctuated around the horizontal line, which means a perfect cohesive material with no friction angle value on the failure line, which is typical for saturated specimens in unconsolidated undrained triaxial tests. Although this fluctuation is normal; Figure 40b could indicate that silica sol starts to show frictional internal forces due to it shows a small inclination in the failure line with an angle of around 4 degrees. To determine whether this is a change in behaviour or just a fluctuation more tests has to be done.



(a) (b)

Figure 40. *Mohr-Coulomb diagrams for unconsolidated undrained triaxial test: (a) 70 days after mixing (b) 91 days after mixing.*

In Figure 41, all the measurements of the strength of silica sol are summarised. The measurements show that the strength of silica sol increases with time in all the tested environments. A comparison of the test results shows similar behaviour during ageing especially among unconfined compression and unconsolidated undrained triaxial tests, which confirms the previous findings and indicates a good correlation between these tests. As it was shown in previous reports by Butrón (2005), fall-cone tests show approximately the same results as long as the undrained shear strength is below about 40 kPa. The stress-strain behaviour was observed in the unconfined compression tests and the unconsolidated triaxial tests; in all tests the material behaved ductile during the first day(s) after mixing. After a longer hardening time the specimens showed brittle failures in the unconfined compression tests without external confining stresses. The unconsolidated undrained triaxial tests in specimens stored immersed in water showed that with a certain confining stress the deformation became elastic-plastic after the initial hardening stage. However, the corresponding tests on specimen stored in pH11 and TDS solutions indicate brittle failures before 35 days after mixing, after failure, a residual strength corresponding to 50% of the peak strength remained and the specimens behaved plastic at further deformations, see appendix D.

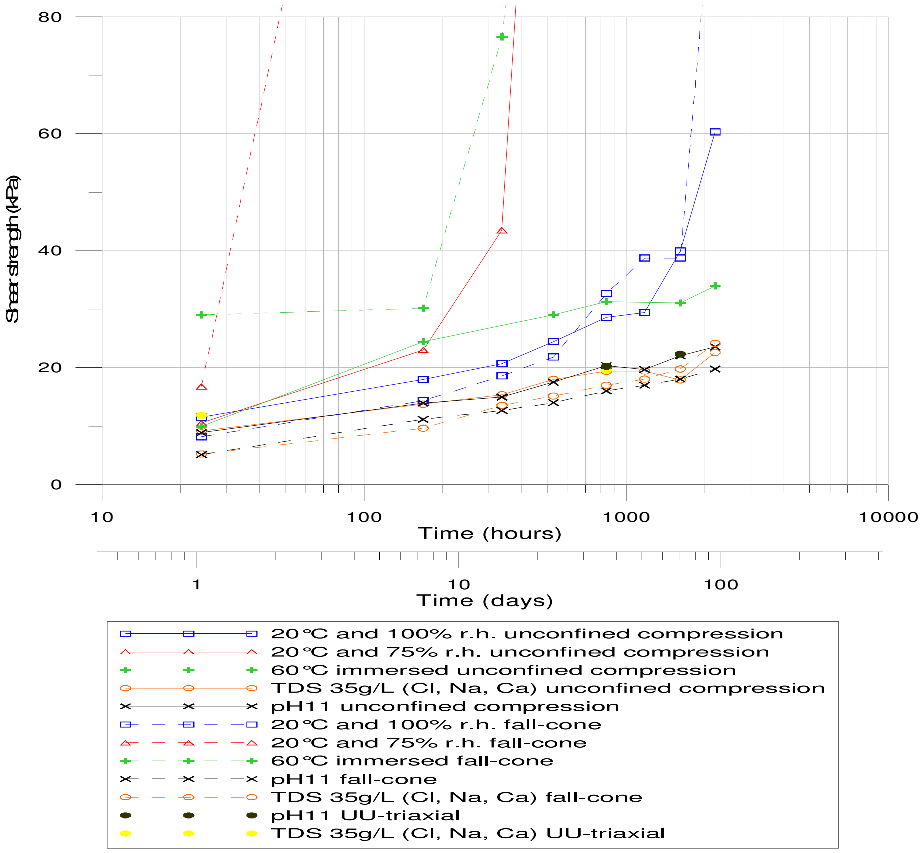


Figure 41. *Comparison of shear strength-time curves for silica sol specimens measured with fall-cone, unconsolidated undrained triaxial and unconfined compression tests.*

Figure 42, shows that most of the compression at consolidation takes place at low effective stresses. At a vertical stress of 100 kPa, 25% of the sample is compressed whereas it takes about 1400 kPa to compress the sample by 50%, see Figure 24a. The CRS tests show similar results during the first 13 days of hardening. Results from the tests 29 days and more after mixing show that a higher stress is needed to compress the specimens, which imply that the molecule bonds are getting stronger. Still, a preconsolidation pressure is not apparent. Figure 42 also shows a typical curve for a preconsolidated soil from which the preconsolidation pressure can be evaluated (a typical clay CRS test result). The results of tests on silica sol stored under water without external stresses do not show this pattern at first loading, and thus no apparent quasi-preconsolidation pressure is created by chemical bonds.

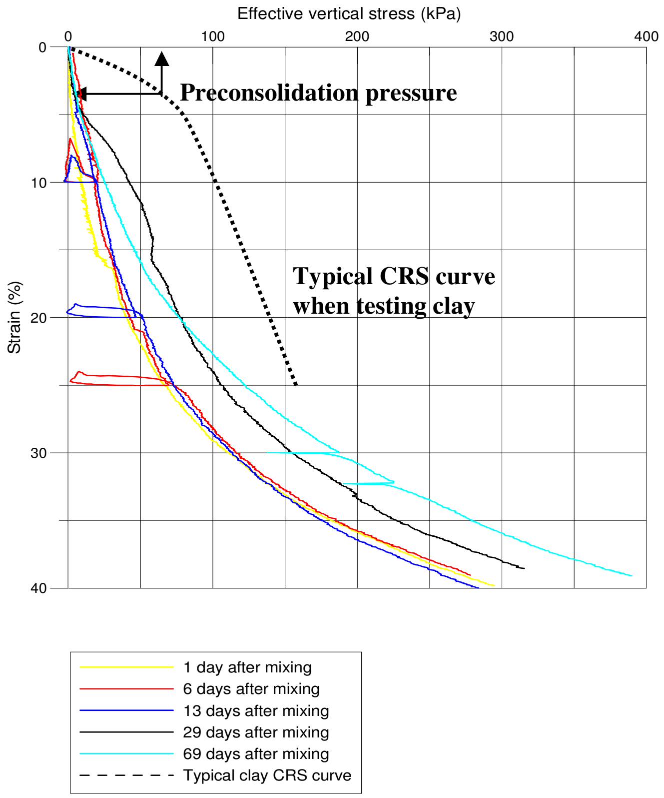


Figure 42. *Results from CRS oedometer test performed five occasions during two months.*

Figure 43 shows the results of two tests with unloading-reloading cycles, one performed 6 days after mixing and the other 13 days after mixing. In both cases the patterns are similar although the reloading was done at different times after mixing. The results show that silica sol specimens swell at unloading but this swelling appears to become smaller as the compression of the specimen increases, which could indicate that the molecules are somehow reorganized and that the elastic strains are not completely reversible as time continues. The reloading of the specimens gave curves showing clear preconsolidation effects with preconsolidation pressures corresponding to the maximum previous effective vertical stresses. Consolidation of silica sol for effective stresses thus results in the same preconsolidation effects as in similar types of materials, e.g. clays. A corresponding pattern can be seen if pore pressure is plotted against strain, see Figure 43. The pore pressure transducer placed at the bottom of the apparatus registered high values at compression of the specimens, which implies that silica sol has low permeability. This is corroborated by the low hydraulic conductivity evaluated from the CRS tests, see Figure 25. The hydraulic conductivity decreases continuously with compression since the pores and the pore volume become smaller. For most of the test, a range can be observed with values between 10^{-10} and 10^{-11} m/s.

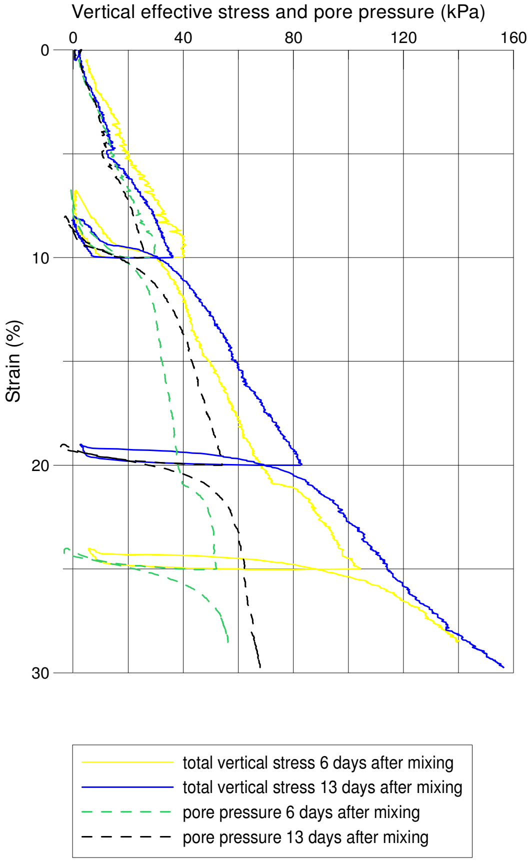


Figure 43. *Results from CRS tests with unloading-reloading cycles*

The specimens in the consolidated undrained triaxial tests were consolidated for the effective stresses shown in Table 2. This resulted in axial and volumetric compressions of the specimens during the consolidation phase. Low rates of loading are applied to silica sol in these tests.

Table 2. *Effective stresses used for the consolidation process and deformation obtained during this stage.*

Test conducted after hardening time (days)	Effective stress σ_1 (kPa)	Effective stress σ_3 (kPa)	Axial deformation (%)
1	13	2	12
6	20	10	10
13	20	2	12
29	20	5	2,7
64	13	2,5	2

The consolidation process generally took about a week, whereupon the undrained shear phase started. The total time for the test was around 10 days. This testing period could have an influence on the test results and the evaluated strength increases with time. About 10 days should therefore be added in a more rigorous analysis of the results. However, no such addition of time has been made in this report.

Figure 44 shows the results of a test conducted on a silica sol specimen 64 days after mixing. Three points on the shear stress-strain curve are identified. The curve starts where the consolidation process was finished, at effective stresses σ_1=13 kPa and σ_3=2,5 kPa and 2% of deformation, see also Table 3. Up to point A the axial strain is small and roughly elastic. Between points A and B there is a transition from small elastic deformations to larger plastic strains. In this zone, the pore pressure stops to increase. After a large plastic deformation Point C is reached. Here the specimen fails and the peak shear stress is obtained. This behaviour was observed for specimens tested 29 and 64 days after mixing. Tests conducted on silica sol specimens 1, 6, and 13 days after mixing did not yield a peak shear stress within the test limits and the specimens appeared to be able to withstand higher shear stresses before failing. However, the limit of the apparatus in terms of maximum compression was reached in these tests and the latter point C was thus not observed. The results, Appendix E, indicate that the effect on the strength of the larger initial compression during consolidation for the "youngest" specimens compensates for or even exceeds the effect of the longer hardening times for the "older" ones. A possible explanation is that "young" silica sols with just cohesive forces acting let silica restructure and withstand more force as the loading continues.

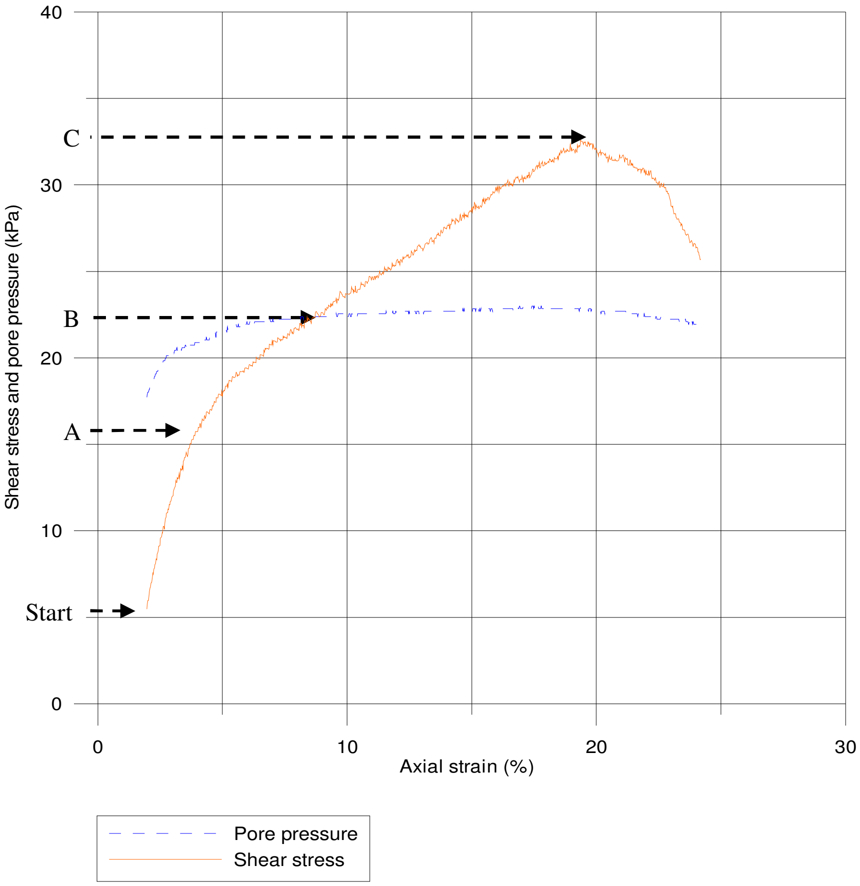


Figure 44. Results from a consolidated undrained triaxial test.

5.1.2. Continuous water loss measurement test

In Figure 45 the loss of water by weight is plotted against time in a log-log graph. The first set of data shows a lot of scatter during the first 10 hours due to the logarithmic scale on the weight loss axis. As described in chapter 3.3, water is assumed to be released from silica sol during ageing both by evaporation and diffusion. In the tests, just one surface was in contact with the surrounding environment. The first stage of the shrinkage process seems to be related to a diffusion process. de Groot and ven der Sloot, (1992) showed that when water release is related to a diffusion process it can be described by a plot with slope 1:2 drawn against time in a log-log diagram, such as that in Figure 45,. In this phase, silica sol specimens release water to the surrounding environment until the diffusion process has continued through the whole length of the specimen.

Three to four days after mixing, a second phase seems to have started independent of the environment. Water is then released by evaporation and whole volume diffusion, where the transport of water consists of flow through the specimen towards the free surface. In this phase, the water-air interaction takes place inwards the silica sol specimen from the surface and this phase is where most of the decrease in volume occurs. The decrease in volume (or shrinkage) will cause cracks to appear if a large and fast shrinkage occurs (high temperature and/or low humidity). This phenomenon was observed in other tests where a larger surface was exposed to an environment with 20°C and 30% relative humidity. The water released during the first and second phases constitutes the bulk water present in silica sol that is not bound to the silica sol particles and is free to move due to hydrodynamic pressure forces. The total amount of water in the mixture of SiO_2 plus $CaCl_2$ is around 68% by weight.

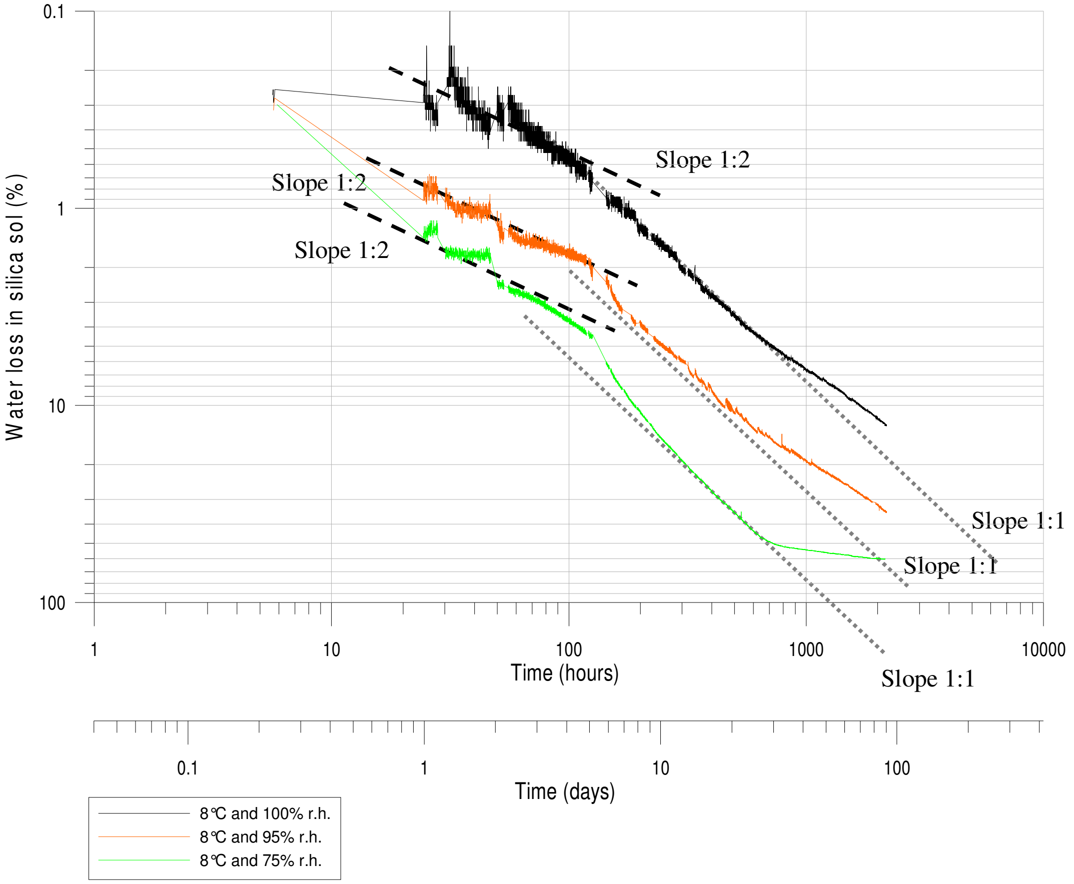


Figure 45. *Results of continuous weighing/drying of silica sol.*

The last phase, which could be observed in the specimen kept at 8°C and 75% relative humidity, occurred one month after mixing and the release-rate then appeared to be slower than a diffusion process. The previous figure, Figure 45, indicates that the remaining pore water in this stage constitutes a small percentage of the total amount of water present in the silica sol (18% of the total weight). At the stage where the curve turns off, the specimen has lost about 50% of its total weight. Assuming that the specimen has remained almost saturated up to this point, this means that about 75% of the original water has left the specimen and the specimen has been compressed by about 60% of its original volume. A further compression of the soil skeleton is hardly possible, (compare the results of the CRS tests in Figure 24a) and the specimen volume has reached its shrinkage limit. A further reduction of the weight by loss of water must then be associated with a replacement of the water in the pores by air, which would imply the start of a different process. At the end of the test almost 90% of the original water had been lost, which indicates that there should be a considerable amount of air in the pores. This final stage should continue until equilibrium is reached, determined by the ambient temperature and relative humidity in which the specimens are kept; faster for a specimen kept in a lower humidity and slower for a specimen kept in a higher humidity. No further change in weight is expected after this phase. There is still the possibility of water that is hard bounded to the silica sol that wont be released during the entire process due to it needs great temperatures in order to be mobilised.

5.1.3. Water loss measurements at varied humidity

In Figure 46 the loss of weight for all tests in this series is plotted against time in a log-log graph. As described in chapter 3.3, water is assumed to be released from silica sol during ageing by both evaporation and diffusion. The results of the tests in this study show a water release to the surrounding environment at a rate that was faster than diffusion when the specimens were kept in an environment with 75% relative humidity, (plotted slope of approximately 1:1). A description of the different phases in the release of water from silica sol is given in previous chapters.

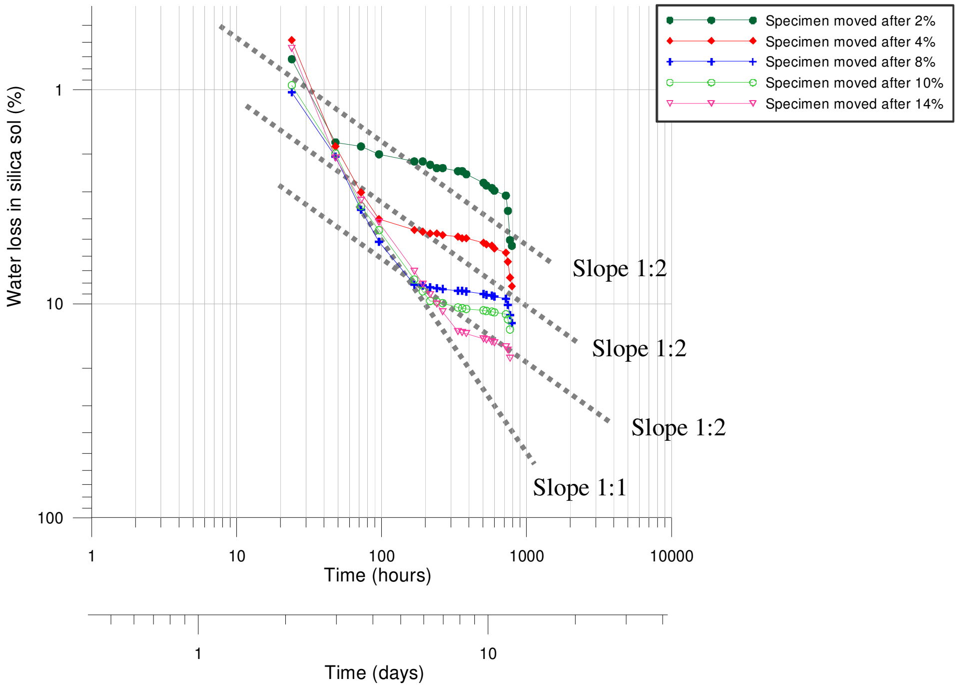


Figure 46. *Plot of weight loss measurements in a log-log diagram.*

Figure 46 also shows that when the specimens were moved to an environment with higher humidity, the resulting inclination of the plotted line is less than a slope of 1:2. The release of water thereby appeared to go on at a rate that was slower than diffusion. This was observed for all test specimens moved at different weight loss stages. When the specimens were moved back to 75% relative humidity, the water release became faster again corroborating the general finding that silica sol releases water to the surrounding environment at a faster rate when the humidity decreases. It is expected that once silica sol is immersed in water, the shrinkage process will end. The low rate of water release after moving the specimens to a high humidity could be seen as an indication of this. However, the results showed that the loss of water continues during ageing if silica sol is not immersed in water, at least within the ranges of relative shrinkage and humidity tested. A test series including specimens immersed in water was not possible to perform since the accuracy of the measurements was expected to be too low and some problems were likely to occur at handling of the specimens, for instance partial drying and detaching of silica sol pieces from the muddy face.

5.1.4. Drying-out tests between transparent plates

As previously described, these tests were done with silica sol grouted between plates with one face in contact with water and the other one in contact with room-air (around 22°C and 30% of r.h.). In Figure 47 the same results as those presented in Figure 31 are plotted in a log-log graph. The results obtained concerning the movement of the water-contact face indicate a diffusion process (slope 1:2 in the graph). At this face, water is transported into the silica sol by diffusion through the whole length of the specimen until it reaches the air-contact face, as was observed during the progress of these tests. The movement of the air-contact face shows a different behaviour, previously explained on earlier reports, which is faster at the beginning and slower at the end.

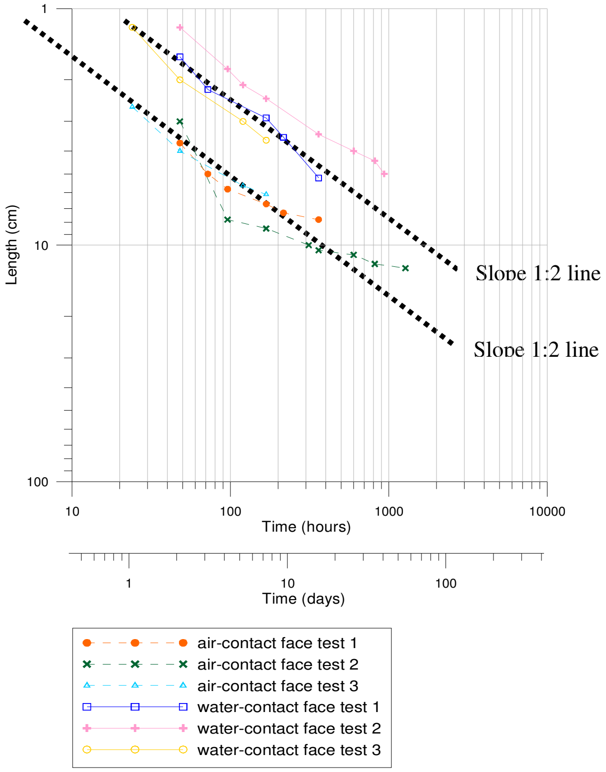


Figure 47. *Comparison of the results from the first three drying-out tests of silica sol.*

It was observed during the tests that once the diffused water got in contact with the air-contact face, the shrinkage stopped. However, no water leakage was observed and the test continued uninterrupted for another month to study a possible breakthrough and measure the resulting flow, but no flow occurred. The whole process can be explained as a diffusion of water molecules through silica sol from a higher concentration to a lower concentration keeping the silica sol intact without any further shrinkage once equilibrium is reached. Probably, the partially dried silica sol is "thirsty", which implies that the diffused water is incorporated in the silica sol and hence no leakage occurs.

5.1.5. Diffusion of chlorides from silica sol

The release of chlorides from silica by diffusion was initially studied with both one and two exposed surfaces at the laboratory work. The tests showed similar results and repeatability for each type of configuration (one or two exposed surfaces) suggesting that the following test should be performed with one exposed surface, due to more stable release and lower concentration of ions.

Tests were performed to measure the release of chlorides from silica sol samples in three different environments, 8°C and immersed in water, 20°C and immersed in water and 40°C and immersed in water. This was done in order to determine how the concentration and diffusivity is influenced by the temperature. Unfortunately, the values in 8°C and 40°C drifted too much from the estimated chloride concentration to be reliable. The main reason is probably the temperature effect on the used electrode, which was calibrated at room temperature.

The obtained value at 20°C should be regarded as an assessment of the diffusion and not an exact value. However, it is still a valuable parameter that can be used to estimate the rate of the chloride release to the surrounding water and its concentrations. Since the diffusivity of chlorides is very similar to that of water, it can also be used to predict the necessary time for water to diffuse through silica sol over a specific distance.

5.2. Field application

Observations on silica sol specimens during ageing show that silica sol shrinks when the humidity is below 100%. It is also shown that no shrinkage occurs when the specimens are kept immersed in water. Relating this to the application of silica sol as a grout, it is likely that water is present at least on one side when silica sol is grouted in rock in order to prevent a water leakage. In the tests, it was also shown that an environment with higher temperature, pH-value up to 11 or addition of ions did not destroy the silica sol.

The tests with transparent plates were performed in order to simulate a real grouting situation. Silica sol is then exposed to water pressure on one side and to air on the other. In Figure 48 the processes in this test are shown schematically. If silica sol is stored in an environment with humidity lower than 100%, shrinkage will occur. The shrinkage was recorded as loss of weight with time in previous tests. A change in volume was observed at the same time, which is an indication that there is then a re-organization of the silica sol skeleton during ageing. On the other hand, if silica sol is surrounded by water no shrinkage and therefore no re-organization of the skeleton will occur.

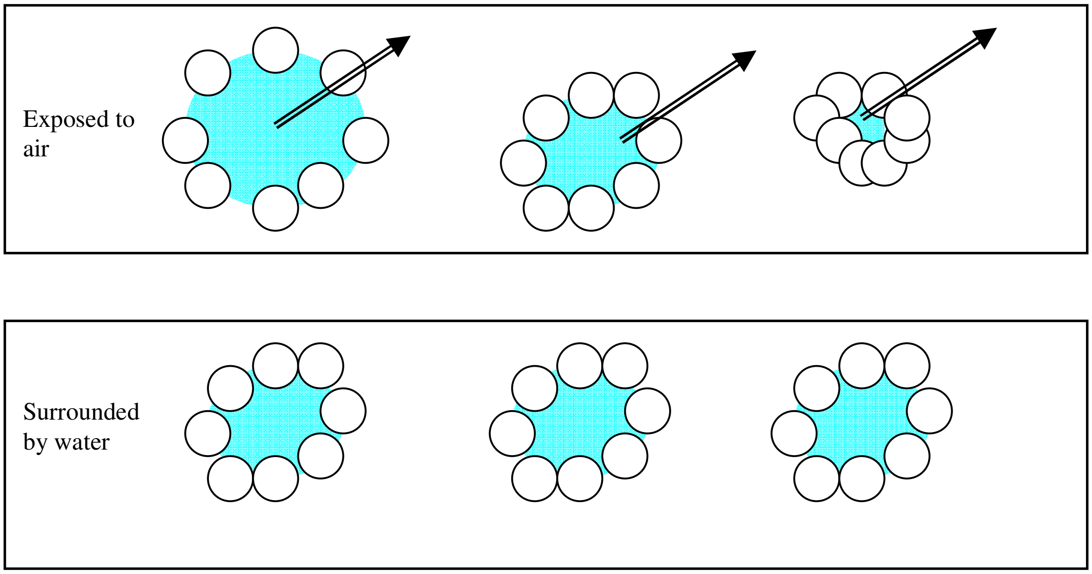
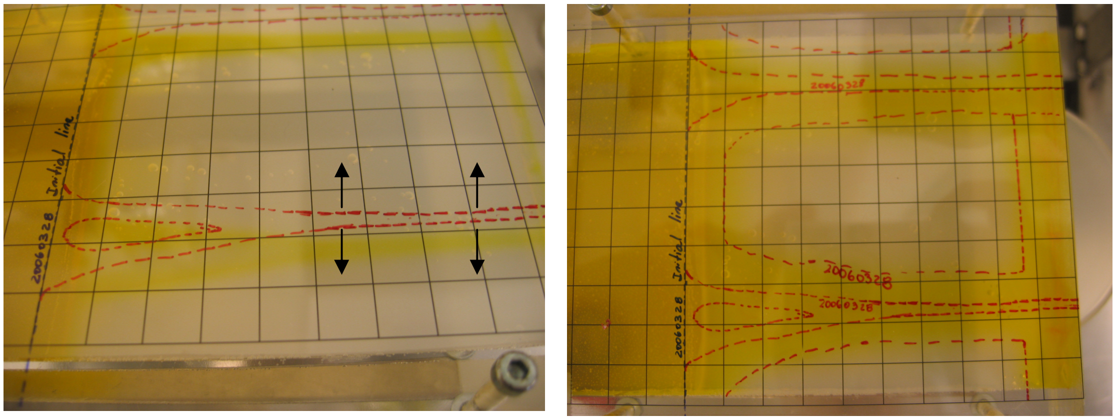


Figure 48. *Schematics of ageing process of silica sol. A possible physical process is drawn where the influence of surrounding environment can be seen. The arrow denotes the release from water to the surrounding*

In earlier studies by Axelsson (2004), it was shown that the flow of water was reduced over time when a rock core grouted with silica sol had water on one side and air on the other, as in the transparent plate test with an initial water breakthrough. The latter tests showed a decrease of the water flow over time until it finally stopped, corroborating the earlier findings. Figures 49a and 49b show the development of the breakthrough channels during the test generated by unfilled spaces during grouting of the transparent plates. In Figure 49a two channels are observed, which are the flow paths for water. Figure 49b shows that water diffused into the silica sol over time along the channels whereby the flow decreased. From the other test results, it is concluded that if shrinkage occurs at the silica sol surface that is directed towards the tunnel, it can proceed until it comes in contact with the front of the water diffusing through the silica sol from the other side in contact with free water in the rock mass. The silica sol that has shrunk will then appear “thirsty” and absorb the further diffusing water. This means that the shrinkage will stop and that there is very low risk of a complete breakthrough of water through a silica sol grouted fracture below the groundwater table.

Taking into account that the diffusion velocity is constant, and that, due to the smaller contact area, the air-contact front movement is slower in a rock fracture than in the drying-out tests between transparent plates; it can be expected that the two fronts will meet quite near the surface in a tunnel environment.



(a) (b)

Figure 49. *Picture taken from a breakthrough test which shows the paths formed and the diffusion of water into grouted silica sol alongside the water channels.*

The mechanical behaviour of silica sol was studied by means of fall-cone, unconsolidated undrained triaxial and unconfined compression tests. In a fully grouted fracture, the conditions will be similar to those in the triaxial test. On the other hand, on the grouting front edge the grout will not be as confined and hence it is useful to also perform tests with different stress conditions. From all test results it is indicated that the shear strength and strain at failure vary with time. The initial strength shortly after gelling is a few kPa and the shear strength then increases with time, whereas the strain at failure tends to decrease with time. This development is faster at high temperatures and low humidity.

In all the tested environments, silica sol at first exhibits ductile behaviour with large strains before failure occurs. Within a few days the behaviour changes to become elastic-plastic in triaxial tests with confining stresses, which are assumed to simulate the field conditions. This means that the behaviour will be ductile during the time that silica sol grouted fractures will normally be exposed to blasting vibrations. This characteristic combined with the above stated ability to absorb water means that there should be little risk of a properly performed silica sol grouting to fail as grout during construction because of its mechanical properties.

The above observation of elastic-plastic behaviour is valid for silica sol stored immersed in regular water. Silica sol that has hardened in a non-normal environment with a pH11 and TDS solutions showed brittle failures in the unconsolidated undrained triaxial tests somewhere before 35 days after mixing. However, after the brittle failures the specimens showed plastic deformation again with remaining strengths of about 50% of the peak strength.

Loading of silica sol to high strains indicates that the molecular structure of silica sol becomes reorganised. Under more “normal” deformations it seems like the silica sol structure behaves more or less elastic-plastic and becomes reshaped after unloading. This indicates that the behaviour is similar to clay, and the response to the initial load will lead to drainage of the pore water followed by an uptake of load by the silica skeleton. This theory is supported by the fact that the “youngest” samples in the consolidated undrained triaxial showed the largest consolidation strains and the highest undrained shear strengths thereafter.

At the surface that was in direct contact with water or pH11 solution, a “muddy” face was observed. The interaction of water lowered the strength of silica sol in this zone, which extended approximately 2 mm into the specimen. Since this zone is the weakest part of the material, concerns may be raised about the risk of erosion at the surface. Figures 35 and 36a show that also the strength in this zone increases with time, entailing that if the erosion forces are not strong enough at the beginning of the injection, silica sol will get strong enough with time to prevent any possible erosion in this zone. A specimen immersed in water during two weeks which presented a "muddy face" was cut in half and immersed once again to see if this "muddy face" would reappear, but this was not observed. This means that the rest of the silica sol presents higher strength values.

Relating the diffusion test to a real rock fracture implies that a lot of assumptions have to be made. Important conditions are the surface of silica sol in contact with water as well as the water flow (renewal of water). However, using the findings in this report and extrapolating them to a fracture plane with a radial grout spread with a radius of 5 metres in a 50 μm wide fracture with almost non-moving water, the release of chlorides would take around a month. However, the rate would be faster in the beginning and a considerable portion would be released during the first weeks. If the water is flowing around the grouted zone the process will be even faster.

6. CONCLUSIONS

The experimental study was performed in order to create a foundation for determining if silica sol is a proper material for grouting in hard rock. The study aimed at gaining knowledge of the mechanical properties of silica sol. Experiments were made on the strength development, response to external loading, shrinkage and drying-out behaviour, water transport mechanisms through silica sol and the release of chlorides. The findings from these experiments then have been interpreted with respect to the situation of a grouted fracture. Considering the strength, following conclusions can be made from the laboratory studies.

1. The strength of silica sol increases during ageing, the rate is depending on the storage environment. The tests showed that a faster shear strength increase takes place when silica sol is kept at high temperatures and/or low humidity.

2. A muddy layer, which has lower shear strength, initially around 2 kPa, is formed when silica sol is in direct contact with water or pH 11 solutions. This layer is about 2 mm thick and is formed due to the interaction between silica sol and water or pH11 solution. However, if the muddy phase is scratched off, a new muddy phase will not be formed.

3. The results indicate that silica sol behaves ductile with large strains before failure during the first day(s) after mixing. The stress-strain then changes with time to gradually smaller strains before yield, which for unconsolidated specimens corresponds to failure. The behaviour after the yield stress has been reached after the initial elastic behaviour depends on the boundary conditions in the loading case. Unconfined specimens fail in a brittle mode whereas specimens with sufficiently large confining stresses behave elastic-plastic (tunnel case). The elastic-plastic behaviour was observed for specimens immersed in water during the hardening process. Specimens stored in pH11 and TDS solutions were not destroyed by the medium and the strength increased as in samples immersed in water. They showed brittle failures also with lateral support whereby about 50% of the strength was abruptly lost somewhere before 35 days after mixing; the specimens then showed plastic deformation at further loadings with a remaining strength of about 50% of the peak strength.

4. Consolidated undrained triaxial tests conducted on silica sol specimens 1, 6, and 13 days after mixing did not present a peak shear stress within the testing range of the apparatus and the specimens appeared to withstand higher shear stresses than the specimens with longer hardening times before consolidation. Same tests conducted on specimens stored immersed in water during the hardening process also showed elastic-plastic stress-strain relations. In this case the yield did not correspond to a failure but the material behaved strain-hardening during the further plastic deformations. The failure strains in these tests were large and could in many cases not be observed due to limitations in the test equipment.

In order to link these findings regarding the strength development, to the use of silica sol as a grout in hard rock, some general statements can be made. The initial strength after mixing will soon be a few kPa and then increase, meaning that the strength will be sufficient to withstand most grouting conditions. The muddy zone at the surface of silica sol that is in contact with water will have a lower strength, and hence larger risk to be affected mechanically by for instance erosion. However, since this muddy zone does not seem to re-appear once silica sol has hardened, the influence in a grouted fracture will be insignificant. Silica sol will also show a plastic deformation during the first time after mixing, which implies that it is not very vulnerable to blasting vibrations.

The effect on the silica sol structure upon loading was investigated in the CRS and consolidated undrained triaxial tests (CU).

5. The CRS tests showed in principle a gradual hardening with time during ageing. None of the test results showed a typical S-shaped curve at first loading and for that reason a possible quasi preconsolidation pressure due to the chemical hardening process could not be evaluated.

6. Unloading-reloading cycles in CRS tests show that silica sol specimens swell somewhat at unloading. Preloaded specimens of silica sol show preconsolidation pressures corresponding to the effective preloading pressure at reloading.

7. The results of the CU triaxial tests indicate that a volumetric compression due to consolidation for confining effective stresses can have the same effect on the shear strength as a longer hardening time or sometimes even higher.

These findings imply that silica sol in general seems to behave as clay, at least initially. The initial load will lead to drainage of the pore water followed by an uptake of load by the silica skeleton. The response of silica sol is more or less elastic-plastic under confined conditions. In silica sol that has hardened for a longer time, the loading is taken up by a stiffer skeleton that yields at lower strains. Provided that the silica sol is sufficiently confined, it will then behave ductile. Silica sol in a fracture below the groundwater will thus generally be able to withstand loading and unloading cycles at fairly large deformations. Silica sol without confinement will not be as resistant to loading/reloading and is therefore subject to a risk of cracking.

The results of continuous water loss measurement tests and water loss tests with varied humidity showed good correlation and repeatability, thereby validating the used test methodology. The methodology assumes that the water loss from silica sol correlates to the shrinkage. As shown in earlier reports, the water loss rate depends on the surrounding environment. The results show a continuous decrease in water content at all times during a period of three months and a consistent trend if the specimens are not immersed in water. Silica sol specimens dried at an oven temperature of 105°C for two days showed an initial water content of 68% by total weight.

8. There is no observable shrinkage in silica sol specimens stored immersed in water or in environments with some solution providing a fully saturated environment.

9. The loss of water, and thereby shrinkage, with time is faster when the humidity is lower. Specimens kept at 8°C temperature and 75%, 95%, and 100% relative humidity had lost water corresponding to 60%, 35% and 14% of their total weight respectively in a period of three months.

10. Three phases were identified in the silica sol shrinkage process. The first stage of the process seems to be related to a diffusion process. The second phase started about one

week after mixing at the prevailing test conditions and the water is then assumed to be released by evaporation and whole volume diffusion processes. The third phase showed a release of water at a rate slower than evaporation or diffusion.

11. The water released during the first and second phases constitutes the bulk of the water present in silica sol that is not bound to silica sol particles and is free to move due to hydrodynamic pressure forces. Most of the shrinkage occurred in the second phase and it is faster for a specimen kept in a lower humidity and slower for a specimen kept in a higher humidity. The slower process during the third phase is assumed to be related to water that can not be removed without being replaced by air in the pores.

12. Increasing the humidity in the surrounding environment leads to a decrease in the drying out rate. However, the loss of water was not stopped completely within the ranges of relative shrinkage and humidity studied in the test series. Moving of the specimens from 75% to 100% relative humidity resulted in a water release at a rate that appeared to be lower than diffusion.

These findings imply that there will always be a risk of shrinkage if silica sol is not in contact with groundwater. However, the tests show that the shrinkage is governed by slow processes at high humidity and that a temporary drying out around the grouted fracture will give a temporary increased shrinkage but this process will slow down as the humidity increases. To test conditions similar to a real grouted fracture, experiments were done between transparent plates. The tests were conducted with water present at one side and air on the other side.

13. Water was transported through silica sol primarily by diffusion. The diffusion process combined through the whole length of the specimen until it reached the air-contact face approaching from the drying end of the specimen.

14. Shrinkage stopped once the air-contact face reached the front of diffused water through the grouted specimen.

From the CRS-tests it can be concluded that the hydraulic conductivity of silica sol is in the range between 10^{-10} and 10^{-11} m/s, which implies that silica sol is a low-permeable material. This is also supported by the visual observations that water was transported through silica sol primarily by diffusion.

The tests have shown that there are two processes acting; the diffusion of water from the “groundwater” side and the shrinkage of silica sol from the “tunnel” side. The results show that the shrinkage will stop as the air-contact face meets the diffusing front of water through silica sol. The part of silica sol that has shrunk will not be saturated and as it comes in contact with free water it will absorb this water. The rate of the shrinkage is depending on the exposed surface whereas the diffusion process is independent on the fracture width. Taking the fracture widths that are expected (tenths to hundred micrometers) into account, the shrinkage process will be considerable slower than the diffusion process. This implies that free diffused water will be available in silica sol already after a short shrinkage distance, stopping further shrinkage. This means that a complete breakthrough related to shrinkage is very unlikely in a fracture with groundwater on one side. This is also supported by the fact that although the tests between transparent plates were conducted at very low humidity (relative humidity around 20%) and fracture widths of centimetres, no breakthrough occurred or, when induced, stopped within a short time.

The gelling of silica sol is initiated by a salt solution that acts as a catalyst. In order to evaluate the release rate of the chlorides in the salt solution, measurements were performed on silica sol samples stored in milli-q water.

15. 10 days after mixing, the surrounding water reached a concentration of chloride ions of around 280 mg/l and 210 mg/l with specimens immersed in water with two and one open surfaces respectively. This means that almost all chlorides had been released from the specimens with two open surfaces whereas around 70% had been released from the specimens with one open surface.

16. Calculations of the diffusion coefficient for the chloride transport through silica sol yielded a value of $1 \cdot 10^{-9}$ m^2/s for a silica sol specimen stored immersed in water at 20°C with one open surface.

The results indicate that the release of chlorides from silica sol is a relatively fast process. In a fracture with flowing water around the grouted surface, the chlorides will be released within a time frame of a month.

As stated earlier, the influence of the surrounding environment is important for the strength increase and shrinkage rates. In Table 3 the influence of different surroundings are summarised.

Table 3. *Influence of different surroundings on the mechanical behaviour for silica sol. A slower rate is marked with - , whereas + means faster rate. A comparison made among all the tests.*

	Strength increase	**Shrinkage increase**	**Time to change from ductile to brittle**
Relative humidity, increase	-	-	-
Temperature, increase	+	+	+
Water at 8°C	-	none	-
Water at 60°C	+	none	+
pH up to 11	-	none	-
TDS of 35 g/L	-	none	-

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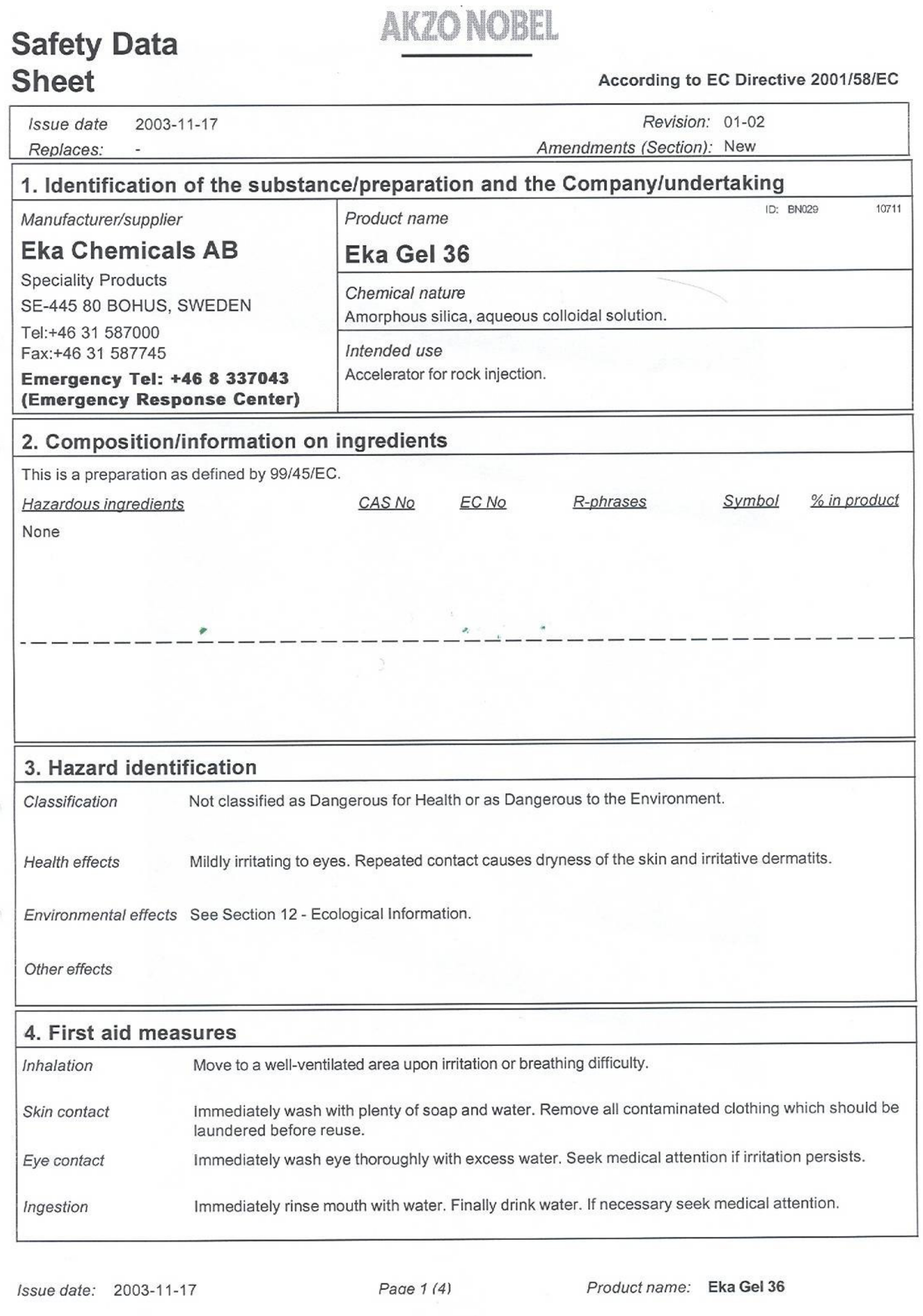
APPENDIX A – Silica sol's safety data sheet.



Safety Data Sheet

AKZO NOBEL

According to EC Directive 2001/58/EC

Issue date	2003-11-17	*Revision:*	01-02
Replaces:	-	*Amendments (Section):*	New

1. Identification of the substance/preparation and the Company/undertaking

Manufacturer/supplier

Eka Chemicals AB
Speciality Products
SE-445 80 BOHUS, SWEDEN
Tel:+46 31 587000
Fax:+46 31 587745
Emergency Tel: +46 8 337043
(Emergency Response Center)

Product name

ID: BN029 10711

Eka Gel 36

Chemical nature

Amorphous silica, aqueous colloidal solution.

Intended use

Accelerator for rock injection.

2. Composition/information on ingredients

This is a preparation as defined by 99/45/EC.

Hazardous ingredients	*CAS No*	*EC No*	*R-phrases*	*Symbol*	*% in product*
None					

3. Hazard identification

Classification	Not classified as Dangerous for Health or as Dangerous to the Environment.
Health effects	Mildly irritating to eyes. Repeated contact causes dryness of the skin and irritative dermatits.
Environmental effects	See Section 12 - Ecological Information.
Other effects	

4. First aid measures

Inhalation	Move to a well-ventilated area upon irritation or breathing difficulty.
Skin contact	Immediately wash with plenty of soap and water. Remove all contaminated clothing which should be laundered before reuse.
Eye contact	Immediately wash eye thoroughly with excess water. Seek medical attention if irritation persists.
Ingestion	Immediately rinse mouth with water. Finally drink water. If necessary seek medical attention.

Issue date: 2003-11-17 *Page 1 (4)* *Product name:* **Eka Gel 36**

AKZO NOBEL

Safety Data Sheet

According to EC Directive 2001/58/EC

5. Fire fighting measures

Extinguishing Media	Does not present a fire hazard.
Usuitable Ext.Media	Not applicable.
Special Protective Equipment	None.
Special Exposure Hazards	None.

6. Accidental release measures

Environmental Cleanup Procedures	Collect as much as possible in a clean container for (preferable) reuse or disposal.
Personal Protection	Goggles, rubber/PVC gloves and full working clothes recommended.

7. Handling and storage

Handling	Normal handling precautions applicable to industrial chemicals.
Storage	To maintain quality; storage temperature > 3°C.
Materials to avoid	No information available.

8. Exposure controls/personal protection

Respiratory protection	Good ventilation should be provided in working areas and a breathing mask is recommende if respirable aerosols or dust occurs.
Hand protection	Rubber/PVC gloves.
Eye protection	Goggles and eyewash station recommended.
Skin protection	Full working clothes recommended. Contaminated clothing should be laundered before re-use.
Air contamination limits	Silica - Amorphous: (ACGIH, TWA: 10 ppm inhalable particle, 3 ppm respirable particle) (MAK, TWA: 4 ppm inhalable particle), (HTP, TWA: 5 ppm)

AKZO NOBEL

Safety Data Sheet

According to EC Directive 2001/58/EC

9. Physical and chemical properties

(These values are typical for the product and should not be considered as a specification)

Form	Liquid	*Vapour pressure*	As water
Colour	Opalescent	*Density*	~1200 kg/m³
Odour	Slight odour.	*Bulk density*	Not applicable.
pH	10-11.4	*Solubility*	Miscible (water).
Melting/boiling points	MPt. 0°C, BPt. 100°C. (Approx.)		
Viscosity	<25 mPas (25°C)	*Partition coefficient octanol/water log Pow*	Not applicable - inorganic product.
Flash point	Not applicable.		
Autoinflammability	Not applicable	*Explosion properties- upper and lower limits*	Not applicable.

10. Stability and reactivity

Hazardous decomposition	None.
Condition to avoid	Frost may lead to container rupture and leakage.
Materials to avoid	None known.
Hazardous reactions	None.

11. Toxicological information

** Estimated from analogous products*

Acute toxicity	LD50 (oral rat) >2000 mg/kg.*
Health effects	
Inhalation	Dust from the dry product/spray may irritate the respiratory tract and cause symptoms of bronchitis.
Ingestion	May cause irritation to the mucous membranes of the mouth, throat and gastro-intestinal tract.
Skin contact	Repeated contact causes dryness of the skin and irritative dermatits.
Eye contact	Mildly irritating. (Rabbit)
Sensitisation data	Not a sensitizer. (Magnusson-Kligmann test)
Carcinogenicity - mutagenicity	No data available.
Subacute, subchronic, chronic effects	Product contains amorphous Silicon dioxide. No cases of Silicosis have been reported from amorphous silica.
Reproductive/ developmental effects.	-

AKZO NOBEL

Safety Data Sheet

According to EC Directive 2001/58/EC

12. Ecological information

** Estimated from analogous products*

Aquatic toxicity	Acute toxicity to fish:LC50 (Brachydanio rerio, 96hr) >5000 mg/l, Acute toxicity to water crustacea: EC50 (48hr, Ceriodaphnia) = 7600 mg/l Toxicity to water plants: (Selenastrum capricornutum) EC50 (48hr,Selenastrum capricornutum) = 440 mg/l, *
Persistence/degradability	Not applicable, product contains only inorganic component(s).
Bioaccumulative potential	Not expected to bioaccumulate.
Mobility	No test results. Transport to air is not expected. Under certain circumstances, transport from earth to water may take place.
Other effects	No information.

13. Disposal considerations

Product disposal	Obtain advice from local authorities.
Packaging disposal	As for product.

14. Transport information

Summary Not classified as Dangerous for Transport.

UN/ID No	-
Packaging group	
ADR/RID (Road/Rail)	-
IMDG (Sea)	-
IATA/ICAO (Air)	-

Proper shipping name

-

15. Regulatory information

R-phrases -

S-phrases -

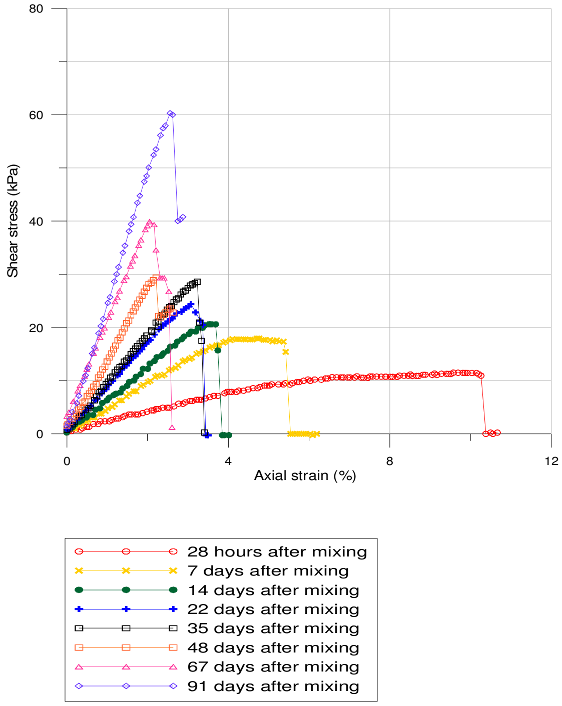
Symbols

16. Other information

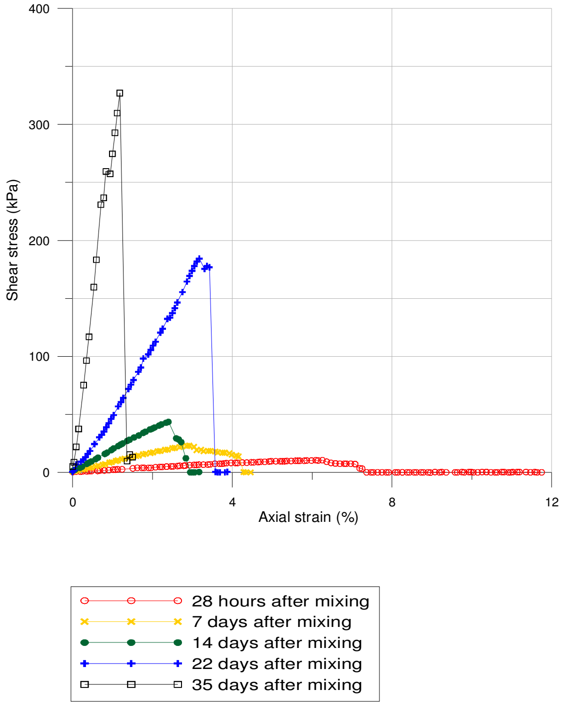
67/548/EEC, 99/45/EC, 2001/58/EC

Issued by: R&D *Print date:* 18-nov-03 *Approved by:* J.Murray

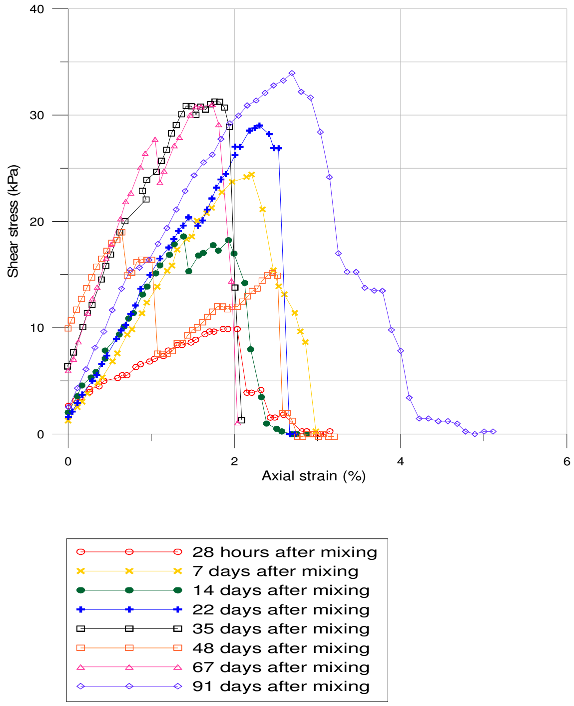
APPENDIX B – Unconfined compression test results for silica sol specimens stored in different environments.



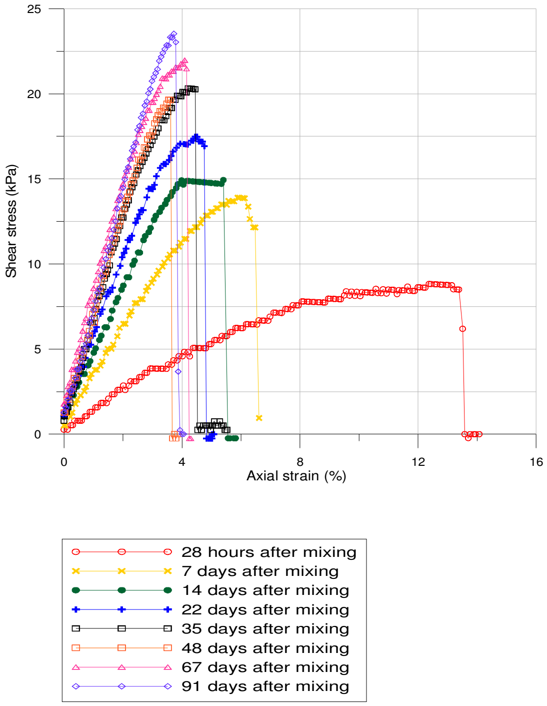
20°C and 100% r.h.



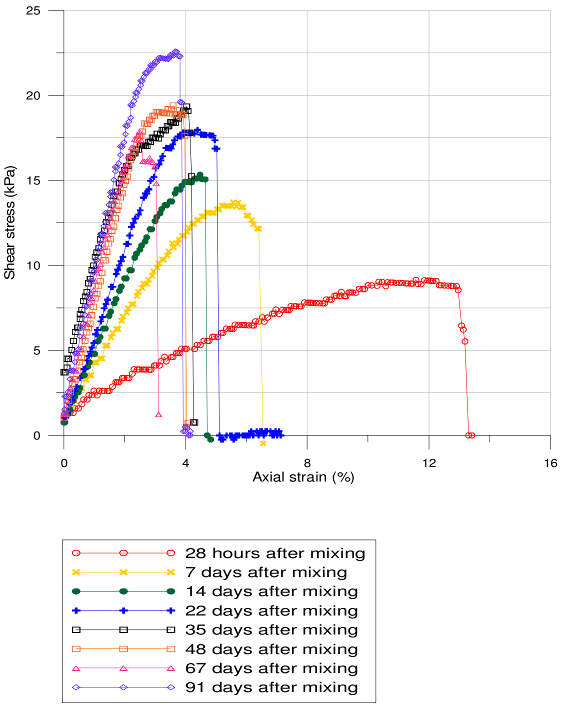
20°C and 75% r.h.



60°C immersed

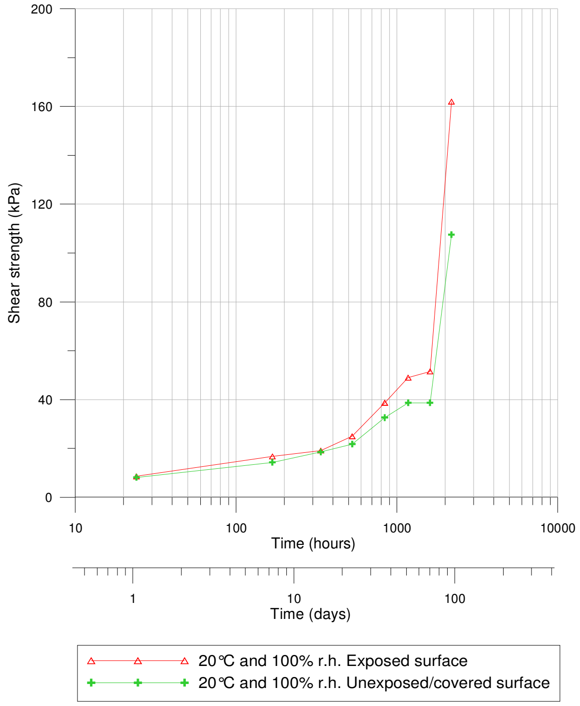


pH11 solution.

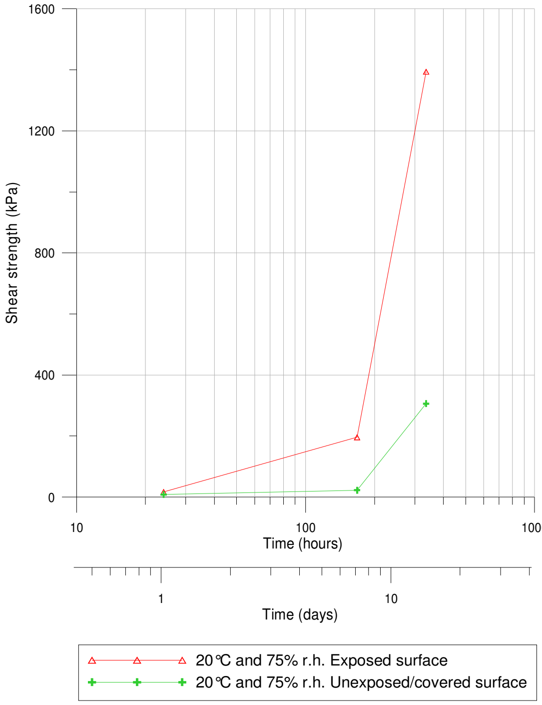


TDS 35g/L (Cl, Na, Ca) solution.

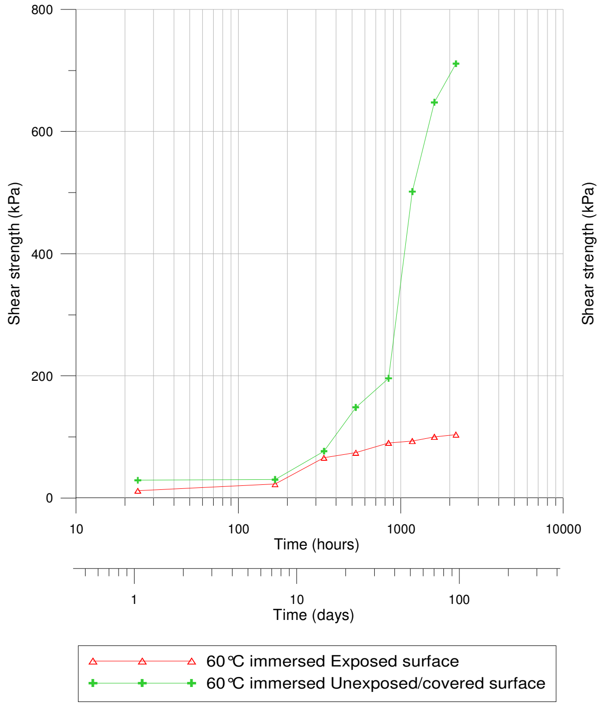
APPENDIX C – Fall-cone test results for silica sol specimens stored in different environments.



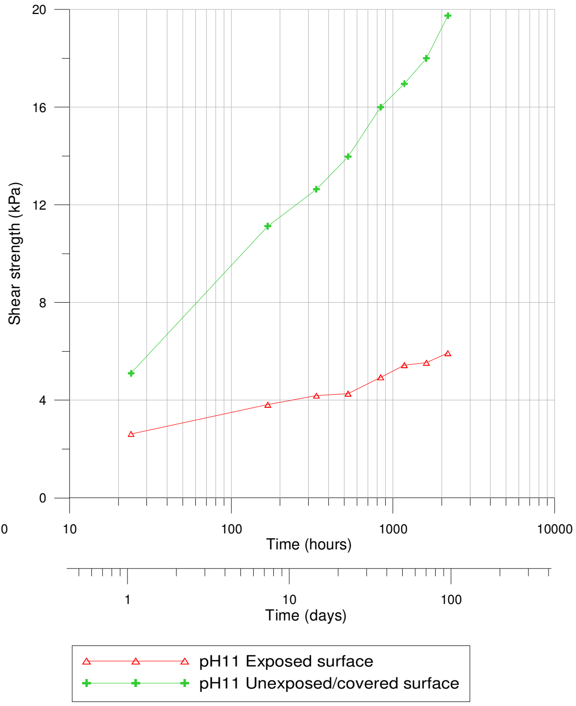
20°C and 100% r.h.



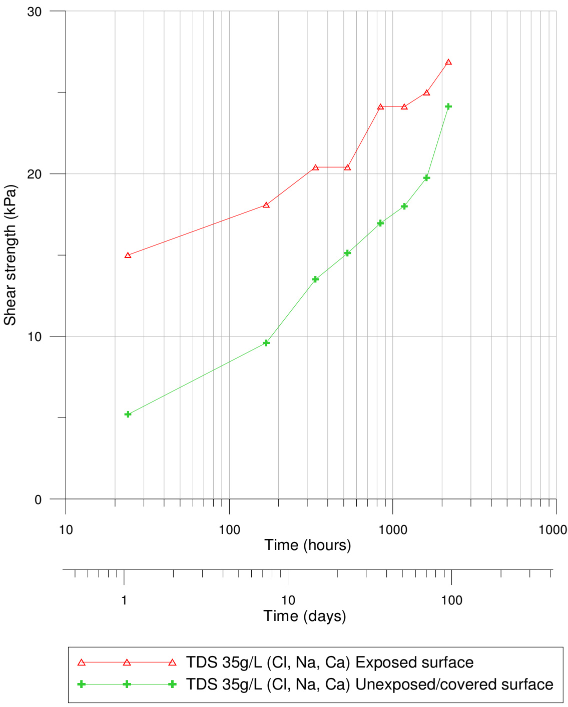
20°C and 75% r.h.



60°C immersed

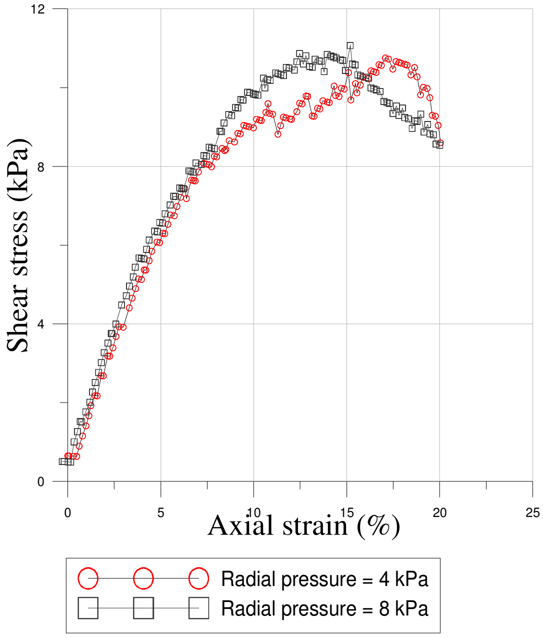


pH11 solution



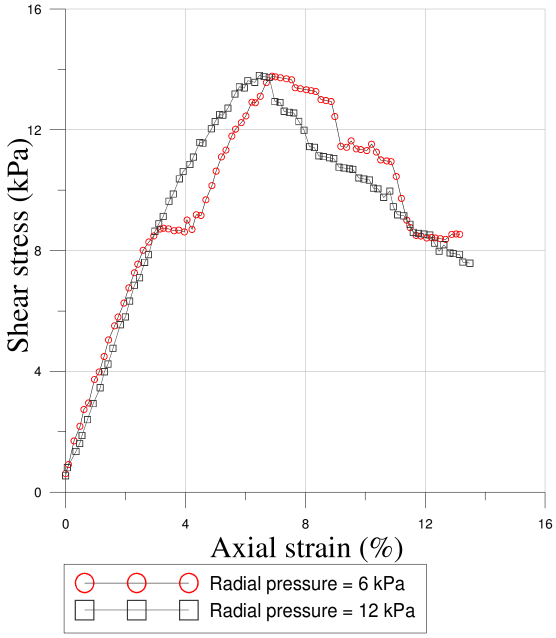
TDS 35 g/L (Cl, Na, Ca) solution

APPENDIX D – Unconsolidated undrained triaxial test results for silica sol specimens stored immersed in water.



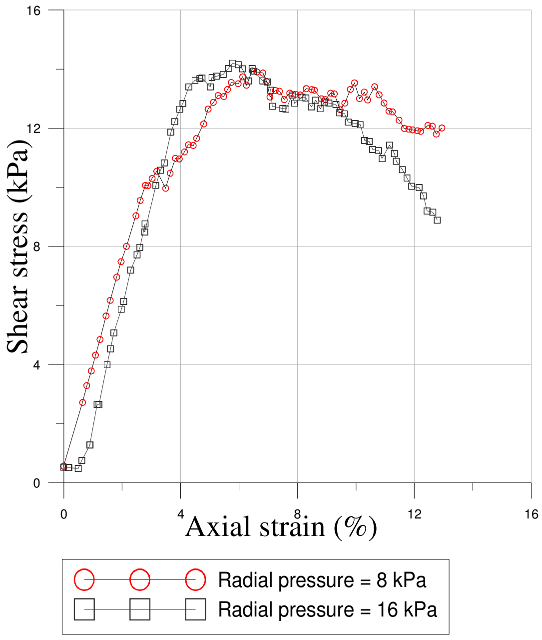
(a)

26 hours after mixing



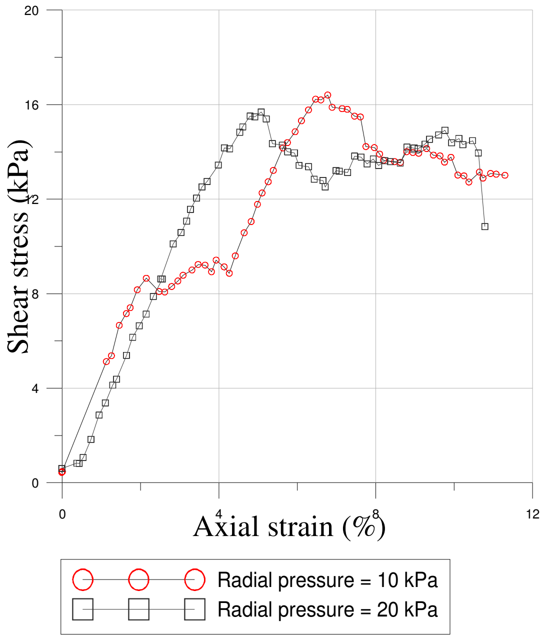
(b)

6 days after mixing.



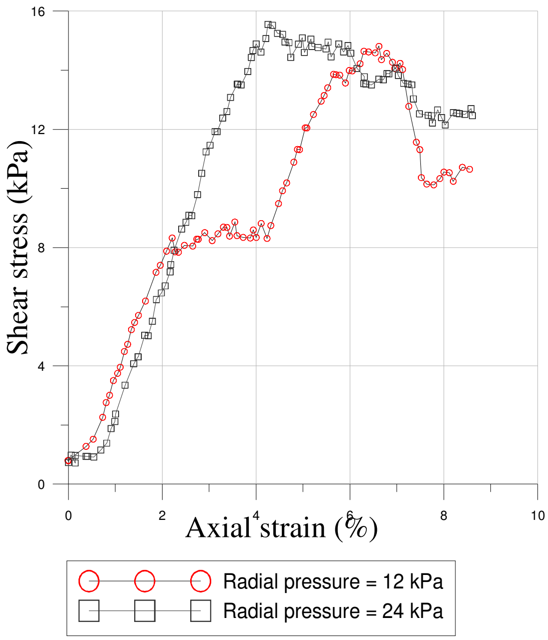
(a)

13 days after mixing

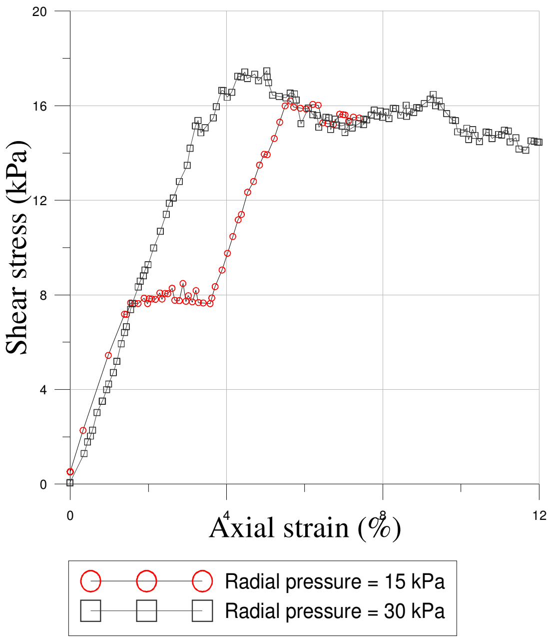


(b)

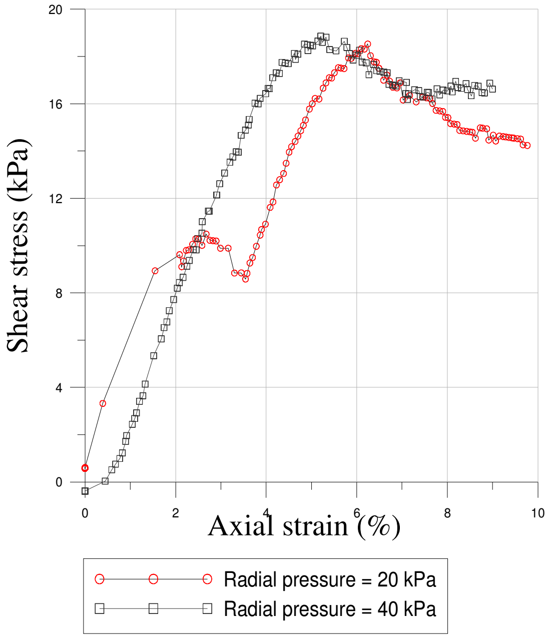
21 days after mixing.



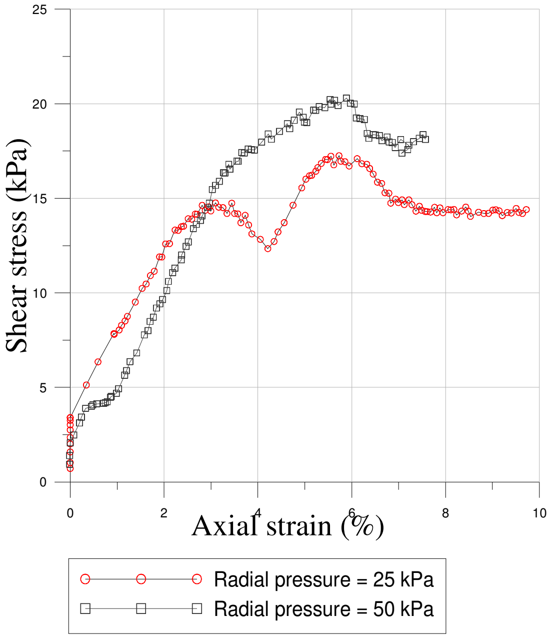
35 days after mixing



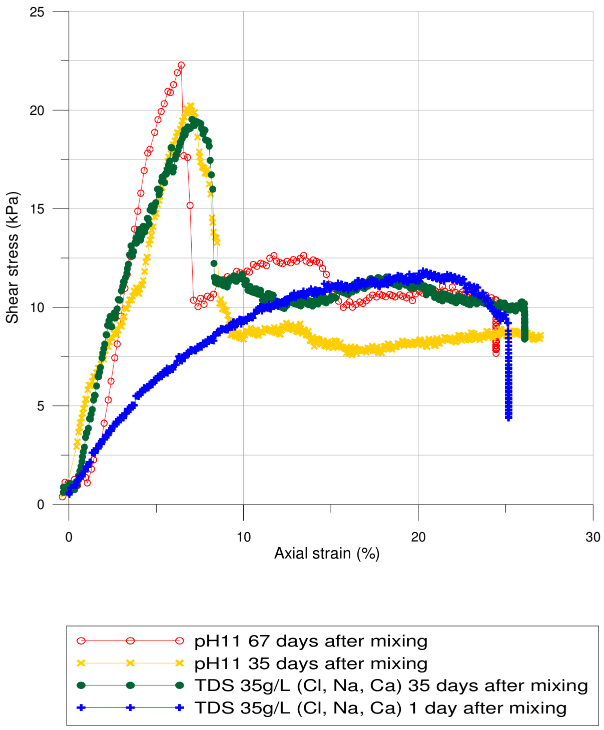
48 days after mixing.



70 days after mixin

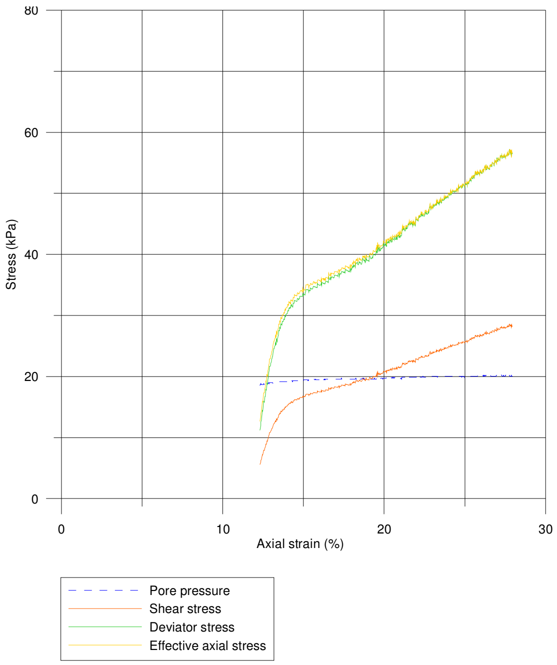


91 days after mixing.

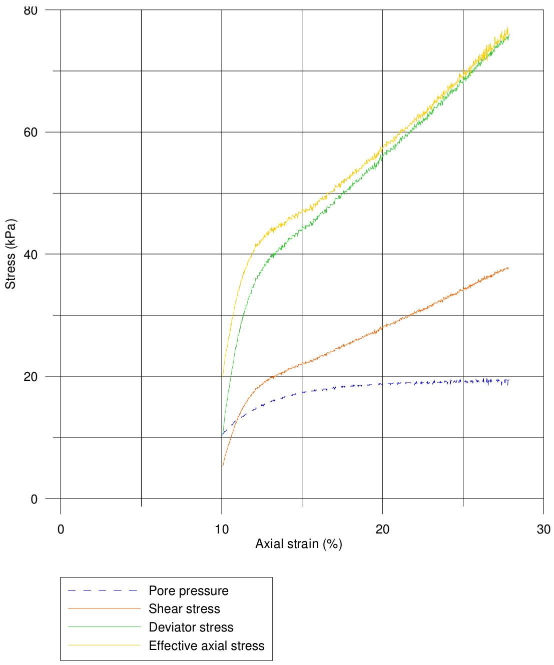


Specimens stored in a pH11 and a TDS 35 g/L (Cl, Na, Ca) solution

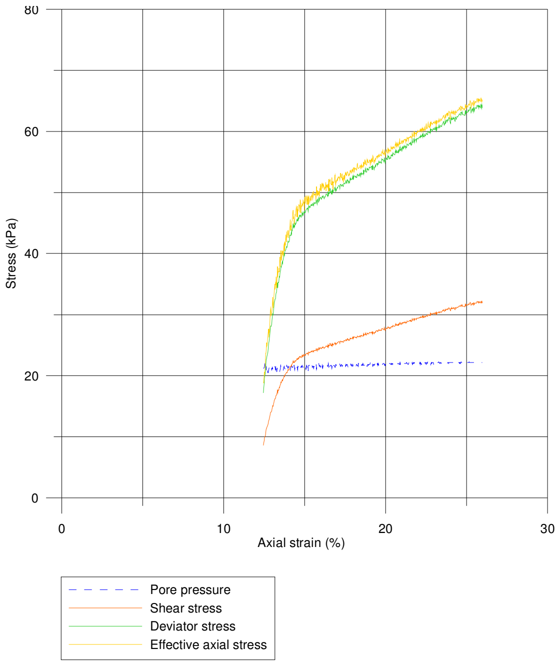
APPENDIX E – Results from consolidated undrained triaxial tests on silica sol specimens stored immersed in water.



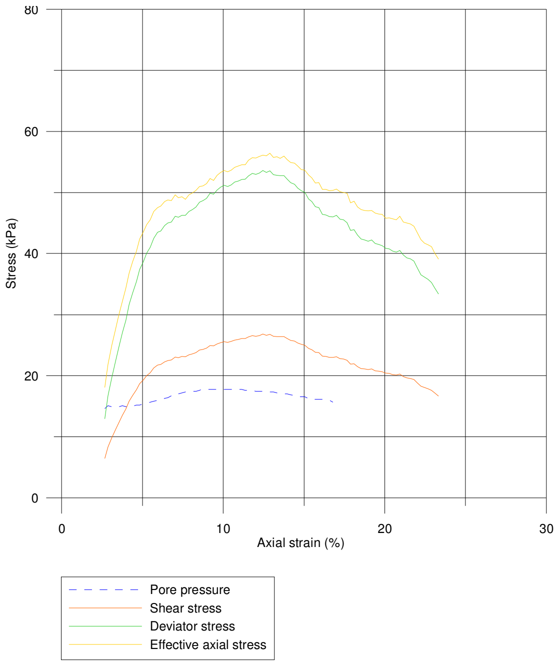
1 day after mixing



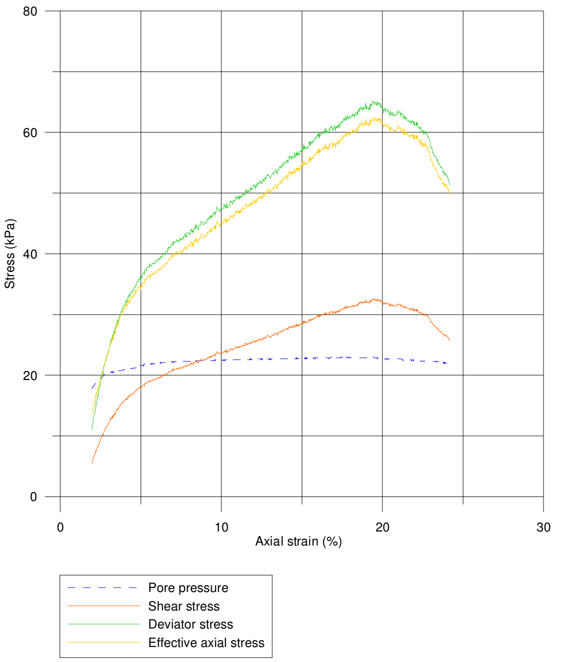
6 days after mixing.



13 day after mixing



29 days after mixing.



64 days after mixing.

APPENDIX F – Test results for Silica sol specimen moved from an environment of 75% relative humidity to an environment of 100% relative humidity after different percentages of weight loss.

All specimens tested were kept in boxes with an internal environment of 8°C and 75% or 100% relative humidity. The yellow colour in the tables designates that measurements were not made due to weekends and/or holidays. The following tests results correspond to silica sol specimens moved from an environment of 75% relative humidity to an environment of 100% relative humidity after different percentages of water (weight) loss.

Specimen No:	Time (hours)	Time (days)	W1 (g)	W2 (g)	W3 (g)	S (%)
41	24	1	55,8	180,7	179,8	0,72
	48	2			178,5	1,76
	72	3			178,4	1,84
	96	4			178,2	2,00
	120	5				
	144	6				
	168	7			178	2,16
	192	8			178	2,16
	216	9			177,9	2,24
	240	10			177,8	2,32
	264	11			177,8	2,32
	288	12				
	312	13				
	336	14			177,7	2,40
	360	15			177,7	2,40
	384	16			177,6	2,48
	408	17				
	432	18				
	456	19				
	480	20				
	504	21			177,3	2,72
	528	22			177,2	2,80
	552	23				
	576	24			177,1	2,88
	600	25			177	2,96
	624	26				
	648	27				
	672	28				
	696	29				
	720	30			176,8	3,12
	744	31			176,1	3,68
	768	32			174,4	5,04
	792	33			174	5,36
	816	34				
	840	35				
	864	36				

After 2% water (weight) loss

Specimen No:	Time (hours)	Time (days)	W1 (g)	W2 (g)	W3 (g)	S (%)
46	24	1	55,8	175,3	174,6	0,59
	48	2			173,1	1,84
	72	3			171,7	3,01
	96	4			170,5	4,02
	120	5				
	144	6				
	168	7			169,9	4,52
	192	8			169,8	4,60
	216	9			169,7	4,69
	240	10			169,7	4,69
	264	11			169,6	4,77
	288	12				
	312	13				
	336	14			169,5	4,85
	360	15			169,4	4,94
	384	16			169,4	4,94
	408	17				
	432	18				
	456	19				
	480	20				
	504	21			169,1	5,19
	528	22			169	5,27
	552	23				
	576	24			168,9	5,36
	600	25			168,7	5,52
	624	26				
	648	27				
	672	28				
	696	29				
	720	30			168,4	5,77
	744	31			167,7	6,36
	768	32			166,3	7,53
	792	33			165,4	8,28
	816	34				
	840	35				
	864	36				

After 4% water (weight) loss.

Specimen No:	Time (hours)	Time (days)	W1 (g)	W2 (g)	W3 (g)	S (%)
1	24	1	55,8	182,4	181,1	1,03
	48	2			179,8	2,05
	72	3			177,8	3,63
	96	4			175,9	5,13
	120	5				
	144	6				
	168	7			172,1	8,14
	192	8			172	8,21
	216	9			171,8	8,37
	240	10			171,7	8,45
	264	11			171,6	8,53
	288	12				
	312	13				
	336	14			171,4	8,69
	360	15			171,4	8,69
	384	16			171,3	8,77
	408	17				
	432	18				
	456	19				
	480	20				
	504	21			171	9,00
	528	22			170,9	9,08
	552	23				
	576	24			170,8	9,16
	600	25			170,7	9,24
	624	26				
	648	27				
	672	28				
	696	29				
	720	30			170,4	9,48
	744	31			169,6	10,11
	768	32			168,1	11,30
	792	33			166,8	12,32
	816	34				
	840	35				
	864	36				

After 8% water (weight) loss.

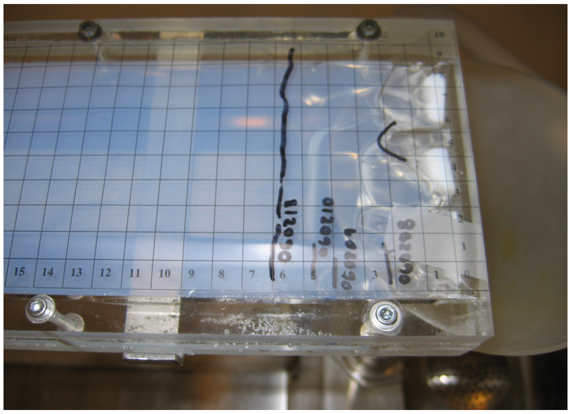
Specimen No:	Time (hours)	Time (days)	W1 (g)	W2 (g)	W3 (g)	S (%)
49	24	1	55,8	181,7	180,5	0,95
	48	2			179,2	1,99
	72	3			177,3	3,49
	96	4			176	4,53
	120	5				
	144	6				
	168	7			172	7,70
	192	8			170,7	8,74
	216	9			169,5	9,69
	240	10			169,4	9,77
	264	11			169,2	9,93
	288	12				
	312	13				
	336	14			168,6	10,41
	360	15			168,5	10,48
	384	16			168,4	10,56
	408	17				
	432	18				
	456	19				
	480	20				
	504	21			168,2	10,72
	528	22			168,1	10,80
	552	23				
	576	24			168	10,88
	600	25			167,9	10,96
	624	26				
	648	27				
	672	28				
	696	29				
	720	30			167,6	11,20
	744	31			166,8	11,83
	768	32			165,1	13,19
	792	33				
	816	34				
	840	35				
	864	36				

After 10% water (weight) loss.

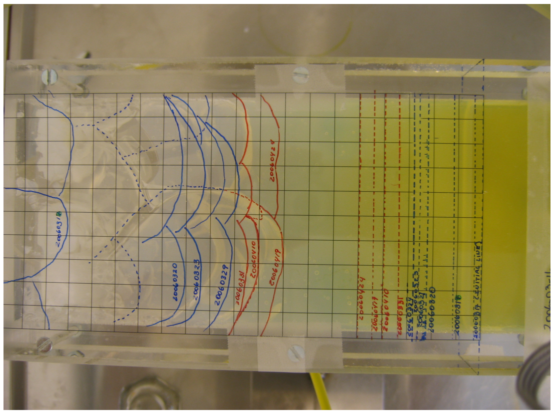
Specimen No:	Time (hours)	Time (days)	W1 (g)	W2 (g)	W3 (g)	S (%)
13	24	1	55,8	180,5	179,7	0,64
	48	2			177,9	2,09
	72	3			176,4	3,29
	96	4			175,3	4,17
	120	5				
	144	6				
	168	7			171,7	7,06
	192	8			170,4	8,10
	216	9			169,2	9,06
	240	10			168	10,02
	264	11			166,9	10,91
	288	12				
	312	13				
	336	14			163,7	13,47
	360	15			163,5	13,63
	384	16			163,3	13,79
	408	17				
	432	18				
	456	19				
	480	20				
	504	21			162,3	14,60
	528	22			162,1	14,76
	552	23				
	576	24			161,7	15,08
	600	25			161,5	15,24
	624	26				
	648	27				
	672	28				
	696	29				
	720	30			160,7	15,88
	744	31			160	16,44
	768	32			158,1	17,96
	792	33				
	816	34				
	840	35				
	864	36				

After 14% water (weight) loss.

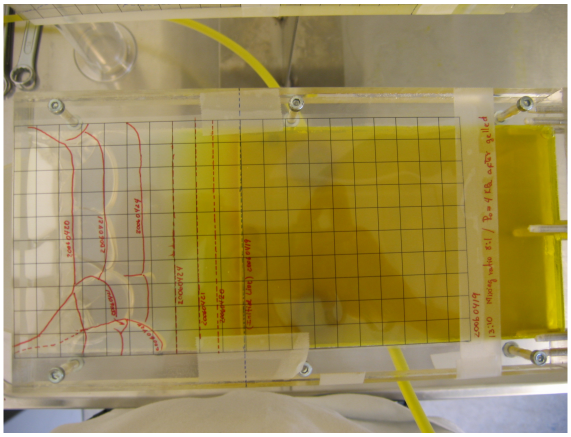
APPENDIX G – Measured movements of air-contact face and water-contact face at different times in drying-out tests between transparent plates.



Tests 1



Test 2



Test 3.

APPENDIX H – Tests results concerning the release of chlorides from silica sol to the surrounding “milli-q” water.

DIFFUSIVITY TEST 1

Mixing ratio 8:1
First test: Specimens 1 and 2 one free surface, specimens 3 and 4 two free surfaces

Gelling time: 1 hour and 10 min

Specimen no.	Time (days)	Time (hours)	Concentration of Cl (mg/l)
1		2	7,04
2		2	7,21
3		2	21
4		2	22,5
1	1	24	72,5
2	1	24	78
3	1	24	157
4	1	24	167
1	6	144	148
2	6	144	165
3	6	144	247
4	6	144	256
1	7	168	166,8
2	7	168	184,8
3	7	168	263,7
4	7	168	274,2
1	8	192	178
2	8	192	196,5
3	8	192	270,04
4	8	192	280,88
1	9	216	188,2
2	9	216	207,6
3	9	216	272,82
4	9	216	283,96
1	10	240	199,9
2	10	240	219,5
3	10	240	274,03
4	10	240	285,15

Diffusivity tests 1, specimens had one or two exposed surfaces.

DIFFUSIVITY TEST 2

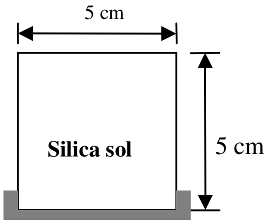
Mixing ratio 8:1
Date started: 2006-06-12
Gelling time: 1 hour and 10 min

Specimen no.	**Time (days)**	**Time (hours)**	**Concentration of Cl (mg/l)**
1	1	24	83,4
2	1	24	78,6
3	1	24	75,5
4	1	24	75,3
1	2	48	119,6
2	2	48	108,4211
3	2	48	106,2
4	2	48	114,7368
1	*3*	*72*	*174,6*
2	*3*	*72*	*150*
3	*3*	*72*	*155,8*
4	*3*	*72*	*144,4444*
1	*4*	*96*	*262,8*
2	*4*	*96*	*207,0588*
3	*4*	*96*	*232*
4	*4*	*96*	*191,7647*
1	*6*	*144*	*315,6*
2	*6*	*144*	*253,75*
3	*6*	*144*	*276,4*
4	*6*	*144*	*270*
1	*8*	*192*	*409,2*
2	*8*	*192*	*353,3333*
3	*8*	*192*	*349,4*
4	*8*	*192*	*349,3333*
1	*21*	*504*	*504,1*
2	*21*	*504*	*468,5714*
3	*21*	*504*	*379*
4	*21*	*504*	*402,8571*
1	*22*	*528*	*516,2*
2	*22*	*528*	*512*
3	*22*	*528*	*410,5*
4	*22*	*528*	*433*
1	*28*	*672*	*548,1*
2	*28*	*672*	*540*
3	*28*	*672*	*443*
4	*28*	*672*	*476*
1	*30*	*720*	*583,1*
2	*30*	*720*	*573*
3	*30*	*720*	*477,5*
4	*30*	*720*	*523*

Diffusivity tests 2, all specimens had one exposed surface, specimens 1 and 2 were stored at 8°C and 3 and 4 at 40°C. Values in red are not considered reliable due to reasons explained in Chapter 5.

APPENDIX I – Calculation of the total amount of chlorides in a silica sol specimen.

The following Figure shows the dimensions of the silica sol specimens used in this study; where the diameter is 5 cm and the height 5 cm.



The volume of a silica sol specimen was calculated as

$$V = H\pi(D/2)^2 = 5\pi(5/2)^2 = 0.1[l] \quad (1)$$

Where:

V is the volume of the silica sol specimen
H is the height of the silica sol specimen, and
D is diameter of the silica sol specimen

The specimens were weighed and corresponded to a mass of 117,75 g of silica sol. The specimens were mixed in a ratio of 8:1 in weight SiO_2 and $CaCl_2$+H_2O respectively, therefore the amount of $CaCl_2$+H_2O can be calculated as:

$$117{,}75 = \mathrm{XmassSiO_2} + \frac{\mathrm{X}}{8}\mathrm{mass(CaCl_2} + H_2O)$$

Solving X, it becomes 104,67 g and dividing by 8 gives the mass of $CaCl_2$ +H_2O = 13,08 g. The salt content in the solution is 2,9% by weight and the amount of $CaCl_2$ in a silica sol specimen is 0,379 g

The chemical reaction of $CaCl_2$ can be written as:

$$CaCl_2 \Leftrightarrow Ca^{2+} + 2 * Cl^{1+}$$

Using this equation, the amount of chloride ions can be calculated from:

$$0{,}379(g)CaCl_2 * \frac{1molCaCl_2}{111(g)CaCl_2} * \frac{2molCl^{1-}}{1molCaCl_2} * \frac{35{,}5(g)Cl^{1-}}{1molCl^{1-}}$$

Which gives 0,24 g of Cl^{1-} as a amount of chloride ions in the salt part of the solution. Adding the 0,05 g of Cl^{1-} that comes from the colloidal silica sol part gives a total estimated amount of chloride ions of 0,29 g. Dividing by 1 litre of water, into which the silica sol specimens released the chlorides, will give a final concentration of 290 mg/l.

APPENDIX J – Calculation of the diffusion coefficient.

For one-dimensional diffusion to or from a piece of height H = 2*l*, Crank (1956) gives an equation for fractional uptake, *F* as a function of time where diffusion occurs from both surfaces simultaneously. For diffusion from one surface only, the same equation can be used, although with H = *l*. The following is the development of Crank's equation:

$$F = \frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[- \frac{D(2n+1)^2 \pi^2 t}{4l^2} \right]$$

The initial mass of chlorides in a silica sol specimen is defined as:

$$M_0 = V_s \varepsilon_p C_s^0$$

Where:

V_s is the volume of the silica sol specimen,
ε_p is the sample porosity, and
C_s^0 is the initial concentration in the interstitial porosity sample.

A mass balance of chlorides gives:

$$V_s \varepsilon_p C_s^0 = V_w C_w^\infty + V_s \varepsilon_p \overline{C}_s^\infty$$

Where:

$\overline{C}_s^\infty$ is the concentration of chlorides in the sample,
C_w^∞ is the concentration of chlorides in the water box, and
V_w is the volume of the water box.

Once at equilibrium of concentration between sample and water:

$$C_w^\infty = \overline{C}_s^\infty$$

The final concentration can be written as:

$$C_w^\infty = \left\lfloor \frac{V_s \varepsilon_p}{V_w + V_s \varepsilon_p} \right\rfloor = \beta C_s^o$$

The term M_∞, which means the total amount of chlorides depleted from the sample, is given as:

$$M_\infty = V_s \varepsilon_p (C_s^0 - \overline{C}_s^\infty) = V_s \varepsilon_p (1-\beta) C_s^0$$

The total amount of chlorides depleted at any given time from the sample is:

$$M_t = V_w C_w$$

C_w can be written as:

$$C_w = \frac{V_s \varepsilon_p (1-\beta) C_s^o}{V_w} * F = C_w^\infty * F$$

Therefore replacing this last term in the first Crank equation of diffusivity, the silica sol equation of diffusivity is written as:

$$\frac{C_w}{C_w^\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right]$$

Where:

C_w is the concentration of chlorides in the water,

C_w^∞ is the final concentration of chlorides in the water,

D is the coefficient of diffusion,

t is the time that takes by diffusion to go from the initial concentration to the final one, and

n is the number of iterations and just positive values greater than zero, and

l is the height of the sample.

However, this equation does not cover the situation where the concentration of salt in the water can not be neglected. It can still be used in order to have an estimation value of the diffusion coefficient of chloride ions from silica sol to the surrounding water.

Using values from Appendix H (diffusivity test 1):

C_w = 7.04 mg/L

C_w^∞ = 285 mg/L

l = 50 mm

t = 856800 s

n = 7

The calculated diffusion coefficient D is approximately equal to $1 \cdot 10^{-9}$ m^2/s. This corresponds to an average of the seven intervals measured each day. The program MatLab was used to solve the equation.