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Investigation of the shear strength of silica sol

Laboratory studies of a grouting agent using mechanical, rheological and hydraulic tests

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Cover: The shape of the silica sol sample after the in-situ shear test had been conducted.

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ABSTRACT

The aim of this study was to investigate and develop theories on the shear strength of silica sol. Four different types of tests were conducted; fall cone tests, rheological tests, in situ shear tests and shearing in pipe tests. Prior to testing, the silica sol was stored in room temperature and 100 % relative humidity.

The purpose of the fall cone and rheological tests was to investigate the shear strength of silica sol during the gelling process. The fall cone test was performed by dropping a conical weight into a sample of silica sol mix and measure the penetration depth, which was used as input data for shear strength calculations. The rheological test involved an oscillating cone-plate set up. The tests measured different kind of parameters of the silica sol sample throughout the early stages of the gelling process, e.g. the shear strength.

The in-situ shear test was performed by filling a tank with silica sol up to different levels and pressurize it with water from a small metallic pipe. This was done in order to investigate the behaviour of the material at gel time. The shearing in pipe test was performed by filling a pipe with silica sol. At gel time, the silica sol in the pipe was pressurized with water to investigate if a certain hydraulic gradient, calculated using a mathematical formula, corresponded to the shear strength of silica sol.

The results from the fall cone tests show increased shear strength with time for a silica sol sample stored in room temperature and 100 % relative humidity. The results from the rheological tests show that the shear strength of silica sol at gel time is somewhere between 60-80 Pa. The in-situ shear tests indicated that silica sol behaves as a moderately ductile material at gel time. And the results from the shearing in pipe-tests confirmed the correlation between the hydraulic gradient and the shear strength of silica sol at gel time.

Key words: silica sol, grouting, shear strength, erosion, oscillatory rheology, gel point, gel time, loss modulus, storage modulus, loss tangent.

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Preface

This master's thesis is part of a larger research project which aims to better understand the grouting agent known as silica sol and its behavior in different kind of environments. The work was performed at Chalmers University of Technology, at the department of Civil and Environmental Engineering in Gothenburg. Johan Funehag has been supervising the work and Åsa Fransson has been the examiner.

I would like to thank my supervisor Johan Funehag for introducing me to the topic and for the opportunity to contribute to this field of work. I am thankful for all the support, the fruitful discussions and for the constant push to think outside the box. In return, I hope that my work will contribute as a piece to the puzzle. I would like to thank Mona Pålsson for the support during my laboratory work in the WET lab and for assisting me with instruments making my crucial rheological tests more accurate. Furthermore, I would like to thank Aaro Pirhonen and Georgios Birmopilis for all the help and support in the Geo Lab.

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Finally, I would like to thank my family and friends for all their support. You are awesome.

Gothenburg, 2017

Goran Tercan

List of notations

Roman upper-case letters

L [m] Length

Roman lower-case letters

g [m/s²] Gravitational acceleration
 $k\beta$ [-] Constant related to cone angle
 m [kg] Mass
 r [m] Radius
 n [-] Critical/relaxation exponent

Greek upper-case letters

ΔH [m] Excess pressure/ Loss of head

Greek lower-case letters

ρ [kg/m³] Density
 τ [Pa] Shear stress
 ω [Rad/s] Oscillation frequency

Mathematical expressions

$G'(\omega)$ [Pa] Storage modulus
 $G''(\omega)$ [Pa] Loss modulus
Tan δ [-] Loss tangent
 $\Delta H/L$ [-] Hydraulic gradient

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1 Introduction

When excavating tunnels or dealing with other types of underground constructions in hard rock, the inflow of water can become an issue. The inflow can cause damage to the underground constructions but also to the surrounding areas above the excavations, due to drawdown of the groundwater level. To reduce the amount of water entering the underground constructions, a method known as grouting is commonly used.

Grouting is a procedure where fractures in the rock are filled with a liquid material, which eventually hardens, hence creating a waterproof screen around the excavation. Traditionally, cement-based grouts have been used in underground applications and is the most common type of grout used in Sweden. However, the fracture penetrability of cement-based grouts is limited, due to the particle size. Stricter regulations regarding the allowed inflow of water has therefore led to an increased demand of other types of grouting agents, e.g. silica sol (Funehag, 2012).

Silica sol is a chemical grout that has an ability to penetrate and seal fractures with a hydraulic aperture down to 0.01 mm. Silica sol is a non-toxic material and the pH is also preferable, compared to the undesirable high pH of cement-based grouts. However, independently of the grouting agent used in grouting applications, grouting can still be unsuccessful. The force and flow of surrounding water can cause failure of the grout and hence allow leakage of water into the underground construction, especially if it is located below ground water level (Butron, Axelsson & Gustafson, 2007).

In the initial phase of grouting, when the penetration of fractures is ongoing, a problem known as fingering could occur. Fingering is the phenomena when the water replaces the grout and creates channels inside of the grouting agent. To reduce the risk of fingering, the flow of the grout should be higher than flow of water inside the fracture, thus excessive pressure when injecting must be sufficiently high. To furthermore reduce the risk of fingering, the viscosity of the grout should be higher than the one for water (Axelsson, 2009).

As penetration rate of the grout decreases, due to increasing viscosity of the grout, the procedure is eventually stopped. With the removal of the packer, the risk of back-flow is present, due to decreasing friction forces working against the water pressure. To reduce the risk of back-flow, sufficient penetration length of the grout is required during the grouting procedure. That is, the grout must be distributed with a certain radius from the borehole so that a sufficiently large area between the grout and the rock surfaces can be obtained. The friction- and cohesion forces between both must be enough to withstand the force of water (Axelsson, 2009).

At the same time, during both the penetration stage and the end stage of the grouting procedure, the risk of erosion could be high. If steep hydraulic gradients are present and the shear strength of the grout is insufficient to withstand the force of flowing water, the grouting agent could erode. Before the pressure from the pump drops and the grouting procedure ends, the shear strength of the grouting agent must be sufficiently high to reduce the risk of erosion. It is therefore crucial to understand the material used in the procedure. The shear strength development for the specific grout

and the hydraulic gradient in the fractures must be understood to achieve a successful sealing. The shear strength of the grouting agent and the shear forces of water are strongly correlated (Axelsson, 2009).

While the mechanisms of fingering and back-flow are well known and can be handled, the problem of erosion is not that clear and more difficult to cope with. This study will therefore focus on the issue of erosion in combination with the grouting agent known as silica sol. As previously mentioned, the use of silica sol has increased in grouting procedures in recent years. The early shear strength of silica sol and the behaviour of silica sol in the presence of steep hydraulic gradients is still quite unclear.

1.1 Aim and objectives

The aim of this study is to investigate the shear strength of silica sol during the gelling processes. The objectives of this study are the following:

- Investigate the shear strength development of silica sol
 - Find the relation between the visual method used to identify gel time and the shear strength development.
 - Find a criterion of the gel point using a rheometer and compare with the visual method.
- Study the mechanical behaviour of silica sol and the type of failure mode at gel time.
- Investigate the correlation between the shear strength of silica sol at gel time and the hydraulic gradient.

2 Literature review

2.1 Gels

There are various types of gels with different properties, hence a simple definition of a gel is hard to describe. The definition of a gel can for example be a soft, semisolid material which has a yield strength. It consists of a multi component system, for example a network of solid particles and a liquid (Miyoshi, 2012) and can generally be divided into two classes; chemical gels and physical gels. The division is due to the bonding types connecting the molecules in the structure. Covalent bindings define chemical gels, while physical interaction between particles define physical gels. Physical gels can also be divided into strong and weak gels. Another property of physical gels is that the bond between the molecules can break if heated; the physical gel is so-called thermos-reversible (Jones, 2002).

Colloidal silica or silica sol is the name of amorphous particles of SiO_2 in liquid phase, defined as a particulate gel with physical character. The use of it can be for multiple purposes and in recent years also more common as a grouting agent. It can penetrate narrow fractures which is an important factor when it comes to grouting. However, the long-term effect of the nano-sized particles on the environment are still unknown (Kobayashi, Juillerat, Galletto, Bowen & Borkovec, 2005).

2.1.1 Gelation and gel point

The formation of a gel is out of a liquid substance containing evenly suspended particles, also known as a sol or gelator. Gelation is the transition from the liquid state (sol/gelator) to the solid state (gel) and initiates in different ways. Changes in pH or temperature or addition of salt to the solution, can for example initiate gelation of physical gels (Chalmers Soft Matter Centre, 2007). When disrupting the solution by any of the stated changes, the particles in the solution start to aggregate and turn into larger molecules. The particles link to each other throughout the whole system and eventually becomes one large mass of molecules, a gel. Gel point is a certain point that marks this transition from sol to gel. The gel point for chemical gels occurs when the largest cluster diverges to an infinite size. Regarding physical gels, the gel point reaches when the so-called correlation length of the molecular movement diverges to infinity (Borsali & Pecora, 2002) and (Rubinstein & Colby, 2003).

2.1.2 Gel point indicators

Three methods to possibly indicate gel point are investigated in the literature review, but only two were used in the laboratory works due to time restrictions. However, the third method is worth mentioning for further studies, since it seems to be a clear method and eventually could work as a complement to the other two.

2.1.2.1 The visual method

The visual method is a commonly used test to identify the gel time, but not necessarily gel point. If the method indicates gel point or not, will be investigated in this study and is one of the objectives. The gel time however, is defined as a certain moment when a plastic tube filled with the silica sol mix is tilted 90 ° and a straight surface of the silica sol mix can be seen. That is, when the gel ceases to flow and the surface stops to deform/change when the tube is tilted 90 °, gel time is reached. Gel time is dependent on the ratio of the components used for the gel mix and can therefore be adjusted according to requirements (Funehag, 2012).

2.1.2.2 Needle penetration test

Another method used to possibly identify the gel point, is with the needle insertion technique. With the needle insertion technique, the gel point is identified when two things occur simultaneously; the tube can be tilted without any flow occurring and the needle can be supported. The needle insertion should not cause breakage of the gel at gel point, since that would indicate a fully solidified silica (Shen, Hankins & Jefferis, 2017).

2.1.2.3 Rheology – Loss modulus (G'') and storage modulus (G')

Another method to possibly determining the gel point is to investigate the rheological properties of the material. There are many ways of identifying the gel point in rheology and a few of them will be investigated in this study. When using rheology to identify gel point, parameters that can be examined are for example the storage modulus (G'), which measures the ability of the gel to storage energy, and the loss modulus (G''), which is related to energy loss (Goodwin & Hughes, 2008). To further clarify, if a gel mix is in a liquid phase, viscous properties are dominant, therefore energy put on the sample will be lost and loss modulus (G'') will have a larger value than the storage modulus (G'). However, when the gel mix reaches a more solid state, elastic properties will dominate. More energy will be stored in the sample rather than dissipated, thus G' will increase and eventually obtain a larger value than G'' . Both G' and G'' can be plotted as a function of time, temperature or frequency etc. (Malvern Instruments, n.d.)

In order to find the gel point using G' and G'' , different criteria's and methods have been developed through out time. Tung and Dynes (1982) suggested that the point at which $G' = G''$ could be used to detect gel point. However, Winter (1987) showed that the definition was only true for certain types of gels, more specific the stoichiometrically balanced network polymers.

A more general criterion to find the gel point was later developed by Winter & Chambon (1987), but not necessarily valid for all kind of gels. The criteria states that gel point is found when the loss tangent, $\tan \delta (\omega) (= G''(\omega)/G'(\omega))$, is independent of frequency (ω). To further clarify, when the loss tangent is plotted for all frequencies, at some point, all the different curves will intersect at one single point. The point in which all curves intersect simultaneously, is the gel point. An example of this can be seen in Figure 1.

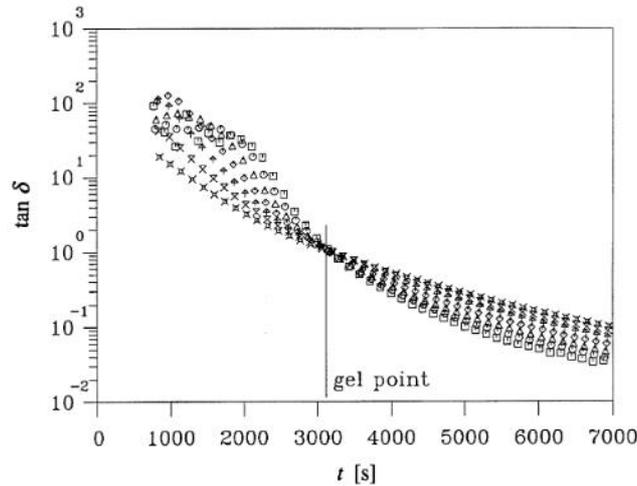


Figure 1. $\tan \delta$ plotted for different frequencies, intersection of all curves in one single point is marked as the gel point (Ewen, Mours, Richter, Shiga & Winter, 1997, p. 222).

Another method to identifying gel point with the storage modulus (G') and loss modulus (G'') could be to do a frequency sweep. With the frequency sweep setup, gel point is indicated when G' and G'' are parallel. Presented in Figure 2 is an example of when G' and G'' are parallel and gel point is reached.

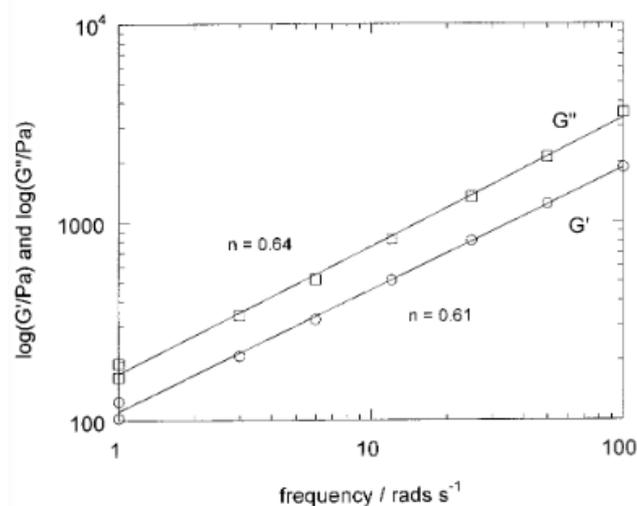


Figure 2. G' and G'' plotted vs. frequency. Parallel lines indicate gel point (Mortimer, Ryan & Stanford, 2001, p. 2978).

Presented in Figure 3 are additional examples of how gel point indication using rheology could look like.

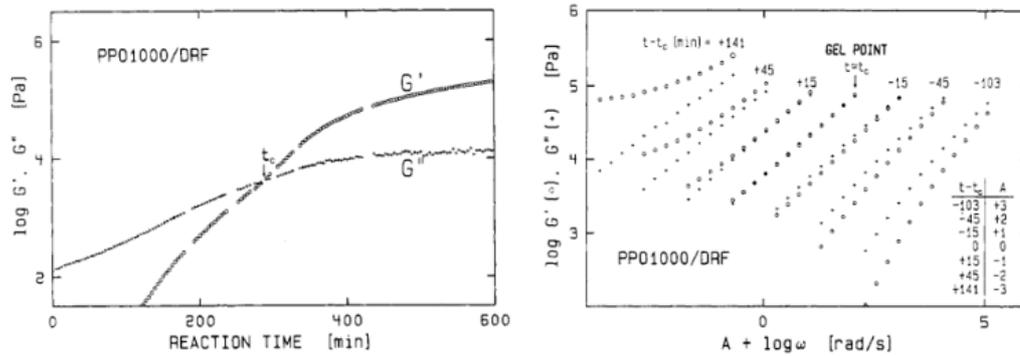


Figure 3. Left picture: G' & G'' plotted vs. time. Intersection of G' & G'' is indicated at a t_c . Right picture: G' & G'' plotted vs. frequency and parallel lines are indicated at t_c (MacKnight, Chambon, Petrovic & Winter, 1986, p. 2147).

However, there are studies (Gosal, Clark, & Ross-Murphy, 2004), (Kavanagh, Clark & Ross-Murphy, 2000) and (Chiou, Raghavan, & Khan, 2001) stating that the Winter-Chambon criterion does not apply for some gels, e.g. physical networks. Storage modulus (G') is greater than the loss modulus (G'') at a very early stage and sometimes an intersection between G' & G'' cannot be indicated at all. The Winter-Chambon criterion is therefore of limited use for such systems, regarding gel point detection.

2.2 Mechanical properties

Fall cone test (FCT) is one way of measuring mechanical properties of viscoelastic material, for example the undrained shear strength. FCT is a simple and cheap test where a cone is placed right on the top of the material that is being tested. As the cone is released, it penetrates the material. The penetration depth is measured and put into a mathematical formula, the undrained shear strength can be obtained.

Fall cone test is one of the most repeated tests on silica sol. Butron, Axelsson & Gustafson (2007) conducted numerous and extensive fall cone tests on silica sol to study the long-term shear strength development. The study included tests on silica sol that had been stored in different types of environment prior to testing, to investigate how different environments affected the shear strength development. The result of interest for this study are the tests conducted on silica sol that had been stored in 20 °C with 100 % relative humidity (r. h.) prior to testing. The results indicate an increase in shear strength with time, from 5-10 kPa after 24 hours up to 50 kPa after 48 days.

Liverios & Nilsson (2016) also conducted fall cone tests on silica sol to study the shear strength development. The samples were stored in room temperature with 100 r.h. The purpose of the study was to compare the shear strength development for two different accelerators, NaCl and KCl. The results obtained from the tests also showed an increase in shear strength with time. The shear strength reached 3 kPa after approximately 1 h and increased to 20 kPa after approximately 120 h.

At the early stages of a gelling silica sol, it is however hard to measure the shear strength using FCT, or other similar tests, due to the low viscosity. Hence there is a lack of knowledge surrounding the early stages of the shear strength development of silica sol, such as at gel time or prior to gel time. Axelsson (2009) tried to predict the shear strength of silica sol at gel time using fall cone test data and predicted a shear strength of 60-80 Pa for silica sol at gel time. Liverios & Nilsson (2017) conducted one rheological tests on silica sol to measure the early shear strength. Results from the single run showed a shear strength at gel time of 60-80 Pa, which is consistent with the predictions made by Axelsson (2009).

2.3 Erosion and hydraulic gradient

Steep hydraulic gradients can cause difficulties and problems in grouting applications in underground constructions, such as erosion of the grout, leading to leakage and unsuccessful grouting. This is especially a problem if the underground constructions are located at great depth ($>100\text{ m}$) (Funehag, 2012). Erosion occurs if the force of water is higher than the strength of the grouting material. There are numbers of tunnels where the grouting procedure have been unsuccessful, and many studies have been conducted on the topic.

Suresh and Tohow (2013) investigated the possibility of designing the grout procedure to better cope with hydraulic gradients and for the grout to better resist erosion. In the study, field tests were conducted in a tunnel in the Gothenburg area where previous grouting attempts had been unsuccessful. Among other things, the results from the field tests and measurements showed a water stress of approximately 26 Pa in the borehole, which they regarded as the minimum that the grout should be able to resist. The new grout was designed to withstand 26 Pa, but when applied, it was still unable to successfully seal the leakage. The conclusion was that the hydraulic gradient probably became higher because of the grouting procedure and that the water stress in the borehole could possibly become 100 Pa or higher, making it a nearly impossible task to seal using only grouting.

Another study conducted by Reynisson (2014) focused on the TASS tunnel, located in Äspö HRL facility. In the study, the author investigated leaking boreholes in the tunnel and created different scenarios where different assumptions regarding the hydraulic gradient were made (theoretical, simplified, worst case and according to geometry). The author also assumed values of the shear strength of the grout. Comparing the different hydraulic gradients with the assumed shear strength of the grout, the conclusions were that most boreholes in the tunnel should have fulfilled the criteria of erosion. That is, the assumed shear strength of the grout was higher than the assumed stress of flowing water and leakage should therefore not have been able to occur. But as the author observed when conducting a field test, the boreholes in the tunnel were still leaking. Reynisson (2014) concluded that the boreholes which intersected the same fracture plane as the one that was grouted, probably was affected by higher water stress levels making the design of the grout not valid for the other boreholes. Another conclusion was that the grout was not designed correctly for the low temperatures in the rock, causing lower grouting time and hence a lower initial shear strength of silica sol and

Liverios & Nilsson (2016) conducted further studies on the topic. The study included an investigation on the susceptibility of silica sol in relation to water stress level. The authors also conducted rheological tests on the material to better understand the silica sol and to obtain actual shear strength of silica sol at different time intervals using rheological instrument. The results were put to test and applied using a fracture replica set where silica sol was injected to the container followed by a water stress of 1 Pa. The results showed no visible erosion of the grout.

2.4 Rheology

The word rheology derives from Greek and is a composition of the words “study of” and “flow”. In rheology is it primarily the flow of liquids, in response to applied stress, that is of interest. Elasticity, plasticity and viscosity are some of the most relevant parameters, that is, flow and deformation properties (Vader & Wyss, n.d.)

The rheological parameters are of high interest in grouting procedures, since they affect the penetration length, pressure requirements etc. Two different types of fluids and their behaviour are of interest when it comes to grouting; Newtonian and Bingham fluids (Funehag, 2012).

A Newtonian fluid has a linear relation between shear stress and shear rate, thus the viscosity remains constant independent of shear applied. Also, a Newtonian fluid has no yield strength, hence when stress is applied to the fluid, it flows proportionally. No threshold value needs to be exceeded for it to flow. The initial phase of silica sol can be described as a Newtonian fluid.

A Bingham fluid however, also has a linear relationship between shear stress and shear rate, but unlike the Newtonian fluid, it has a yield strength. For a Bingham fluid to flow, an initial stress must be exceeded. Cementitious grouts can be described as Bingham fluids and also the later phase of silica sol, since the gelation results in an increase of viscosity. The viscosity is defined as the resistance of the fluid to be deformed by stress, the higher the viscosity, the higher stress is required to deform the fluid (Axelsson, 2009) and (Funehag, 2012).

The methods to measure mechanical parameters of viscoelastic materials and fluids differ from steel, wood etc. Due to the intermediate state between a liquid and solid, the methods for measuring mechanical parameters are quite complicated. However, there is an established and capable instrument used in this matter; the rheometer.

2.4.1 Rheometer and oscillatory rheology

A rheometer is a device that can apply force to fluids, slurries or suspensions and measures the behavior and response due to that force. The material of interest is placed in a certain geometrical arrangement and stress, strain or strain-rates is applied. The environment can also easily be controlled in the rheometer, such as temperature etc. Together with other practical features, the rheometer is regarded as a useful instrument when studying properties of viscoelastic material.

There are different set ups and modes when using a rheometer. A common rheological test is the oscillation testing. The set up induces a sinusoidal shear deformation at an angular frequency, ω , in the material and at the same time measures the stress response. From these tests storage modulus (G'), loss modulus (G'') amongst others can be obtained. Advantages of oscillatory tests are for example the ability to not disturb the sample when performing the tests, keep certain parameters constant etc., making the rheometer a precise and flexible instrument to use (Schramm, 2004).

In a study conducted by Ågren & Rosenholm (1998), both rheological methods and the visual method was used to identify the gel point. The authors studied the

behaviour of tetraethylorthosilicates for different polyethylene glycol to study the difference. The parameters studied were the storage modulus (G') and loss modulus (G'') for different frequencies. The authors found that the gel time identified using the visual method corresponded relatively well with the gel point identified with the rheometer. The Winter- Chambon criterion was used for the identification.

Other studies however, states that the Winter- Chambon criterion is of limited use for some physical network gels, due to the G' being greater than G'' in the early stages of the measurements, as previously mentioned (Gosal, Clark, & Ross-Murphy, 2004), (Kavanagh, Clark & Ross-Murphy, 2000) and (Chiou, Raghavan, & Khan, 2001).

3 Methodology

3.1 Gel time

The gel time of the silica sol mix needs to be consistent for all the tests to ensure comparable results, hence a recipe for the silica sol mix is required. The first step of the laboratory tests is therefore to determine the amount and ratio of silica sol and saline solution required for the mix.

In this study, the silica sol used was Meyco MP 320 and the accelerator used was NaCl, mixed with ultrapure water in a 2 M solution. The weight of all three components was measured before any mix occurred. The aim was to obtain a silica sol mix with a gel time of 20 minutes at room temperature (21 °C). The gel time was indicated with the visual method.

Following steps were performed to obtain the required gel time for the silica sol mix:

1. Place a plastic cylindrical tube on a scale with an accuracy of at least two decimals and fill with a certain amount of silica sol. Prepare ultrapure water in another tube and measure NaCl in a frictionless plastic cup. Pour the salt into the tube with ultrapure water and mix.
2. Mix the silica sol with the 2 M saline solution and start the timer as soon as it is done.
3. Gently turn the tube 90° when estimated gel time is close to being reached. Check the surface of the gel. This is done every 30 seconds up to gel time.
4. When the gel no longer flows and has a straight surface, gel time is reached. Note the time.
5. Adjust the amount of salt and water but keep the ratio of 2 M and keep the exact amount of silica sol. The test is repeated until a gel time of 20 min is observed.

3.2 Shear strength tests

This section contains the methods used in order to determine the shear strength of silica sol. As previously mentioned, silica sol is a viscoelastic material and can therefore behave like a fluid, semi-solid and a solid material depending on different factor. Consequently, different measuring techniques are needed in order to investigate the shear strength parameters throughout the different phases of the silica sol during gelation. Also, combining different measuring techniques can give better and more exact values of the shear strength parameters. The tests conducted in this study were fall cone tests and rheological tests.

The aim of fall cone tests was to investigate the long-term shear strength of silica sol. The aim of the rheological tests was to investigate the shear strength development for silica sol during the early stages of the gelling process and particularly to identify the shear strength of silica sol at gel time.

3.2.1 Fall cone test

The first test of fall cone was conducted 1 hour after gel time. Further tests were conducted with an interval of 20-24 hours except for longer gaps due to weekends. A total of 10 tests were conducted. The test tubes were prepared with 100 g of silica sol mix and were stored in room temperature. In order to prevent the silica sol mix of drying, all samples were covered with a small amount of water on the top and sealed using parafilm, duct tape and other plastic material for maximal prevention of water molecules leaving the tube containing silica sol mix, hence maintain 100 % r. h. in the tube.

Following steps were performed in order to measure the undrained shear strength of silica sol after gel time using the fall cone test set up:

1. Prepare ten cylindrical plastic tubes, each with a height of 45 mm and an inner diameter of 50 mm, with 100 g silica sol mix.
2. Position the cylindrical tube filled with silica sol mix under the cone of the test apparatus.
3. Lower the cone until it almost touches the surface of the silica sol mix and stop.
4. Drop the cone into the mix.
5. Read the penetration depth of the cone.
6. Put in the necessary values in Equation (1) in order to calculate the undrained shear strength of the silica sol sample (Hansbo, 1957). The properties of the cones used in the fall cone tests are stated in Table 1.

$$\tau_u = k_\beta \left(\frac{m \cdot g}{d^2} \right) \quad (1)$$

Where;

| | |
|---|---------------------|
| k_β = constant related to the angle of the cone | [-] |
| m = the weight of the cone | [g] |
| g = gravitational constant | [m/s ²] |
| d = penetration depth | [mm] |

According to Butron et al. (2007) a cone with apex angle of 30 should be used, even though Butron et al. (2007) states that it gives unreasonably high values.

Equation (1) is only valid for penetration depth between 7-20 mm. Cone number 1 was therefore used for the first test. The choice of cone for the next test was therefore dependent on the outcome and penetration depth of the previous test. Two drops were made in one sample and an average depth was calculated.

Table 1. Properties of the two cones used in the fall cone tests.

| Cone | m | β | k_β |
|------|-------|---------|-----------|
| 1 | 100 g | 30 ° | 1.0 |
| 2 | 400 g | 30 ° | 1.0 |

3.2.2 Rheological test

The rheometer used was an Anton Paar Physica MCR 300 Rheometer. The test set up installed was a cone-plate geometry in oscillation and further settings used in the rheometer are stated in Table 2.

To be able to identify the shear strength at gel time, the visual method was conducted simultaneously as the rheological tests. Since the environment was the same for the tube filled with silica sol mix (visual method) as for the silica sol mix in the rheometer, the visual method would indicate gel time and thus indicate when to read the shear strength value from the rheometer.

Table 2. Rheometer set up information.

| Cone angle | Gap | Frequencies | Temperature | Strain |
|------------|-----------|----------------|-------------|--------|
| 1° | 0.0052 cm | 0.1, 0.5, 1 Hz | 24.5 °C | 0.5 %. |

Following steps were performed in order to measure the shear strength using the rheometer and also identifying the shear strength of silica sol at gel time using the visual method mountainously:

1. Fill one tube with silica sol and another tube with the saline solution, i.e. the ultrapure water + NaCl.
2. Mix the contents of both tubes by pouring the saline solution into the silica sol for 5 seconds and stir with magnetic stirrer for 15 seconds.
3. Measure the temperature of the silica sol mix.
4. Set the temperature of the rheometer to the measured temperature obtained in step 3.
5. Take a small amount from the mix and place between cone and plate.
6. If water bath is available, set it to the same temperature as rheometer, seal the tube and place it inside the water bath in order to have a constant temperature for the silica sol mix in the tube.
7. Start the test. Note the time difference between when mixing ends and when the rheometer starts. This is done to be able to compensate for time differences when comparing different tests.
8. Visual method: Tip the tube containing silica sol mix 90 ° every 30 seconds when approaching expected gel time and note the time when gel time is reached.
9. The most important task is to read the shear strength on the computer at the same moment as gel time is obtained in the tube indicated with the visual method!

3.3 Investigation of a gel point criterion

As previously mentioned, rheology can be used to identify gel point. The rheology studies were used not only to investigate the shear strength of silica sol, but also to use the data in order to investigate the gel point. The aim was to investigate the Winter- Chambon criterion of gel point and whether it can be applied to the silica sol.

Using the data from the rheological studies, following steps were conducted in order to investigate the gel point criterion:

1. Investigate the storage modulus (G') and loss modulus (G'') for each of test conducted using the rheometer. The method for the rheological tests is presented in section 3.2.2. Investigate if any intersection between G' and G'' occurs, by plotting the parameters as a function of time for each of the tests. Particularly observe if intersection happens at gel time for each of the tests.
2. Investigate the loss tangent ($\tan \delta$) for each of the test conducted. Plot $\tan \delta$ for all the different tests in one single plot as a function of time. Observe if intersection for the different loss tangents occurs at one single point at the same time, which would indicate gel point according to the Winter- Chambon criterion.

3.4 Pipe flow tests

This section contains the methods used in order to investigate the behaviour of silica sol at gel time in response to stress induced by water.

The aim of the in-situ shear tests was to investigate the mechanical behavior of the silica sol mix at gel time. The aim of the shearing in pipe- tests was to investigate the correlation between the shear strength of silica sol at gel time and the hydraulic gradient.

3.4.1 In-situ shear test

Silica sol and saline solution was mixed according to 20-minute gel time, see section 3.1. Following steps were thereafter performed to investigate the mechanical behavior of the silica sol mix at gel time:

1. Arrange set up according to Figure 4. Connect a pressure regulator to a water tank with the volume of 1-2 liter via a pipe. Connect the water tank to another tank containing silica sol mix via a second pipe. Mount a metal pipe at the bottom of the tank containing the silica sol mix and let it stand inside.
2. Fill the tank with silica sol mix up to a length of 1 cm above the metal pipe outlet at the top. Let the outlet be far up in the tank, since friction forces and self-weight of the silica sol mix is required in order to prevent an uplift of the sample, when the water pressure is put on.
3. Let the silica sol mix reach gel time. Increase water pressure slowly but steady, observe the pipe outlet carefully. Note the pressure at failure/flow of water in silica tank and measure radius of shear geometry.
4. Repeat for 2, 3 and 5 cm of silica sol mix above pipe outlet.

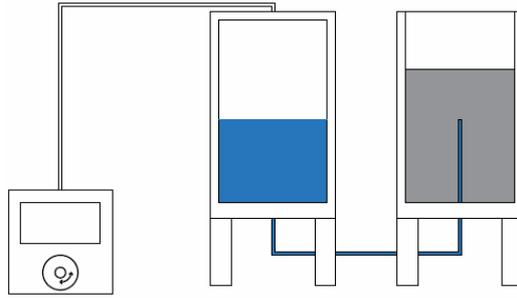


Figure 4. From the left: Pressure regulator, a tank containing water and a tank containing silica sol mix. Connected via plastic pipes. The tank to the right has a metal pipe standing in it and is connected to the bottom of the tank.

3.4.2 Shearing in pipes test

Another relation of interest is the shear strength of silica sol at gel time and the hydraulic gradient ($\Delta h/L$). In order to test this, the gradient needed to shear the silica sol at gel time was calculated using Equation (2) (modified from Axelsson, 2009). The shear strength (τ) of 60-80 Pa was assumed for the silica sol mix at gel time (Liverios & Nilsson, 2016).

To further clarify, the hydraulic gradient, which is based on the shear strength of silica sol at gel time, is used to induce failure of the silica sol mix in the pipe at gel time. Correlation between the formula and the shear strength of silica sol was obtained if silica sol is pushed out from the pipe at the specific hydraulic gradient. The tests were conducted for various lengths of pipes.

$$\Delta h = \left(\frac{\tau \cdot L \cdot 2}{\rho \cdot g \cdot r} \right) \quad (2)$$

(Note: The formula was rearranged to simplify and excess water pressure (Δh) was used further on, instead of hydraulic gradient ($\Delta h/L$))

| | | |
|--------|--|----------------------|
| Where; | τ = shear strength | [Pa] |
| | L = length of sample | [m] |
| | g = gravitational acceleration | [m/s ²] |
| | ρ = density of sample | [kg/m ³] |
| | Δh = excess pressure/ loss of head | [m] |
| | r = radius of sample | [m] |

Following steps were performed to conduct the shearing in pipe-test:

1. Arrange set up according to Figure 5. Connect pressure regulator to a water tank with the volume of 1-2 liter via a pipe. Connect the water tank to a second plastic pipe in the other end.
2. Fill the second plastic pipe with the silica sol mix and seal the end of the pipe that isn't connected to anything.
3. When gel time is reached, start the test.
4. Remove sealing from the end of the second plastic pipe. Slowly increase the pressure and observe the end of the plastic pipe.
5. Note the pressure when the silica starts to pour out from the end of the plastic pipe.
6. Push through the remaining visible silica and let the pipe dry.
7. Inspect the inside surface of the plastic pipe to see if remains of any silica can be observed, for example by pushing a dark textile through the pipe.

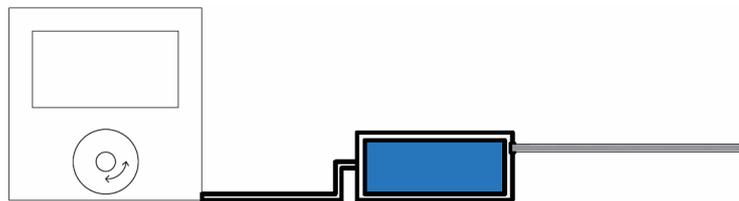


Figure 5. From left: Pressure regulator, tank containing water and a plastic pipe containing silica sol mix.

In order for the test to be valid, shear failure must occur within the silica material. If there is material left along the inner surface of the plastic pipe after test is conducted and pipe is dried, it is assumed that shear failure within material has in fact occurred. On the contrary, if all the silica in the pipe is simply gone and nothing can be found during inspection, shearing between particles has not occurred. In that case, it is the shear strength between pipe and silica that is measured, which would disqualify the test, and/or the type of pipe used.

4 Results

4.1 Gel time

Presented in Table 3 are the components used in the silica sol mix. Depending on ratio, different gel time was achieved. For the first test, a gel time of more than 24 minutes was achieved and therefore the amount of saline solution was decreased successively.

Table 3. Different ratios of the three components result in different gel times.

| Salt [g] | Ultrapure water [g, at room temp.] | Silica sol [g, at room temp.] | Gel time [min] |
|----------|------------------------------------|-------------------------------|----------------|
| 0.52 | 4.46 | 24.0 | >24 |
| 0.53 | 4.5 | 24.0 | ~24 |
| 0.54 | 4.6 | 24.0 | ~23 |
| 0.55 | 4.7 | 24.0 | ~23 |
| 0.56 | 4.8 | 24.0 | ~22 |
| 0.57 | 4.9 | 24.0 | ~21 |
| 0.58 | 4.95 | 24.0 | ~20 |
| 0.59 | 5.05 | 24.0 | ~18 |

To achieve a gel time of approximately 20 minutes for the silica sol mix, the ratio of 0.58 g NaCl, 4.95 g ultrapure water and 24.0 g of silica sol was required, see blue marked row in Table 3..

4.2 Shear strength tests

Presented in Figure 6 are the results from the ten fall cone tests that were conducted on the silica sol mix. The shear strength of the silica increases with time.

4.2.1 Fall cone test

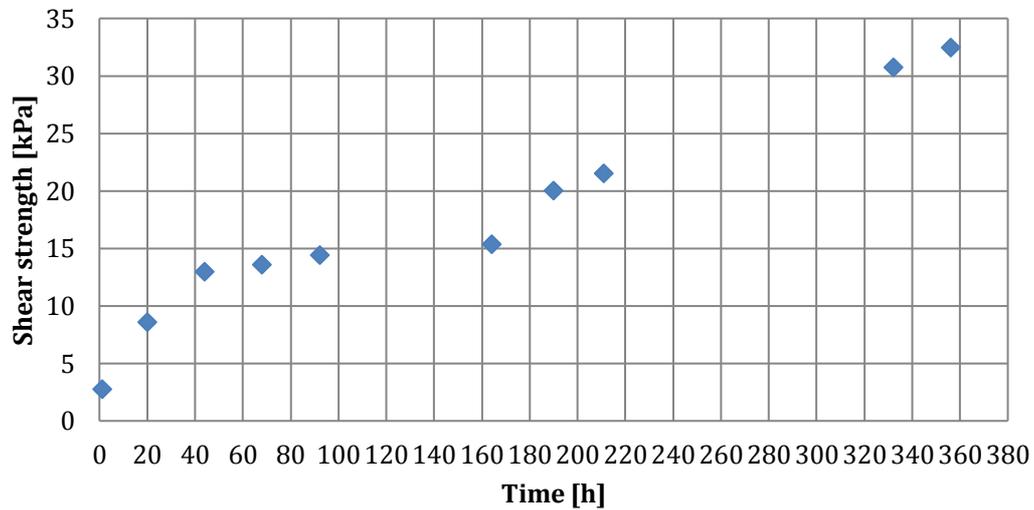


Figure 6. Fall cone test data indicating increased shear strength of silica sol with time.

4.2.2 Rheological test

Presented in Figure 7 are the results of eight test runs with the rheometer. The curves show the measured shear strength development for the silica sol during the gelling process. The yellow lines represent the gel time observation using the visual method for each of the tests and was conducted parallel to each of the rheological test.

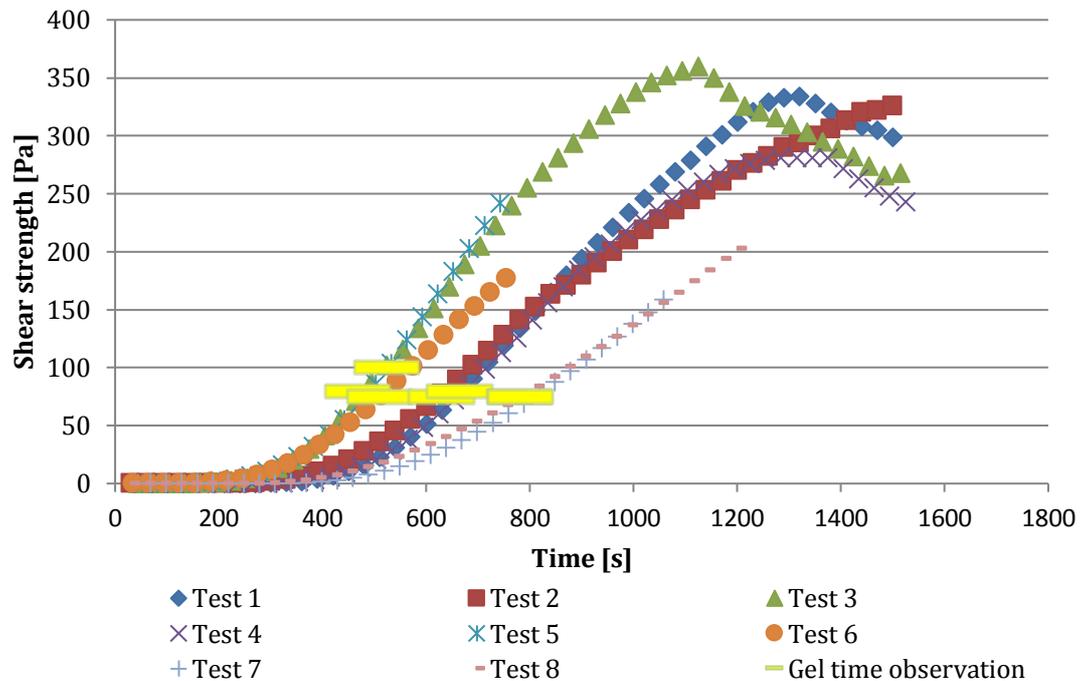


Figure 7. Shear strength development for the eight tests. Gel time observation for each of the tests is marked with a yellow, horizontal line.

The shear strength at gel time for all the tests range approximately 60-80 Pa, with one exception. As can be seen in Figure 7, the gel times are slightly scattered. The reason for the gel times being below 20 minutes (1200 s) and scattered along the x-axis, is because of the high and varying room temperature (23-24.5 °C) at the lab and no available water bath, hence a shorter gel time. Time differences between start up for the different tests have been compensated for.

4.3 Investigation of gel point criterion

During the rheological tests not only shear strength was measured, but also a number of other different parameters, e.g. storage modulus (G') and the loss modulus (G''). Presented in Figure 8 are the G' and G'' parameters measured in one of the rheological tests. The results of the storage and loss modulus measurements for the seven other tests are presented in Appendix 1 - Oscillating cone plate raw data.

No intersection of G' and G'' can be observed for the test presented in Figure 8. The results from the visual method, which was conducted parallel with the rheological test, indicated the reach of gel time at 665 seconds, which is marked with a vertical green line. The results for the other seven tests presented in “Appendix 1 - Oscillating cone plate raw data” have a similar look as the one presented in Figure 8. That is, the results from the seven other tests showed no intersection of G' and G'' curves or intersection at a very early stage, long before reach of gel time.

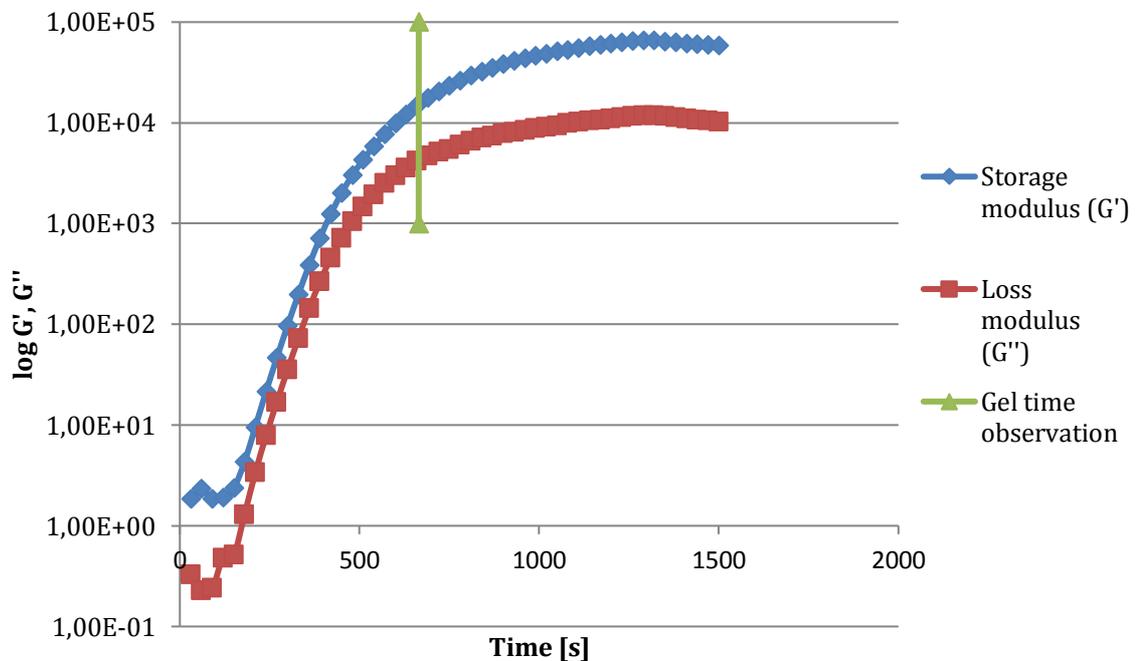


Figure 8. Storage modulus (G') and loss modulus (G'') vs. time

The loss tangent ($\tan \delta$) for all eight tests are presented in Figure 9. Time differences between start up for the different tests have been compensated for. As can be seen, the curves for all the eight tests are not met in one single point at the same time. Gel point is therefore difficult to observe/ cannot be observed for the silica sol mix and this test set up.

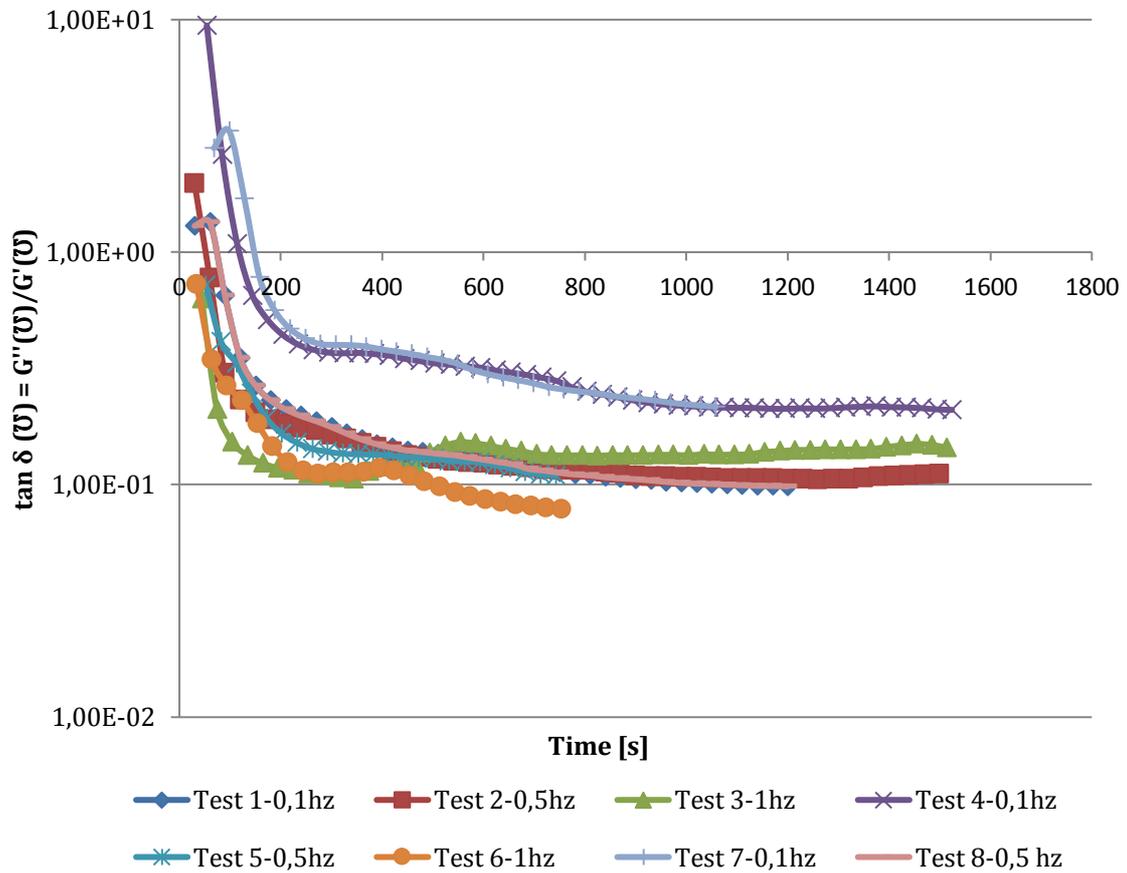


Figure 9. The loss tangent ($\tan \delta$) presented for three different frequencies vs. time.

4.4 Pipe flow tests

4.4.1 In-situ shear test

Presented in Figure 10 are the pressure requirements to lift/push the various amount of silica located above the pipe outlet. The higher amount/ length above pipe outlet, the more pressure was required to lift the silica. The diameter of the tank was, as previously stated, 8 cm.

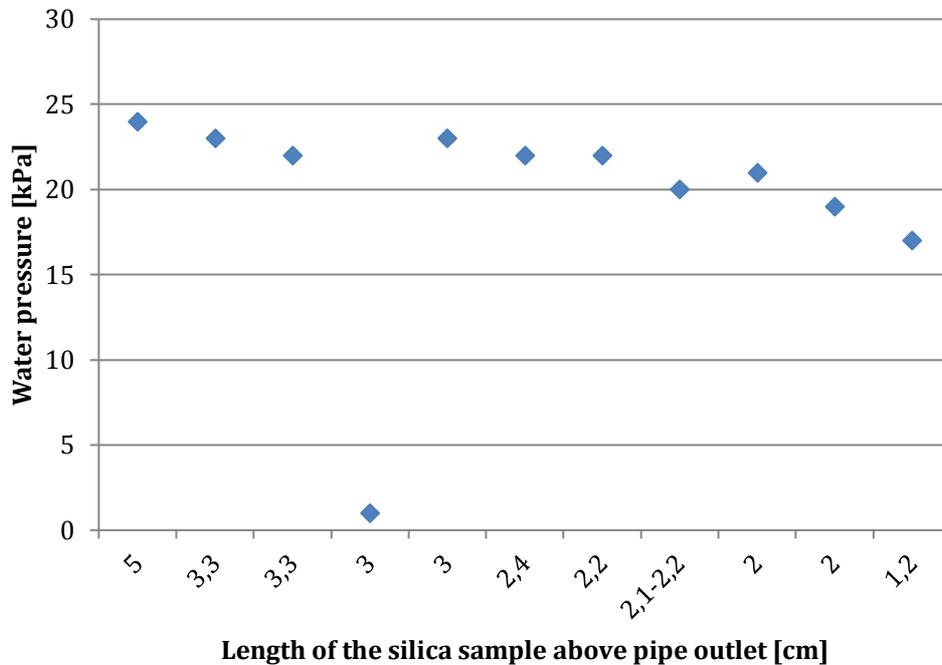


Figure 10. Tests results from eleven in-situ shear tests.

The tank to the right presented in Figure 11 shows the fracture failure of the silica sol mix after water had pushed through. Interestingly, the geometry of the fracture failure after break through of water had the shape of a half-sphere. Because of the profile view, the half-spherical shape is presented as a half circle in Figure 11, see tank to the right.

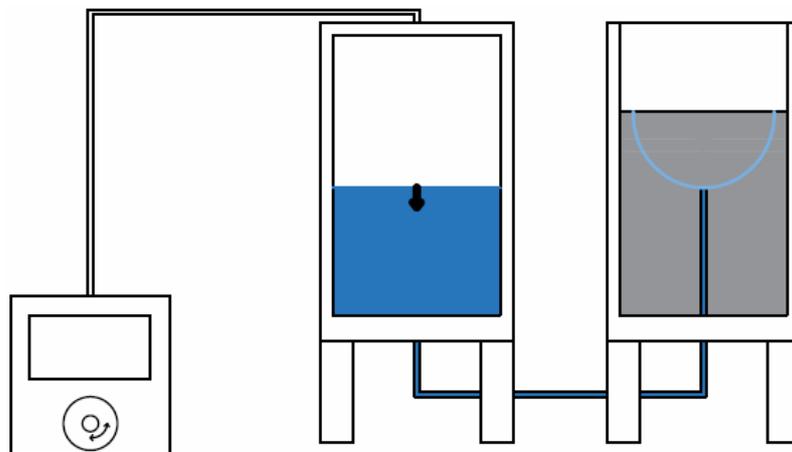


Figure 11. The half-spherical geometry obtained in the tank to the right.



Figure 12. Half-spherical failure geometry of the silica sol at gel time

The half-spherical geometry obtained in the silica sample during the tests can also be seen in Figure 12. The two left pictures show the results of the testing for a length of 3 cm silica above pipe outlet and a diameter of 8 cm of the half-spherical geometry. The right picture shows the results of the testing for a length of 2 cm of silica above pipe outlet and the failure geometry with a diameter of around 5 cm.

4.4.2 Shearing in pipes test

Presented in Figure 13 are the test results from the shearing in pipe- tests. The red (square) and the green (triangle) markings represent the hydraulic gradient required to shear the silica sol at gel time according to the calculations, using equation (2) presented in section 3.4.2 based on the assumptions that the silica sol has a shear strength of 60 and 80 Pa at gel time. The blue (diamond) marking represent the actual hydraulic gradient needed to push the silica through the pipe for each test. The hydraulic gradient used to push the silica sol during the test did correspond relative well to the calculated theoretical values based on the assumed shear strength of 60-80 Pa.

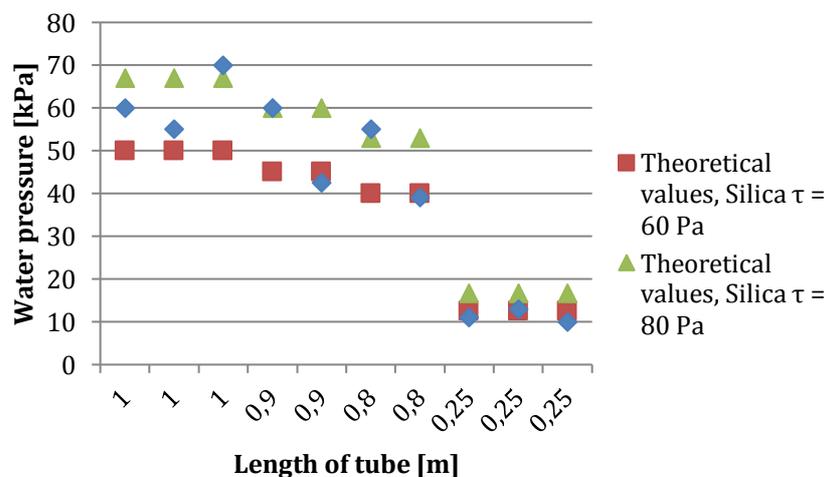


Figure 13. Pressure required to push silica sol mix through the rough pipes at gel time, for different lengths.

In order for the test to be valid, shearing was required to occur within the silica sol itself. If the silica sol simply slipped out of the pipe without shearing, the test would not have been valid. Remains of silica sol had to be present in the washed out plastic pipes in order for the test to be valid. A dark textile was therefore pushed through each of the pipes after the testing, to investigate the remains of silica sol along the inner surface. Presented in Figure 14 is the textile after it had been pushed through the shortest (0.25-m) pipe used in the test. It was difficult to measure the amount of gelled silica sol scratched off from the inner surface, but the amount was visible to the bare eye.



Figure 14. Dark textile used to clean the inside of the plastic pipes. Remains of silica sol was detected.

5 Discussion

5.1 Mechanical behaviour

One objective of this study has been to investigate the mechanical behaviour of silica sol and the type of failure mode in the material at gel time. The in-situ shear test was set up to achieve this. The results of the in-situ shear tests are quite unexpected due to the half-spherical failure geometry that was obtained. It is difficult to state exactly what causes the failure, since the test wasn't monitored with electronic equipment and therefore it is difficult to state whether it is a true shear failure, tensile failure or a combination of both that is occurring. However, the half-spherical shape could demonstrate a cup- and cone failure.

The cup- and cone geometry is typically obtained when subjecting moderately ductile material to tensile stresses, in contrast to the conical fracture geometry obtained for fully ductile material and the plain/straight fracture surface obtained for brittle material. The failure geometry obtained during the in-situ shear test therefore suggests the silica sol to be something between a fully ductile material and brittle material at gel time, if the test set up in fact induced tension stresses on the silica sol. The latter could be true, since the water beam in the in-situ shear test did not penetrate the silica at first and instead lifted the silica at the pipe outlet (the bottom of the silica sample), so that a small puddle of water was created beneath the silica sample. As water pressure was ongoing, an uplifting effect was created and possibly caused tension stresses inside the silica sample. In a study conducted by Axelsson (2006), the author states that silica sol behaves like a ductile material at gel time. The results from the in-situ shear tests in this study therefore consistent with the findings of Axelsson (2006).

Furthermore, the different shear strengths result from the fall cone tests, rheology tests and the pipe tests are summarized in Figure 15.

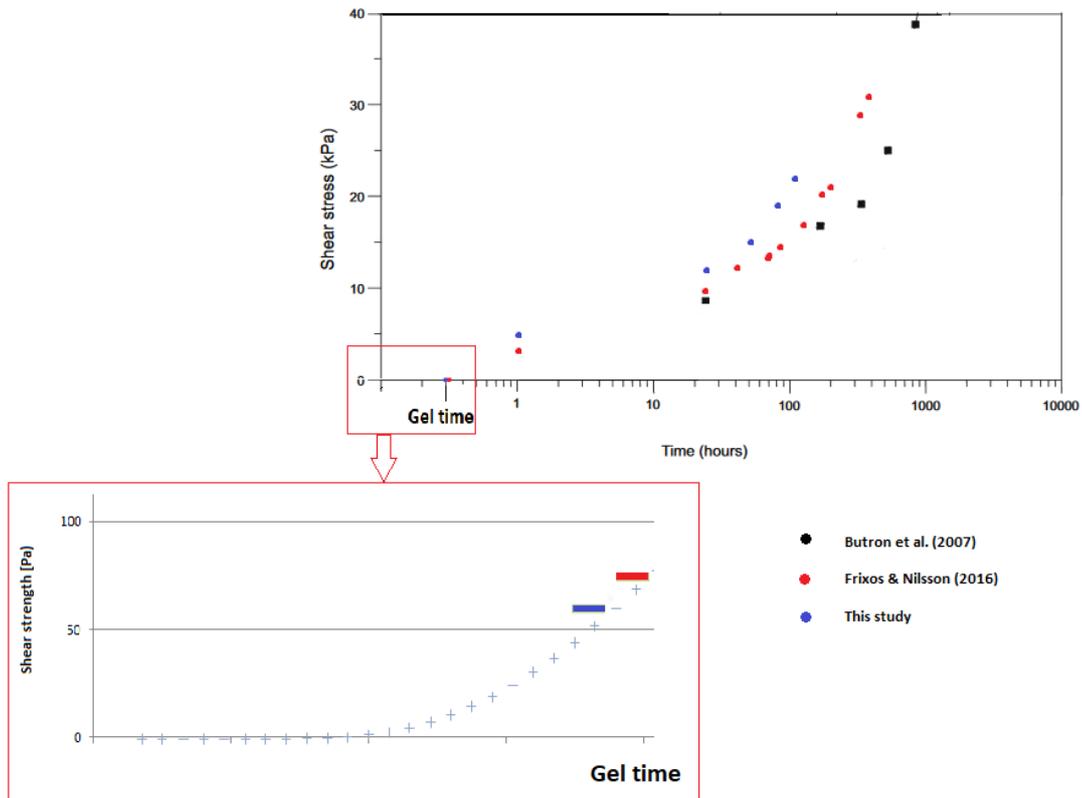


Figure 15. Shear strength development for silica sol.

The shear strength values obtained during this study corresponds relatively well to the values obtain in previous studies, such as the one conducted by Butron et al. (2007) and Liverios & Nilsson (2016). The values obtained in this study are slightly lower compared to the values obtained by Liverios & Nilsson (2016) and slightly higher than the values obtained by Butron et al. (2007).

Lastly, while the fall cone tests only can measure the shear strength of silica sol past gel time, the rheometer measures the shear strength before and at gel time. As mentioned before, previous rheological studies by Liverios & Nilsson (2016) on silica sol shows shear strength of 60-80 Pa at gel time. Also, Axelsson (2009) forecasted values of 60-80 Pa for silica sol at gel time, based on predictions from fall cone test data. As stated before, the results obtained from several runs with an Anton Paar rheometer in this study, at different frequencies, are consistent with the results of both Liverios & Nilsson (2016) and Axelsson (2009).

5.2 Hydraulically driven shear failure

Another objective of this study was to investigate the correlation between shear strength of silica and the hydraulic gradient. The results obtained from the tests show that a certain hydraulic gradient and the equivalent shear force the water creates, corresponds to the same shear strength value of the silica sol. To further clarify, 60-80 Pa was used as input data to calculate the hydraulic gradient using the formula and as the results from the test show, the calculated hydraulic gradient corresponded well to the shear strength of silica sol at gel time, which is 60-80 Pa. However, the results are only valid if no slip occurs in the pipe. Slip would mean that the results obtained is not in fact the failure within the material itself, and in that case, it is not the shear strength of silica that is measured. Instead the results would only imply the force it takes to push silica sol through a plastic pipe.

The fact that the silica sol could be found along the inner surface of the plastic pipes proves the validity of the test method and the set up. That is, the method is believed to measure the actual shear strength within the silica sol, and not the shear failure between silica sol and the pipe. Worth mentioning is that remnant of silica sol could be found even though high water and air pressure had been pushed through the pipe prior to examination of the plastic pipe.

It is believed that the test set up of shearing in pipes could be used as a complement to other shear strength measuring methods, in order to measure the shear strength of silica sol, but further tests have to be conducted and with known surface roughness's for the plastic pipes.

Finally, the shearing in pipe- test is conducted to try to simulate reality. The scenario which the tests aims to replicate is when a borehole is grouted in combination with presence of steep hydraulic gradients. During grouting procedures, water may flow towards the grout with high force. If the silica sol doesn't have enough internal shear strength to withstand the water, it will naturally fail. The results from the shearing in pipe- tests indicates that if the silica sol is let to reach gel time, and thus reach shear strength of 60-80 Pa, it will have a better chance to withstand steep hydraulic gradients.

5.3 Gel point study

Another objective of this study was to find a gel point criterion and compare it with the visual method using rheology, to find a correlation. As previously stated, a criterion of the gel point developed by Winter & Chambon is investigated and used during the rheological tests.

As could be found in the literature, results from numerous tests are consistent with the Winter- Chambon criteria, which states that G' and G'' intersects at the gel point and that the gel point can be found by studying the intersection of the loss tangents ($\tan \delta$). However, the results obtained during this study, the rheological tests barely showed intersection of G' and G'' . The few occasions G' and G'' intersected, was at a very early stage. G' was usually of a higher magnitude than G'' , thus indicating a predominately elastic characteristic of the material, even at an early state. Therefore, correlation between gel point and gel time could not be found or seen.

The loss tangent ($\tan \delta$) was also investigated. Intersection of different loss tangents at one specific point could not be seen, which furthermore states that the Winter- Chambon criterion is not true for the type of silica sol used in this study. However, due to time limitations, the frequency sweep which measure G' and G'' for all different frequencies, was not conducted. Therefore, it is not fully clear whether the Winter-Chambon criteria is true or false for the type of silica sol used. But according to the tests conducted within this study and the results obtained, the Winter- Chambon criterion do not seem to be of much use. The results of this study seem to consist better with the studies and conclusions of Gosal et al. (2004), which states that some gels with physical character do not satisfy the Winter- Chambon criterion, as previously mentioned.

5.4 Sources of error

During the rheological studies, no water bath was available, and the room temperature varied and was relatively high, 23-24.5 °C. This caused gel time to occur earlier than 20 minutes and slightly affected the synchronization between rheometer and visual method. Since temperature in the room varied slightly, the temperature for the silica sol in the tube also varied slightly, which could have been avoided if a water bath was available. However, throughout all the tests the temperature in the tube was measured, at the beginning and the end of the test, to make sure it didn't change drastically.

Pre-aggregation effects of the silica material could possibly be the cause of the limited use of the Winter- Chambon criterion. Due the long-time storage, the silica sol material could have pre-aggregated prior to the tests.

6 Conclusions

To reach the aim and objectives, three types of tests were conducted - Fall cone tests, with the purpose to investigate the shear strength development during 2.5 weeks; rheological tests in order to find the early shear strengths and to investigate the gel point criterion of Winter and Chambon; And finally, hydraulically driven shear tests, to study the mechanical behavior of silica sol at gel time in an environment that simulated reality, where steep hydraulic gradients can be present. Following conclusions can be drawn from the results of this study:

- The results obtained from the fall cone tests in this study, regarding the shear strength of silica sol, are relatively consistent with the results obtained in the studies by Liverios & Nilsson (2016) and Butron et al. (2007).
- Shear strength of silica sol at gel time is approximately 60-80 Pa and consistent with predictions made by Axelsson (2009) and the rheological studies conducted by Liverios & Nilsson (2016).
- Mechanical behavior of silica sol at gel time indicates a moderately ductile material and is consistent with the finding of Axelsson (2009).
- The Winter- Chambon criterion was of limited use in this study and for the certain type of set up used for the rheometer.
- No apparent correlation between gel point and gel time could be found.
- Correlation between hydraulic gradient and the shear strength of silica sol could be detected using the shearing in pipe- tests.

7 Further investigations

- Conduct shearing in pipe- test using different kind of pipes with known roughness.
- More in-depth rheology measurements. For example, further investigation of the loss tangent as a function of time and investigate the intersection point for all curves. Also, conduct a frequency sweep test, that is, plot G' and G'' as a function of frequencies and look for parallel lines, see Figure 2 and Figure 3.

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Appendix 1 - Oscillating cone plate raw data

The figures presented below show the results obtained during the rheological tests. The parameters G' and G'' are studied in order to investigate the Winter- Chambon criterion.

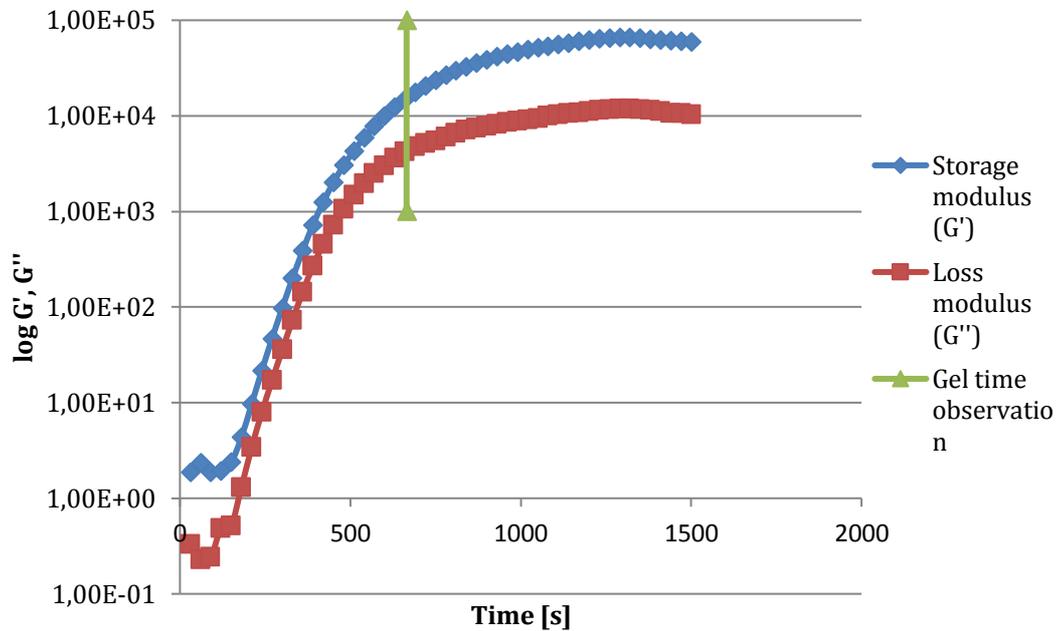


Figure 16. Test 1, 0.1 Hz

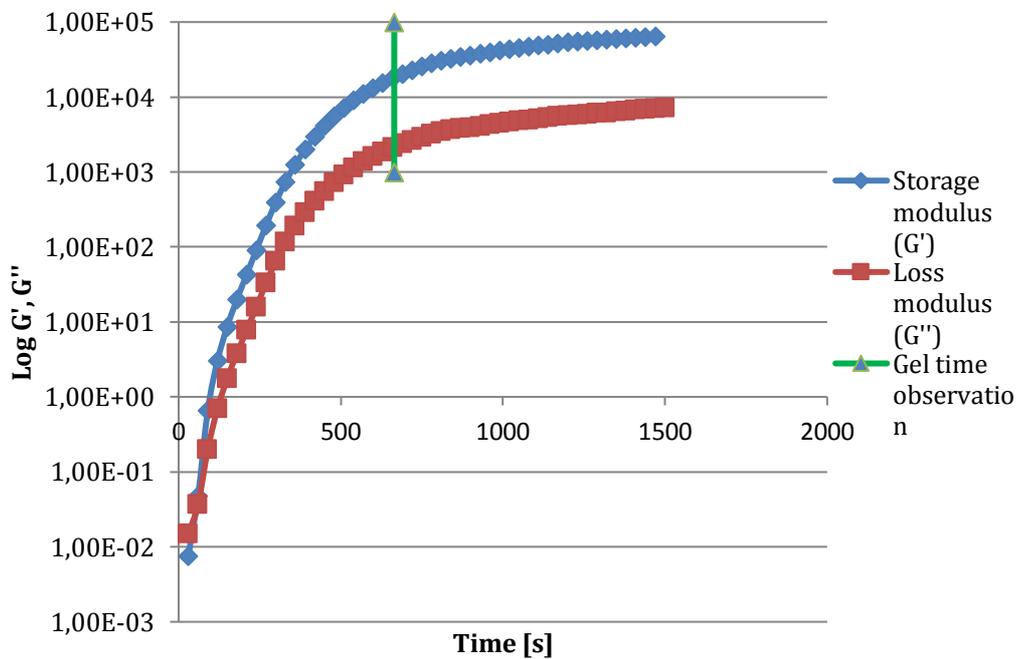


Figure 17. Test 1, 0.5 Hz

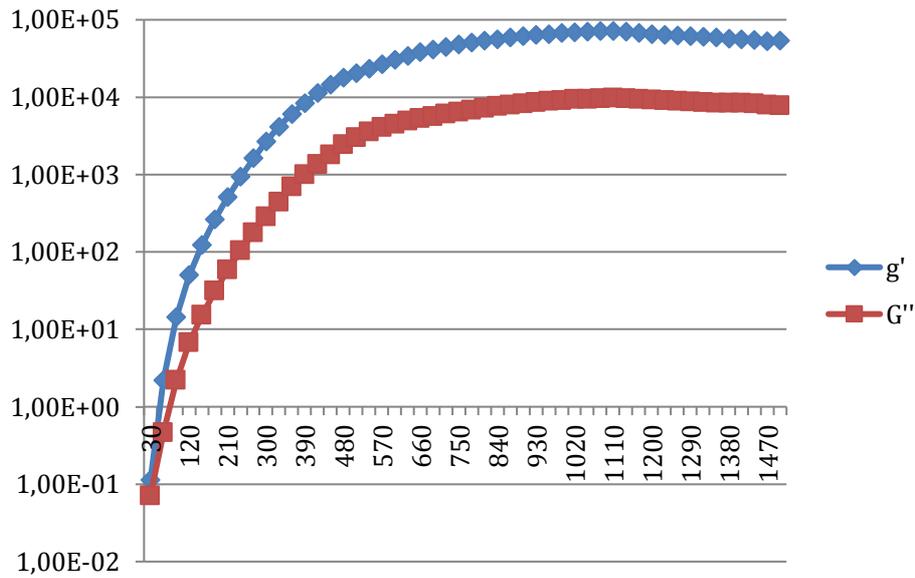


Figure 18. Test 1, 1 Hz

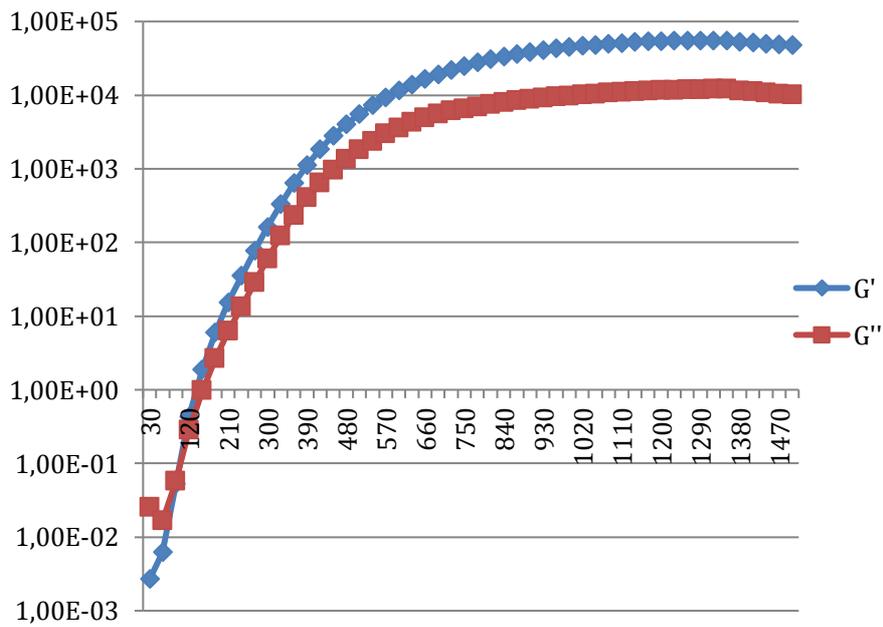


Figure 19. Test 2, 0.1 Hz

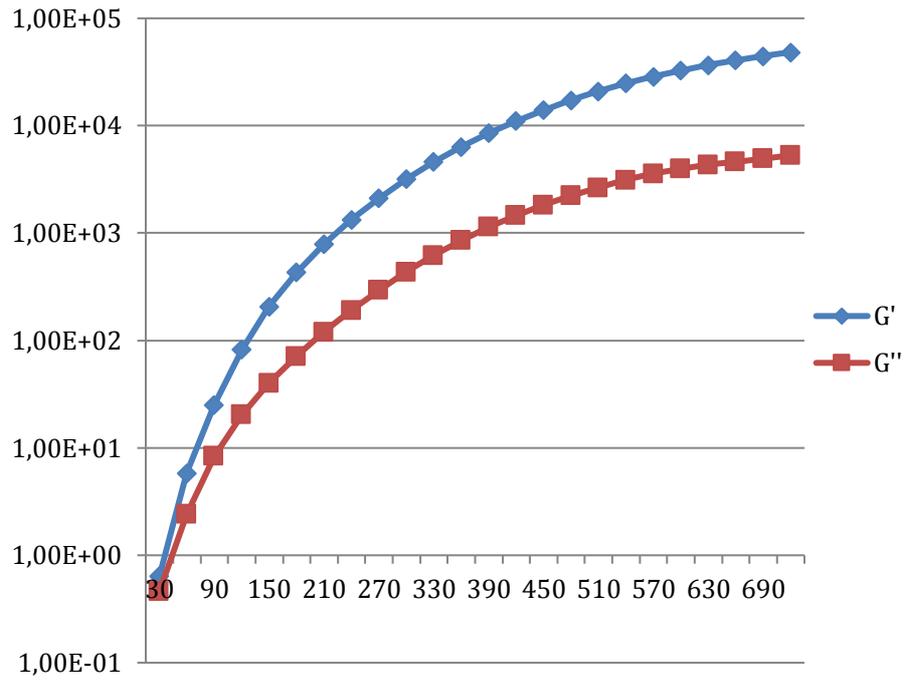


Figure 20. Test 2, 0.5 Hz

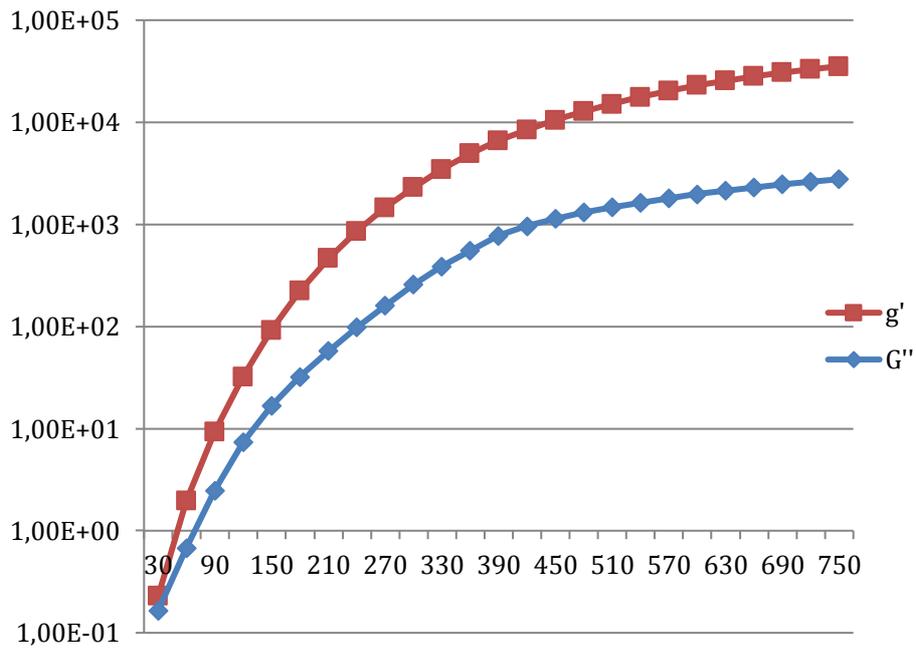


Figure 21. Test 2, 1 Hz

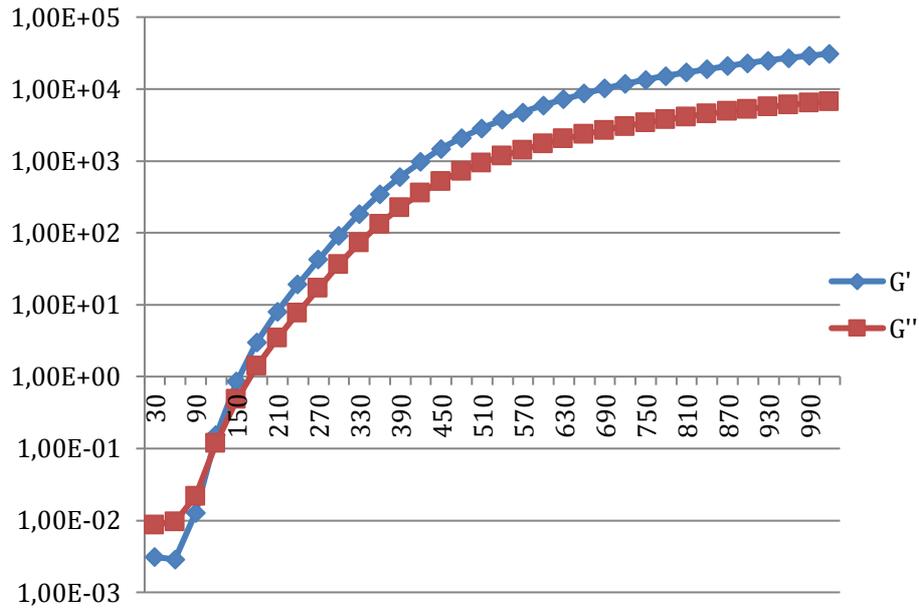


Figure 22. Test 3, 0.1 Hz

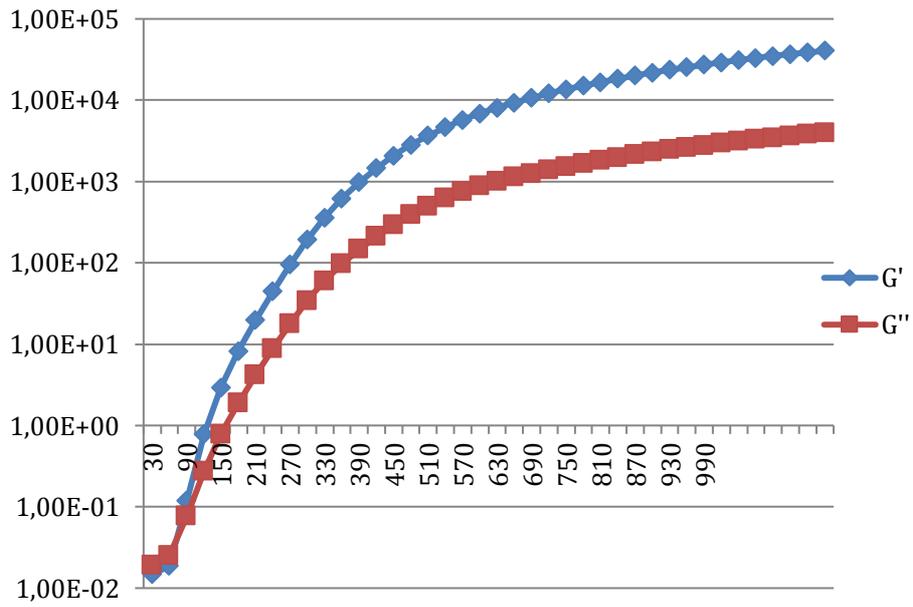


Figure 23. Test 3, 0.5 Hz