Silicate gels in civil engineering: The effect of organic matter content of soils on the hydraulic conductivity and strength of silicate gels

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Summary

Due to an increasing demand in space in urban areas, underground construction is becoming increasingly popular. To enable these constructions, silicate grout is injected to reduce the inflow of groundwater or to strengthen the soil. Unsuccessful grouting operations in the past have shown the need to investigate how environmental conditions affect grouting. This thesis focusses on how organic matter affects silicate grouting. Exploratory experiments were done focusing on three different aspects of the silicate grout, namely i) syneresis, ii) permeability and iii) Uniaxial compressive strength. Gel samples and grouted soil samples with increasing organic mass fractions were prepared and tested on these aspects. The syneresis experiments show that the shrinkage of silicate gels decreases with organic mass fraction. The syneresis experiments show that, in contrast to common belief, the permeability of grouted soils is not inherent to the grout, but rather to the imperfections in grouting procedures. The strength experiments show that an organic mass fraction of 8% may decrease the uniaxial compressive strength of grouted soil samples by up to 50%. In addition, the dehydration of grouted soil samples may also decrease the strength by 50%.

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1. Introduction

1.1 General

In urban areas, underground constructions are becoming more popular due to an increasing demand in space. Underground constructions in coastal areas require working with soft soils such as peat and clay as well as sandy aquifers. To enable underground constructions, measures need to be taken to either reduce inflow of groundwater or strengthen the soils. A popular methodology in the Netherlands is the application of so-called silicate grout, which is a fluid that can be injected in-situ and turns in to a gel.

Silicate grouting is typically used in civil engineering to either decrease a soil's permeability or to increase soil strength in aquifers below construction projects (Littlejohn et al., 1997). The technique of silicate grouting was developed to strengthen or reduce flow in soils where the porosity was too low to support the use of traditional Portland-cement suspensions (US Army Corps of Engineers, 1995). The first grouts were based on the reaction between sodium silicate and metal salts with the aim to bond the particles of soil or rock and to fill in the pore spaces to reduce permeability. Nowadays, organic curing agents are being used to control the reaction of the injected solution, thereby modifying the strength of the formed gel. Sodium silicate grouts are the most popular grouts for soil stabilization and reducing groundwater flow due to their safety and relatively low environmental impact (Avci, 2017). This type of grouting solution will also be mainly considered in this research.

A silicate grouting solution has three constituents: Dissolved silicate (commercially known as *water glass*), water and a curing agent. The ratio of these constituents varies based on the application of the grouting solution. For the permeability reduction of the soil, a so-called soft gel grout is used. This type of grout has a relatively low silica content. The soil permeability is lowered as the gel fills up the pore space between the soil grains. For soil stabilization, a so-called hard gel grout is used which has a relatively high silica content. The high silica content allows the grout to form stronger connections with the soil, thereby increasing the soil strength. (Sweijen et al., 2019)

A silicate grout will erode over time due to passing groundwater flow (Dekker et al., 2020). Consequently, silicate grouts have a lifetime, which is important as it determines the applicability of silicate grout civil engineering projects. For example, silicate grout shows an increase in permeability with time, which was shown by Avci (2017) who monitored an increase in soil permeability up to 160 days after the grouting was applied. They measured a total permeability increase of two to five orders of magnitude. The permeability increase is mainly attributed to syneresis (Mollamahmutoğlu & Avci, 2016), which is the shrinkage of a gel during which liquid is expulsed from the pores (Scherer, 1989).

Silicate grout can also decrease in strength because of leaching of components out of the grout. For example, Yonekura & Kaga (1992) measured a continuous decrease in strength in silicate grouted soil during a period of 1.000 days. In this period, the strength of the soil has decrease by half of the initial value. Leaching of grout and syneresis are caused by several factors. Past studies have focused on how these factors can be best controlled to achieve desired results in grouting projects. Tognonvi et al. (2011) studied the influence of the silicate content and the pH on the amount of syneresis occurring for 100 days. They found that high silicate concentrations resulted in more syneresis, while a higher alkalinity decreased the resulting syneresis. Syneresis also decreases when the content of curing agent is increased and the soil strength significantly increases more with a higher silicate content when a larger volume of curing agent is present (Littlejohn et al., 1997). How such factors are influenced by environmental conditions has however received little attention in literature.

An important environmental condition is the presence of organic matter in sandy soils. In this research, we hypothesize that gelation of a silicate grout is influenced by the presence of organic matter in the soil. This hypothesis is based on field data of projects in the Netherland where the strength of silicate grouting decreases with organic matter content.

Despite these observations, the effect of the soil organic mass fraction on the integrity of silicate grout has not been intensively studied. However, research by Kazemian et al. (2012) does indicate that grouted organic soils have a lower strength and higher permeability. They measured the conductivity and strength of grouted organic soil samples with an organic content larger than 25% using multiple grouts. Typically, sand layers are used for grouting in construction in which the organic content is significantly lower than 25%. For these soils, it is still important to understand the effects of organic matter on the grouting process.

1.2 Problem definition & research aim

In construction projects where grouting is applied, the effectiveness of the grout bears a big responsibility. Should a soft gel grout fail, construction fields could flood which brings additional costs and delays the construction. An example of such a case is the construction of 'de Haagse tram tunnel' (van Tol, 2004). In case a hard gel grout fails, the consequences could be even more catastrophic, like the collapse of overlying structures. This research aims to investigate how the soil organic mass fraction influences the effectiveness of silicate grouting. To realize this aim, the following research question is posed: What is the effect of organic matter in soils on silicate grouting, in terms of shrinkage, permeability and strength?

To answer this question, the following objectives were set:

- To show the effect of organic matter on the shrinkage of the gel.
- To show the effect of organic matter on the permeability of grouted soils.
- To show the effect of organic matter on the strength of grouted soils.
- To discuss the underlying processes responsible for the relation between organic matter and silicate grouting.

2. Theory

This chapter introduces two important concepts in this study, namely: i) Grouting operations and ii) Silicate grouting chemistry. The introduction of these concepts is intended to provide an understanding of the processes involving the practical applications of silicate grouting. The paragraph 'Grouting operations' discusses the execution of silicate grouting on a field scale and elaborates on the application of grouting. The paragraph 'Silicate grouting chemistry' provides the processes that precede gelation[1].

2.1 Grouting operations

Grouting for civil engineering applications can be done with various grouting techniques. The main techniques are permeation grouting, compaction grouting, hydro fracture grouting, jet grouting, rock grouting, compensation grouting and deep mixing method (Kazemian & Huat, 2009). Figure 2.1.1 provides a schematic overview of these techniques. In the experiments conducted in this study, soil samples are grouted with sodium silicate grout with particular interest in permeability and strength of the soils. As permeation grouting is applied under similar conditions, this technique is mainly discussed here.

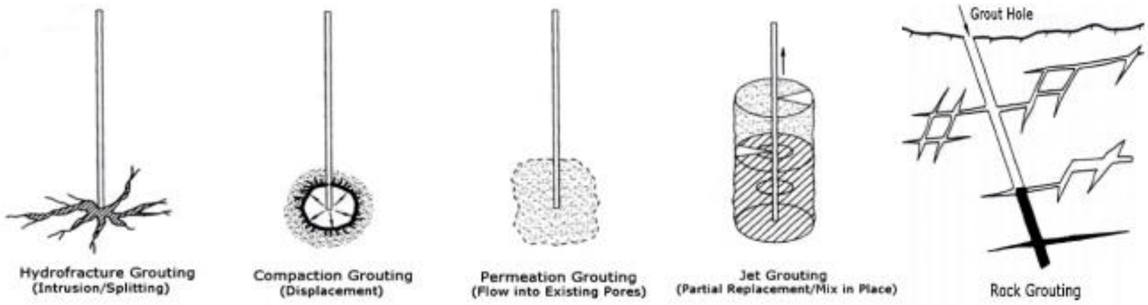

Figure 2.1.1 Civil engineering grouting techniques. (Kazemian & Huat, 2009)

[1] Gelation is the solidification of a gel.

2.1.1 Permeation grouting

The penetration of grout is dependent on the permeability of the soil. Permeation grouting is therefore limited to soils with relatively high porosities, like sand or gravel (Celik, 2019). Grout is injected into the soil through injection tubes, which are placed in a desired grid within a construction area (B&P Bodeminjectie, 2012a). When injected, the grout diffuses from the tube exit through the pore spaces of the soil (Yanbin et al., 2019) (Figure 2.1.2). The grout diffused from different injection tubes interlinks and solidifies to form a semi-impermeable layer.

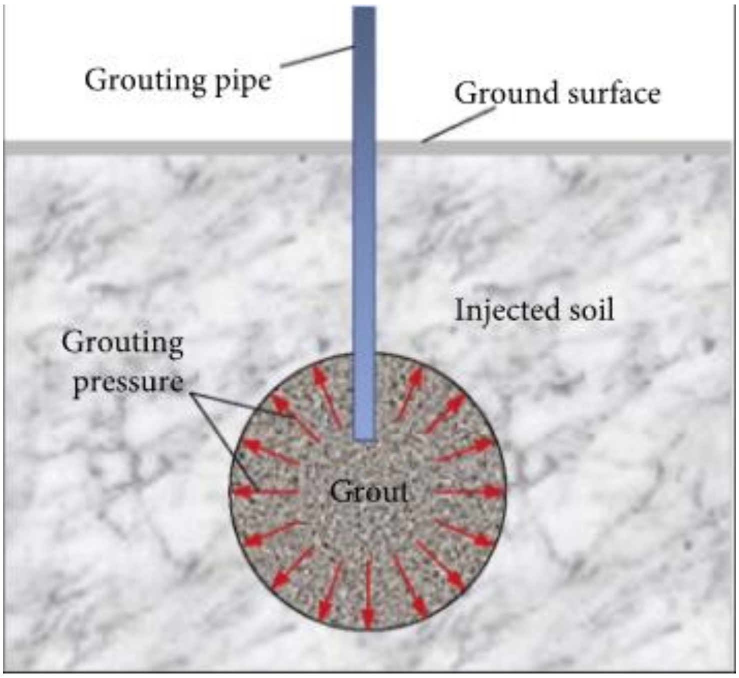

Figure 2.1.2 The diffusion of grout in permeation grouting. (Yanbin et al., 2019)

Ground stabilization

Beside permeability reduction, permeation grouting is also used for increasing soil strength. Ground stabilization is particularly applied in construction next to already existing constructions. With the injection of grout with high silica content (hard gel) into the soil, the bordering ground can be excavated without support mechanisms (Figure 2.1.3).

Figure 2.1.3. An injected soil underlying an existing foundation (B&P Bodeminjectie, 2012b).

2.2 Silicate grouting chemistry

In this paragraph the two major components of sodium silicate grout, namely sodium silicate and the curing agent, are discussed and the chemical processes leading to the formation of a silicate gel explained.

2.2.1 Sodium silicate

Dissolved silicates can be represented by the following formula: (M_2O) * n (SiO_2), in which M is the alkali metal used in the formation of the silicate, sodium in this case, and n is the number of moles of silica (SiO_2) per mole of alkali metal oxide (M_2O) (CEES, 2004). Silicates are identified by the SiO_2:M_2O ratio, which can be provided in terms of weight ratio (WR) and molar ratio (MR) (PQ corp, 2004). In this study a sodium silicate solution with a molar ratio >3.2 is used (PQ Corporation, 2016).

2.2.2 Curing agent

When a dissolved silicate solution is exposed to acid forming products, the formation of silica polymers is induced (PQ corp, 2004). For the acid forming product an organic ester solution (Triacetin 70-100%; Vescolub, 2017) is used in this study. The organic esters undergo a process of hydrolysis, whereby the pH of the silicate solution is lowered. As a result, silica polymerization is induced.

2.2.3 Silica polymerization

Silica polymerization is the process leading to the formation of colloidal silica (gelation) (Lunevich, 2019). During polymerization, silicate ions can from chains and networks with dimensions depending on the molar ratio of the silica (Figure 2.2.1). The polymerization reaction can be represented by the condensation reaction of silicic acid (PQ corp, 2004):

$$2\,Si(OH)_4 \rightarrow (OH^-)_3 - Si - O - Si(OH)_3 + H_2O$$

The molecule $Si(OH)_4$ is only stable in a particular pH range (Sweijen et al., 2019). Therefore, when an acid forming product is added to a dissolved silica solution, the above polymerization reaction is induced. The polymerization of sufficient $Si(OH)_4$ molecules can cause the formation of colloids. The presence of natural silica (e.g., in sand) can allow the colloids to grow on the particle surface (Figure 2.2.1).

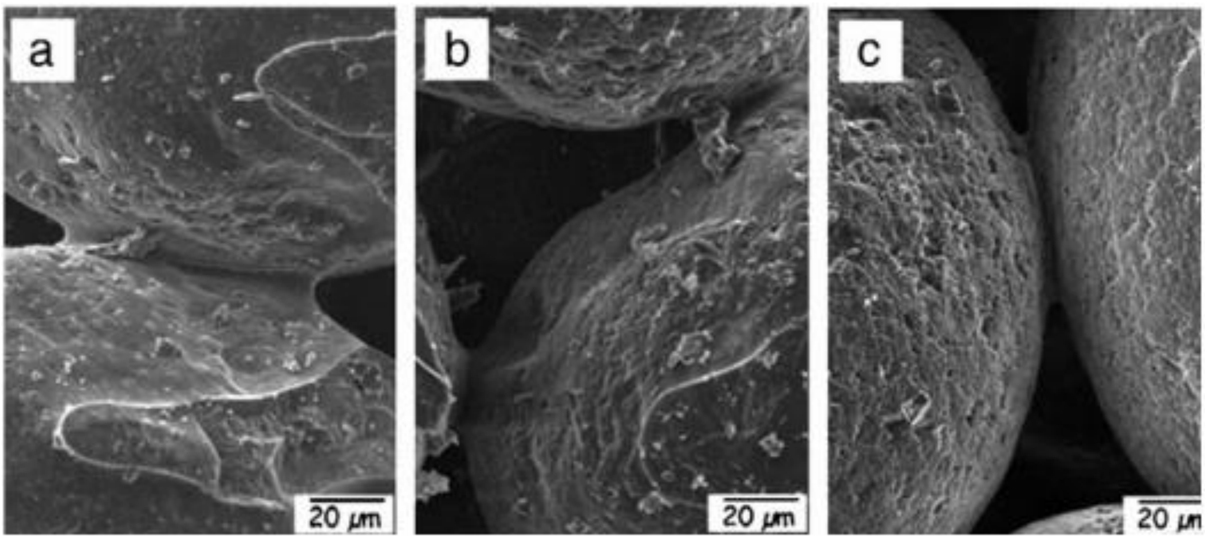

Figure 2.2.1 The coagulation of sand particles for different silica concentrations (a 18 wt%, b 13 wt% and c 7 wt%). (Sweijen et al., 2019)

There are various degrees of silicate polymerization, quantified by the number of Si-O-Si bonds. In general, more Si-O-Si bonds suggests a stronger polymer and in turn a stronger gel structure. Figure 2.2.2 provides an overview of different degrees of polymerization. During polymerization, water is expulsed from the silicate compounds. This process is called syneresis. The more syneresis takes place, the denser the structure of the gel becomes. (Sweijen et al., 2019)

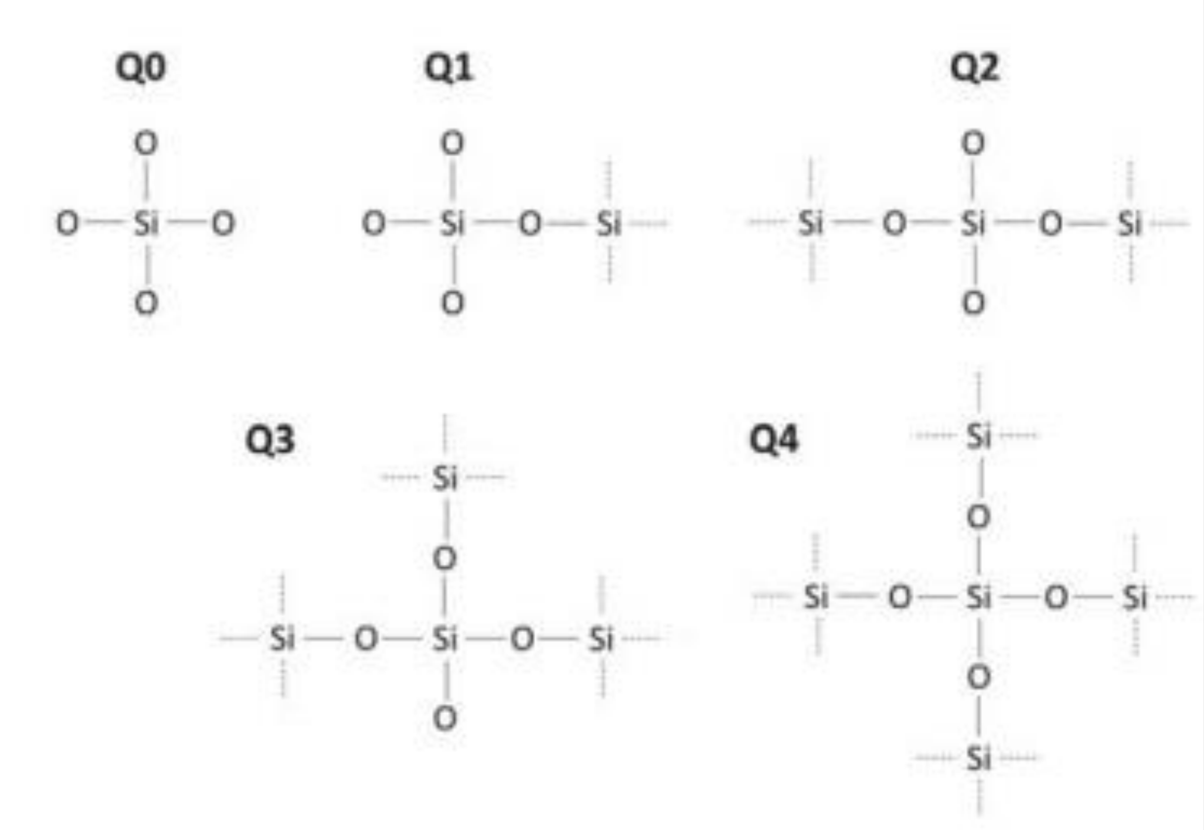

Figure 2.2.2 Different degrees of polymerization. Q4 (four Si-O-Si bonds) is further polymerized than Q1 (one Si-O-Si bond). (Sweijen et al., 2019)

3. Methods

3.1 General

This research consists out of three experimental approaches, namely experiments to determine: i) syneresis, ii) soil strength and iii) permeability. The experimental approach is designed to fully investigate the parameter space of hard gels and soft gels and their respective soil strength and permeability. The research aims to correlate findings and to give insights on how macro-scale properties are defined by pore- and gel scale phenomena.

The syneresis and permeability measurements were conducted at the workshop of B&P Bodeminjectie in Vianen. The experiments on soil strength were conducted at TUDelft, at the soil mechanics lab.

3.2 Silicate grouting

Silicate grouting was done in all three experiments and refers to the injection or addition of a silicate gel mixture to the soil pore space. The gel mixture is produced from mixing a sodium silicate solution (PQ Corporation, 2016), an organic ester (Triacetin; Vescoclub, 2017) and water. The mixing proportions depend on the desired gel type (Table 3.2). To produce the gel mixture, all components are added together and mixed for five minutes.

3.3 Sand and organic matter

For the grouted soil in the permeability and UCS experiments, commercial crusher sand was used. The physical properties of the sand are unknown. For computational purposes, the bulk density was assumed at 1650 kg/m^3 and the porosity was assumed at 0.35. As organic matter, black peat by Pokon was used with an organic matter content larger than 90% and a pH of 3.5 – 4.2. Further constituents of the black peat are unknown.

The proportions of silicate grout and organic matter in the syneresis experiments were derived from computations (Appendix 1). For the soil strength experiments, the proportions of organic matter added to the sand were determined as follows: First, the mass of a volume of sand was determined. This volume was considered as a mass fraction 100% minus the required organic mass fraction. Organic matter was then added until the total mass was reached.

3.4 Syneresis experiments

The syneresis experiments were conducted in five batches. In each batch, six containers of 250 ml were prepared with organic matter, corresponding to a variety of organic mass fractions[2] (Table 3.1). In each container, silicate grout was added bringing the total sample volume to 200ml (Table 3.3). The grout was prepared separately in volume of approximately 2L. The constituents and proportions of the samples are provided in Table 3.2.

Sample	1	2	3	4	5	6
Hard gel batch 1	0%	2%	4%	6%	8%	10%
Hard gel batch 2	0%	2%	4%	6%	8%	10%
Soft gel batch 1	0%	2%	4%	6%	8%	10%
Soft gel batch 2 (water)	0%	2%	4%	6%	8%	10%
Soft gel batch 3	0%	0,5%	1%	1,5%	2%	2,5%

Table 3.1 An overview of the executed syneresis experiments. The '%' indicates the organic mass fraction of the sample. Soft gel batch 2 was executed with an initial water layer of 30ml on top of the gel.

[2] Defined as percentage of the sample mass that is organic. Appendix 1 provides the derivation of the organic mass values.

The experiments were done for both hard gels and soft gels. Based on earlier syneresis experiments conducted by for example Eyubhan (2017), Littlejohn, et al. 1997), the required time steps for measuring the amount of syneresis data were estimated. The actual time steps were however based on the measured data during the experiments. When seemingly no additional syneresis was measured compared to the previous time step, the time interval between measurements was increased.

<u>Hard gel</u>		***<u>Organic matter</u>***	
Curing agent	*8%*	*Organic content*	*min. 90%*
Water	*42%*	*pH*	*3.5 – 4.2*
Water glass	*50%*	*Moisture content*	*max. 80%*
<u>Soft gel</u>			
Curing agent	*2.5%*		
Water	*84%*		
Water glass	*13.5%*		

Table 3.2 Constituent information of the water glass gel samples as percentage of the total volume.

3.4.1 Sample preparation

First, organic soil was added to the containers with a mass according to Table 3.3. To measure the weight a balance was used with an accuracy of 0,01 grams. Then, the silicate gel mixture was prepared. Next, each container was filled with a volume of silicate gel mixture depending on the organic mass fraction of the sample (Table 3.3). The samples were then additionally stirred to increase the reaction surface between the silicate gel and organic soil. The containers were closed with a lid to reduce the impact of evaporation during the experiments. The containers were weighed beforehand and after preparation of the sample to determine the initial mass of the samples.

Organic mass fraction	Mass of black peat (grams)	Volume silicate gel mixture (ml)
0%	0	200
2%	12	181
4%	22	165
6%	30	152
8%	37	141
10%	44	131

Table 3.3. The mass of organic soil and silicate gel mixture added to the samples.

3.4.2 Data collection

Syneresis was measured four times after preparation of the samples. Before measuring syneresis the samples were weighed. The syneresis liquid was then poured from the container into a measuring cylinder by hand. The container (and gel) was weighed again and the volume of syneresis was determined from the measuring cylinder. Hereafter, the syneresis liquid was poured back into the container and the container was weighed again to determine possible weight loss from the sample because of the procedure. The measuring cylinder was additionally weighed before adding the syneresis liquid, when the syneresis liquid was added and when the cylinder was emptied again. This was done to compare potential weight loss of the sample with weight gain of the measuring cylinder.

3.5 Permeability experiment

To investigate the permeability of sandy soils injected with soft gels, an experimental setup was designed that was able to cope with high pressure values. This was required because of the low permeable nature of silicate gels.

3.5.1 Test setup

Figure 3.5.1 shows a schematic overview of the experimental setup. The experimental setup was designed after a constant head test coping with large pressures (up to $5*10^5$ Pa). The setup contains an acrylic column (1) in which the grouted sample was placed. A second, longer, acrylic column was used as water reservoir (2). The columns were connected by tubing. Water valves were placed below the grouted sample and at the top of the water column to regulate pressure and water flow (7). A tube was connected directly below the grouted sample to allow for measurements of water pressure (6). At the top of the water column (2) a constant pressure was applied using an air compressor (5). An air valve at the top of the acrylic tube allowed for the release of air pressure from the system (3). The top boundary conditions were at a constant pressure, such that the groundwater flowed at a constant volumetric rate.

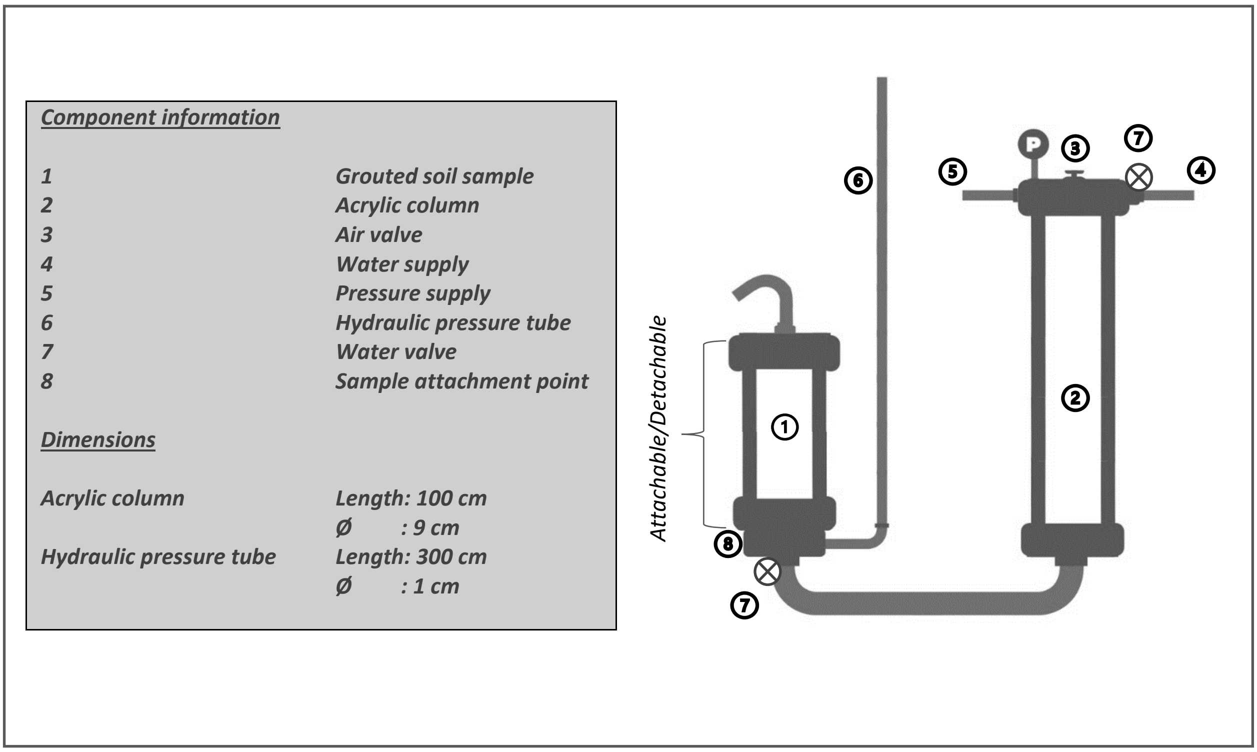

Figure 3.5.1 A schematic overview of the constant head test setup.

3.5.2 Procedure

The permeability experiments were conducted using two different grouting methods, namely i) mixing of the grouting and ii) gravity permeation.

3.5.2.1 Mixing grout method

A surplus amount of sand was first added to a bucket. Then a soft gel grout mixture was prepared, after which the mixture was added to the sand and stirred until fully saturated. The mix of grout and sand was then poured into the sample case, while intermittently compacting the sample through manual pressurization. When filled, the sample was left to solidify for at least two hours before use.

3.5.2.2 Gravity permeation grouting method

In this method sand was added to the sample case first and the gel mixture was added on top to allow saturation under gravity. To prevent excessive gel mixture remaining on top of the samples, the bottoms of the samples were closed by an elastic lid that allowed gel mixture and air to come through when manual pressure was applied on the sample. Before adding the gel mixture, the sample was covered with a permeable cloth to prevent distortion of the sample surface. After gelation, the sample was covered with a column of dry sand and closed off at the top (Figure 3.2).

3.5.3 Computations

To determine the permeability of the silicate grouting, we use Darcy's law. Permeability is defined as '*K*' ($m \cdot s^{-1}$) as follows:

$$Q = K * A * \frac{dh}{dz} \qquad \text{or converted:} \qquad K = \frac{Q}{A} * \frac{dz}{dh}$$

In which Q ($m^3 s^{-1}$) is the volumetric flow rate, A (m^2) is the surface area of the flow, dz (m) is the sample length and dh (m) is the hydraulic head difference between both ends of the sample. The head difference was set equal to the air pressure in the water column ($3*10^4$ Pa), which was significantly higher than the water Table in the injected sample ($1{,}01325*10^2$ Pa). In the gravity permeation grouting experiment, the top of the sample was covered with a sand column (Figure 3.5.2). The head difference was computed using soil pressure data and the sand column thickness. The volumetric flow rate in this setup was estimated from the increasing saturation level of the sand column above the sample (Figure 3.5.3).

Figure 3.5.2 The gravity permeation grouting sample. First dry sand was added, and then semi saturated sand was added on top.

Figure 3.5. An overview of the saturating sand column. The blue markings indicated saturation levels 30 minutes apart. The bottom line represents t=0.3

3.6 UCS experiments

To determine the effect of organic matter on the strength of soils grouted with hard gel, experiments were conducted with using a Uniaxial Compressive strength (UCS) test (Figure 3.5.4). In this test, a grouted soil sample is placed in between and compressed by two metal discs at a constant rate of 0,01 mm/sec, thereby increasing vertical load on the sample. The stress that the metal discs experience is recorded. Due to the constant strain, the sample will fail by fracturing at which point the UCS test is turned off.

Figure 3.5.4 The device used in the UCS experiments. The red markings demonstrate the metal plates that enclose the sample.

3.6.1 Sample preparation

Two batches of UCS experiments were conducted. In both batches five samples were prepared with varying organic matter content following Table 3.4. The samples were prepared by pouring a mixture of hard gel grout, sand, and organic soil into a mold. The mixture was pressurized manually during addition to improve sample compaction. A volume of sand of about twice the sample volume was first added to a container. Then a quantity of organic soil corresponding to the mass fraction of the respective sample was added and mixed with the sand. Next, the silicate gel mixture was prepared (section 3.1.1) and mixed with the sand and organic soil before the entire mix was added to the mold. After preparation, the samples were left for six days before being used in the UCS device.

The surfaces of the samples were straightened using a thin layer of gypsum (Figure 3.5.5). This procedure was mostly required for the first batch as for the second batch the packing method was altered slightly to produce evenly shaped surfaces. Although improved, the sample surfaces of the first batch were not ideally flat for the UCS device.

Figure 3.5.5 The UCS samples of the first batch.

4. Results

4.1 Syneresis experiments on hard gels

This paragraph presents the experimental results on syneresis experiments on hard gel samples. The data is presented in Figures 4.1.1 and 4.1.2. The amount of syneresis is defined as the volume of fluid of the gel caused by shrinkage of the gel and the initial volume of the gel. Figure 4.1.1 shows the amount of syneresis against time. Syneresis typically started occurring within hours and decreased as a function of the degree of organic matter for approximately 4 days.

Syneresis in Figure 4.1.1 is given as a percentage of the initial volume of the silicate gel. This initial volume does not include organic matter and therefore solely shrinkage of the gel is reflected. The addition of organic soil to the samples resulted in less syneresis. This difference in syneresis is more expressed closer to the maximum syneresis position of the samples.

The maximum amount of syneresis, derived from the equilibrium volume of syneresis in Figure 4.1.1, was plotted against the organic mass fraction (Figure 4.1.2). Furthermore, the change in gel density was plotted against time. Lastly, both an estimation of mass loss due to evaporation and measurement uncertainties are given and discussed (Figure 4.1.3).

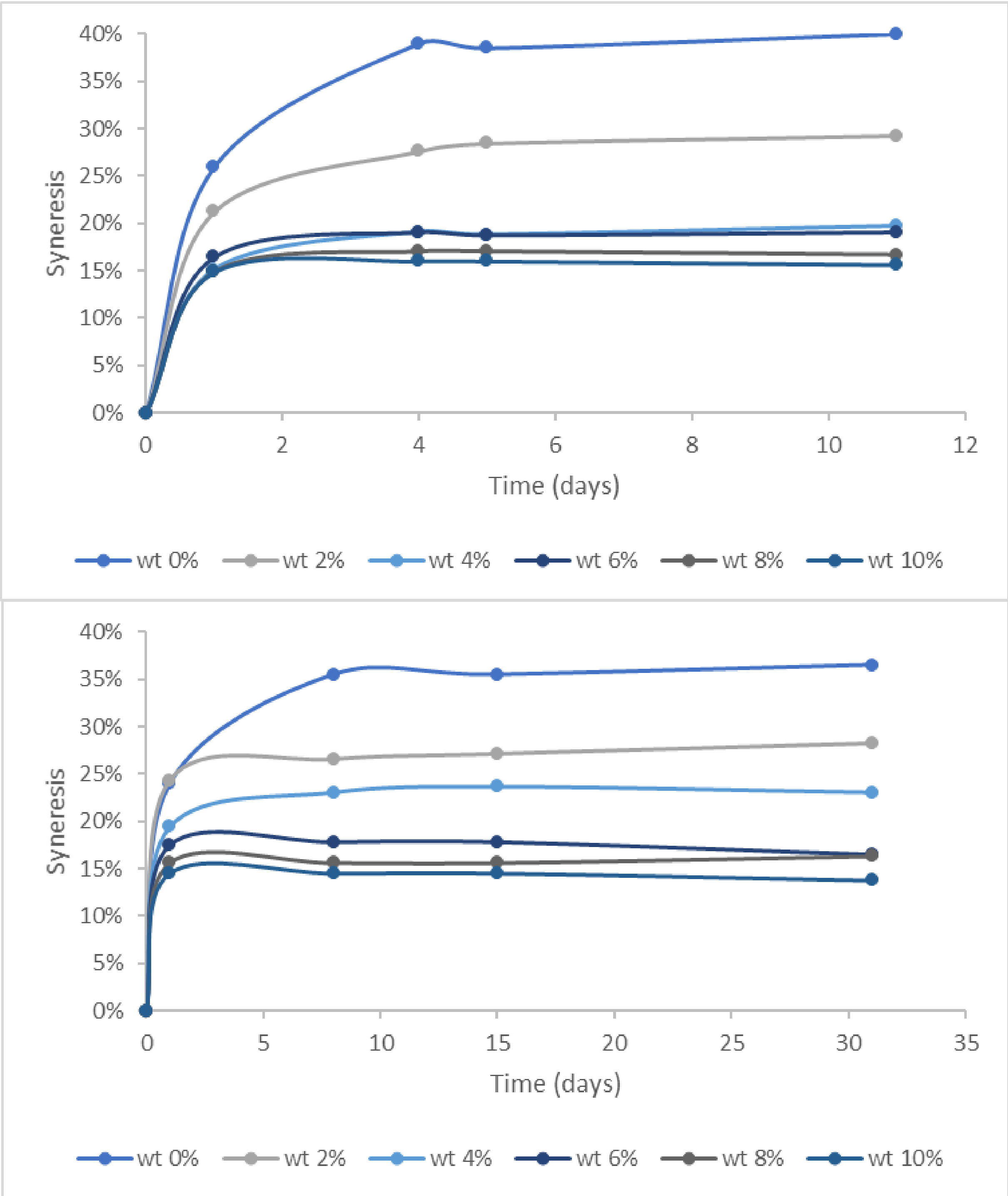

Figure 4.1.1 Syneresis of the hard gel samples of the first batch (top) and the second batch (bottom). The syneresis is expressed as a percentage of the initial gel volume.

4.1.1 Total syneresis vs organic mass fraction

The graph in Figure 4.1.2 shows a decrease in total syneresis with increasing organic mass fraction. The graph connects the averaged data from the two batches. The error margin on the graph provides a maximum error resulting from the measuring procedure. This margin is drawn on the averaged data and therefore differs slightly from the actual error margin (section 4.1.2). The graph shows that organic matter decreases the total amount of syneresis occurring in the gel. The concave shape of the graph indicates a decreasing effect of organic matter for higher organic mass fractions.

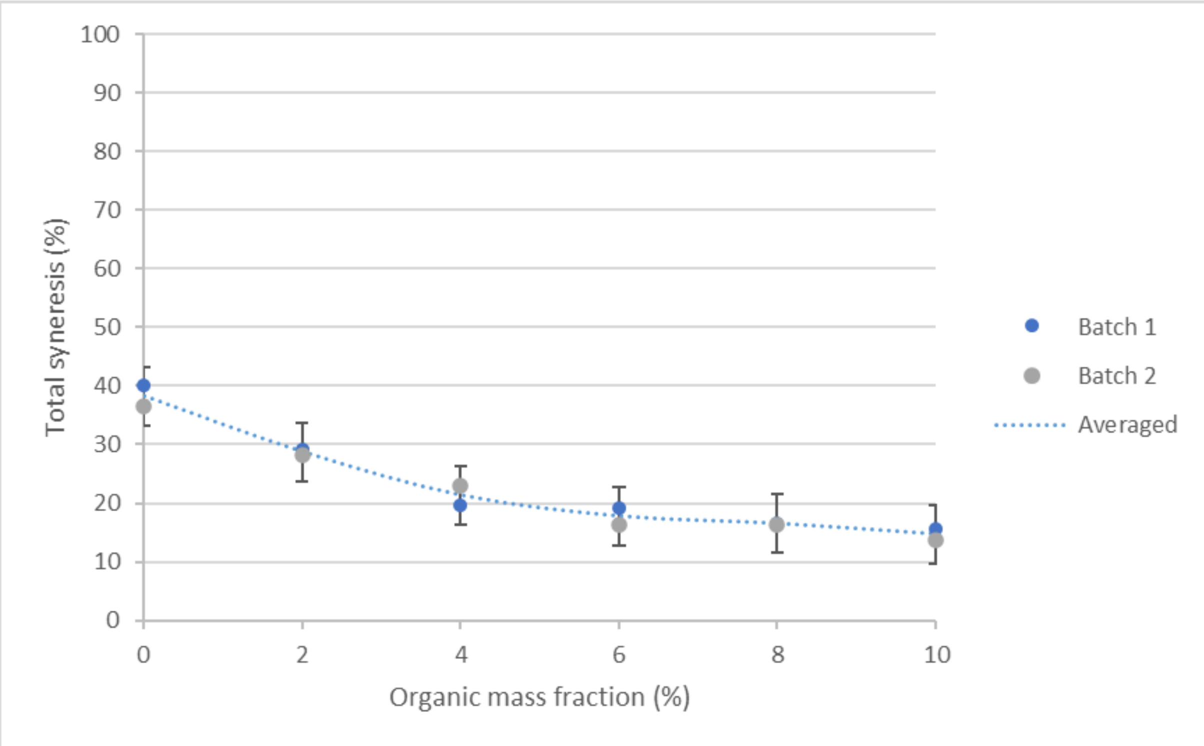

Figure 4.1.2. The total syneresis for different organic mass fractions. The dotted line represents the average values between the data points. The error margin is provided on the averaged data points. The x-axis describes the organic mass fraction in the sample and the y-axis describes the total syneresis relative to the initial sample volume.

4.1.2 Measuring error

The error margin caused by the measuring procedure was determined from the weight change of the container. Figure 4.1.3 shows the resulting error margin from the measurements. The data is grouped by day of measurement and plotted against the mass loss given in grams. When the total mass loss is compared to the total syneresis, the net loss values less than 5%. Most of the mass loss is recorded in the weight gain of the measuring cylinder. The mass loss not shown in weight gain of the measuring cylinder describes the error margin of the mass loss (Appendix 2).

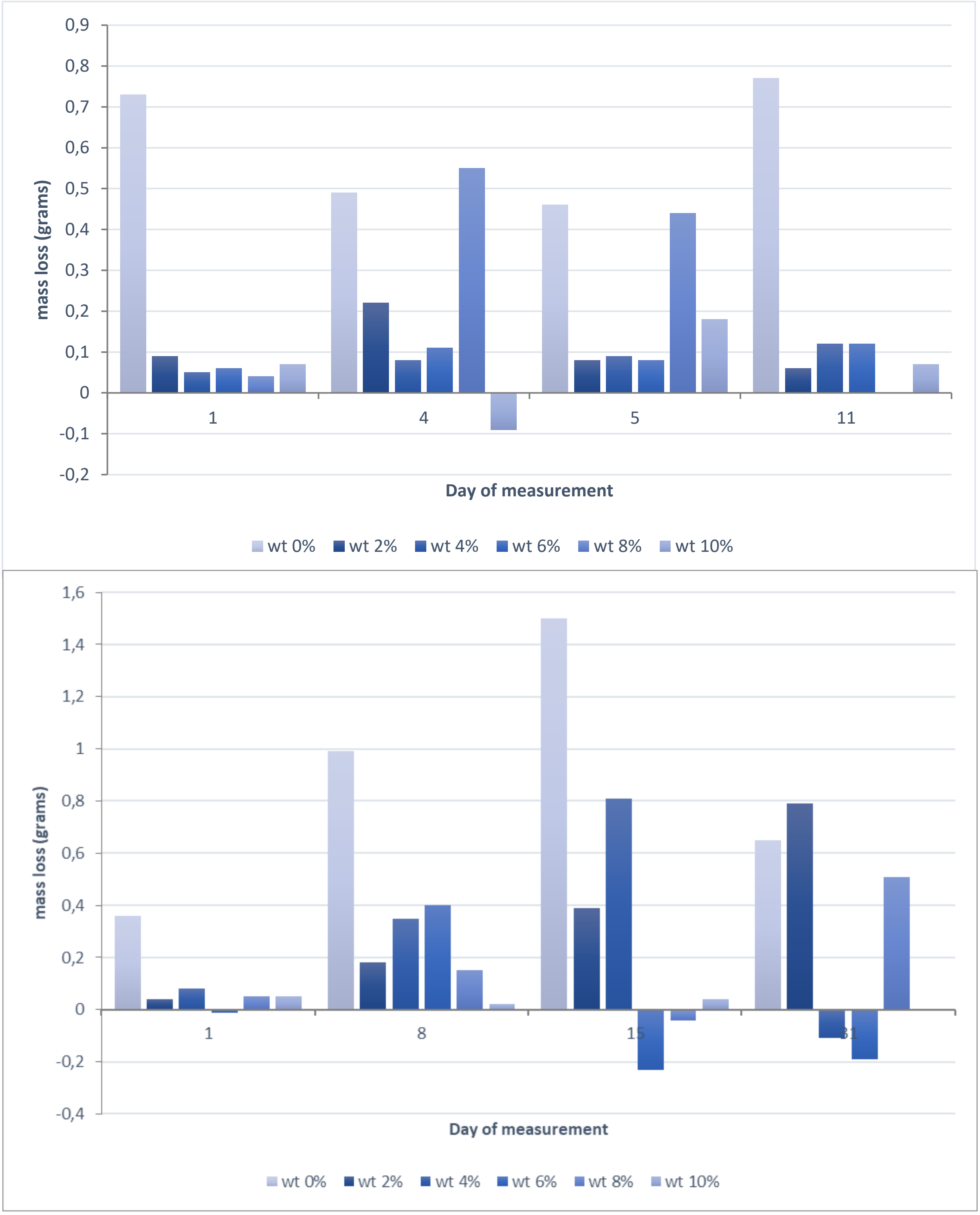

Figure 4.1.3 The mass loss resulting from the measurements in the first batch (top) and second batch (bottom). The x-axis shows the samples measured on 4 separate days and the y-axis shows the accompanying mass loss from each measurement. The samples are distinct in the mass fractions shown in the legend.

4.2 Syneresis experiments on soft gels

After several weeks of observation, all soft gel samples ceased shrinking and syneresis remained constant, with values of no more than 2% of the initial gel volume (Figure 4.2.1). During the first and second batch, samples were prepared with organic mass fractions 0% - 10%. Furthermore, a third batch was prepared with organic mass fractions 0% - 2,5%.

Total syneresis of about 5ml was measured for the soft gel without organic soil. The soft gel sample containing an organic matter content of 2% measured a total syneresis of about 3ml. The remaining samples showed very little to no syneresis. The syneresis liquid that was present in these cases was too little to measure accurately (less than 1% of the initial volume). One week after the soft gel samples were prepared, mold was observed on the samples with organic matter contents of 4% and higher. Visual observation after one month indicated the growth of mold on samples with low organic matter content (2%). When mold started showing on the first batch of soft gel samples, it was chosen to prepare the second batch differently, namely by adding 30ml of additional water on top of the already formed gels. For the second batch, no significant syneresis was observed (only 1ml after two weeks). During the second batch, no mold was observed anymore indicating that the additional water prevented mold growth by reducing the oxygen supply at the top of the gel.

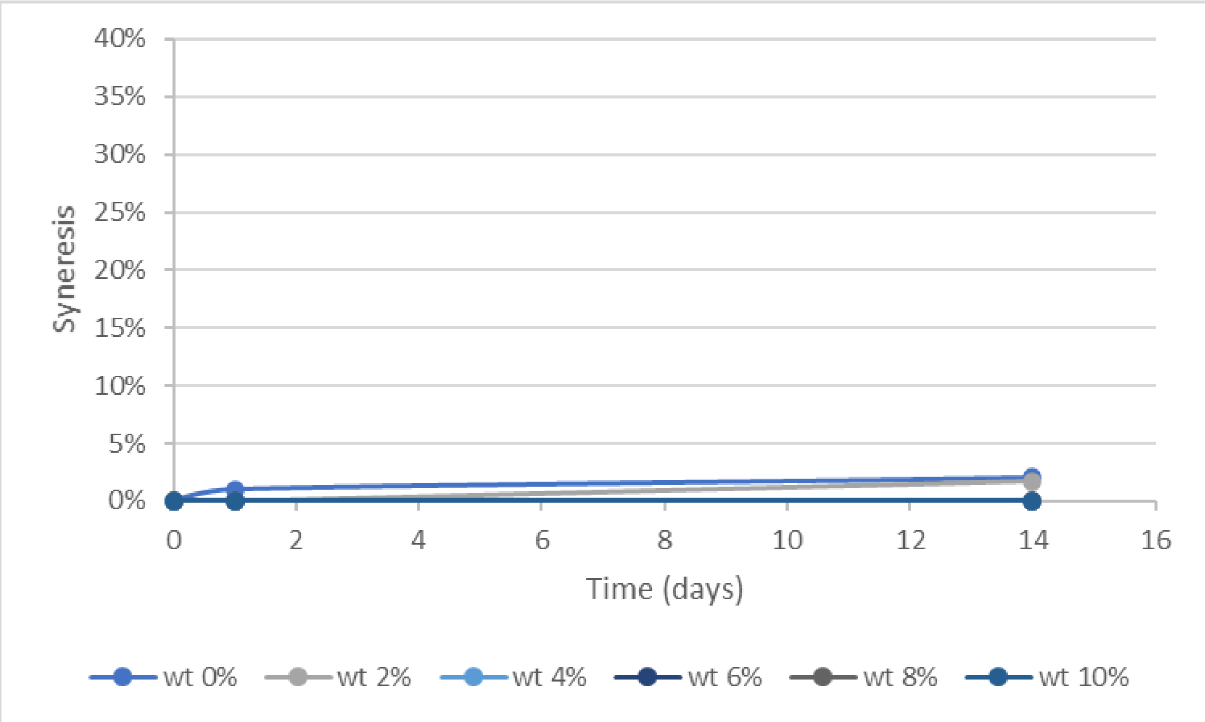

Figure 4.2.1 Syneresis of the soft gel samples of batch 1. Syneresis is given as a percentage of the initial volume.

4.2.1 Error margin curing agent

This experiment was done to determine if fluctuations in the addition of curing agent during sample preparation could attribute to a significant error in the syneresis results. Three samples of 500ml silicate gel were prepared with varying content of curing agent. The first sample contained 4% curing agent, 13.5% water glass and 82.5% water. The second sample contained 6% curing agent, 13.5% water glass and 80.5% water. The third sample contained 8% curing agent, 13.5% water glass and 78.5% water. After several weeks only very little difference in syneresis volume was observed. A higher content of curing agent did cause increased syneresis in the sample, but not enough to affect the syneresis results in any way.

4.3 Discussion of syneresis experiments

The discussion below mainly represents the results of the hard gel samples. Although a decrease in syneresis was observed for the soft gel samples (Figure 4.2.1), it cannot be said with complete certainty that a relation exists here. The error margin values for measurements of the hard gel samples (Figure 4.1.3) lie close to the measured syneresis in the soft gel samples. It is however likely that the same processes involved in the syneresis reduction for hard gels apply for soft gels too.

4.3.1 Inhibited syneresis of organic samples

The results indicate that organic matter in soils reduces the amount of syneresis in the silicate gel. As the process of polymerization of a gel is set on by the lowering of the pH with an organic acid, it is expected that further lowering of the pH by the addition of black peat (pH 3.5 – 4.2) would enhance polymerization. Figure 4.3.1 shows that following the solubility of silica with pH, polymerization is expected to increase. The reduced syneresis of gels containing a high organic mass fraction however implies that the polymerization process is inhibited. This observation may be explained by one of the following hypotheses:

4.3.1.1 Total dissolved solids (TDSs)

Past research has shown an inhibiting effect of total dissolved solids on the polymerization of silica (Zulh & Amjad, 2013). They also found that the inhibiting effect of divalent cations inhibited polymerization much more strongly than monovalent cation. Natural peat has a large capacity for storing cations, in particular Na^+, Ca^{2+}, Mg^{2+} and K^+ (Urban et al., 1995). However, black peat is known to have a low nutrient content (van Eysinga, 1965), and therefore the addition of cations in the experiments may have been limited. Still, the addition of total dissolved solids may well have contributed to decreased syneresis. Additionally, the presence of dissolved solids decreases the reaction surface between silica molecules, which may decrease polymerization.

4.3.1.2 Curing agent neutralization

Most organic matter consists for 60-80% of humic acids (Sanderman & Amundson, 2014). These acids often have a strong polarizing power and can therefore easily adsorb to other polar surfaces (Graveland, 1981). The curing agent triacetin contains three acid groups with such polar surfaces. By adsorption of the humic acids to the triacetin acid groups, the curing agent can become partly neutralized and will be unable to react with silicic acid. Another important bond that may neutralize the curing agent is the hydrogen bond. Research by Chen et al. (2017) has shown that hydrogen bonds can significantly lower the polymerization of silica.

4.3.1.4 Increasing silica solubility

A hypothesis was posed that the reduction of syneresis was a result of the increasing solubility below pH 7 (Figure 4.3.1). The effect of organic matter on the pH was calculated to verify this possibility. The hypothesis was rejected when found that the pH of the samples does not reduce below 10,5 after the addition of both the curing agent and the organic soil.

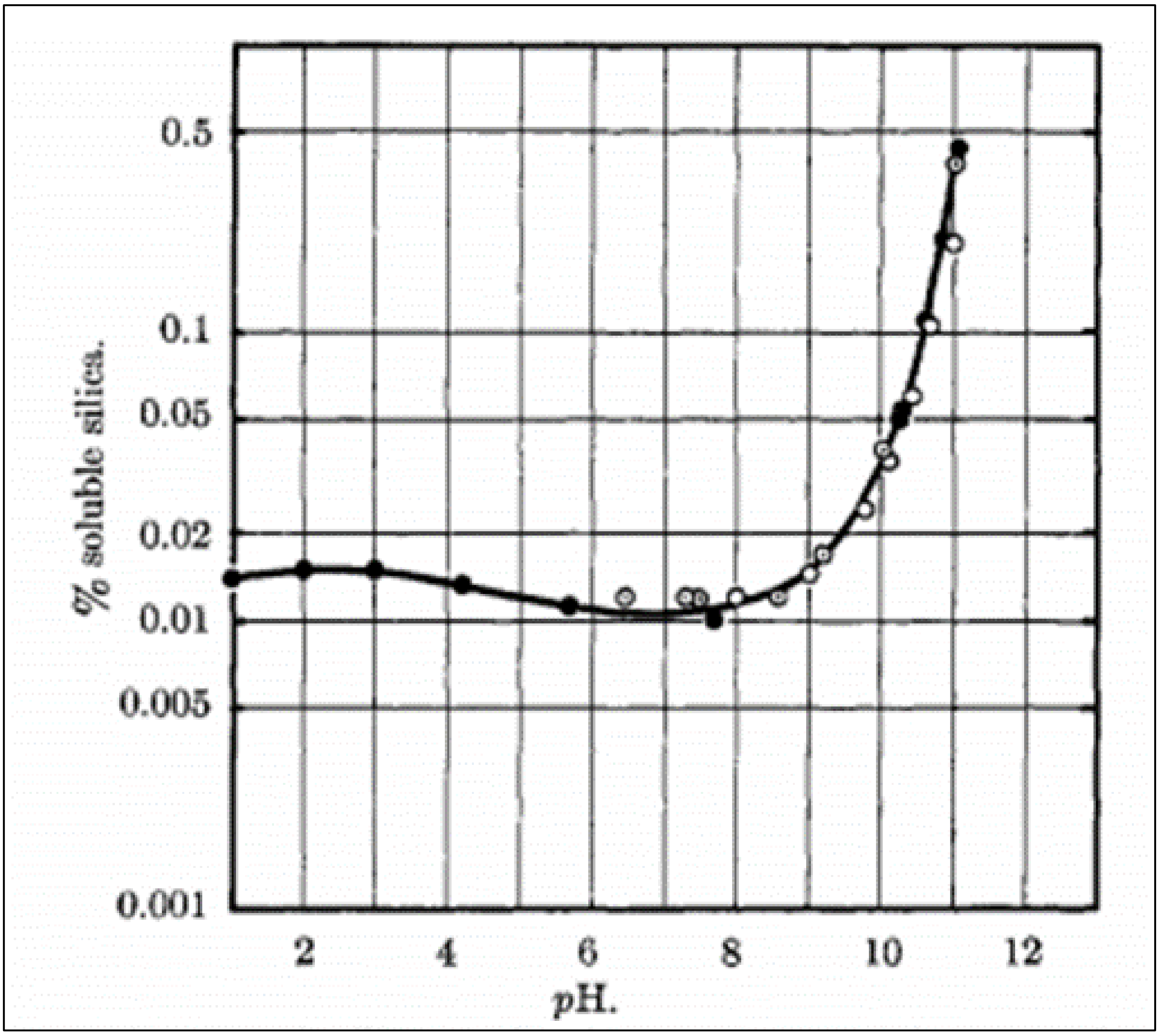

Figure 4.3.1 The solubility of amorphous silica. (Alexander, Heston & Iler., 1954)

4.3.2 Mold occurrence

The mold was solely observed at the gel-air interface and was not present within the gel. It can therefore be assumed that the mold growth was induced by optimal conditions at this interface: The presence of water, oxygen, and sufficient nutrients (organic matter in this case) (Block, 1952). For mold to grow, dissolved organic matter must be available as already bound organic matter cannot be used as a nutrient. This implies that it is unlikely for mold to grow on a gel but rather grows on the supernatant fluid on the gel that contains dissolved organic matter.

The growth of mold was earlier observed in the soft gel samples but was later also observed in the hard gel samples. The relatively large volume of syneresis fluid expulsed from the hard gel may have diluted the concentration of dissolved organic matter and thereby extended the time until mold growth. The syneresis fluid in the hard gel samples likely also had a lower concentration of dissolved organic matter as more dissolved organic matter was used to inhibit syneresis. In the soft gel samples, where syneresis without the presence of organic matter was already relatively low, the concentration of organic matter in the syneresis liquid would have been much higher, allowing for an earlier onset of mold growth. In the batch of soft gel samples where a 30ml water volume was added after gelation, the addition of water could have diluted the syneresis liquid enough to prevent mold growth for a long period. This is especially the case considering that after expulsion of syneresis liquid, the water volume on top of the samples would be stratified such that most dissolved organic matter exists at the bottom.

As grout is typically injected below the groundwater table where very little oxygen is present, mold growth should generally not occur in soil engineer practices.

4.4 Permeability experiments

This paragraph presents the permeability data obtained from the mixing grout method and the gravity permeation grouting method. Samples prepared with the mixing grout method resulted in no flowthrough after 3 hours of constant pressure ($2.5*10^4$ Pa), after which it was decided to conclude the experiment. A maximum permeability of this grout can be estimated by assuming flowthrough occurred with a volume lower than could be observed (1ml) and a sample porosity reduced by 99% of the initial porosity (0,35 > 0,0035). This estimate yields a permeability of $6.35*10^{-9}$ ms^{-1} (Appendix 3).

Samples prepared with the gravity permeation grouting method resulted in flowthrough after several minutes. The dry sand on top of the grouted sample saturated non-uniformly, indicating the presence of preferential flow paths within the sample (Figure 4.4.1). The permeability of both samples grouted with gravity permeation was computed at $2.2*10^{-7}$ ms^{-1} (Appendix 3).

Figure 4.4.1 The onset of saturation of the sand column above the grouted soil. Top of the duct tape indicates the top of the grouted soil. The uneven saturation indicates the presence of preferential flow paths.

4.5 Discussion of permeability experiments

4.5.1 Result implications

The experiments with the mixing grout method resulted in no flow through the grouted sample. This indicates that the sodium silicate grout has an exceedingly low hydraulic conductivity from which no intrinsic permeability can be derived in this experimental setup. Mixing the grout with sand resulted in complete saturation of the pores with grout, thereby allowing no flow through the sample.

In contrast, the gravity permeation grouting method did allow for flow through the sample. It can be assumed that the permeability resulting from this grouting method is realized through an imperfect saturation of the sample with grout. The gravity permeation grouting method better resembles the permeation grouting method used in the field. This is reflected in the similarity between the permeability commonly used in literature (10^{-7} ms^{-1}), the permeability obtained in previous studies (e.g., Gerssen et al., 2017; [$1{,}8*10^{-6}$ – $1{,}3*10^{-7}$ ms^{-1}]) and the permeability in this study ($2{,}2*10^{-7}$ ms^{1}). Permeability data obtained from permeation grouting should therefore not be considered a result of the intrinsic permeability of the silicate gel, but rather of imperfect saturation of the soil with grout.

It was intended to determine the effect organic soil has on the permeability of a grouted sample. Considering the implications on grouting practices mentioned above it was decided against this. If grouting imperfections influence the permeability, the consolidation of the soil may be of such importance that it would be difficult to differentiate between the effect of consolidation and organic soil. Furthermore, the syneresis experiments on soft gels resulted in very little to no difference in syneresis between gel samples with different organic mass fractions, which implies that the volume of soft gel in the soil is very similar when exposed to different quantities of organic soil.

4.5.2 Recommendations

The permeability in these experiments was obtained from an improvised grouting technique and cannot fully represent permeation grouting in the field. The compaction of the sand was done manually and therefore the obtained permeability is likely overestimated. Furthermore, the small scale of this experiment provides a relatively large surface/volume ratio, which increases the possible effect of barriers (acrylic column walls in this case) on grouting. Permeation grouting experiments should be done with grout injection to obtain more accurate permeability data and the scaling (barrier) effect should be further investigated.

From the data it can be expected that organic matter is grouted soils should not affect the permeability to an extent that measures need to be taken. From the soft gel syneresis results it follows that organic matter has very little impact on the silicate grout. The final gel volume appeared to remain closer to the initial volume in the presence of organic matter. This could indicate that the volume of gel in the soil pores is larger in the presence of organic matter and that thereby the permeability reduction is induced.

4.6 UCS experiments

This paragraph presents the results on the UCS experiments. UCS is compared with i) the organic mass fraction and ii) the bulk density of the soil sample. The batches are plotted separately in all figures due to their difference in preparation.

4.6.1 Organic mass fraction

The graphs in Figure 4.6.1 show a decrease in UCS (MPa) with organic mass fraction (%), which indicates that organic matter decreases the strength of a grouted soil sample. The samples from the second batch consistently reach higher UCS values. This may be attributed to their difference in preparation (section 3.6.1). The uneven sample surfaces of the first batch caused concentrated pressure on smaller (point) surfaces, thereby weakening the sample. Appendix 4 provides the difference in UCS projections between the first and second batch. The difference in strength between batches may also be attributed to the wetness of the samples. The samples of the first batch had been exposed to air for six days before testing, which had significantly reduced the wetness of the samples. One sample of the second batch (0% wt) had also dried for a week before testing. The data point is encircled in Figure 4.6.1. The difference in UCS between the 0% organic mass fraction samples is an indication that the overall UCS difference between the batches may be largely attributed to the difference in wetness.

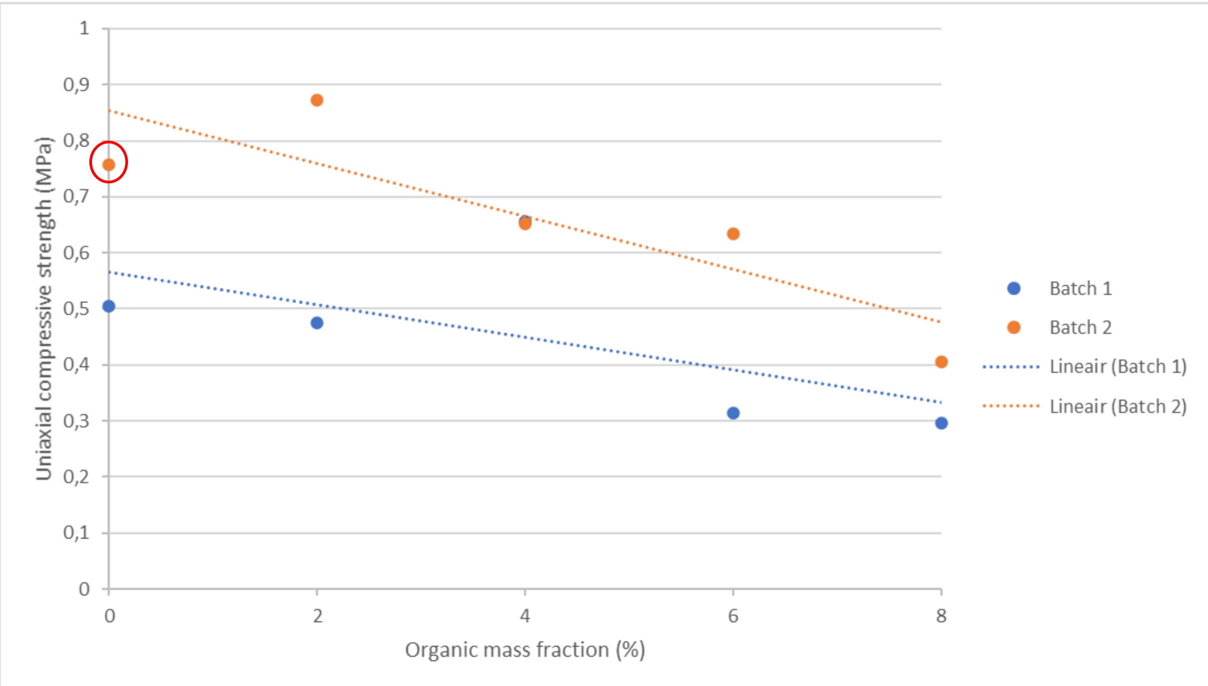

Figure 4.6.1. The Uniaxial Compressive Strength with increasing organic mass fraction. The red circle displays the dried sample in Batch 2.

4.6.2 Bulk density

Figure 4.6.2 shows the increase of UCS with bulk density. The effect of bulk density on UCS should be considered indirect, as the experimental data shows the bulk density to be a function of i) the organic mass fraction, ii) the compaction of the soil, and iii) the water content.

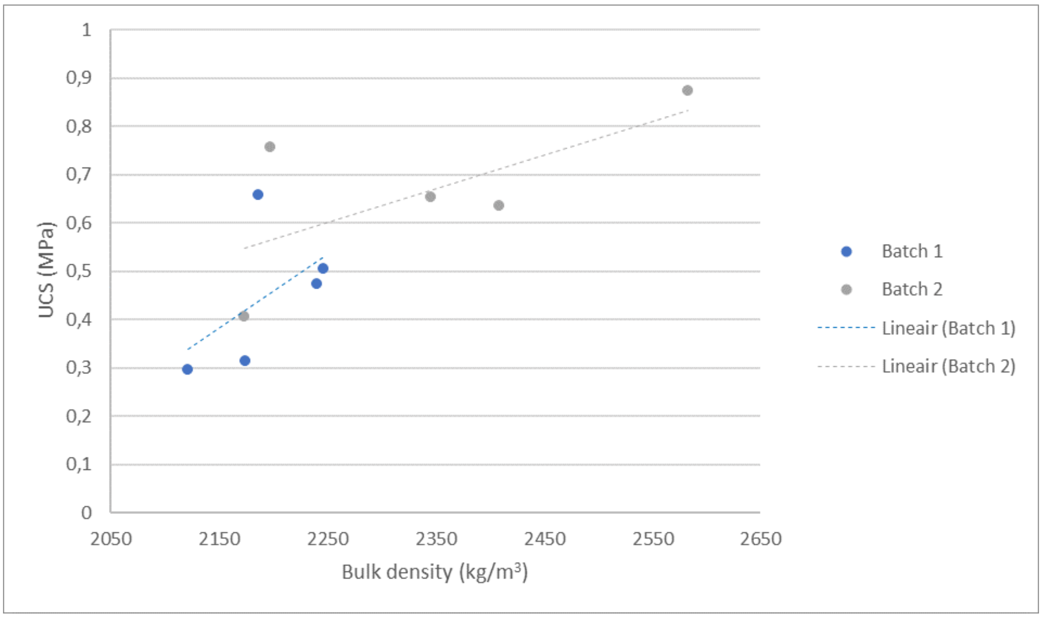

Figure 4.6.2 The Uniaxial Compressive strength compared to the bulk density.

The UCS experimental data was also compared to previous experimental data (unpublished). From this, the relation between UCS and bulk density becomes more evident (Figure 4.6.3). A trendline was drawn for field samples with a high organic matter content. The resulting trajectory is very similar to the experimental data of the second batch.

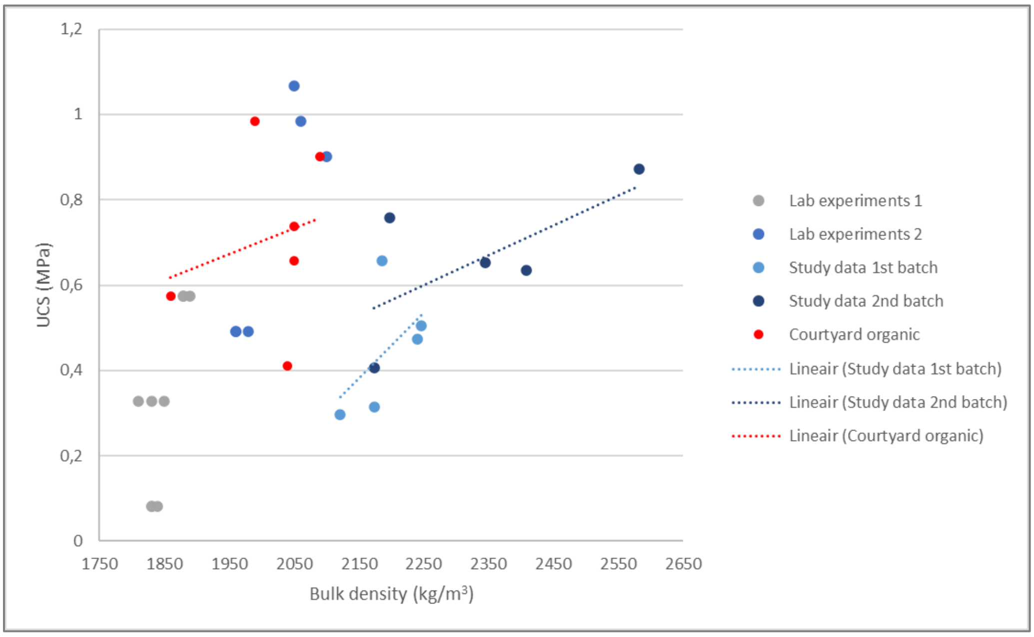

Figure 4.6.3 The relation between UCS and bulk density projected over multiple studies. The courtyard organic samples are field samples rich in organic matter. The other data points all represent laboratory experiments.

4.6.2.1 Organic mass fraction

A distinct relation can be derived between the bulk density and the organic mass fraction (Figure 4.6.4). This is expected as the replacement of sand with organic matter should lower the bulk density of the soil. The nonlinear position of the datapoints implies that the bulk density was further affected by another mechanism, namely the compaction of the soil. The bulk densities in the second batch lie considerably further apart. This indicates the variance in compaction between the samples to be much larger than for the first batch. Additionally, the wetness of the samples causes a difference in bulk density between the batches. The samples of the first batch had been exposed to air for a week before testing, while the samples of the second batch had remained confined within the mold. Overall, Figure 4.6.4 shows that the sample bulk density decreases with organic matter content.

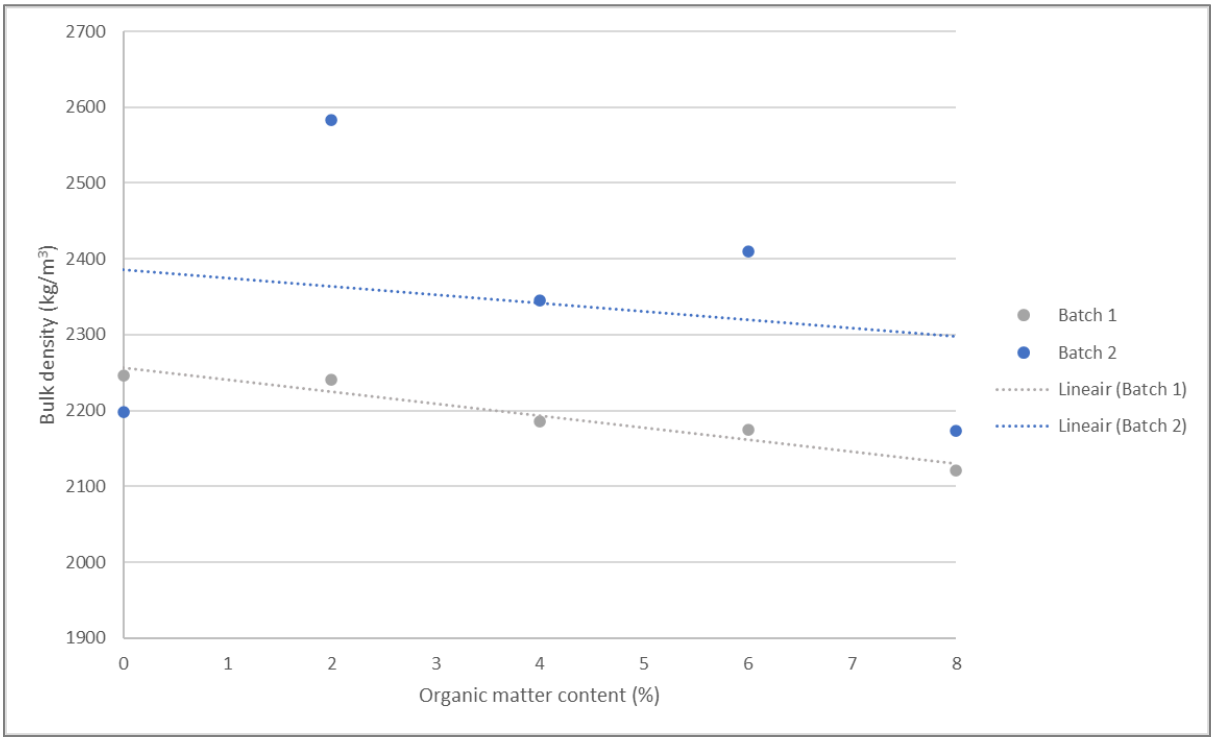

Figure 4.6.4 The relation between organic matter content and the sample bulk density.

4.7 Discussion of UCS experiments

4.7.1 Organic mass fraction

The main result from the UCS experiments is that a high soil organic mass fraction could decrease the strength of grouted soil samples up to 50% for an organic mass fraction of 8%. The reduction in strength is likely an indication of an inhibition in the formation of silica polymers, which we can attribute to i) the TDSs effect (section 4.3.1.1), ii) the neutralization of curing agent (section 4.3.1.2), and iii) a reduction of the silica content. The addition of organic matter in the UCS samples was paired with the removal of sand, since a constant sample volume was prepared. As the silica in sand can act as a reaction surface for the formation of silica polymers, the removal of sand reduces the reaction surface between silica molecules. As a result, fewer silica polymers may form, and the grouted sample strength is reduced.

4.7.2 Bulk density

The bulk density appears to be a significant factor in the strength of grouted soils (Figure 4.6.2). Therefore, obtaining and maintaining high bulk densities in silicate grouting is deemed a priority. From the experiments in this study the following drivers of bulk density have been identified: The organic mass fraction, the compaction of the soil and the water content. The organic mass fraction and consolidation of the soil are difficult to control in grouting practices. Keeping grouted soil saturated with water can however be maintained. The experimental data in this study shows that a dry soil may reduce the uniaxial compressive strength by up to 50%, which stresses the importance of wetting grouted soils.

4.7.3 Recommendations

Firstly, the strong relation found between the UCS and the soil organic mass fraction should be taken well under advisement. It accentuates the importance of preliminary research on organic matter in soils, as high contents could lead to insufficient grouted soil strengths. Should the soil be rich in organic matter, it is advised to take the potentially lower grouted soil strength well into account before starting any grouting operations.

Secondly, the relation found between the UCS and the hydration of the soil stresses the importance of soil saturation. Additionally, it is advised to hydrate core samples for testing the grouted soil strength in grouting operations. Not doing so, could significantly underestimate the grouted soil strength.

6. Conclusion

The syneresis experiments have shown that organic matter inhibits the polymerization process in silicate grouts. The reduction in polymerization leads to a lower gel density and strength, which is unfavorable for the application of hard gels. The inhibition of syneresis was much less pronounced for soft gels. Considering that the measuring error value obtained from the hard gel experiments lies very close to the observed syneresis in the soft gels, we cannot with certainty suggest a relation between organic matter and syneresis in soft gels. The permeability experiments have shown that the permeability of a grout is a function of the imperfections in grouting. The intrinsic permeability of the grout itself is too low to be measured from the experiments done in this study. However, a maximum grout permeability was determined at $6.35*10^{-9}$ ms^{-1} when assumed that grouting done with the mixing grout method reduces the soil porosity by 99%. From the gravity permeation grouting method, a permeability of $2.2*10^{-7}$ ms^{-1} was obtained. The order of magnitude of the permeability is consistent with commonly used permeability values for silicate gels (10^{-7} ms^{-1}) and thereby corroborates the narrative that the permeability is caused by grouting imperfections. The UCS experiments have shown that a strong relation is present between the organic mass fraction of the soil and the strength of grouted soils. An organic mass fraction of 8% could lead to a 50% reduction of the uniaxial compressive strength. The experiments have additionally stressed the importance of keeping grouted soils saturated, as dehydration of the soil has shown an up to 50% decrease of the uniaxial compressive strength as well.

7. Acknowledgements

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Appendix 1

Computations on the required organic soil

$$V_{organic} + V_{water\ glass} = 200ml$$

$$V_{organic} = \frac{V_{water\ glass} * \rho_{bulk,sand}}{\eta * 1000 * f} * wt\%^{i}$$

$$\frac{V_{organic}}{V_{water\ glass}} = \frac{\rho_{bulk,zand} * wt\%}{\eta * 1000 * 0{,}9} = R$$

$$R * V_{water\ glass} + V_{water\ glass} = 200ml$$

$$V_{water\ glass} = \frac{200ml}{1 + R}$$

$$V_{organic} = 200 - V_{water\ glass}$$

$$M_{organic} = \frac{V_{organic} * \rho_{bulk,organic}{}^{ii}}{1000}$$

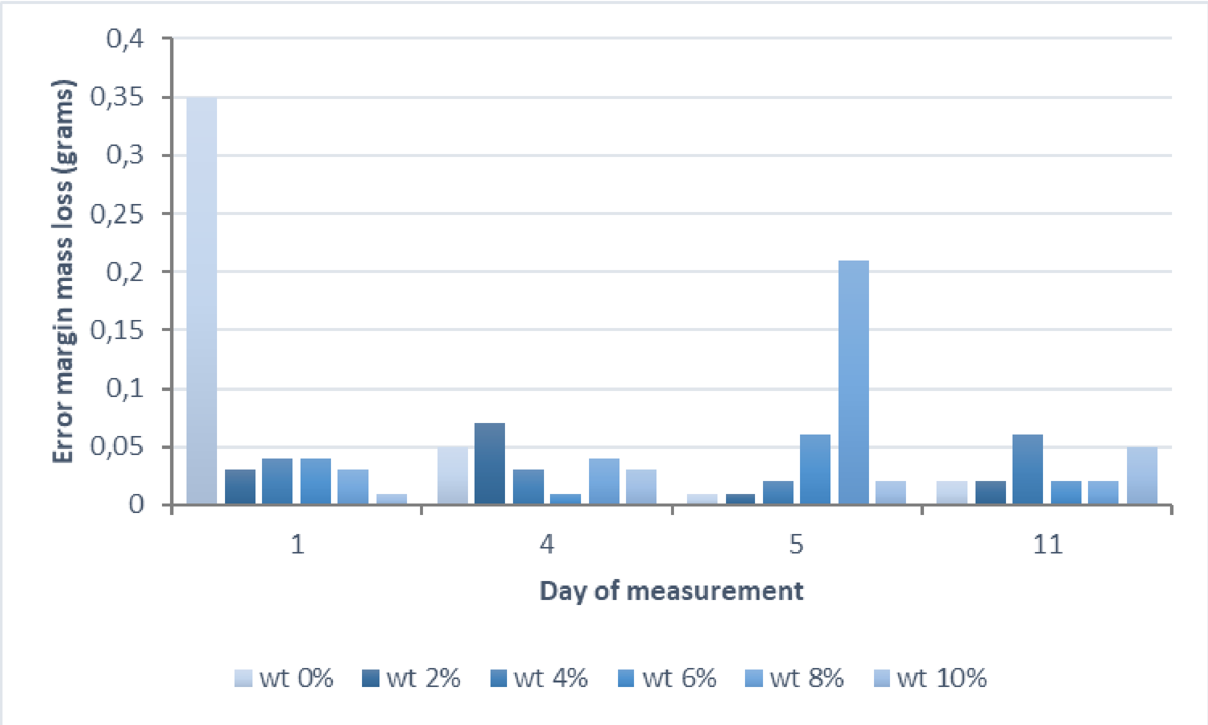
$\rho_{bulk,sand}$ (bulk density of sand)	1650 kg/m^3
η (porosity)	0.35
f (conversion factor)	0.9
$wt\%$	Organic mass fraction
R	Ratio $V_{organic}/V_{water\ glass}$
$\rho_{bulk,organic}$ *(bulk density of organic soil)*	633,75 kg/m^3

[i] The volume of water glass, bulk density of sand and porosity are used to determine a soil volume corresponding to the water glass volume. A conversion factor '*f' is used as the organic soil is 90% organic. The wt% is defined as a ratio (i.e., wt2% = 0.02).*

[ii] The bulk density of the organic soil was determined by means of the immersion method.

Appendix 2

The error margin of mass loss in the syneresis measurements



The figure shows the difference between the measured weight change of the gel sample and the measured weight change of the measuring cylinder for batch 1 of the hard gel samples. The y-axis shows the error margin in grams and the x-axis shows the six samples for each day of measurement. The error margin is well below the syneresis volumes obtained in the experiments and is therefore considered insignificant.

Appendix 3

Computations on the hydraulic conductivity (permeability)

The following tables provide the computed values of the variables used in the calculation of the hydraulic conductivity according to Darcy's Law:

$$K = \frac{Q}{A} * \frac{dz}{dh}$$

Volumetric flow 'Q'	$5{,}05*10^{-10}$ m^3s^{-1}
Surface area of the flow 'A'	$6{,}4*10^{-3}$ m^2
The sample length 'dz'	0,2 m
The hydraulic head difference 'dh'	2,5 m

The Table provides the computed values for the estimation of the maximum hydraulic conductivity of the silicate grout in which the soil porosity is assumed to be reduced by 99%.

Volumetric flow 'Q'	$2{,}24*10^{-7}$ m^3s^{-1}
Surface area of the flow 'A'	$6{,}4*10^{-3}$ m^2
The sample length 'dz'	0,15 m
The hydraulic head difference 'dh'	1,95 m

The Table provides the computed values of the first permeability experiment using the gravity permeation grouting method (3.5.2).

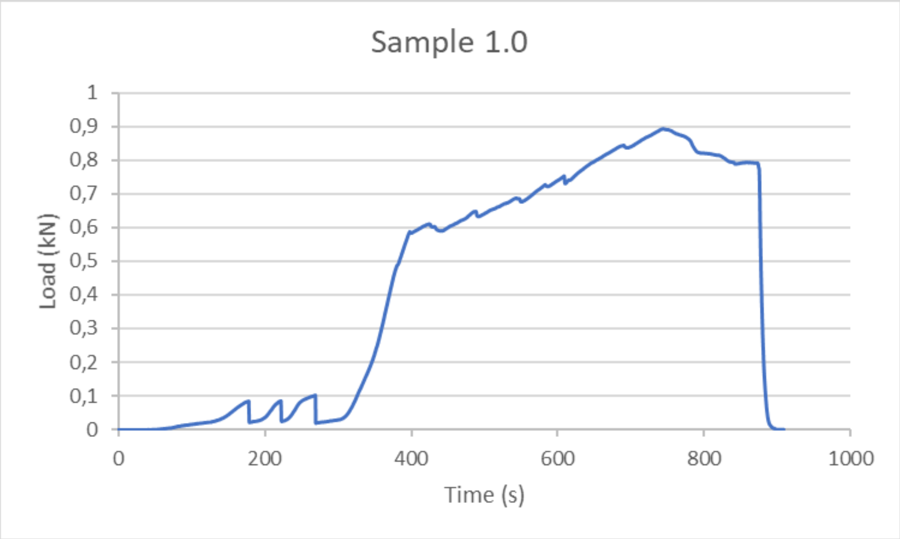
Volumetric flow 'Q'	$2{,}21*10^{-7}$ m^3s^{-1}
Surface area of the flow 'A'	$6{,}4*10^{-3}$ m^2
The sample length 'dz'	0,125 m
The hydraulic head difference 'dh'	1,87 m

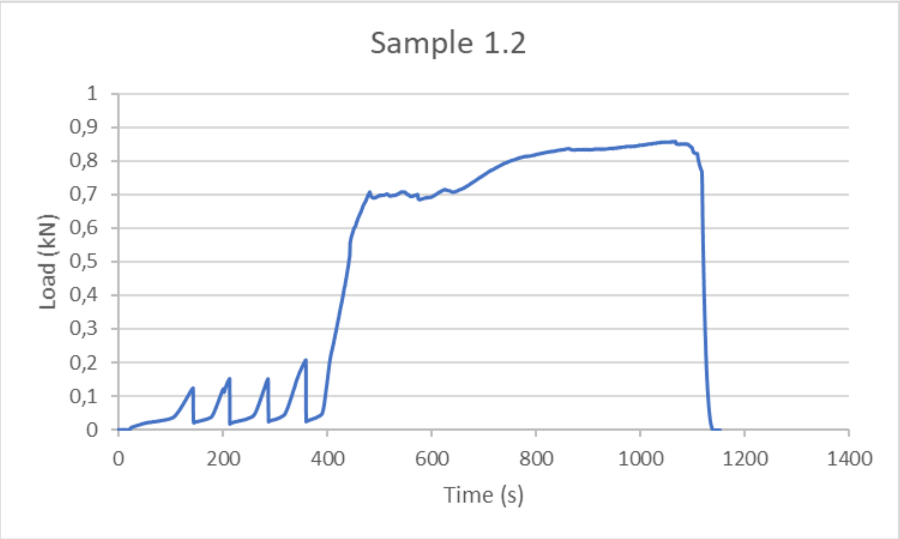
The Table provides the computed values of the second permeability experiment using the gravity permeation grouting method (3.5.2).

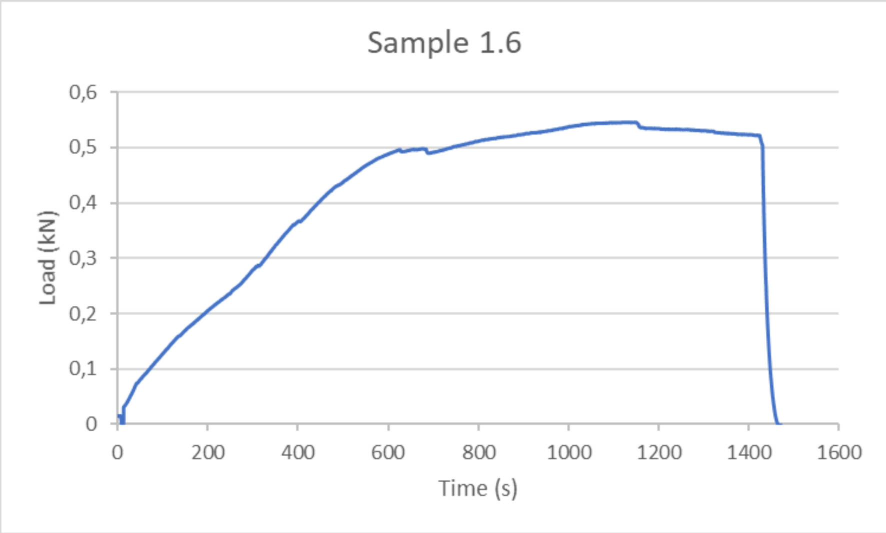
Appendix 4

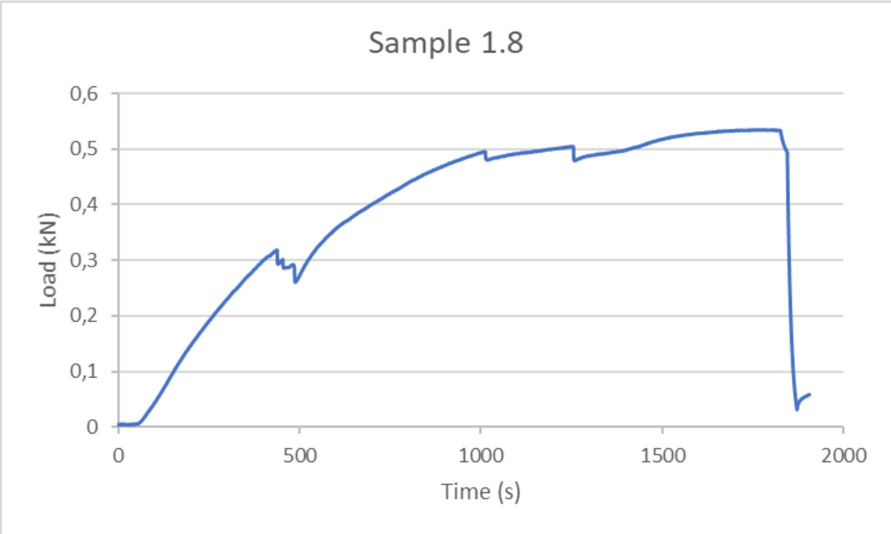
The following figures show the projections of the Load (UCS) against time for the samples of the first batch (1.0 – 1.8) and the second batch (2.0 – 2.8). The value behind the sample decimal point refers to the organic mass fraction in the sample (i.e., sample 1.0 refers to batch 1; 0% wt).

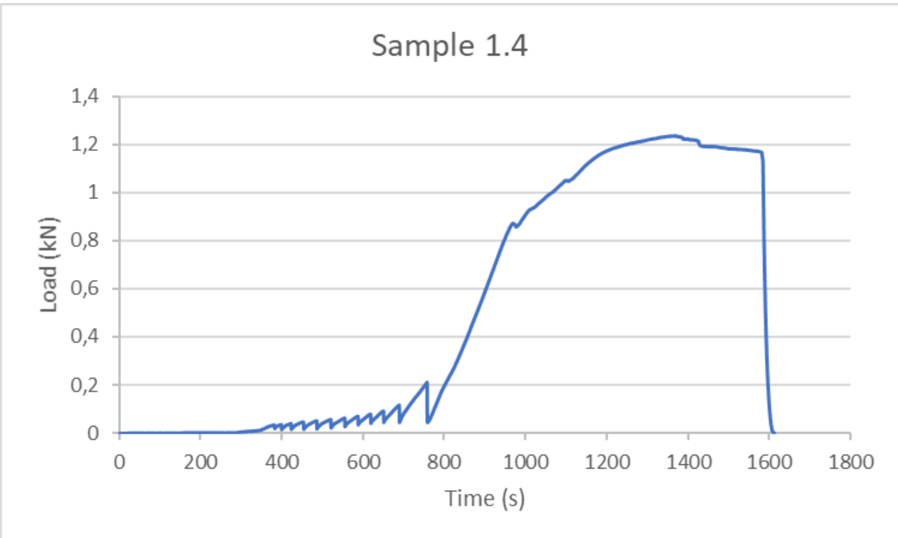
The UCS projections of batch 1



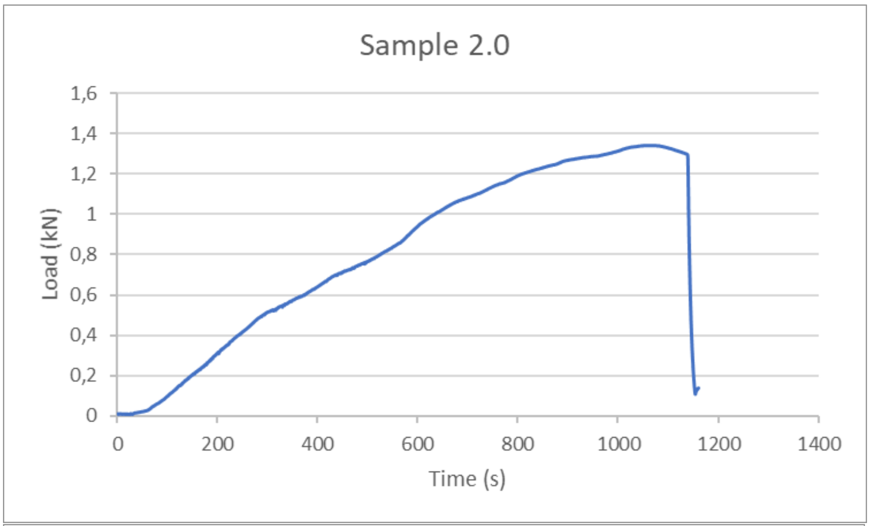


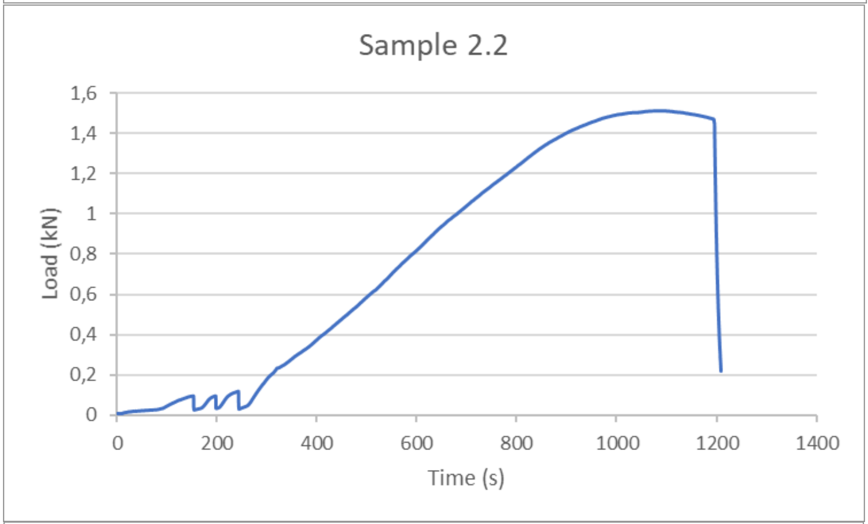

Sample 1.6
0,6
0,5
0,4
0,3
0,2
0,1
0
Load (kN)
0
200
400
600
800
1000
1200
1400
1600
Time (s)

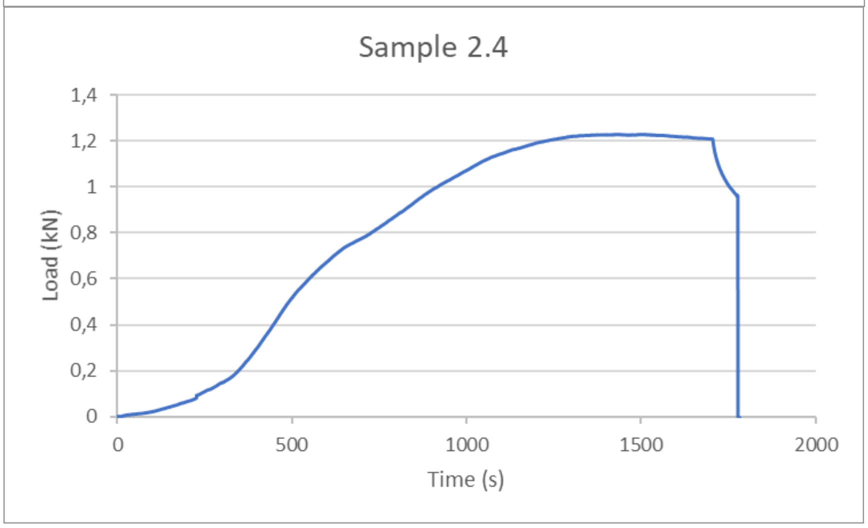

Sample 1.8
0,6
0,5
0,4
0,3
0,2
0,1
0
Load (kN)
0
500
1000
1500
2000
Time (s)

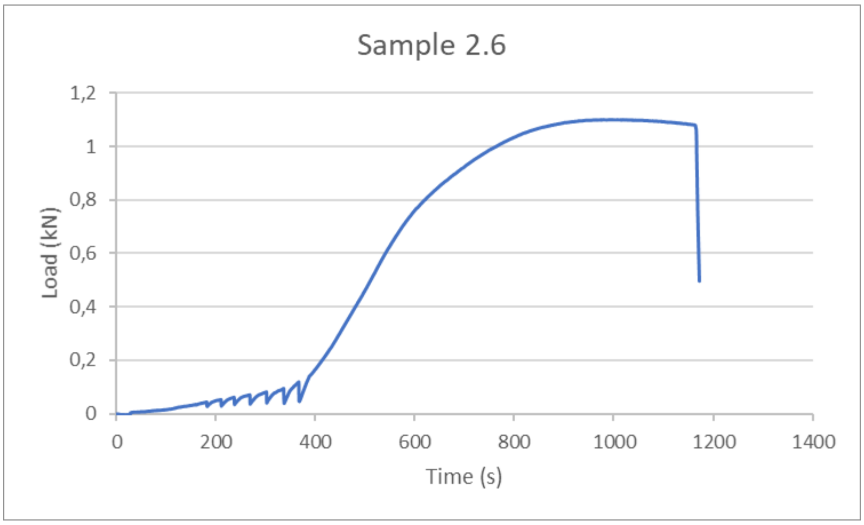

Sample 1.4
1,4
1,2
1
0,8
0,6
0,4
0,2
0
Load (kN)
0
200
400
600
800
1000
1200
1400
1600
1800
Time (s)

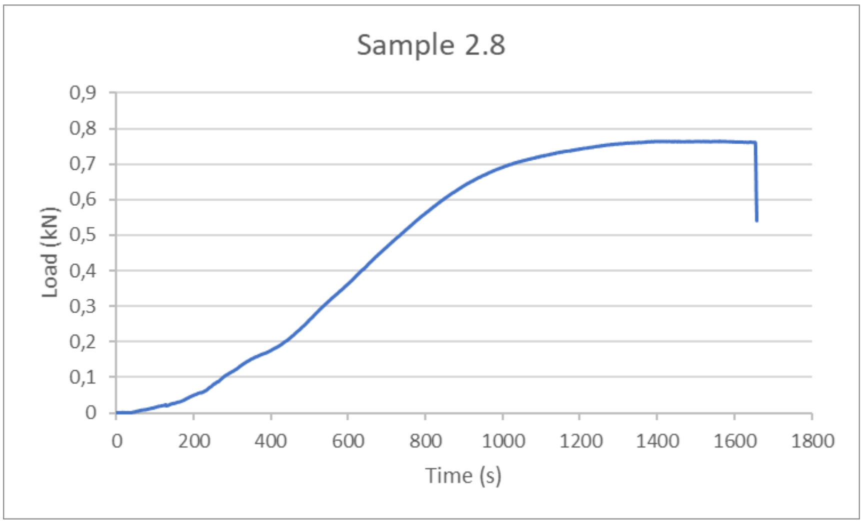
The UCS projections of the second batch








Sample 2.6
1,2
1
0,8
0,6
0,4
0,2
0
Load (kN)
0
200
400
600
800
1000
1200
1400
Time (s)


Sample 2.8
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Load (kN)
0
200
400
600
800
1000
1200
1400
1600
1800
Time (s)