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## Abstract

A common problem for maturing oil fields is excessive water production. Ultimate oil recovery could be increased considerably by implementing an appropriate water production management. Solutions for managing excess water production may include the use of smart-well completions, downhole water separation and disposal, as well as mechanical and chemical means of delaying, reducing or shutting off excess water production. As such, an in-depth placement of blocking agent can reduce water influx in the borehole and contribute to lower water cut and, thus, extend the lifetime of an oil production well.

Low impact on the environment revitalized sodium silicate systems in the oil industry for zonal isolation. This thesis focuses on the laboratory evaluation of sodium silicate as zonal isolation chemical for water control applications. Sodium silicate solution forms gel when pH is reduced below 11. For pH control, two different crosslinkers (HCl and glyoxal) were used in this work. Gelation time and strength of the formed gel play an important role in designing successful water shutoff treatment in a field trial. Gelation time is defined as the time required for the gel to become rigid. Gelation codes are introduced to distinguish the macroscopic changes of the gel.

This thesis also discusses the parameters affecting gelation time for gels formed by crosslinking sodium silicate with glyoxal. These parameters are: sodium silicate and glyoxal concentrations, temperature, salinity and presence of divalent ions in the makeup water. It is shown that gelation time is reduced for increased sodium silicate and glyoxal concentrations. NaCl and CaCl<sub>2</sub> act as catalysts and decrease gelation time. A more rapid gelation was observed at higher temperatures.

AcoustoSizer from Colloidal Dynamics was tested to determine particle size distribution for sodium silicate crosslinked with HCl. Results showed that the AcoustoSizer underestimates particle diameter for polymerizing particles and, therefore, further testing was abandoned.

Finally, gel strength is studied and expressed as the applied pressure drop required to compromise the gel's integrity in a testing tube. Sodium silicate gels' strength, formed using various crosslinker (HCl and glyoxal) concentrations, is tested at different temperatures.

Pressure tests have shown that stronger gels could be created using higher glyoxal concentrations. An increase in sodium silicate or HCl concentrations only slightly increases gel strength.

# Table of Contents

Acknowledgements .....	I
Abstract .....	II
Table of Contents .....	III
List of Figures .....	VI
List of Tables.....	VIII
1 Introduction.....	- 1 -
2 Literature Survey .....	- 3 -
2.1 Water production sources .....	- 3 -
2.2 Handling of water production.....	- 6 -
2.3 Impact of produced water on environment and treatment costs .....	- 7 -
2.4 Water control solutions .....	- 7 -
2.4.1 Completion designs and well placement .....	- 8 -
2.4.2 Downhole separation .....	- 9 -
2.4.3 Chemical water shut-off .....	- 10 -
2.4.4 Gelling systems .....	- 11 -
2.4.5 Disproportional permeability reduction.....	- 13 -
2.4.6 Strategies of attacking water production .....	- 14 -
3 Theoretical Background.....	- 18 -
3.1 Chemistry of sodium silicate .....	- 18 -
3.2 Gel formation .....	- 19 -
3.3 Gelling agents.....	- 22 -
3.3.1 Hydrochloric acid.....	- 24 -

3.3.2	Glyoxal .....	- 24 -
3.3.3	Esters .....	- 25 -
3.4	Gel codes .....	- 27 -
3.5	Silicate gel kinetics.....	- 28 -
3.6	Gel syneresis.....	- 31 -
3.7	Gel strength .....	- 33 -
4	Laboratory Equipment and Experimental Procedures .....	- 34 -
4.1	Sodium silicate crosslinked with HCl .....	- 34 -
4.1.1	Bulk gelation time .....	- 35 -
4.1.2	AcoustoSizer tests .....	- 36 -
4.2	Sodium silicate crosslinked with glyoxal .....	- 39 -
4.2.1	Glyoxal concentration effect of on gelation time .....	- 39 -
4.2.2	Salinity and divalent ion effect on gelation time .....	- 40 -
4.2.3	PH time dependency.....	- 43 -
4.2.4	Temperature effect on gelation time.....	- 44 -
4.2.5	Effect of silicate concentration on gelation time .....	- 45 -
4.3	Gel strength .....	- 46 -
5	Results and Discussion .....	- 47 -
5.1	Sodium silicate crosslinked with HCl .....	- 47 -
5.1.1	Bulk gelation time .....	- 47 -
5.1.1	AcoustoSizer tests .....	- 49 -
5.2	Sodium silicate crosslinked with glyoxal .....	- 54 -
5.2.1	Glyoxal concentration effect on gelation time .....	- 54 -
5.2.2	Salinity and divalent ion effect on gelation time.....	- 55 -

5.2.3	PH time dependency .....	- 64 -
5.2.4	Temperature effect on gelation time.....	- 66 -
5.2.5	Silicate concentration effect on gelation time .....	- 67 -
5.3	Gel strength .....	- 71 -
5.3.1	Sodium silicate crosslinked with HCl .....	- 72 -
5.3.2	Sodium silicate crosslinked with glyoxal .....	- 75 -
6	Conclusions and Recommendations .....	- 80 -
	References .....	- 82 -
	Appendix A .....	- 87 -
	Appendix B .....	- 91 -

## List of Figures

Figure 1: Sources for water production during primary recovery <sup>1</sup> .....	- 4 -
Figure 2: Sources for water production during secondary recovery <sup>1</sup> .....	- 5 -
Figure 3: Sources for water production caused by mechanical failures <sup>1</sup> .....	- 5 -
Figure 4: The concept of downhole separation <sup>1</sup> .....	- 9 -
Figure 5: The concept of gel treatment <sup>1</sup> .....	- 10 -
Figure 6: Relative permeabilities before, and after gel formation <sup>18</sup> .....	- 14 -
Figure 7: Schematically illustration of polymerization of silica <sup>21</sup> .....	- 19 -
Figure 8: Simplified silicate polymerization <sup>22</sup> .....	- 20 -
Figure 9: Structure of glyoxal <sup>24</sup> .....	- 24 -
Figure 10: General structure of an ester <sup>26</sup> .....	- 25 -
Figure 11: General formula of ester hydrolysis .....	- 26 -
Figure 12: Progress of syneresis in porous medium .....	- 32 -
Figure 13: Representation of the testing tube for pressure extrusion test .....	- 33 -
Figure 14: AcoustoSizer from Colloidal Dynamics .....	- 36 -
Figure 15: Setup of pressure extrusion tests.....	- 46 -
Figure 16: Gelation time (gel code 1) versus HCl concentration.....	- 48 -
Figure 17: Particle size distribution at different times .....	- 50 -
Figure 18: Average particle size development .....	- 51 -

Figure 19: Particle size distribution at different times when water is replaced by a 750 ppm Xanthan solution .....	- 52 -
Figure 20: Average particle size development when water is replaced by a 750 ppm Xanthan solution .....	- 52 -
Figure 21: Gelation time versus glyoxal concentration .....	- 54 -
Figure 22: Gelation time versus NaCl concentration .....	- 56 -
Figure 23: Gelation time versus CaCl <sub>2</sub> concentration.....	- 58 -
Figure 24: Gelation time versus NaCl and CaCl <sub>2</sub> concentrations, 25°C.....	- 60 -
Figure 25: Gelation time versus NaCl and CaCl <sub>2</sub> concentration, 60°C .....	- 60 -
Figure 26: Gelation time (hrs) versus NaCl and CaCl <sub>2</sub> concentrations.....	- 62 -
Figure 27: PH versus time.....	- 65 -
Figure 28: Gelation time versus the inverse absolute temperature .....	- 67 -
Figure 29: Gelation time versus silicate concentration, 60°C.....	- 68 -
Figure 30: Gelation time versus silicate concentration, 25°C.....	- 69 -
Figure 31: Gel shrinkage when cooled down.....	- 73 -



## List of Tables

Table 1: Excessive water production sources and suggested treatments <sup>11</sup> .....	- 16 -
Table 2: Stability of silicate species in solution when the pH is reduced .....	- 21 -
Table 3: Gelling agents for sodium silicate.....	- 23 -
Table 4: Classification of gel codes based on macroscopic gel structure observations .....	- 27 -
Table 5: Compositions of bulk gelation samples .....	- 35 -
Table 6: Summary of the AcoustoSizer tests .....	- 38 -
Table 7: Compositions of glyoxal samples .....	- 39 -
Table 8: Compositions of NaCl samples.....	- 41 -
Table 9: Compositions of CaCl <sub>2</sub> samples.....	- 42 -
Table 10: Compositions of NaCl-CaCl <sub>2</sub> samples.....	- 43 -
Table 11: Compositions of pH samples .....	- 44 -
Table 12: Compositions of temperature samples .....	- 45 -
Table 13: Compositions of silicate samples .....	- 45 -
Table 14: Gelation times for HCl bulk gel test .....	- 48 -
Table 15: Input parameters and respective values selected for the AcoustoSizer tests .....	- 49 -
Table 16: Gelation times for glyoxal samples.....	- 54 -
Table 17: Gelation times for NaCl samples .....	- 56 -
Table 18: Gelation times for CaCl <sub>2</sub> samples .....	- 57 -

Table 19: Gelation times for NaCl-CaCl <sub>2</sub> samples .....	- 59 -
Table 20: Measured and calculated gelation times for all salinity samples .....	- 63 -
Table 21: The pH values for the pH samples .....	- 64 -
Table 22: Gelation times for pH samples .....	- 64 -
Table 23: Gelation times for temperature samples.....	- 66 -
Table 24: Gelation times for silicate samples .....	- 68 -
Table 25: Constants derived for the general equation.....	- 70 -
Table 26: Pressure drop values.....	- 71 -
Table 27: Pressure extrusion results for silicate/HCl systems .....	- 72 -
Table 28: Pressure extrusion results for silicate/HCl systems with Xanthan.....	- 74 -
Table 29: Pressure extrusion results for glyoxal samples .....	- 75 -
Table 30: Pressure extrusion results for low glyoxal concentrations.....	- 76 -
Table 31: Pressure extrusion results for salinity test.....	- 77 -
Table 32: Pressure extrusion test results for silicate concentration test.....	- 78 -

# 1 Introduction

A common problem for maturing oil fields is excessive water production. This often leads to rapid reduction in productivity and a big increase in costs. As a result of high water production, some wells might have to be shut prematurely.

When oil or gas is produced to the surface, some water is produced and brought to surface in mixture with hydrocarbons. The produced water contains low concentrations of heavy metals, organic acids, radioactive materials and a fraction of chemicals added during the production process.

In order to maximize the total oil recovery and minimize production costs, water production has to be controlled. It is essential to identify where the produced water comes from, and what is the cause of the excessive water production.

Methods for water production reduction can be grouped into two main categories: mechanical and chemical. Mechanical solutions are effective near the wellbore, whereas chemical solutions work usually deeper in formation.

A zone or a layer, which is not producing enough hydrocarbons to achieve economic viability, is preferably shut off. It can be done by a mechanical isolation, cement squeeze, solids injection or by injecting preformed or gelant gel systems. There are two main groups of gel systems: polymers crosslinked with chromium or organic crosslinker and sodium silicate crosslinked with an acid or another chemical capable of reducing the pH of silicate solution. In this thesis, the focus is placed on sodium silicate systems.

Aqueous sodium silicate solution is crosslinked with an acid or other gelling agent to form a rigid gel. When the gel is formed in reservoir conditions it has to be strong enough to withstand pressure gradients and it should keep its rheological properties over a long period of time to ensure that the zone stays completely shut.

Objectives of this thesis are to test glyoxal as a gelling agent, which factors affect gelation time and derive a general equation for the gelation time calculations. Moreover, to evaluate gel strength by carrying out pressure extrusion tests with different crosslinkers (HCl and glyoxal). In addition, to measure the particle size and their distribution during the polymerization process of sodium silicate crosslinked with HCl.

## **2 Literature Survey**

A thorough review of available books and scientific papers is presented in this section. Problems caused by excessive water production and a growing demand for the best solution, is the motivation behind this thesis. Firstly, the importance of water production problems is reviewed. Secondly, a short overview of possible solutions to handle excessive water production is presented. And lastly, a closer look to gelling systems is presented; where and how they should be used, what factors influence their effectiveness and how the total profitability of an oil field can be increased by an implementation of them

### **2.1 Water production sources**

When oil or gas is produced, water is brought to the surface in a mixture with hydrocarbons. The produced water contains low concentrations of heavy metals, organic acids, radioactive materials and a fraction of chemicals added during production process. Physical properties and the chemical composition will vary depending on reservoir which is producing.

It is convenient to differentiate between produced water problems which occur during the primary and the secondary oil recovery. During the primary oil recovery, some of typical problems are a natural fracture to aquifer, coning or cusping effects caused by pressure drop at the wellbore. These problems are illustrated in figure 1. The upper left panel of figure 1 shows a moving oil-water contact. When oil is produced from the oil zone, volume of produced oil is replaced by water from the underlying aquifer. When water reaches perforations, the well will start producing more water. The upper left panel shows coning effect for a vertical well and cusping for a horizontal well. Coning and cusping effects are inevitable, but can be delayed by lower production rates. The lower panels illustrate faults and fractures from water layer for vertical and horizontal wells. These fractures can be natural, or caused by drilling fluid, or high pressure gradients appeared during the production process.

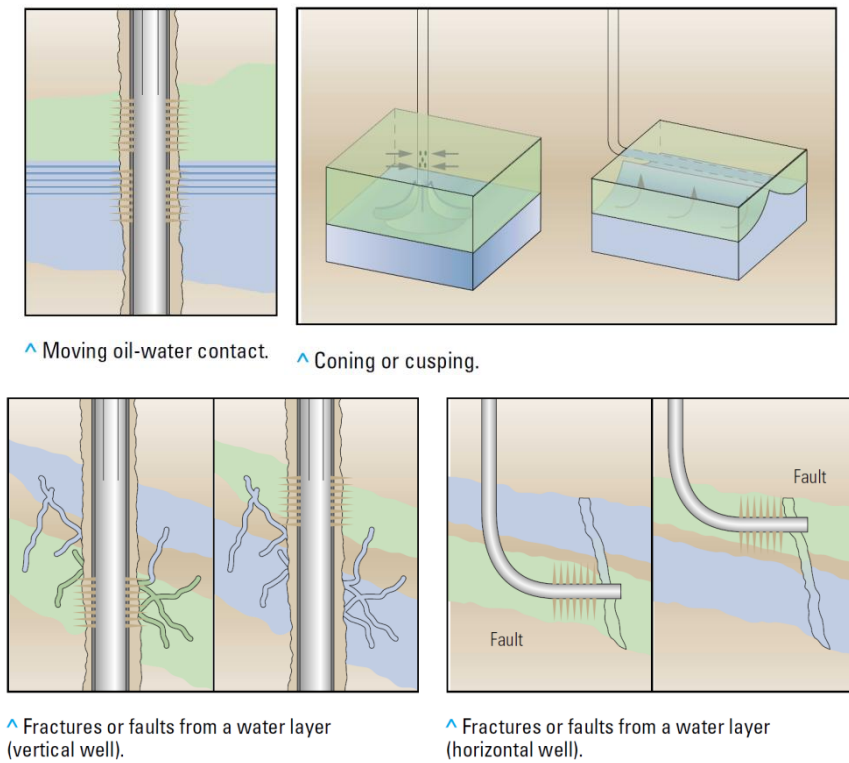
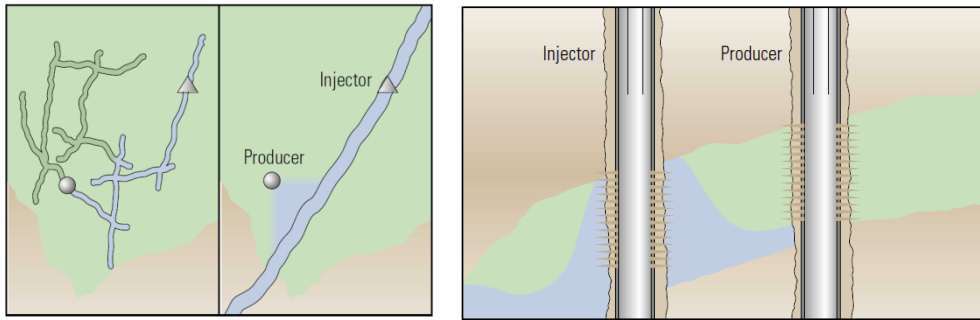


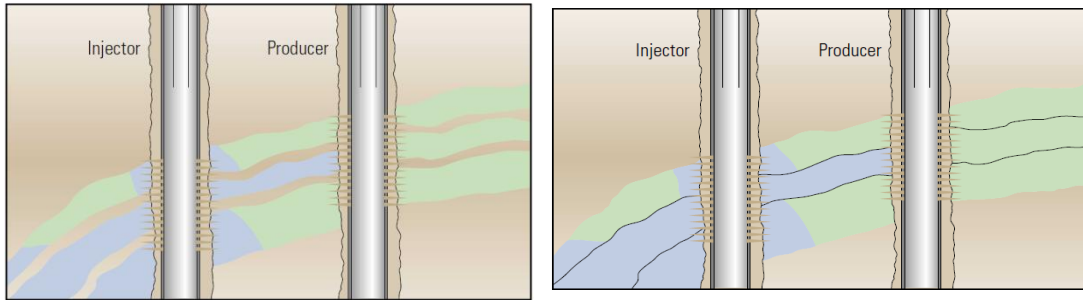
Figure 1: Sources for water production during primary recovery<sup>1</sup>

Water production problems, which might occur during secondary oil production, are illustrated in figure 2. The upper left panel shows how a fracture or a fault can connect an injector to a producer and thus, increase water cut significantly. Again, these fractures might be natural, or caused by high pressure drops between the injector and the producer. In water flood, when the displacing fluid has a larger density than the formation fluid, gravity segregation will take place. It can be a cause for an early water breakthrough, as illustrated in upper right panel in figure 2. The lower panels show layers with different permeabilities. Layers with the highest permeabilities are produced first and, after the injected water breaks through, they will mostly produce water and will contribute to higher water cut for the well.



^ Fractures or faults between an injector and a producer.

^ Gravity-segregated layer.

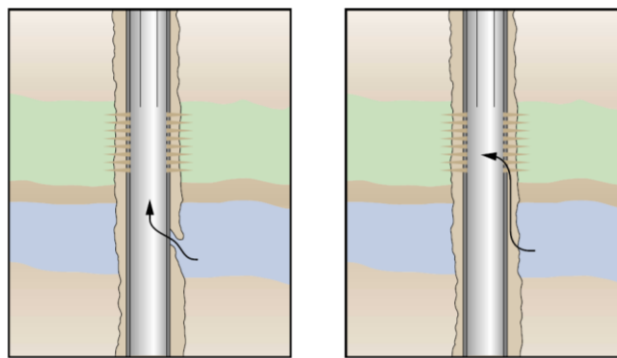


^ Watered-out layer without crossflow.

^ Watered-out layer with crossflow.

Figure 2: Sources for water production during secondary recovery<sup>1</sup>

Figure 3 presents additional failures which occur close to the borehole due to bad cementing job or mechanical failure of casing or packers. Even if water volumes flowing into the annulus are not as high as for secondary recovery problems, such problems can be more difficult to detect and apply the necessary treatment.



^ Casing, tubing or packer leaks.

^ Flow behind casing.

Figure 3: Sources for water production caused by mechanical failures<sup>1</sup>

## 2.2 Handling of water production

When produced water reaches the surface it has to be separated and then treated. Separation is a time-consuming and costly operation and the separators can be quite large and require sufficient space on the rig. In addition, chemicals are used in the separation process and for large produced water volumes; their cost can be significant. After the oil is separated from the produced water, there are several ways to treat the separated water<sup>2</sup>:

- **Discharge.** Produced water can be discharged directly to the ocean for offshore production. Depending on regulations and laws of the location of the field, the produced water has to be treated to a certain level of purity. For example, oil concentration cannot be higher than 9 mg/l according to the Norwegian regulations. OSPAR has set 30 mg/l as a maximum level<sup>3</sup>.
- **Underground injection.** After the produced water has been separated from the oil and gas, it can be re-injected in the reservoir for pressure control or secondary recovery in EOR processes. In case there is no beneficial effect on re-injection in the reservoir, the produced water can be injected into the formation for disposal purposes only. The formation has to be non-leaking and the produced water needs to be treated so it is chemically compatible with the receiving formations.
- **Evaporation.** Not widely used, but applicable for rather small amounts of produced water. Water is placed in a pond with large surface area and left for evaporation. Geographical position here is essential and hot, dry regions are naturally preferred.
- **Offsite water treatment.** When onsite water treatment facilities are unavailable, the produced water can be transported to an offsite facility.
- **Beneficial reuse.** The produced water may be reused for agricultural and industrial purposes, such as crop irrigation, livestock watering, etc.

Even though around 95% of produced water is re-injected<sup>2</sup>, which is beneficial for EOR processes, reduction in produced volume means huge savings. Therefore, it is crucial to minimize water production downhole by reducing production rates, diverting water production, or shutting-off water producing zones.



### **2.3 Impact of produced water on environment and treatment costs**

The biggest part of the pollution in the oil industry is connected to produced water<sup>4</sup>. Total volumes of are quite difficult to compute, but it has been estimated, that in 1999 a total of about 77 billion bbl water has been produced worldwide, which is some 3 times higher than the total oil production the same year<sup>5</sup>.

It has been projected, that the total size of the market opportunity for the final stage produced water treatment systems will be around \$4.3 billion for years 2010-2014. For the same period market opportunity for topside produced water re-injection systems can reach \$9.8 billion<sup>6</sup>.

These numbers prove once again that huge savings can be achieved by reducing water production.

### **2.4 Water control solutions**

When the source of the water production is identified, appropriate actions of attacking the problem should be taken. Water production can be slowed down by a reducing of production rates, water can be diverted, or the layers with high water cut can be completely shut off. production Prate reduction and diversion of water flow in the formation is only a way to delay water production, water shut-off is a permanent treatment to completely or partially block flow of unwanted fluids. Water shut-off can be classified in two different types: mechanical and chemical<sup>7</sup>.

Each problem type has solution options that range from relatively simple and inexpensive mechanical and chemical solutions, to the more complex and cost-demanding completion and work-over solutions. In case of multiple produced water sources, a combination of several solutions may be applied. The following sections present some solutions to control water production.

### **2.4.1 Completion designs and well placement**

In order to extend the lifetime of a well, unwanted fluid production has to be minimized and more importantly, avoided in the early stages of the production. Instead of treating water production after a breakthrough downhole, a well can be placed in a very well calculated way to ensure maximum recovery.

Placing a well horizontally, instead of vertically, will have a positive effect on coning problems. Pressure drop over a much larger perforated area will be lower, so coning from underlying aquifer or overlying gas zone will be delayed. Advanced drilling techniques allow controlling drilling trajectory with extreme accuracy, so the placement of the borehole is feasible using azimuthal resistivity tool, and with integration of Inflow Control Devices (ICDs) coning is not only delayed, but any water that might flow into the wellbore can be choked back.<sup>8</sup>

Implementation of smart wells is another good option for water control. They have valves and sensors that can be controlled independently. These options give an opportunity to select which reservoir fluids to produce and select zones which should be shut-off for production. The downside of smart wells is their cost. Net present value is not necessarily increased when a smart well solution is chosen. This is because of high additional investments<sup>9</sup>.

If a water influx to the annulus is caused by casing failure, or other type of mechanical failure. Mechanical solutions can be applied to keep water production from entering the wellbore. Metal or plastic patches can be used to isolate the inside of the casing. For a successful operation, the depth of the source must be known. These patches cannot, on the other hand, be used for longer intervals of damaged casing.

## 2.4.2 Downhole separation

If the produced fluid has a higher water cut than the economical limit for that particular field, production of such fluid should be stopped. To reduce lifting and disposal costs, produced water can be separated downhole. When water is separated from the produced fluid, the hydrostatic head in the wellbore is reduced and the lifetime of a well is, as a result, increased. In addition, downhole separation leads to significant reduction of surface facilities for produced water treatment. These installations are often used in wells of little value, with a low oil production and a high water cut<sup>10</sup>.

A downhole separation system, usually, consists of a hydrocyclone and an electrical submersible pump (ESP). The fluid is drawn in the pump where the velocity is increased before it enters the hydrocyclone. At high fluid velocities, gravity separates fluids with different densities (water-oil or water-gas) and water can be reinjected back into the formation. Huge savings in both capital and operational costs come from smaller and more compact surface facility. In addition, when the produced water is separated and reinjected downhole, there is a reduced demand for injection wells<sup>10</sup>. An illustration of downhole separation is shown in figure 4.

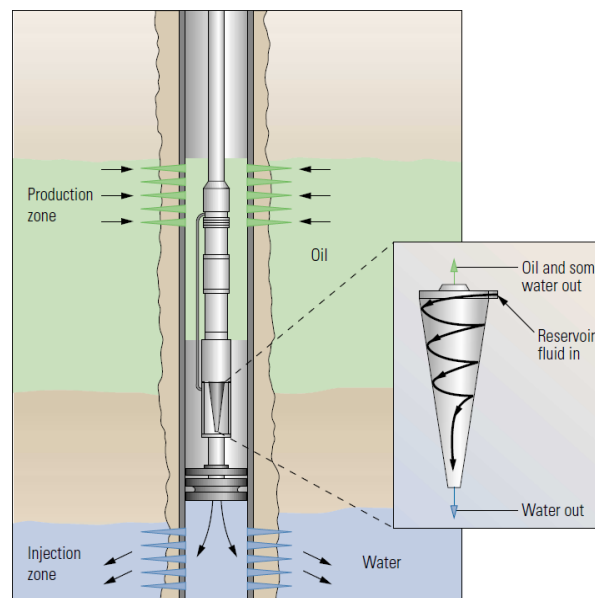


Figure 4: The concept of downhole separation<sup>1</sup>

### 2.4.3 Chemical water shut-off

Mechanical methods for water shut-off have been implied for many years and are still applicable for some particular problems discussed earlier. Chemical methods, on the other hand, have become more used and more successful in the last decade<sup>11</sup>.

Mechanical treatments cannot always ensure that water is completely kept away since they are efficient for near-wellbore problems solving. For a deeper and more efficient blockage of water flow chemicals methods can be used. Figure 5 illustrates the principle of gel system treatment.

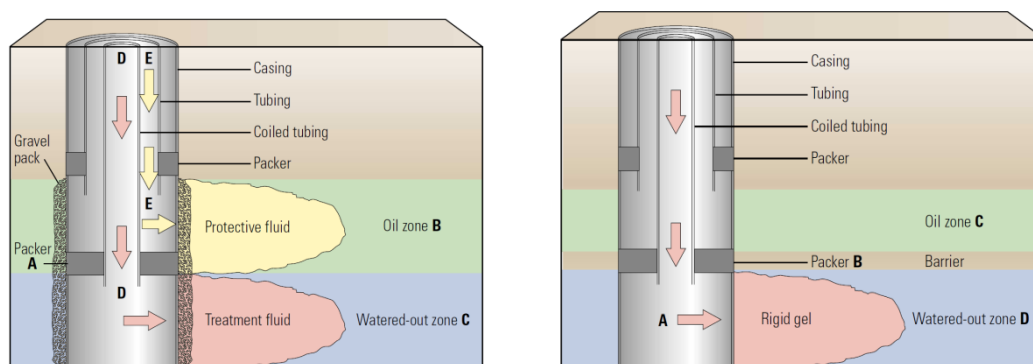


Figure 5: The concept of gel treatment<sup>1</sup>

Two different cases are presented in figure 5. In the first case, in the left panel, a coiled tubing dual injection is shown. The placement of the treatment fluid is critical, so the packers must be set at the right depth. The protective fluid keeps the oil zone free from gelant. When the gel is formed and it is able to withstand formation pressure gradients, the production can resume and watered-out zone will be shut-off permanently. In this particular situation there is a communication between oil and water layers, so coning effect might cause a water breakthrough later. The breakthrough can be delayed by reducing the production rate or an increase of the treatment zone.

On the right panel in figure 5, a simple chemical shut-off operation is shown. There is no communication between the layers, so the gelant can be pumped straight into the watered-out

zone. To assure that there is no gelant flowing in the oil zone, a packer inside the casing is necessary. Gel will completely shut-off the watered-out zone and water production will be stopped from that zone. A later breakthrough might occur only if the gel is not strong enough, or if the placement was not sufficient.

#### **2.4.4 Gelling systems**

Gelling systems are divided into two main groups according to the chemical which is polymerized during the process. These groups are polymer and silicate gels. Polymer gels are created by crosslinking a polymer with a gelling agent, such as chromium or an organic crosslinker. Silicate gels are made by an addition of acid or another gelling agent to an aqueous solution of sodium silicate.

Polymer gels are differentiated to preformed gels and gelants. The term “preformed gel” refers to any gel state that does not flow into or through porous medium. Such gels are formed in advance on surface and have high viscosities. Gelants, however, have lower viscosity and can penetrate the formation rock. Gelant systems are created by injecting the chemicals before the gelation leads to an increase of viscosity<sup>12</sup>. Silicate gel systems are considered to be gelants.

Silicate gels for petroleum applications have been introduced as early as 1922<sup>13</sup>. Despite the fact that silicate gels have been discovered much earlier, polymer systems have been one of the most extensively applied in the last two decades<sup>7</sup>. They have been applied in many field cases and have shown great pay-off values with relatively low investments. However, they certainly have limitations. Key issues with polyacrylamide systems are<sup>14</sup>:

- Environmental and safety issues over crosslinker chromium
- Limited penetration depth
- Polymer shear degradation
- Polymer absorption on reservoir rock
- Polymer precipitation under harsh reservoir conditions.

Krumrine and Boyce's paper presents a controversial fact that silicate use was inequitably neglected in favor of polymer treatments in commercial applications<sup>15</sup>. Now, however, silicate systems are being revitalized. It is so, mostly because of the low impact on the environment and their cost, but also chemical processes are better understood and desired properties of the gel can be created.

The main disadvantages of silicate systems are<sup>16</sup>:

- Gel is rigid and prone to fracture
- Gel shows syneresis and reduction in blocking efficiency
- Precipitation of water insoluble salts in contact with formation water
- The gelation time is hard to control.

Silicate gel systems have number of advantages over polymer systems in situations where polymers are limited to shear degradation and syneresis, or are inadequate to shut-off major thief zones. The main advantages can be summarized as follows<sup>16</sup>:

- Low, water-like viscosity
- Short to moderate pumping times before gel is rigid
- Flexible chemical mechanism
- Excellent thermal stability
- Easy gel breaking in case of fail placement
- Simple and cost-effective surface technology.

In addition to all of the above, sodium silicate is considered to be a “green” chemical which means that it does not have any negative effect on the environment. Conveniently, silicate gels can be crosslinked with “green” gelling agents. This is very important in the industry which is focused on the environment now more than ever before.

New gel aggregates were recently introduced<sup>17</sup>. Such gels are created by the synthesis of microspheres. A system can consist of a simple monomer or polymer, crosslinked with a metal or organic crosslinker. Polymer or monomer is crosslinked, and then the mixture is slowly sprayed to heated oil while stirring. Later, oil is separated from the mixture.

Microspheres accumulate at the bottom. Similar process is taking place when the mixture is injected in the formation. The microspheres block pores and, thus, can be used as a blocking agent. Such microspheres have several characteristics which make them ideal for field use. They have high tolerance for formation salts, they have high injectivity. Their elasticity allows deeper placement of the gelant and increased oil sweep.

#### **2.4.5 Disproportional permeability reduction**

When a zone or a layer is producing water and some oil, it is not desirable to shut-off the whole zone and leave the unproduced oil behind. Gelling systems can be used to reduce the relative water permeability while the oil relative permeability is kept close to constant. This process is called disproportional permeability reduction (DPR). Sufficient results can be achieved by using an emulsion of oil and water with gelling agents dissolved in the water phase. In the reservoir, gravity causes separation of emulsion into oil and water phase. Water phase forms a gel while oil is in continuous phase and is mobile in the formation. This creates segregated flow at pore levels which is the base a DPR model construction. This phenomenon has been observed earlier but was not fully understood. There are still a lot of different opinions on which factors have the biggest influence on efficiency of this concept, but the most recent papers show that segregated pathways are most likely to be true<sup>18,19,20</sup>.

Figure 6 shows an example of how relative permeabilities may look like after a formation of in-situ gel. Relative permeabilities are  $k_{rw}$  and  $k_{ro}$  prior to the treatment, and  $k_{rw2}$  and  $k_{ro2}$  after an in-situ gel formation.

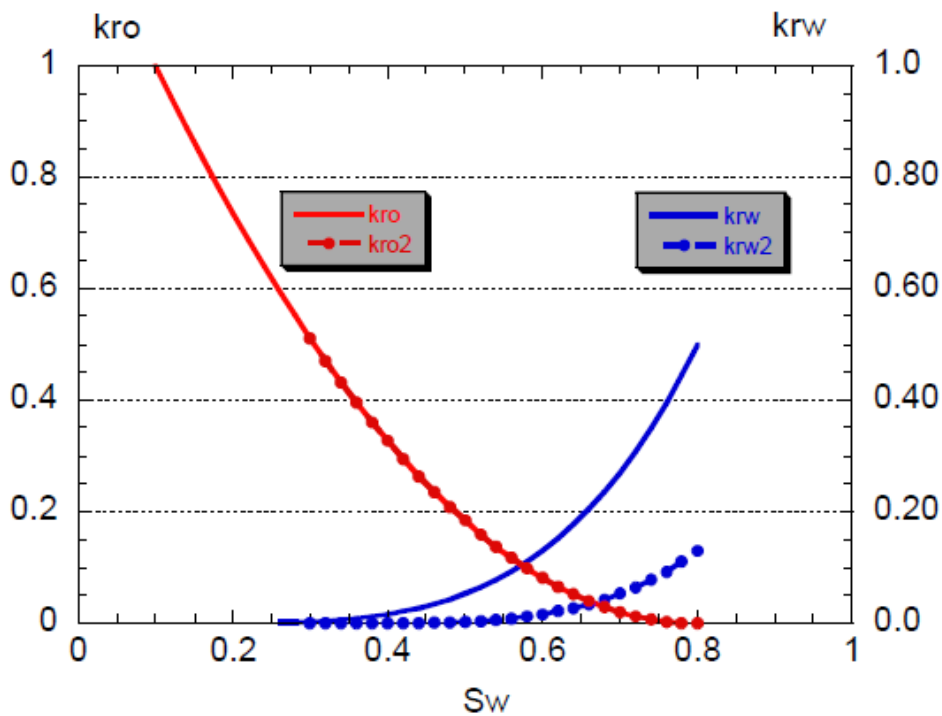


Figure 6: Relative permeabilities before, and after gel formation<sup>18</sup>

#### 2.4.6 Strategies of attacking water production

Seright presents a strategy for attacking excessive water production<sup>11</sup>. The main message presented in his paper, is that the simplest problems should be attacked first. Conventional methods, such as simple cement squeeze or mechanical water control devices are cheaper and should be used for treatment of relatively uncomplicated problems. For near wellbore treatments, the strength of the cement is very important since pressure gradients are at their highest values.

Gel treatments can be used where the cement is impossible to squeeze, for example, when flow behind casing occurs. Gels have higher injectivity than cements and can be placed where cement placement is limited.



A fault or a fracture, connected to an aquifer or producer, should be treated with gels. Gels have near water viscosity and they can be injected deeply in the formation and assure that the fault or fracture is plugged.

More complex problems, such as a fracture crossing a horizontal well should be treated with preformed gel. Even though, a preformed gel cannot penetrate the formation, it can be a good barrier closer to the borehole.

The most important part of water production treatment choice is to determine where the problem is and what the cause is. It is essential to use data which is already available to apply the necessary treatments quickest possible.

Summarizing sources of excessive water production and their treatment options, table 1 is presented. Problems are grouped into 4 categories according to difficulty of treatment in increasing order.

Table 1: Excessive water production sources and suggested treatments<sup>11</sup>

Category A: “conventional” treatments normally are an efficient choice

- Casing leaks without flow restrictions
- Flow behind casing without flow restrictions
- Unfractured wells with effective barriers to crossflow

Category B: Treatments with gelants normally are an efficient choice

- Casing leaks with flow restrictions
- Flow behind casing with flow restrictions
- “Two dimensional coning” through a hydraulic fracture from an aquifer
- Existence of natural fractures connecting a production well with an aquifer

Category C: Treatments with preformed gels are an efficient choice

- Faults or fractures crossing a deviated well
- Single fracture causing channeling between wells
- Natural fracture system allowing channeling between wells

Category D: Difficult problems where gel treatments should not be used

- Three dimensional coning
- Cusping
- Channeling through strata (no fractures), with crossflow

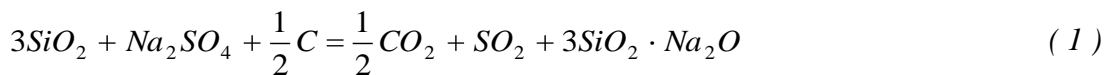
Chemical methods for water shut off have been applied successfully for field applications in the recent years<sup>16</sup>. In-depth placement of a blocking agent can increase sweep efficiency, reduce water cut and thus, increase the profitability of the field. It is believed that this subject will remain central in the near future. Additionally, the impact, caused by chemicals injected in the formation, on the environment has to be minimized, as the oil industry is expanding towards more sensitive environments. Sodium silicate is one of the few environmentally friendly chemicals that can be applied in water management problems. Therefore, the primary aim for this thesis is to analyze sodium silicate gels, their rheological properties and possible gelation agents.

### 3 Theoretical Background

This section presents the theoretical background required for this study. A thorough review and evaluation of chemicals and their properties, basic chemical equations, and gelling processes are presented in this chapter. Additionally, a general equation for gel kinetics is also derived. Understanding the chemical processes is essential in all experimental research.

#### 3.1 Chemistry of sodium silicate

Chemistry of water-soluble silicates is very complex and not completely understood. Sodium silicate is manufactured by heating silica and sodium carbonate to temperatures above 1300°C to form a water-soluble glass referred as “water glass”. Iler presents these reactions<sup>21</sup>:



Sodium silicates are commercially produced as glasses having  $SiO_2 : Na_2O$  molar ratios of 1,6-3,9.

When sodium silicate is dissolved in water, different silicate species tend to dominate at varying pH. Equilibrium equations describe which species dominate and are listed as follows<sup>21</sup>:



Equilibrium constants for equations 3-7 are  $10^{-9,8}$ ,  $10^{-12,16}$ ,  $10^{-9,8}$ ,  $10^{-12,8}$ , 2200 respectively. By using these equilibrium constants, it is possible to calculate the concentration of each silicate species at different pH.

### 3.2 Gel formation

At higher pH values, dimer species dominate but when the pH is reduced, silicate will react to form gel through a polymerization process. To initiate gel formation the pH has to be reduced to a value below 11. The development of the gel can be described with the following steps<sup>21</sup>:

1. Polymerization of monomer to polymer
2. Growth of particles
3. Linking of growing particles to form polymer chains and forming a gel.

These steps are shown in figure 7.

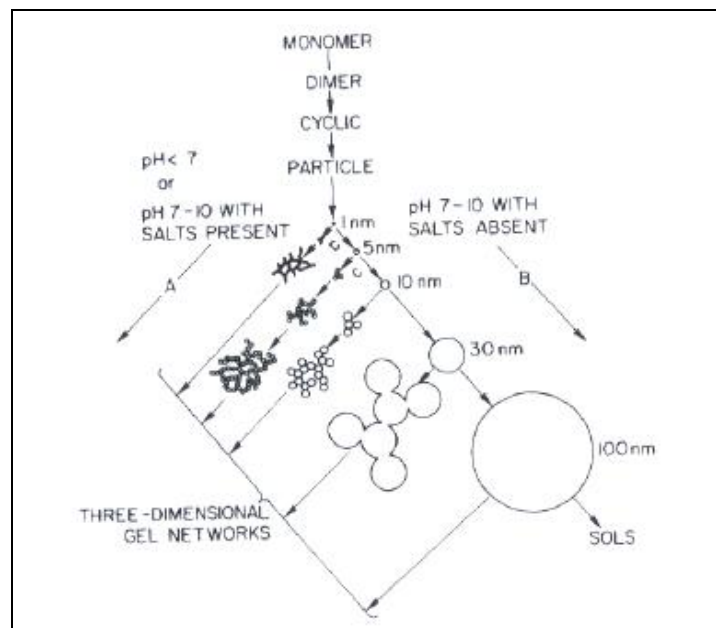


Figure 7: Schematically illustration of polymerization of silica<sup>21</sup>

In solution, molecules will grow by linking to other silica molecules, resulting in a polymer creation. This process is complicated and not very well understood. Water molecules are “captured” and locked in a network of silicate molecules. There are many configurations of polymerization. One (simplified) configuration is illustrated in figure 8. The degree of the polymerization increases as the processes move down in the figure 8.

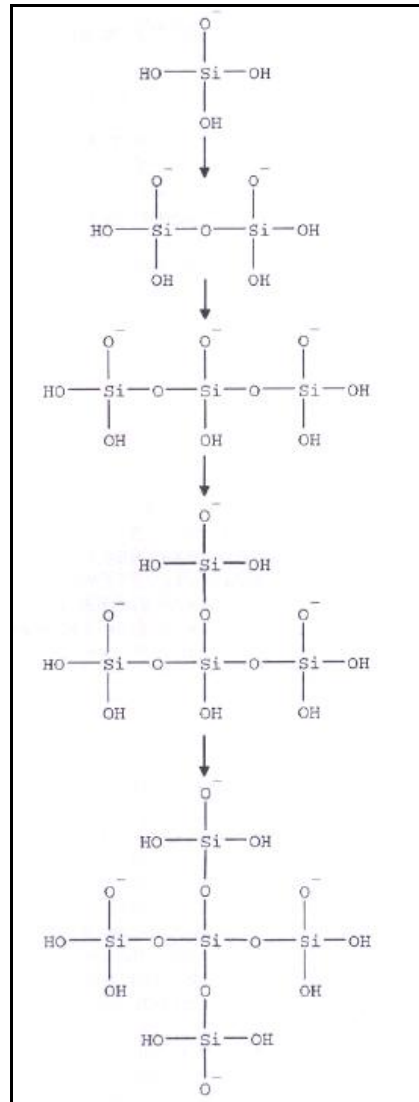


Figure 8: Simplified silicate polymerization<sup>22</sup>

The rate and extent of sodium silicate polymerization is affected by several factors. To understand and control gelation time, these factors must be taken into account. Summary of which and how different factors effect gelation time is presented as follows:

- PH: When the pH of solutions decreases, the process will move down in figure 8.
- Molar Ratio: An increase in silica ratio will result in higher degree of polymerization.
- Dilution rate: dilution at constant pH will de-polymerize silica (process moves up in figure 8).
- Salts: Act as catalysts and increase the rate of polymerization (moves down in figure 8)
- Temperature: Process is accelerated at higher temperatures.

The main factor, controlling gelation time for sodium silicate, is the pH of the solution. However, this relationship is not linear for all pH values. Therefore, this correlation can be divided into several pH intervals, where a change in the pH will follow a certain trend. This is shown in table 2 where the pH values of an aqueous solution of sodium silicate are decreased and the effect of this reduction, in given intervals, are presented.

*Table 2: Stability of silicate species in solution when the pH is reduced*

pH interval	Gelation time	Reason
$11 \leq \text{pH} \leq 14$	Does not gel	Solution is stable
$5,5 \leq \text{pH} < 11$	Decrease in gelation time	Reduction in negative charge
$2 \leq \text{pH} < 5,5$	Increase in gelation time	Catalyzed by $\text{OH}^-$
$0 \leq \text{pH} < 2$	Decrease in gelation time	Catalyzed by $\text{F}^-$ from metal ions

### 3.3 Gelling agents

This section describes chemicals which initiate gelling of sodium silicate. First, an overview of possible gelling agents is presented. Later, the chemicals used in the experimental work of this thesis (HCl and glyoxal) are discussed for oilfield applications. Finally, esters and their properties are evaluated and their applicability to form gels for water control applications is discussed.

The simplest way to reduce pH of the solution is to add acid. Such systems have been applied for many years and a lot of work has been done on optimizing silicate/acid systems for the petroleum production purposes<sup>13, 16, 23</sup>.

Despite the fact that acids have been widely used as gelling agents, there are plenty of other chemicals that can be used. Krumrine and Boyce have presented a good overview of such agents<sup>15</sup>. Most of them are shown in table 3.



Table 3: Gelling agents for sodium silicate

Type	Compound(s)	Examples
Inorganic	Acids	HCl, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub>
	Ammonium Salts	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , NH <sub>4</sub> Cl
	Alkali Metall Salts	Na <sub>2</sub> ZnO <sub>2</sub> , NaHSO <sub>4</sub> , KF, K <sub>2</sub> ZnO <sub>2</sub> , NaCl
	Polyvalent Metal Salts	Cations Al, B, Ti, Zr, Fe, Cu, Si with anion HCO <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , OH <sup>-</sup>
Organic	Acids	Formic, acetic, propionic and corresponding Al, Ba, Ca, Mg, Zn salts
	Aldehydes	Formaldehyde, paraformaldehyde, glyoxal, benzaldehyde
	Polyhydric Alcohols	Ethyleneglycol, dextrin, cellulose, glycerin, starches, sugars
	Esters, Amides, Lactones	Ethylacetate, ethyl chloroformate, formide dimethylformide,
	Polymers	Polystyrene, dipolvynilbenzene, polyesrer resins, latex polyvinyl alcohol
	Surfactants	Most nonionic and many anionic surfactants
	Organic Compounds	Proteins, polypeptides, gelatins, asphalt
Natural Minerals	Inorganic Compounds	Clay, fly ash, shale, gypsum, sulfur

### 3.3.1 Hydrochloric acid

Addition of almost any acid will cause gelation of sodium silicate. In this work, hydrochloric acid (HCl) was chosen as a gelation agent for some experiments to verify results found in the literature and to compare HCl with glyoxal as a reacting agent.

HCl is a solution of hydrogen chloride in water. HCl is a good and cheap gelling agent for silicate systems. Concentrated acid (37 wt%) has a pH value of -1,1. At the point HCl is added to sodium silicate solution the pH value drops. However, use of concentrated acid is limited because it causes immediate gelation in mixture with sodium silicate. In this work, HCl was diluted to 2M solution, a value which is also found in the literature for pH control in field applications<sup>23</sup>. The pH of diluted solution is 0,3. The biggest advantages of HCl as a gelling agent for silicate gels are price, availability and little, if any, damage on environment.

### 3.3.2 Glyoxal

Glyoxal is the smallest double aldehyde (two aldehyde groups) with chemical formula OCHCHO. Its structure is shown in figure 9.

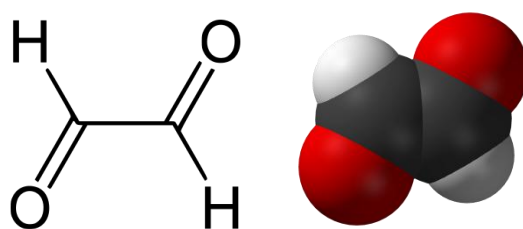


Figure 9: Structure of glyoxal<sup>24</sup>

Glyoxal and sodium silicate were combined as early as 1964 to form hard, cement-like coatings<sup>25</sup>. Very hard substances have been created in the past by using high (around 50 wt%) glyoxal concentrations. Such gels are extremely hard, cohesive and water insoluble. For water control applications, glyoxal concentrations must be lowered to reduce the cost of the gel system and adjust required gelation time. For casing repair, on the other hand, hard substances created with high glyoxal concentration might be an alternative.

As mentioned, sodium silicate pH has to be reduced to a value under 11; an addition of a sufficient amount of glyoxal can be used to achieve that. For this system, the reduction of pH is highly dependent on temperature and, therefore, this system has an advantage when gelation has to be delayed until it is injected deeply in reservoir. Ideally, there should exist a system of sodium silicate crosslinked with glyoxal which would be close to stable, i.e. it would not gel at room temperatures, but once the necessary temperature is reached, it would form a strong and water insoluble gel. Parameters that have an effect here are: sodium silicate concentration, glyoxal concentration and ions in dilution water.

### 3.3.3 Esters

Even though esters were not used in the experiments for this work, they are a very interesting alternative for petroleum applications as gelling agents. In reaction with water, esters produce acid and alcohol and, thereby, can initiate polymerization. Esters are organic compounds derived by reacting an oxoacid with a hydroxyl compound, such as an alcohol or phenol. An example of ester structure is shown in figure 10.

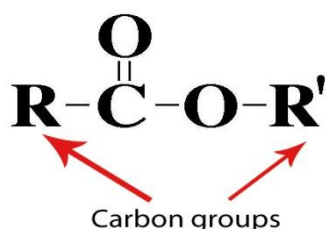


Figure 10: General structure of an ester<sup>26</sup>

Esters react with water. This reaction is called hydrolysis and general formula is presented in figure 11.

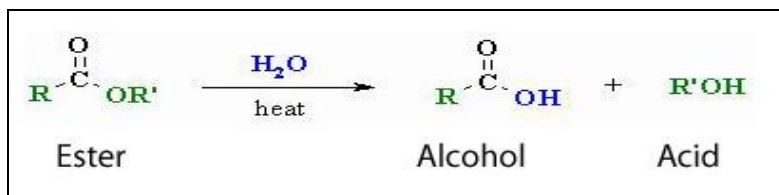


Figure 11: General formula of ester hydrolysis

The products from the hydrolysis reaction will provide the necessary delay if the concentrations and surrounding conditions are suitable. Temperature plays an important role in ester hydrolysis as the rate of reaction increases exponentially with an increase in temperature.

By selecting specific esters and catalysts, a highly temperature-dependent system could be created and optimized. As discussed earlier, such systems have an advantage when gelation has to be delayed for deep gelant placement. A review of available literature shows that similar systems have been created<sup>27</sup>, however, no attempt to optimize these systems was made.

### 3.4 Gel codes

Polymerization of silicate particles is a continuous process. Gel is formed in several stages; these stages are identified and denoted as gel codes. In literature, many different gel code notations can be found but in this work, gel codes introduced by Stavland et al. will be used<sup>23</sup>. Following denotation is based on visual inspection of the gelling fluid in a clear sample glass. Classification of gel codes is presented in table 4.

*Table 4: Classification of gel codes based on macroscopic gel structure observations*

<b>Gel code</b>	<b>Description</b>
<b>0</b>	Clear and low viscous fluid
<b>1</b>	Cloudy and low viscous fluid
<b>2</b>	Cloudy and high viscous fluid
<b>3</b>	Rigid gel

In addition, it has been reported that a gel with code 1 plugged 3  $\mu\text{m}$  Milipore filter. These gel codes have been introduced for sodium silicate crosslinked with HCl, gelation process for other gelling agents is different and some of these codes may not be applicable. Generally, gel code 0 and gel code 3 will be a part of all gelled systems, while codes 1 and 2 may exist for a period which is too short to be identified, or there is no clear boundary between different stages. Visual inspection is relatively precise as long the boundaries are well defined and the person making observations is consistent. A better way to distinguish gel codes would be a numerical measurement of some sort, for example, viscosity, turbidity or, ideally, average particle size.

### 3.5 Silicate gel kinetics

As discussed earlier, time to form a gel is a function of several variables. Gelation time can be defined as time to reach a certain gel code. Stavland et al. defined gelation time as the time required to reach gel code 1, and derived a formula for the gelation time when sodium silicate is crosslinked with HCl<sup>23</sup>. Time to reach gel code 1 is given by equation 8.

$$t_{gel} = \mu \times e^{\alpha[Si]} \times e^{\beta[HCl]} \times e^{\gamma[Ca^{2+}]} \times e^{E_a/RT} \quad (8)$$

Where:

$t_{gel}$ = gelation time [days]

[Si]= silicate concentration [wt%]

[HCl]= HCl concentration [2M wt%]

[Ca<sup>2+</sup>]= concentration of calcium [ppm]

R= gas constant,  $8,314 \times 10^{-3}$  [kJ/mol·K]

T= absolute temperature [K]

$\mu = 2,1 \times 10^{-8}$  [days],  $\alpha = -0,6$ ,  $\beta = -0,7$ ,  $\gamma = -0,1$  and  $E_a = 77$  kJ/mol

In this work, the formula for gelation time is presented based on a modification of equation 8. In the equation, derived in this work, the gelation time is given in hours and it is defined as the time required for the gel to become rigid, i.e. to reach gel code 3 (see table 4). Gel code 3 is chosen because it is easier to distinguish the boundary when the gel becomes rigid. Additionally, some glyoxal systems would not become cloudy; thereby they “skip” gel code 1. An increase in viscosity is a part of all systems, but it might be extremely difficult to identify the transition visually. Moreover, salinity effects are also taken into account in derivation of the equation.

A general equation will be derived with respect to these variables:

- Temperature
- Sodium silicate concentration
- Glyoxal concentration
- Salinity and divalent ion concentration

A general equation which can be used to describe the gelation time as a function of these parameters is as follows:

$$t_g = \zeta \times e^{A[Si]} \times e^{B[Gl]} \times e^{C[Ca^{2+}] + D[NaCl]} \times e^{-E_a/RT} \quad (9)$$

Where:

$t_g$ = gelation time [hrs]

[Si]= silicate concentration [wt%]

[Gl]= glyoxal concentration [wt%]

[Ca<sup>2+</sup>]= concentration of calcium [ppm]

[NaCl]= concentration of sodium chloride [wt%]

$E_a$ = activation energy [kJ/mol]

$\zeta$ = multiplication factor [hrs]

A, B, C, D= constants

Numerical values for A, B, C, D and  $\zeta$  will be presented later in this thesis as a part of discussion and calculations performed with the results obtained from experimental part of this work.

In order to find these unknown constants, gelation time has to be measured for different silicate and glyoxal concentrations. Additionally, salinity and calcium content in the makeup

water has to be varied. Some of these experiments have to be done for different temperatures to estimate the effect of temperature on gelation time.

Equation 9 is divided into four parts where gelation time becomes a function of only one variable, when the others are kept constant.

1. Gelation time as a function of silicate concentration only

$$t_g = \zeta_1 \times e^{A'[Si]} \quad (10)$$

2. Gelation time as a function of glyoxal concentration only

$$t_g = \zeta_2 \times e^{B'[Gl]} \quad (11)$$

3. Gelation time as a function of NaCl and CaCl<sub>2</sub> concentrations only

$$t_g = \zeta_3 \times e^{C'[Ca^{2+}] + D'[NaCl]} \quad (12)$$

4. Gelation time as a function of temperature only

$$t_g = \zeta_4 \times e^{-Ea/RT} \quad (13)$$

Constants A', B', C', D',  $\zeta_1$ ,  $\zeta_2$ ,  $\zeta_3$  and  $\zeta_4$  are determined experimentally for each system.

However, the constants in the general equation are obtained by matching the measured data to the general equation.

Arrhenius equation is valid for most chemical reactions, and it is used as a base to describe temperature dependence in this equation.



$$k = Ae^{-E_a/RT} \quad (14)$$

Where:                    k= rate constant [s<sup>-1</sup>]  
                              A= pre-exponential factor [s<sup>-1</sup>]  
                              E<sub>a</sub>= activation energy [kJ/mol]  
                              R= gas constant [kJ/mol·K]  
                              T= absolute temperature [K]

### 3.6 Gel syneresis

Long term studies showed that silicate and polymer gels tend to expel water by contracting. This process is called syneresis and affects long time stability of the gel. It is believed that syneresis is an inevitable part of any gelation process<sup>27</sup>.

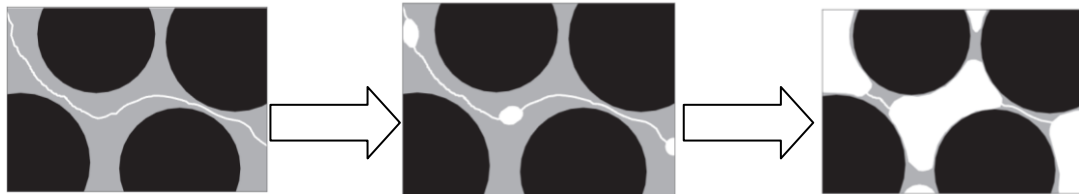
Although the permeability of gel-treated porous medium does increase as syneresis proceeds, the degree of permeability reduction in core samples remains technologically useful even when 95 % syneresis is observed in bulk samples.

As gelation process is finished and the gel has eventually become a solid, the remaining crosslinker will continue to react. It causes shrinking of the gel and expulsion of water which is captured by gelled sodium silicate or polymer particles. Depending on the composition of the gel, volume of expelled water may reach 95 %. Factors which affect the degree of syneresis are silicate/polymer and gelling agent concentrations, temperature, salinity and divalent cations<sup>28</sup>. The degree of syneresis increases with time.

It may look like high degree syneresis in bulk samples affect the choice of gel system for a field trial. Quite possibly, a gel that is reduced to 5% of its primary volume would not be favored to be used for water shut-off applications. However, experimental results show that occurrence of syneresis in a bulk gel has little, or no bearing, on the ability of that same gel to

reduce the permeability of a porous medium. It is worth mentioning, that extent of syneresis is similar for bulk and core samples, but the rate can be significantly slower in cores<sup>28</sup>.

Syneresis of a polymer gel is illustrated in figure 12.



*Figure 12: Progress of syneresis in porous medium*

To the left, the gel is formed and no syneresis has developed yet. White line indicates a possible fluid flow through a channel or a gel fracture. In the middle, low degree of syneresis is observed. Some pockets of expelled water are present in the pore space. On the right side, a high degree of syneresis has developed. Water pockets have expanded to fill the porous space, leaving only thin layers of the gel at the pore walls. However, the remaining gel is still a barrier for any fluid flow.

Finally, it is close to impossible to predict the effect of syneresis on gel's efficiency in water control operations only by looking at bulk samples. Core experiments give much more accurate results for this type of problem.

### 3.7 Gel strength

Gels must withstand required pressure gradients, when used in water control applications. These pressure gradients will be the highest closer to the borehole and will get weaker deeper in the formation. So, independently on where the gel is placed it needs to be strong enough to block water flow through formation. Such gel strength is quite difficult to measure, and time-consuming core tests should be carried out to obtain precise data. There is, however, a way to test bulk gel strength which have been used to evaluate different gelling systems<sup>14</sup>. A gel, formed in a test tube, is forced through a small hole by water flow, as shown in figure 13. The walls of the test tube are smooth, so the outlet hole has to be smaller than the tube diameter to ensure that gel stays in the tube. When water is displacing the gel, a piston-like displacement is dubious. Water has a much higher mobility and will try to create a fracture, or some kind of viscous fingering in the tube. Pressure difference,  $\Delta P$  in the tube will deviate a lot from a core samples. Despite that, this test can be used for relative gel strength evaluation. Higher  $\Delta P$  will always mean stronger gel. So, this simplified and quick test is a good solution for comparison of gel strength for different gels.

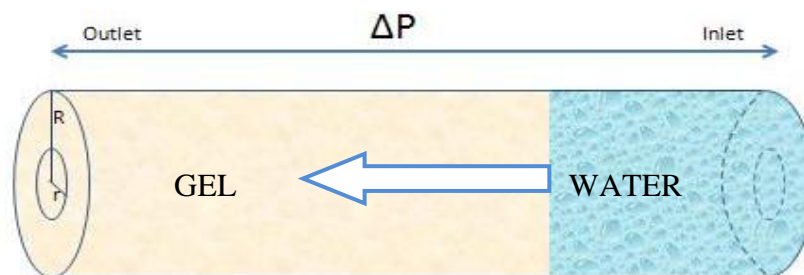


Figure 13: Representation of the testing tube for pressure extrusion test

## 4 Laboratory Equipment and Experimental Procedures

This section describes which experiments were carried out in this work, which chemicals and equipment have been used. In addition, it gives a brief explanation on the experimental procedures. Experiments are grouped according to the objective of each experiment series.

In all experiments, commercial sodium silicate Krystazil 40 (K40) from vendor BIM Norway was used. The  $\text{SiO}_2:\text{Na}_2\text{O}$  molar ratio was 3.4 and  $\text{SiO}_2$  concentration at 27.84 wt%. It had a pH value of 11,3. A 4 wt% sodium silicate concentrate was used in the majority of experiments presented in this work. This choice was based on sodium silicate concentrations reported in the literature<sup>23</sup>.

### 4.1 Sodium silicate crosslinked with HCl

The amount of HCl added is reported as wt% of 2M solution which was prepared from concentrated 37 wt% HCl by diluting it with distilled water. Acid was added slowly to water while mixing carefully. Following amounts were used:

803g	d H <sub>2</sub> O
<u>197g</u>	<u>37 wt% HCl</u>
=1000 g	2M HCl

The pH value was measured to be 0,30 of the 2M solution at room temperature.

### 4.1.1 Bulk gelation time

Gelation times have been estimated in literature for sodium silicate crosslinked with HCl, this test is used to verify the gelation time data and the newly computed data is used for later AcoustoSizer tests.

**Test purpose:** Find out times required to reach gel code 1 for HCl concentrations 8,5- 11,0 wt% at 25°C and 60°C. Accordingly to test results, a sample with appropriate gelation time is chosen for testing procedures in AcoustoSizer.

**Test procedure:** K40 is weighed in a glass beaker, then the calculated amount water is added to the same beaker and the solution is put aside for mixing on a magnetic stirrer. HCl is weighed in a separate beaker and then slowly added to the sodium silicate solution under mixing to avoid quick local gelation. The final solution is then mixed for at least 5 minutes before poured in a sample glass and placed in the oven or placed in room temperature. Time to reach gel code 1 is determined visually and reported.

Compositions of samples are calculated and presented in the table 5.

*Table 5: Compositions of bulk gelation samples*

Sample	1-1	1-2	1-3	1-4	1-5	1-6
Sample size [g]	50	50	50	50	50	50
HCl wt%	8,5	9	9,5	10	10,5	11
K40 [g]	7,184	7,184	7,184	7,184	7,184	7,184
dH <sub>2</sub> O [g]	38,566	38,316	38,066	37,816	37,566	37,316
2M HCl [g]	4,25	4,5	4,75	5	5,25	5,5

#### 4.1.2 AcoustoSizer tests

Polymerization process and silicate particle growth is very poorly understood. For a better awareness of gelation progress AcoustoSizer was employed to measure particle size distribution during gel formation of sodium silicate.

**Equipment used:** AcoustoSizer II from Colloidal Dynamics. The setup is shown in figure 14.

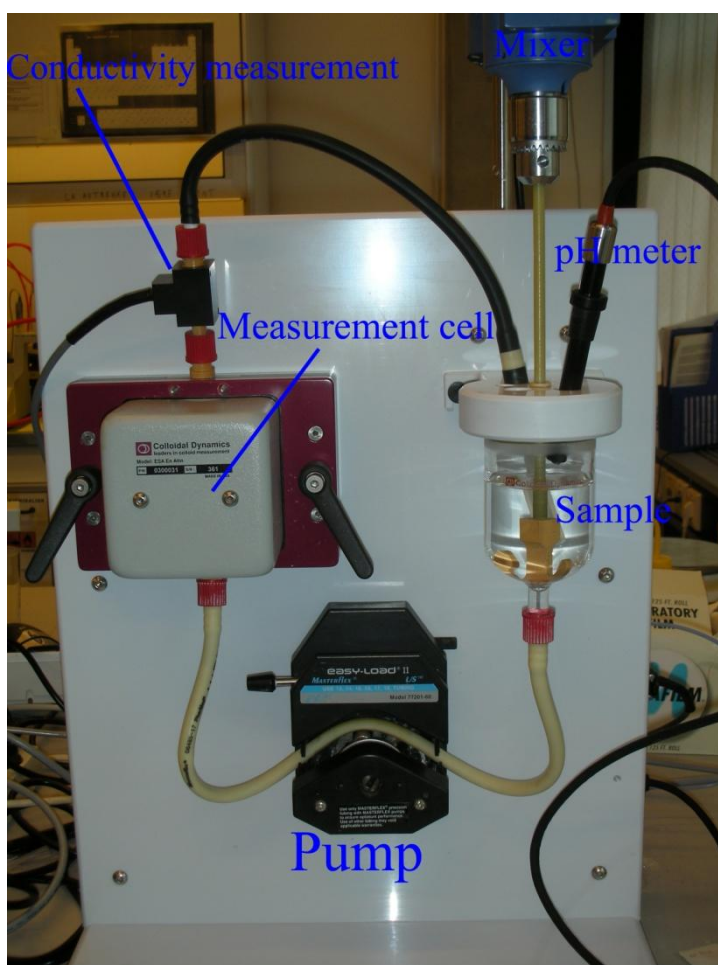


Figure 14: AcoustoSizer from Colloidal Dynamics

**Working principle<sup>29</sup>:** The AcoustoSizer uses multifrequency electroacoustic technology to obtain zeta potential, particle size and conductivity. The sample is pumped through the system and a high frequency electric field is applied in the measurement cell. The motion of the electrically charged particles in the alternating field generates ultrasound which is measured. Two measurement techniques are employed: electroacoustics and ultrasonic attenuation.

If particle size is less than 70 nm, it is better to use attenuation option to obtain particle size. For larger particles, ESA gives better results. Required input data for AcoustoSizer:

- Solvent type: polar or non polar
- Wt% of solids in solution
- Particle type: density and dielectric constant

The output is:

- Particle size distribution with numerical D50, D15 and D85 values
- Two different distribution functions: log- normal and bidisperse
- pH, temperature, conductivity, zeta potential, dynamic mobility, fit error.

The AcoustoSizer does all measurements at the same time, so re-analysis with different input values can be performed after the initial test is carried out.

For every experiment it is essential to find out which type of measurement and which distribution function to use. Re-analyzing the measured data gives different fit error values. The method with the lowest value is clearly preferred. One might, as well, try different particle types to get the best results. All the input data can be changed in the re-analysis.

Table 6 summarizes tests performed with the AcoustoSizer.

*Table 6: Summary of the AcoustoSizer tests*

Test	Purpose	Procedure
4% sodium silicate solution without HCl	Determine the measurement type and the distribution function which fits best for the sodium silicate gel particle size distribution measurements	K40 is diluted to 4 wt% solution with distilled water, no gelling agent is added. AcoustoSizer is then run with different input properties
4 wt% sodium silicate with 11 wt% HCl	Measure and record particle size distribution variations with time. Compare the results with available particle size data and evaluate applicability of AcoustoSizer for gelation time and gel strength evaluation	100 g of sample <b>1-6</b> is prepared and particle size distribution measurements are carried out
4 wt% sodium silicate with 11 wt% HCl and 750 ppm polymer	Examine the effect of polymer presence in the makeup water on particles sizes and growth pattern	Distilled water in sample <b>1-6</b> is replaced with 750 ppm Xanthan solution and 100 g of such mixture is prepared

750 ppm Xanthan solution was prepared by dissolving 0,75 g Xanthan EX 9230 (supplied by vendor Kelco) into 1 liter distilled water while mixing, and left for slow mixing over night. The solution had a slightly higher viscosity than distilled water.



## 4.2 Sodium silicate crosslinked with glyoxal

The main part of this thesis is dedicated to test glyoxal as a possible gelling agent for water control applications. Parameters that affect gelation time are evaluated in this section. Data obtained from these experiments is used to determine numerical values of constants in the general equation (see equation 9) describing gelation time for silicate/glyoxal systems.

### 4.2.1 Glyoxal concentration effect of on gelation time

Adjusting the concentration of the crosslinker, glyoxal in this case, is, probably, the best way to control gelation time. The range of possible glyoxal concentrations is determined in this test. Glyoxal was supplied by Sigma-Aldrich and was delivered as a 40 wt% aqueous solution.

**Test purpose:** Estimate the effect of glyoxal concentrations on the gelation time

**Test procedure:** 4 wt% sodium silicate solution is prepared by diluting K40 with distilled water. Glyoxal is weighed in a separate glass beaker and added to silicate solution while stirring. The gelant is then left for 5 minutes to mix properly on a magnetic stirrer. Each set of samples is placed in the 60°C preheated oven and left in the room temperature to gel. Time to reach gel code 3 is measured and reported.

Compositions of glyoxal samples are presented in table 7.

Table 7: Compositions of glyoxal samples

Sample	2-1	2-2	2-3	2-4	2-5
Sample size [g]	50	50	50	50	50
<b>40% glyoxal wt%</b>	<b>2</b>	<b>2,5</b>	<b>3,5</b>	<b>4,5</b>	<b>6</b>
4% glyoxal wt%	20	25	35	45	60
K40 [g]	7,184	7,184	7,184	7,184	7,184
dH <sub>2</sub> O [g]	41,816	30,316	25,316	20,316	12,816
4 % glyoxal [g]	—	12,5	17,5	22,5	30
40 % glyoxal [g]	1	—	—	—	—

Note that samples 2-2 through 2-5 are prepared using a diluted glyoxal solution. The original 40 wt% solution was diluted 10 times, to 4 wt%, for more precise weighing procedures. Glyoxal is water soluble so dilution did not have any effect on gelation time, as long as true glyoxal wt% in sodium silicate solution was kept the same. To ensure that, a sample with 6 wt% original glyoxal solution was compared to as sample with 60 wt% diluted glyoxal. No difference in gelation time was observed.

#### **4.2.2 Salinity and divalent ion effect on gelation time**

For up-scaling to a field trial, it is important to investigate salinity effects on gelation time. In the field, the makeup water is some kind of tap water with both  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions present. Formation water is usually rich in metal ions and it will have an effect on gelation time. In some cases, it might cause precipitation of calcium or magnesium silicate. Results from the following tests will show how gelation time is affected by a presence of  $\text{NaCl}$  or  $\text{CaCl}_2$  separately, and by a combination of both salts. If concentrations of either of these ions are too high in the treatment formation, there will be a need for a pre-flush with low salinity water. Results from the following tests will show how an eventual pre-flush should be designed and how much effect its salinity will have on gelation time. Firstly, effects of each salt are evaluated separately. Later, a combination of both is used to determine which ions have a bigger impact.

##### **NaCl test**

$\text{NaCl}$  is present in sea water and will always be in the formation water. It is important to be aware of  $\text{Na}^+$  ion effect on gelation time to properly design gel treatment for a field case.

**Test purpose:** Evaluate the effect of  $\text{Na}^+$  ions on the gelation time.

**Test procedure:** Samples with constant concentration of glyoxal were prepared and small amounts of NaCl were added to each sample. Gelation time to gel code 3 is reported.

Compositions of NaCl samples are presented in table 8.

*Table 8: Compositions of NaCl samples*

Sample	3-1	3-2	3-3	3-4
Sample size [g]	50	50	50	50
4% glyoxal [wt%]	25	25	25	25
<b>NaCl [wt%]</b>	<b>1</b>	<b>0,5</b>	<b>0,2</b>	<b>0</b>
K40 [g]	7,184	7,184	7,184	7,184
H <sub>2</sub> O [g]	29,816	30,066	30,066	30,316
4% glyoxal [g]	12,5	12,5	12,5	12,5
NaCl [g]	0,50	0,25	0,10	0

### CaCl<sub>2</sub> test

Calcium ions react with sodium silicate to form calcium silicate which has very low solubility in water. Precipitation of water-insoluble salts causes pore plugging when silicate solution is injected in the formation. It is important to investigate how calcium concentration affects gelation time and find out when precipitation of calcium silicate occurs.

**Test purpose:** Evaluate the effect of Ca<sup>2+</sup> ions on gelation time.

**Test procedure:** Several samples with constant glyoxal concentration were prepared and CaCl<sub>2</sub> was added to solution. The amounts of CaCl<sub>2</sub> had to be kept very low to avoid precipitation of calcium silicate. In one sample, distilled water was exchanged with tap water with 20 ppm calcium concentration.

Compositions of all samples are presented in table 8.

Table 9: Compositions of CaCl<sub>2</sub> samples

Sample	4-1	4-2	4-3	4-4	4-5
Water type	Distilled	Distilled	Distilled	Tap	Distilled
Sample size [g]	50	50	50	50	50
4% glyoxal [wt%]	25	25	25	25	25
<b>Ca<sup>2+</sup> [ppm]</b>	<b>1000</b>	<b>500</b>	<b>200</b>	<b>12</b>	<b>0</b>
K40 [g]	7,184	7,184	7,184	7,184	7,184
H <sub>2</sub> O [g]	30,316	30,316	30,316	30,316	30,316
4% glyoxal [g]	12,5	12,5	12,5	12,5	12,5
CaCl <sub>2</sub> [g]	0,05	0,025	0,01	0,00	0,00

Sample **4-4** has the total calcium concentration of 12 ppm since the fraction of tap water in the solution is 0,6 and tap water had 20 ppm Ca<sup>2+</sup> concentration. Sample **4-5** is prepared without CaCl<sub>2</sub>.

### Combination of NaCl and CaCl<sub>2</sub>

Effects of Na<sup>+</sup> and Ca<sup>2+</sup> ions have been estimated separately, but for a complete picture, it is important to know how presence of both ions affects gelation time. It is the most probable scenario in field applications.

**Test purpose:** Estimate the effects of Na<sup>+</sup> and Ca<sup>2+</sup> ions concentrations on the gelation time

**Test procedure:** Samples are prepared with same sodium silicate and glyoxal concentrations as in previous salinity tests. Sample **4-1** has the highest concentration of NaCl and the lowest concentration of CaCl<sub>2</sub>. NaCl concentration is then reduced while CaCl<sub>2</sub> concentration is increased for samples **4-2**, **4-3** and **4-4**. **4-5** is prepared without addition of any salts.

Compositions of all samples are presented in the table 10.

Table 10: Compositions of NaCl-CaCl<sub>2</sub> samples

Sample	5-1	5-2	5-3
Water type	Tap	Distilled	Distilled
Sample size [g]	50	50	50
4% glyoxal [wt%]	25	25	25
<b>NaCl [wt%]</b>	<b>1</b>	<b>0,5</b>	<b>0,2</b>
<b>CaCl<sub>2</sub> [ppm]</b>	<b>12</b>	<b>200</b>	<b>500</b>
K40 [g]	7,184	7,184	7,184
H <sub>2</sub> O [g]	29,816	30,065	30,214
4% glyoxal [g]	12,5	12,5	12,5
NaCl [g]	0,50	0,25	0,10
CaCl <sub>2</sub> [g]	0,0000	0,0010	0,0025

#### 4.2.3 PH time dependency

Gelation process is mainly controlled by the pH of the solution. However, the pH changes with time after crosslinker is added to the solution. The development of pH will be dependent on what type of gelation agent is used.

**Test purpose:** Investigate the behavior of the solution pH after the crosslinker is added to the sodium silicate.

**Test procedure:** In this test, HCl and glyoxal are used as gelling agents. Samples are prepared and set for gelation in room temperature. The pH is measured at different times until gel is formed.

Compositions of the pH samples are presented in table 11.

Table 11: Compositions of pH samples

Sample	6-1	6-2	6-3	6-4	6-5	6-6
Water type	Distilled	Tap	Distilled	Tap	Distilled	Distilled
Sample size [g]	50	50	50	50	50	50
40% glyoxal wt%	2	2	2,5	2,5	6	
2M HCl wt%	—	—	—	—	—	11
K40 [g]	7,184	7,184	7,184	7,184	7,184	7,184
H <sub>2</sub> O [g]	41,816	41,816	30,316	30,316	12,816	37,316
40% glyoxal [g]	1	1	—	—	—	—
4% glyoxal [g]	—	—	12,5	12,5	30	—
2HCl [g]	—	—	—	—	—	5,5

As it is shown in table 11, two samples were prepared with the original 40% glyoxal solution, other three with the diluted, 4% glyoxal solution. Sample 6-6 was prepared with HCl for pH behavior comparison between the two crosslinkers.

#### 4.2.4 Temperature effect on gelation time

Temperature is one of the main factors which control the pH of crosslinked sodium silicate and, thus, the gelation time. It is important to investigate how much the gelation time is affected by an increase in temperature and which correlations can be applied to predict gelation time in a field case.

**Test purpose:** Estimate the temperature effect on the gelation time for different glyoxal concentrations.

**Test procedure:** 4 temperatures were used to derive the parameters for gelation time equation. Gelation time was measured in temperatures 25°C, 40°C, 60°C and 80°C. Each set of samples were prepared with distilled and tap water to evaluate the salinity effect at different temperatures.

Compositions of all samples are presented in table 12.

Table 12: Compositions of temperature samples

Sample	7-1	7-2	7-3	7-4
Water type	Distilled	Tap	Distilled	Tap
Sample size [g]	50	50	50	50
40% glyoxal wt%	2	2	2,5	2,5
K40 [g]	7,184	7,184	7,184	7,184
H <sub>2</sub> O [g]	41,816	41,816	41,566	41,566
40% glyoxal [g]	1	1	1,25	1,25

#### 4.2.5 Effect of silicate concentration on gelation time

Silicate concentration can be adjusted to achieve desired properties of a gel. Usually, higher silicate concentrations result in stronger gel with shorter gelation time. However, gels with high silicate are subject to high degree of syneresis. Even though some degree of syneresis may not cause major problems, silicate concentrations were kept in the interval 1- 6 wt%.

**Test purpose:** Estimate the effect of silicate concentration on the gelation time

**Test procedure:** Sodium silicate concentrations were varied while glyoxal concentrations were kept constant for each series of samples. The gelation time was measured in 25°C and 60°C and reported. The samples are grouped according to silicate concentration and amount of water added is presented for each sample according to glyoxal concentration. The amounts of glyoxal are not included in the table, but they can be calculated by a simple subtraction.

Compositions of the samples are presented in table 13.

Table 13: Compositions of silicate samples

Wt% glyoxal	Sample	1% silicate	2% silicate	3% silicate	4% silicate	5% silicate	6% silicate
	Sample size [g]	50	50	50	50	50	50
	K40 [g]	1,796	3,592	5,388	7,184	8,980	10,776
3,5	H <sub>2</sub> O [g]	46,454	44,658	42,862	41,066	39,270	37,474
4,5	H <sub>2</sub> O [g]	45,954	44,158	42,362	40,566	38,770	36,974
6	H <sub>2</sub> O [g]	45,204	43,408	41,612	39,816	38,020	36,224

### 4.3 Gel strength

One of the main reasons why glyoxal was chosen as a gelling agent is its ability to create very strong gels in mixture with sodium silicate. This section describes how bulk gel was tested in this thesis. Effects of silicate and glyoxal concentrations are evaluated. In addition, some samples were prepared with HCl for bulk strength comparison of each gel system.

To evaluate and compare bulk gel strengths, gel is left in a tube to gel for a period of time which is much larger than the gelation time of that particular gel. Later, the gel is displaced by a water flow at constant rate. Pressure at the inlet of the tube is measured and reported.

**Equipment used:** Gilson pump, Rosemount pressure gauge and test tubes with inner diameter equal to 1/2 inch. Test tubes were mounted caps on each end with a 1/8 inch diameter size hole. A smaller hole than the tube's diameter at the outlet is necessary to keep gel in tube when pressure is applied. A bottle to collect the extruded gel is placed at the outlet of the testing tube. The setup is shown in figure 15.

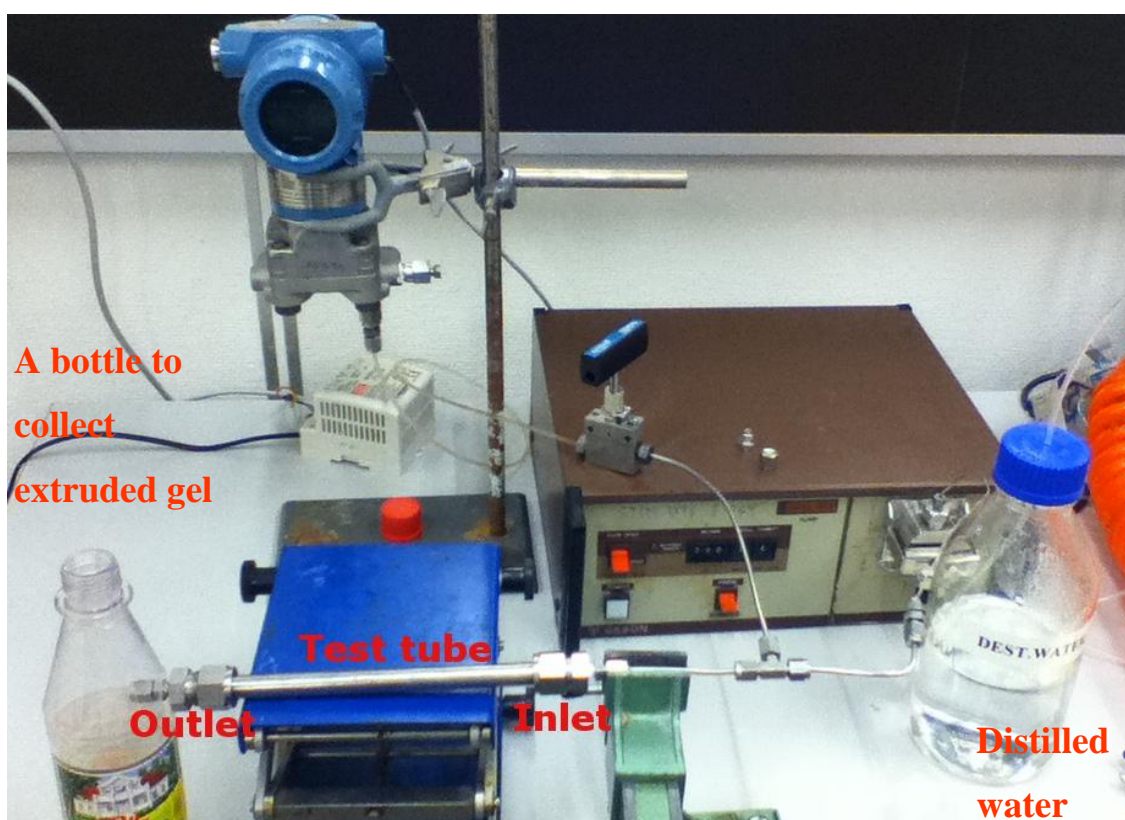


Figure 15: Setup of pressure extrusion tests



## **5 Results and Discussion**

In this section, results from all experiments are presented. This section is subdivided into three main parts. First, results from particle size growth and distribution experiments are displayed and evaluated.

Second, gel formation with glyoxal is presented. Effects of temperature, silicate and glyoxal concentrations, salinity and presence of divalent ions are calculated and reported.

Finally, gel strength measurements are reviewed and discussed.

### **5.1 Sodium silicate crosslinked with HCl**

Behavior of sodium silicate crosslinked with HCl is well known and described in literature. However, AcoustoSizer measurements have not been done for such gel systems as per today's date. To start with, bulk gelation times are measured. Later particle size distribution data is presented and discussed.

#### **5.1.1 Bulk gelation time**

Table 14 shows the pH of each sample, 5 minutes after crosslinking, and the gelation time based on the test data presented in table 5 at two different temperatures: 25°C and 60°C.

Table 14: Gelation times for HCl bulk gel test

Sample	HCl wt%	pH	Gelation time [hrs:min]	
			25°C	60°C
1-1	8,5	10,89	21:55	05:25
1-2	9	10,79	17:03	04:18
1-3	9,5	10,77	09:05	02:53
1-4	10	10,75	03:58	02:11
1-5	10,5	10,7	02:25	01:30
1-6	11	10,63	01:30	01:10

The gelation times, shown in the last two columns of table 14, are plotted versus HCl concentration in figure 16.

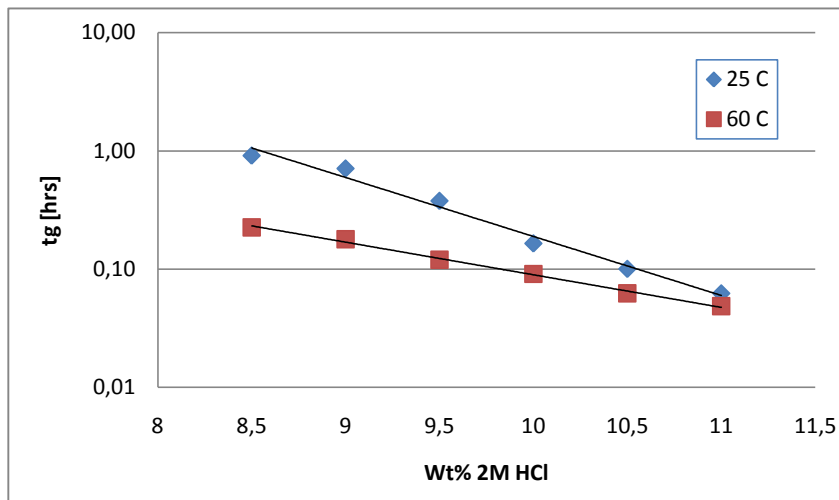


Figure 16: Gelation time (gel code 1) versus HCl concentration

Figure 16 shows a good correlation for both temperatures, however, the data for 60 °C is slightly better correlated. Gelation times are shorter for higher temperatures, and it is easier to see the transition to code 1 in a rapid process than in a slower one. These observations are made visually and the effect of human factor must be taken into account.

The main objective of this test was to find out which concentration is the most suitable for later tests in the AcoustoSizer. The gelation time has to be low enough for the AcoustoSizer to measure the change in particle growth, but cannot be so low that the sample plugs the measuring cell and causes problems. To satisfy these conditions, sample **1-6** was chosen.

### 5.1.1 AcoustoSizer tests

Three tests were run in the AcoustoSizer. Results from these tests are presented and discussed in this chapter.

#### 4% sodium silicate solution without crosslinker

To identify the most suitable parameters in the AcoustoSizer, a 4 wt% sodium silicate solution without crosslinker was tested with different input parameters. The measured data was later re-analyzed and the input parameters giving lowest fit error were determined. The following settings were chosen for the AcoustoSizer tests:

*Table 15: Input parameters and respective values selected for the AcoustoSizer tests*

Input	Value
Distribution function	Lognormal
Particles properties	Density- 2,2 g/ml, dielectric constant 4,5
Measurement technique	Attenuation

#### 4 wt% sodium silicate with 11 wt% HCl

The sample was circulated in the AcoustoSizer and measurements of particle size distribution were carried out continuously. Main objective in this test was to check whether measured particle size would match the expected particle size when the gel reaches code 1. Particle size estimation was obtained from other literature for parallel systems<sup>23</sup>. Figure 17 presents the distribution of particle diameters at 3 different times.

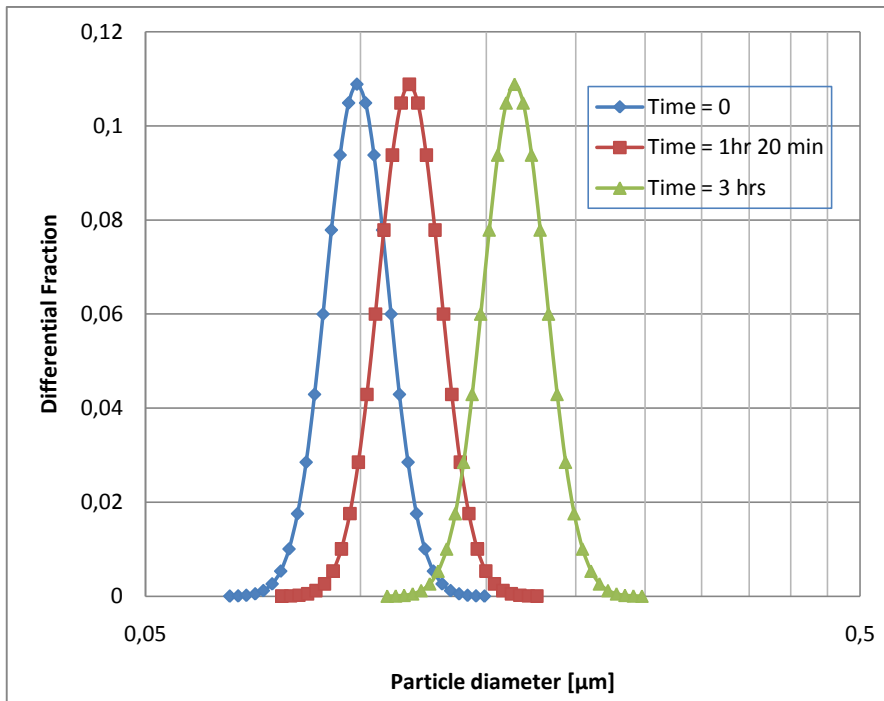
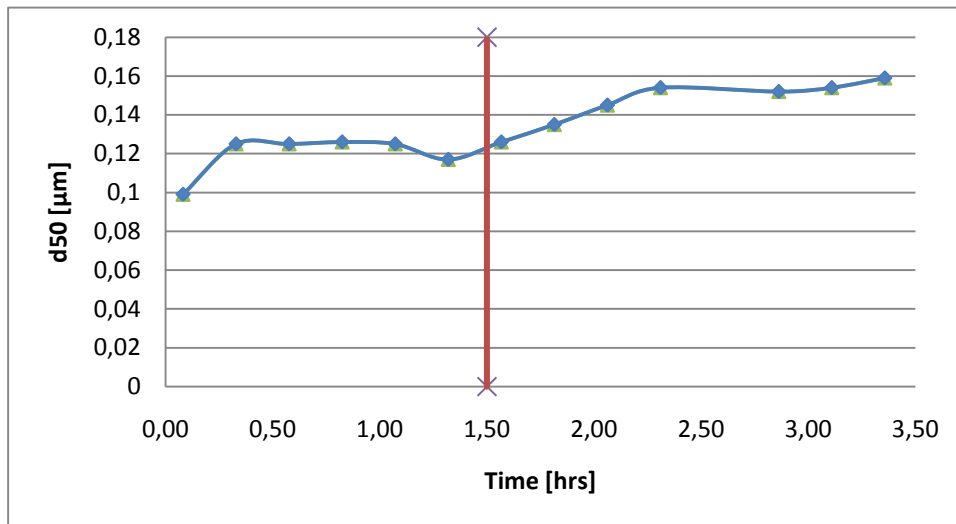


Figure 17: Particle size distribution at different times

From figure 17, it is clear that sodium silicate particles are growing with time. Gelation time for this system at room temperature is 1,5 h. Red curve indicates the measurements taken just before the sample reached gel code 1. Sizes of the majority of particles at this time should reach values around 1  $\mu\text{m}$  according to Stavland et al.<sup>23</sup>. The sample was left for measurements for longer time, since the expected values was not measured. After 3 hours the sample was on the verge to reach gel code 3 and the experiment was abandoned. Still, even at times longer than gel code 1, the AcoustoSizer did not report values in the right magnitude.

The growth of particles can be illustrated by plotting the average particle size (d50) values versus time. This is presented in figure 18 where the vertical red line indicates time needed to reach gel code 1.



*Figure 18: Average particle size development*

Figure 18 gives a clear indication that particles are growing in the solution. However, the growth is far from the extent which is expected. Possible reasons for unsuccessful measurements are discussed later in this chapter.

#### **4 % sodium silicate with 11 wt% HCl and 750 ppm polymer solution**

Distilled water was replaced by a 750 ppm Xanthan solution to investigate what effect presence of a polymer has for particle growth. Figure 19 presents the measured particle distribution data.

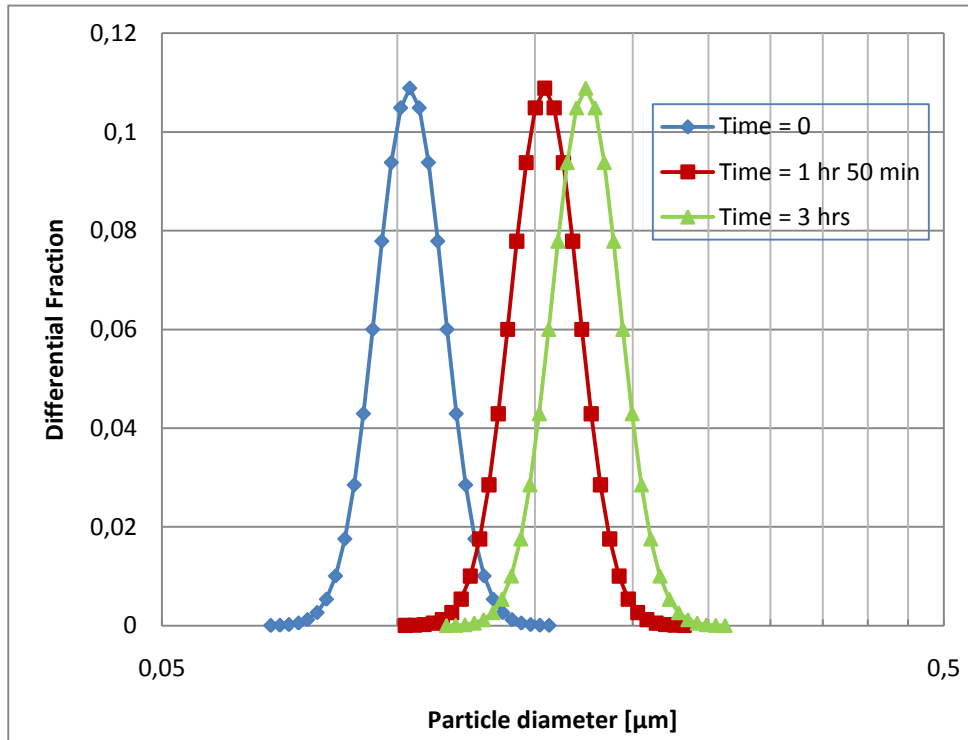


Figure 19: Particle size distribution at different times when water is replaced by a 750 ppm Xanthan solution

D50 values for this sample are plotted versus time in figure 20. The red line, again, indicates time required to reach gel code 1.

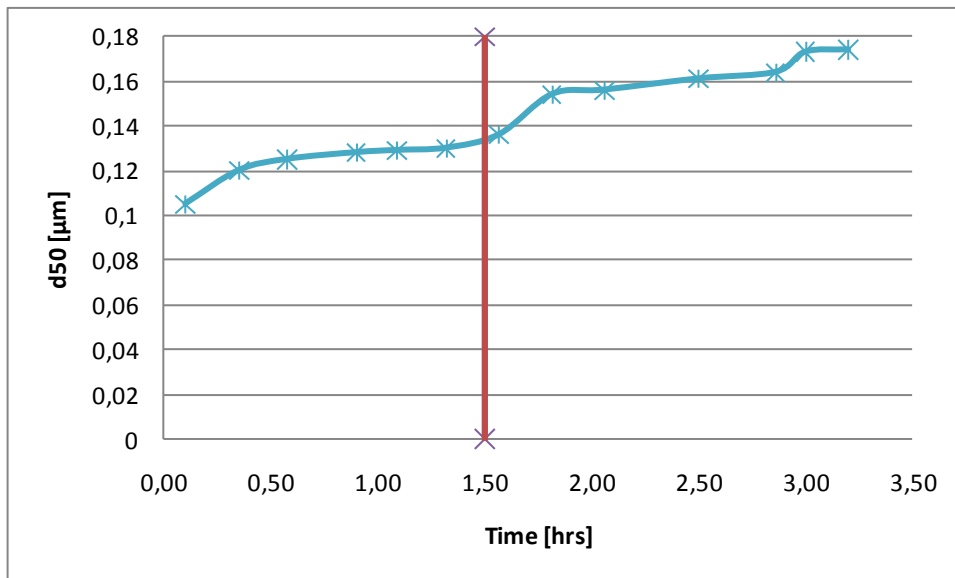


Figure 20: Average particle size development when water is replaced by a 750 ppm Xanthan solution

From figures 17-20, it can be observed that there is almost no difference between the two tests. In both experiments, sodium silicate and HCl concentrations are kept the same.

From these two tests, it can be concluded that AcoustoSizer is unable to measure the actual size of polymerizing silica particles.

The problem, most probably, lies in the inability to predict change of particle properties by the AcoustoSizer. While the particle density is kept constant in AcoustoSizer calculations throughout the whole measuring process, density of polymerizing silicate particles changes when the structure is growing and water molecules are captured.

Early in the process, particle size is measured close to expected values, which means that the equipment is able to detect particles and measuring process is, actually, working. The fact that this equipment does accurate measurements for solutions with constant properties leads to conclusion that it should be possible to measure particle size distribution for each time step if the input values could be varied accordingly to polymerization of the particles. Calculations of input properties should be extremely complicated to compute and might require some very advanced software.

Polymerization process is very complex and not understood to a degree where software could model density of growing silicate particles. In addition, the AcoustoSizer should be able for a dynamic data input as time progresses.

After two series of inaccurate measurements, it was decided to abandon the AcoustoSizer for particle size distribution measurements.

## 5.2 Sodium silicate crosslinked with glyoxal

In this section, glyoxal is evaluated and discussed as a possible gelation agent to form gel in water control applications for petroleum production purposes. Results from all experimental procedures are presented and equations for gelation times are derived.

### 5.2.1 Glyoxal concentration effect on gelation time

Gelation times were measured for 4 wt% silicate gels with different glyoxal concentrations. Table 16 presents the gelation times at two different temperatures: 25°C and 60°C.

Table 16: Gelation times for glyoxal samples

40% Glyoxal [wt%]	Gelation time [hrs : min]	
	25°C	60°C
6	1:41	0:16
4,5	2:57	0:21
3,5	10:00	1:10
2,5	53:57	20:37
2	315:25	64:25

Gelation times from table 16 are plotted versus glyoxal concentration in figure 21.

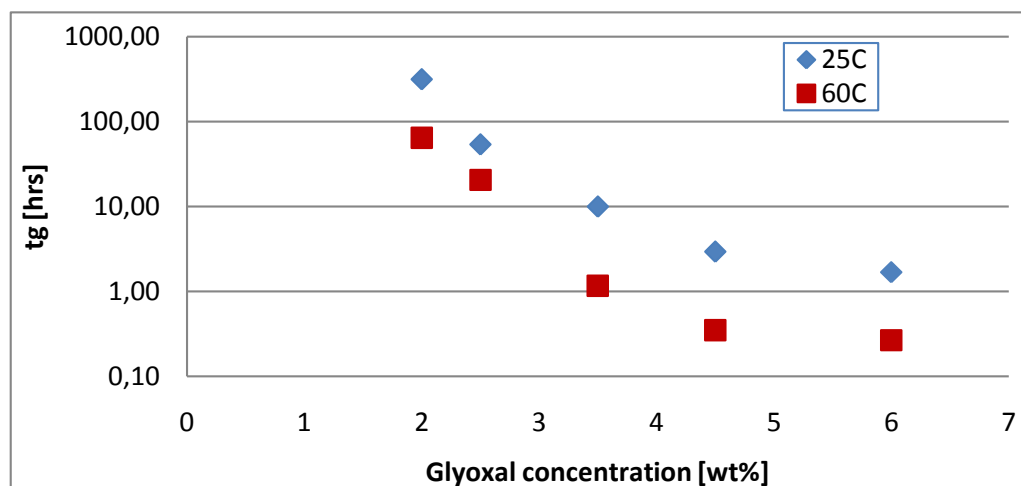


Figure 21: Gelation time versus glyoxal concentration



It is clear, that the gelation time decreases with increasing glyoxal concentrations. At 60°C, and concentrations above 4,5 wt% the gelation is almost instantaneous (less than 20 minutes) and does not decrease much with increased concentration of glyoxal. At 25°C, the same trend can be observed. The line flattens out for concentrations above 4,5 wt%.

Glyoxal concentrations 2 – 4,5 w%, however, give good correlation for both temperatures. Equations for gelation time in this interval are as follows:

Constants in equation 11 are derived based on samples with glyoxal concentrations in the range 2-4,5 wt% So, the equation for 4 wt% sodium silicate and distilled water becomes:

$$\text{At } 25^{\circ}\text{C} \quad t_g = 5934,9e^{-1,743[G]}]$$

$$\text{At } 60^{\circ}\text{C} \quad t_g = 4114,6e^{-2,159[G]}]$$

Three samples with lower concentrations were prepared as well. After 1,5 months in 60°C the sample with 1 wt% glyoxal has not yet reached gel code 3, but some local gelation was observed. Samples with 0,25 wt% and 0,5 wt% glyoxal have become cloudy, similar to gel code 1 for silicate crosslinked with HCl. However, in room temperature, the same samples stayed clear and have not shown any indication of gelation.

### **5.2.2 Salinity and divalent ion effect on gelation time**

Addition of NaCl and CaCl<sub>2</sub> has catalyst effect on gelation. The effect of each salt was evaluated separately first. Later, a combination of both salts was used to investigate gelation times when both salts are present and, thus, determine which ions have a greater effect.

## Effect of Na<sup>+</sup> ions on gelation time

The gelation times for samples with NaCl are presented in table 17.

Table 17: Gelation times for NaCl samples

NaCl [wt%]	Gelation time [hrs : min]	
	25°C	60°C
1	01:37	00:34
0,5	03:42	01:42
0,2	10:13	04:07
0	53:57	20:37

Gelation times from table 17 are plotted in figure 22 versus square root of NaCl concentration at two different temperatures.

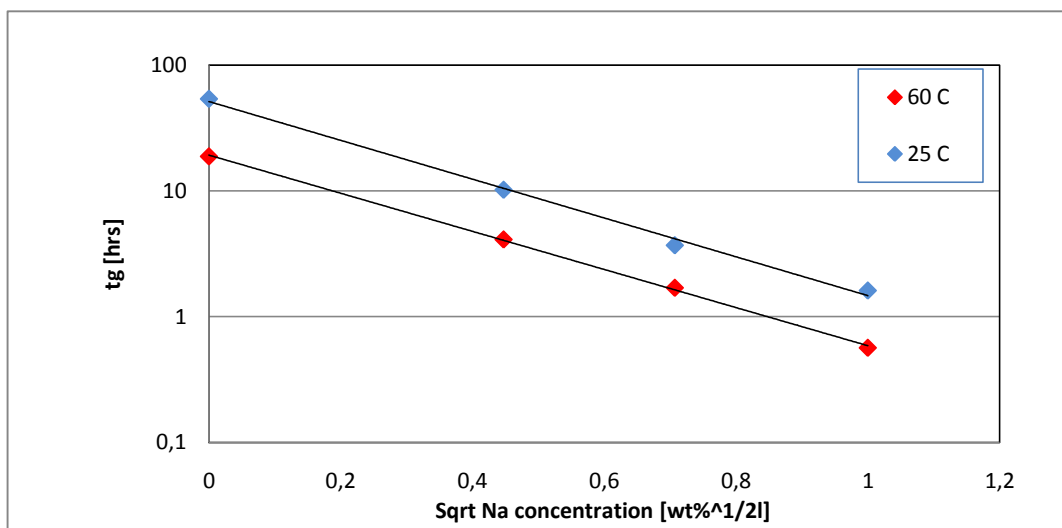


Figure 22: Gelation time versus NaCl concentration

Figure shows that a very good correlation is developed when gelation time is plotted versus square root of NaCl concentration instead of the concentration itself.

Gelation time as a function of salinity is derived. The two following equations are valid for 4 wt% sodium silicate, 2,5 wt% glyoxal concentration and distilled water.

At 25°C:  $t_g = 51,378e^{-3,55\sqrt{[Na^+]}}$

At 60°C:  $t_g = 19,26e^{-3,49\sqrt{[Na^+]}}$

The slopes for both temperatures are nearly identical, so it is safe to assume that this correlation would be valid for other temperatures as well.

### Effect of Ca<sup>2+</sup> ions on gelation time

The gelation times for samples with CaCl<sub>2</sub> are presented in table 18.

Table 18: Gelation times for CaCl<sub>2</sub> samples

Ca <sup>2+</sup> [ppm]	Gelation time [hrs : min]	
	25°C	60°C
500	19:48	5:33
200	22:00	11:00
12	50:51	18:51
0	53:57	20:37

Gelation times from table 18 are plotted in figure 23 versus square root of CaCl<sub>2</sub> concentration at two different temperatures.

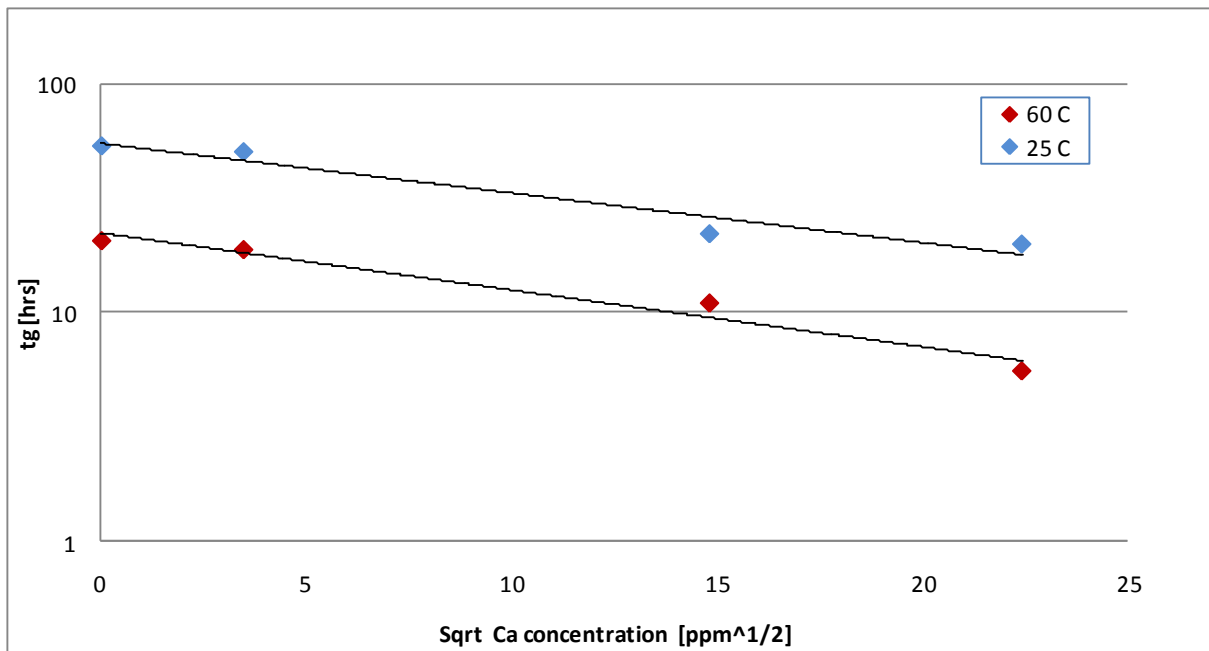


Figure 23: Gelation time versus  $\text{CaCl}_2$  concentration

Measured data fits better when the gelation time is plotted against the square root of calcium concentration instead of calcium concentration. Figure clearly shows that gelation times are reduced with increased  $\text{Ca}^{2+}$  ion concentration. However, reduction of gelation time is not as significant as for NaCl samples.

Gelation time as a function of calcium concentration is derived. The two following equations are valid for 4% sodium silicate, 2,5 wt% glyoxal concentration and distilled water and are given at two different temperatures.

$$\text{At } 25^\circ\text{C:} \quad t_g = 55,05e^{-0,050\sqrt{[\text{Ca}^{2+}]}}$$

$$\text{At } 60^\circ\text{C} \quad t_g = 22,263e^{-0,057\sqrt{[\text{Ca}^{2+}]}}$$

Again, the slopes are similar and the effect of  $\text{Ca}^{2+}$  concentration on gelation time would be similar for other temperatures as well.

In sample **4-1**, with 1000 ppm  $\text{Ca}^{2+}$  concentration, an immediate precipitation was observed and the sample was not taken into gelation time calculations even though it did gel with precipitated calcium silicate on the bottom of sample glass. So, somewhere between 500 ppm

and 1000 ppm there is an upper limit for  $\text{Ca}^{2+}$  concentration in the formation water for field applications. A sufficient pre- flush with lower  $\text{Ca}^{2+}$  concentrations is required to ensure that there is no precipitation of calcium silicate in the pores of the formation. However, this should not be generalized since these experiments were performed for 4% silicate gels and lower concentrations of silicate would need higher calcium concentrations to cause precipitation.

It is worth mentioning, that gels with higher  $\text{Ca}^{2+}$  concentrations seemed to have higher gel strength. The strength was evaluated visually by making the gel ring and by poking it with a small metal stick.

### Combination of NaCl and $\text{CaCl}_2$

Presence of both  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions is a very probable scenario in field applications. Therefore, it is important to estimate the magnitude of each ion concentration, when both are present in the makeup water. Results from earlier tests showed that increasing concentrations of each salt decreased the gelation time. Precipitation of calcium silicate is the limiting factor when increasing amount of  $\text{CaCl}_2$  added. Much larger concentrations of NaCl lead to higher degree of reduction in gelation time in previous samples.

Results from this test are presented in table 19.

Table 19: Gelation times for NaCl- $\text{CaCl}_2$  samples

		Gelation time [hrs : min]	
NaCl [wt%]	$\text{Ca}^{2+}$ [ppm]	25°C	60°C
1	0	1:37	0:34
1	12	1:34	0:24
0,5	200	3:12	1:12
0,2	500	7:04	2:14
0	500	19:48	5:33
0	0	53:57	20:37

Table 19 shows a general trend which was expected. High NaCl concentration causes almost immediate gelling at 60°C. Gelation times for the three NaCl/CaCl<sub>2</sub> samples are plotted in the figures 24 and 25 versus NaCl and CaCl<sub>2</sub>.

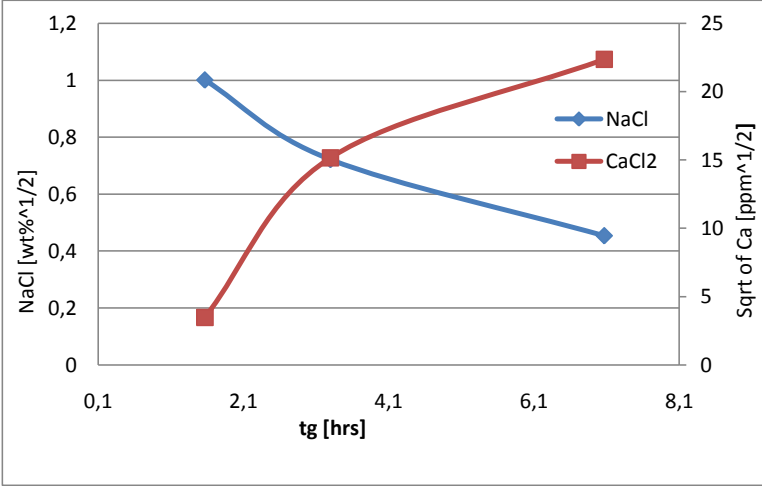


Figure 24: Gelation time versus NaCl and CaCl<sub>2</sub> concentrations, 25°C

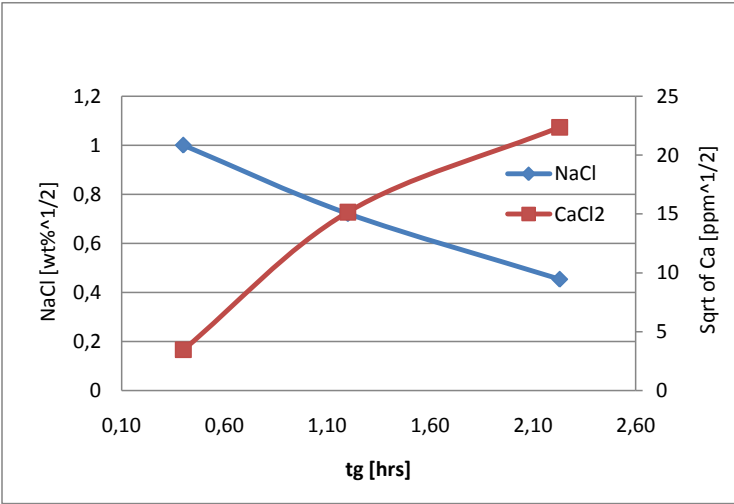


Figure 25: Gelation time versus NaCl and CaCl<sub>2</sub> concentration, 60°C

Figures 24 and 25 indicate that gelation time is reduced when either of the concentrations is increased. When sodium silicate and glyoxal concentrations are kept constant at given temperature for these samples, the only variables are NaCl and CaCl<sub>2</sub> concentrations. However, no equations for gelation time can be obtained directly from these graphs, so a general equation has to be derived for all salinity samples.

For calculation of the constants, a method of least squares in Maple was used. Since there are two variables, a 3D problem was solved. To do so, surface curves were fitted for each temperature data set and constants giving lowest error value for each temperature were derived.

Equation 12 is presented with the calculated constants. The following equations are valid for 4 wt% sodium silicate and 2,5 wt% glyoxal at two given temperatures.

$$\text{At } 25^{\circ}\text{C:} \quad t_g = 47,57e^{-0,0302\sqrt{[\text{Ca}^{2+}]} - 3,3079\sqrt{[\text{NaCl}]}}$$

$$\text{At } 60^{\circ}\text{C:} \quad t_g = 19,54e^{-0,0378\sqrt{[\text{Ca}^{2+}]} - 3,4794\sqrt{[\text{NaCl}]}}$$

Magnitude of the effect that each metal ion has on gelation time can be presented visually. Gelation time is plotted in Maple against the NaCl and CaCl<sub>2</sub> concentrations in figure 26.

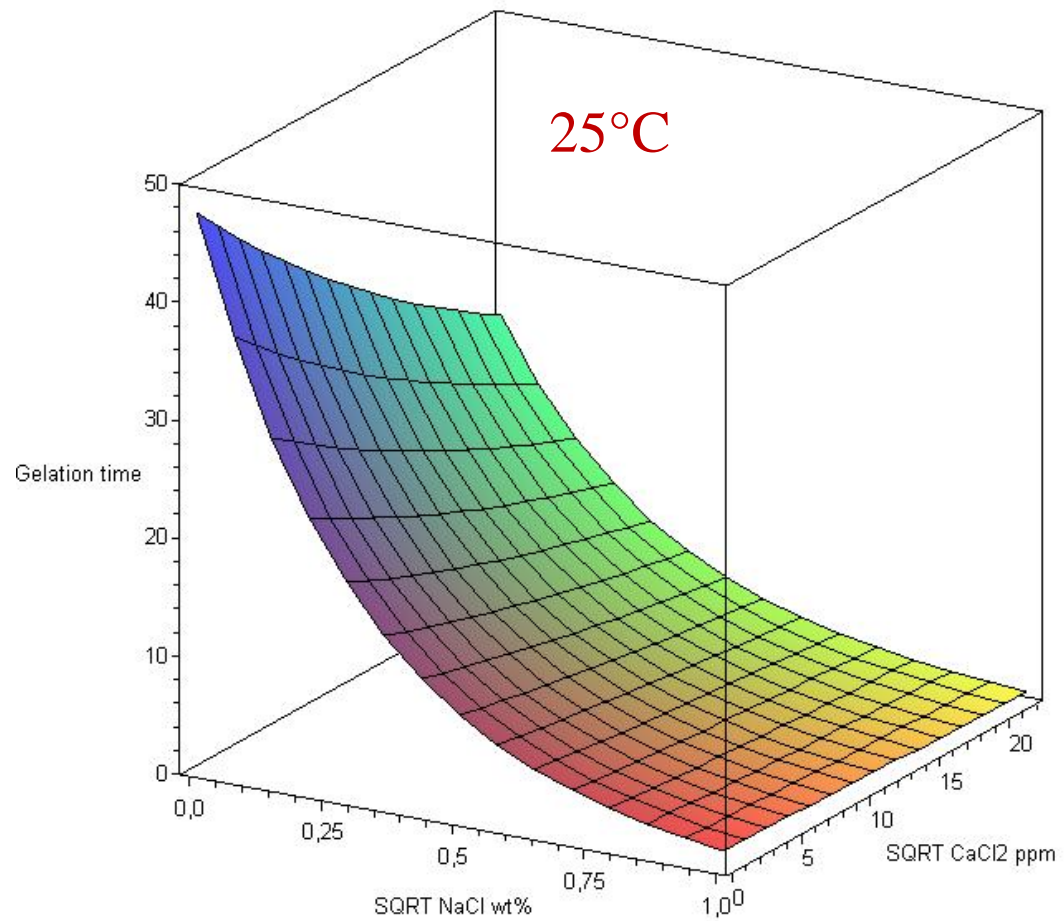
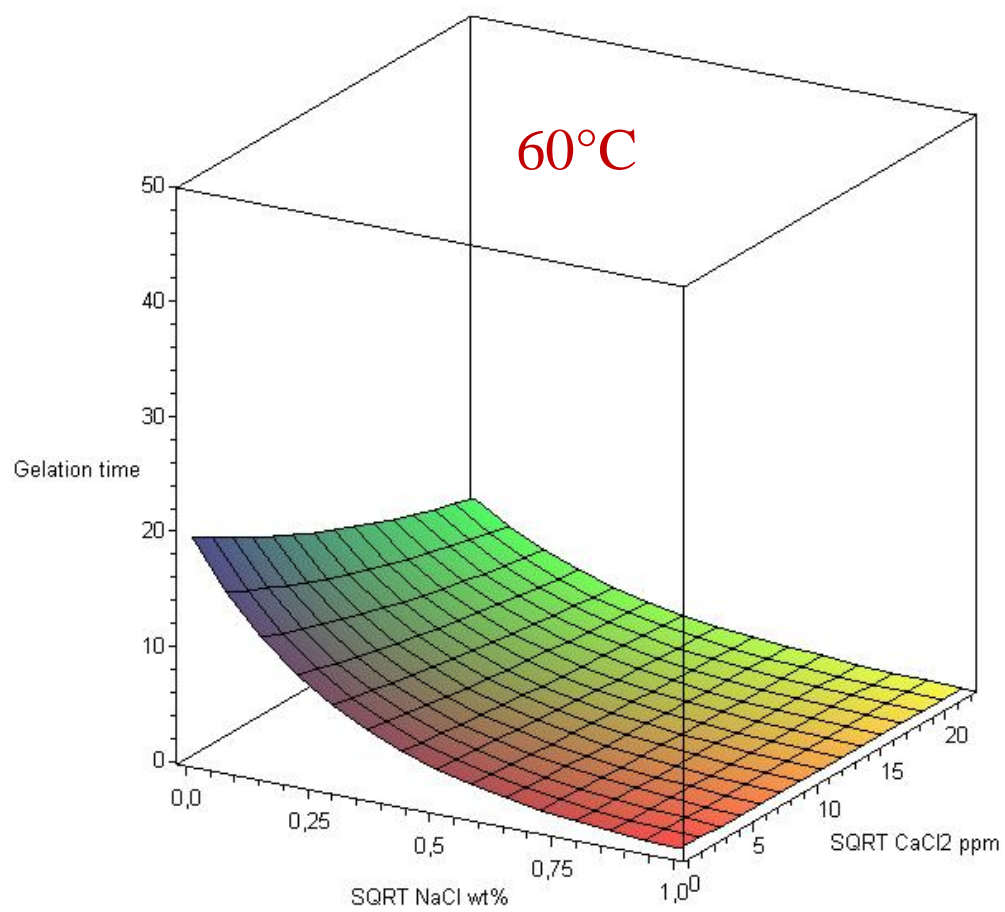


Figure 26: Gelation time (hrs) versus NaCl and CaCl<sub>2</sub> concentrations



As seen from figure 26, addition of NaCl has a much greater effect on gelation time. It is so, because of the total amount added to the solution. Larger amounts of  $\text{Ca}^{2+}$  ions result in precipitation. Numerical values can be tricky to obtain from looking at the two 3D graphs, so calculated gelation times are presented in table 20. In addition, measured values are displayed for comparison purposes.

Table 20: Measured and calculated gelation times for all salinity samples

		Gelation time [hrs : min]		Gelation time [hrs : min]	
		25°C		60°C	
NaCl [wt%]	Ca <sup>2+</sup> [ppm]	Measured	Calculated	Measured	Calculated
1	0	1:37	1:44	0:34	0:36
0,5	0	3:42	4:35	1:42	1:40
0,2	0	10:13	10:50	4:07	4:07
0	500	19:48	24:13	5:33	8:23
0	200	22:00	31:02	11:00	11:27
0	12	50:51	42:51	18:51	17:08
1	12	1:34	1:34	0:24	0:31
0,5	200	3:12	2:59	1:12	0:58
0,2	500	7:04	5:31	2:14	1:46
0	0	53:57	47:34	20:37	19:32

Table 20 shows a quite small deviation between the measured and the calculated data. Calculations are based on quite simple function and constants are derived from 10 samples. To obtain more accurate results, one might have to have more measurements and evaluate other functions as well. Table 20 shows that the calculated values deviate mostly at high  $\text{Ca}^{2+}$  concentrations. It does not cause much trouble for the applicability of the equation, since in a field trial, low concentrations of  $\text{Ca}^{2+}$  ions are expected.

### 5.2.3 PH time dependency

It is important to know how the pH of a sodium silicate solution changes with time to understand the gelation process. Generally, the pH value measured right after crosslinker is added would not stay constant. The behavior will be diverse for different gelation agents. The trend of how the pH develops can contribute to better understanding of different gelling systems.

The measured pH values for given times are presented table 21.

Table 21: The pH values for the pH samples

6-1		6-2		6-3		6-4		6-5		6-6	
2 wt% glyoxal Dist. water		2 wt% glyoxal Tap water		2 wt% glyoxal Dist. water		2,5 wt% glyoxal Tap water		6 wt% glyoxal Dist. water		11% 2M HCl Dist water	
Time [min]	pH	Time [min]	pH	Time [min]	pH	Time [min]	pH	Time [min]	pH	Time [min]	pH
0	11,08	0	11,17	0	11,01	0	11,08	0	11,03	5	10,58
10	11,07	25	11,03	5	11,01	40	10,91	15	10,92	20	10,69
35	10,99	65	10,97	45	10,91	75	10,91	30	10,83	35	10,73
75	10,96	100	10,96	80	10,9	120	10,91	45	10,75	79	10,79
110	10,96	145	10,97	125	10,93	1135	11,03	60	10,66	94	10,8
155	10,97	1100	11,05	1140	11,01			75	10,6	124	10,81
1110	11,07							100*	10,5	142	10,82
										180*	10,83

\* Gel code 3 is reached

Gelation times for samples 6-1 through 6-4 are much larger than the pH test. Table 22 is presented to display time required to reach gel code 3.

Table 22: Gelation times for pH samples

	6-1	6-2	6-3	6-4
	2 wt% glyoxal Dist. water	2 wt% glyoxal Tap water	2 wt% glyoxal Dist. water	2,5 wt% glyoxal Tap water
Gelation time [hrs : min]	315:25	211:47	53:57	50:51

For a graphical representation, the pH values from table 21 are plotted versus time in the figure 27.

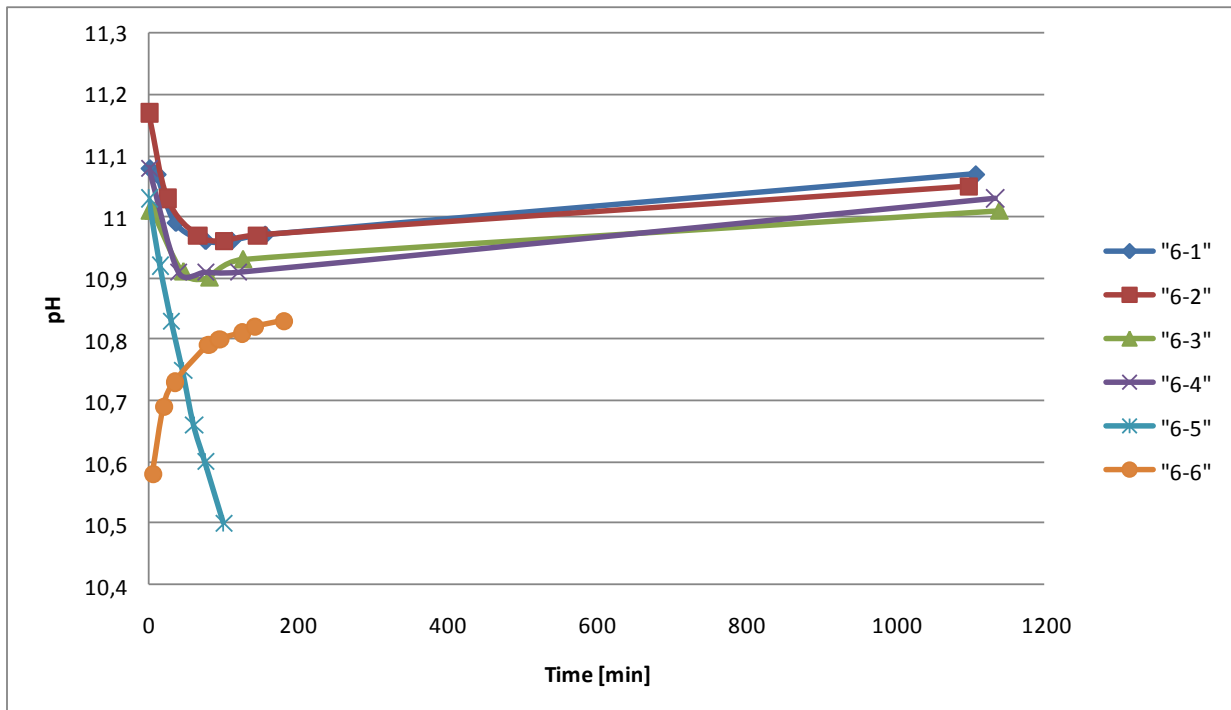


Figure 27: PH versus time

When glyoxal is used as gelation agent, pH values decrease from the initial values. The opposite behavior is observed for gelation agent HCl, where the initial pH is the lowest and it increases with time. For samples with lower glyoxal concentrations (2-2,5 wt%), pH drops to a certain value and then slowly increases until gel is formed. The pH of sample **6-5** drops rapidly until gel is formed due to its high glyoxal concentration (6 wt%).

Samples **6-5** and **6-6** are similar in gelation time, but the pH development is completely opposite. This can be explained by the very nature of the gel system. Glyoxal is reacting with water and produces more  $H^+$  ions whereas  $H^+$  ions from HCl are used by sodium silicate faster than they are created by the acid.

There exists an upper limit for pH where sodium silicate still gels. When the pH is higher than this limit the solution should be stable. In literature, this limit was stated at  $pH= 11$ . Here, we can see that it is not the case, since all test samples created gel at pH values slightly higher

than 11. The pH of 4% sodium silicate solution without crosslinker was measured to be at 11,33, so the limit must lie between 11,1 and 11,33.

A system, where pH value would not drop below this limit would be stable. An example of such system could be a gel with 4 wt% sodium silicate and 1 wt% glyoxal solution. It has a gelation time of around 1,5 months in 60 C, but a significantly longer gelation time in room temperatures. Maybe it would not gel at all. Problem with this particular system is its gel strength. Gel is not rigid and it might be unable to withstand larger pressure gradients in the reservoir. Such system is impossible to create with an addition of acid. As figure 27 shows, the lowest pH value is at time 0, so polymerization of silica starts at the very moment acid is added to the solution. From these observations, it follows that if amount of acid added is sufficient to create gel, such gel would be created at all temperatures, only in different gelation times.

#### 5.2.4 Temperature effect on gelation time

Temperatures vary significantly in different reservoirs. The effect of increased temperature for gelation time is very important. Earlier, it was assumed that Arrhenius's equation should be applicable in these calculations. Gelation times for temperature samples are presented in table 23.

Table 23: Gelation times for temperature samples

Temperature	Gelation time [hrs : min]			
	2 wt% glyoxal		2,5 wt% glyoxal	
	7-1	7-2	7-3	7-4
25	315:25	211:47	53:57	50:51
40	186:50	136:39	40:50	38:42
60	64:25	40:17	20:37	18:51
80	7:27	6:34	4:06	2:45

Table clearly shows that gelation times are significantly reduced for increased temperatures. Arrhenius equation can be satisfied by correlating the gelation time with the inverse absolute temperature.

The gelation times are plotted versus the inverse absolute temperature in figure 28.

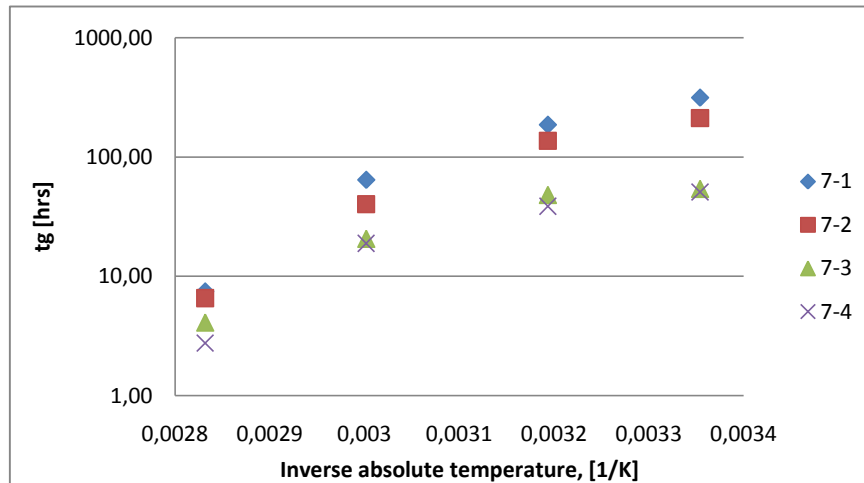


Figure 28: Gelation time versus the inverse absolute temperature

Figure 28 shows that samples **7-1** and **7-2** are in straight line at temperatures above 25°C. Samples with slightly higher glyoxal concentrations have a little worse correlation for temperatures below 60°C. Temperature dependence is rather more complicated than first anticipated and cannot be generalized by one simple equation. However, for data matching Arrhenius's equation will be used as base.

### 5.2.5 Silicate concentration effect on gelation time

For field applications, the required properties of a gel for water shut-off can be achieved by varying silicate concentration. Gelation time is reduced by increasing concentration of silicate in the solution. In addition, gels with higher silicate concentrations seem to have higher strength. This will be investigated later in the research. Table 24 presents gelation times for samples with different silicate concentrations.

Table 24: Gelation times for silicate samples

Silicate wt%	Gelation time [hrs : min]					
	60°C			25°C		
	3,5 wt% glyoxal	4,5 wt% glyoxal	6 wt% glyoxal	3,5 wt% glyoxal	4,5 wt% glyoxal	6 wt% glyoxal
1	1:38	1:10	1:03	52:33	32:39	27:35
2	1:06	1:22	0:48	4:11	16:32	12:41
3	0:50	0:41	0:37	4:18	3:45	3:15
4	1:10	0:21	0:16	4:40	2:57	1:41
5	1:15	0:20	0:18	4:07	2:49	1:55
6	1:08	0:17	0:20	3:28	2:00	1:21

Gelation time data for 60°C is plotted in figure 29.

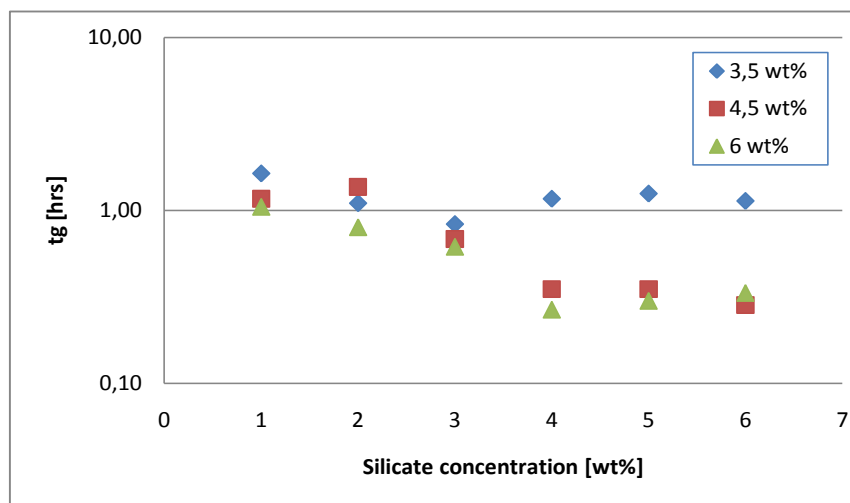


Figure 29: Gelation time versus silicate concentration, 60°C

Figure 29 shows a general trend that the gelation time is reduced with increasing silicate concentration. However, some data points are not following this trend. This is especially visible for samples with 3,5 wt% glyoxal. Gelation times for 4,5 and 6 wt% glyoxal samples with silicate concentrations higher than 4 are so low, that the process can be described as instant gelation.

Gelation time data for 25°C is plotted in figure 30.

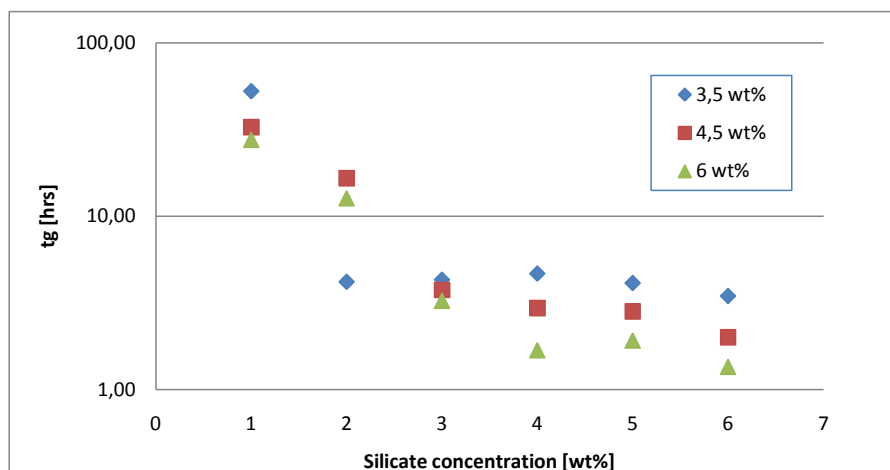


Figure 30: Gelation time versus silicate concentration, 25°C

At a lower temperature, the same trend is observed. Again, the trend is not so clear for higher silicate concentrations. It is interesting to observe that gelation times for 3,5 wt% glyoxal samples are nearly constant for all silicate concentrations, but increases dramatically for 1 wt% silicate.

It is worth mentioning, that gels formed with 1 wt% silicate are clear even after reaching gel code 3. Gels gain more color and turn yellow/brown for higher silicate and glyoxal concentrations.

All samples, except the ones with 1 wt% silicate, had created hard, ringing gels. In fact, gel structure formed by 1 wt% samples was so weak, that it could easily be broken down by a rather weak shaking of the sampling glass. Further research of gel strength follows in the next chapter.

After all experiments were carried out and gelation times for various conditions, the constants in the general formula (see equation 9) for gelation time are computed. Computation was carried out by matching measured data to the derived equation. Least square method in Maple was used to find the constants which give lowest deviation from the measured values.

Several attempts with a selection of specific data points were made to achieve the best correlation. Table 25 presents the constants used in the following equation.

$$t_g = \zeta \times e^{A[\text{Si}]} \times e^{B[\text{GI}]} \times e^{C\sqrt{[\text{Ca}^{2+}] + D\sqrt{[\text{NaCl}]}} \times e^{-E_a/RT} \quad (9)$$

Table 25: Constants derived for the general equation

Selection of samples	$\zeta$ [hrs]	A	B	C	D	$E_a$ [kJ]
All samples	$2,12 \times 10^{-4}$	-0,243	-1,1	-0,025	-3,27	-40,4
Samples with 4 wt% silicate concentration only	$6,45 \times 10^{-5}$	—	-1,406	-0,4106	-3,56	-40,6
All, but the samples used in silicate concentration test and 6 wt% glyoxal samples.	$2,46 \times 10^{-4}$	-0,262	-1,127	-0,025	-3,27	-40,3
Samples tested at temperatures higher than 25°C	$2,26 \times 10^{-8}$	-0,0391	-1,190	-0,020	-3,11	-64,5

Table 25 shows how the constants change when different selection of samples is used. As expected, correlations are quite complex and several equations for specific situations should be used. Sodium silicate and glyoxal concentrations have high ranges and one equation for both ranges will not be very accurate. For more accurate results, an equation developed for selected region should be applied. It is also convenient to calculate gelation time as a function of fewer variables when others can be kept constant. Equation 9 can be used for a rough estimation of gelation time, but one must be aware that it can deviate quite a lot from the actual time. In order to improve the quality of the equation, more samples could be tested, or the equation could be modified.



### 5.3 Gel strength

Results from gel strength tests are presented on this chapter.

A general trend was observed for all samples. At the start of every pressure test, the tube is completely filled with gel and water is pumped at the inlet of the tube to increase pressure. Later, as the pressure builds up to a value where the gel is not strong enough to withstand the applied pressure. Failure of the gel can either be described as water breakthrough from the tube, or extrusion of the gel itself. Water may create a fracture through the gel, or make a path along the tube wall. After the pressure is increased to the value at which gel fails, the pressure drops. When the pressure has dropped to the lower value, it increases again until next step of gel failure occurs, as the water is pumped at a constant rate. The number of such pressure buildups is a function of gel strength. Hard and more rigid gels allow much higher increase in pressure before any kind of failure. The volume of extruded gel, however, is much larger at higher pressures. Additionally, pressure does not drop to the same value in all experiments. It has been noticed that for a certain buildup value, there is an approximate lower value to which pressure will drop after the maximum pressure is reached. These values are presented in table 26.

*Table 26: Pressure drop values*

<b>Build-up [bar]</b>	<b>Drop [bar]</b>
0 - 0,2	0,05- 0,1
0,2 - 1	0,1 - 0,25
1 - 3	0,5 - 0,7
3 - 8	0

Gel strength is reported as a series of pressure build- up values. Light blue colored cells, in some tables, indicate that some gel was left in the tube at the end of pressure extrusion test. A typical time step between pressure buildups is usually around 30 seconds or slightly more. If pressure did not increase for several minutes, it was concluded that water has made a fracture to flow freely and the gel is not able to re-structure itself to block water flow. In some cases, even after a water breakthrough and a period of water flow, the gel would still be able to

block the flow and the experiment could be resumed. If such “recovery” of the gel was not observed, the experiment was abandoned and marked with light blue cells in tables where results are displayed. Time shown in all tables refers to the time of the gel prior to the test. This time is much longer than the gelation time.

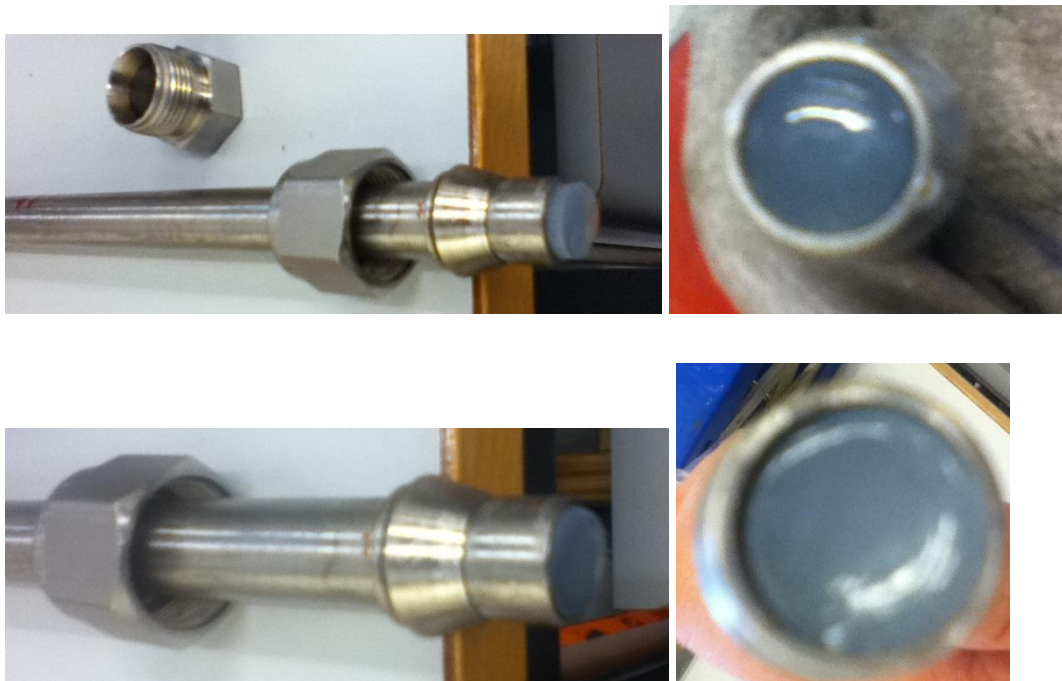
### 5.3.1 Sodium silicate crosslinked with HCl

One point of worry for silicate/HCl systems is the gel’s tendency to have the same gel strength for different HCl concentration. High concentrations of HCl were used in this test and gels created at three different temperatures were tested. Table 27 presents pressure at each buildup step for all tests.

Table 27: Pressure extrusion results for silicate/HCl systems

Temperature [°C]	25				60				80			
HCl wt%	9,5		10,5		9,5		10,5		9,5		10,5	
Time [hrs]	48		24		22		22		20		20	
Rate [ml/min]	1,5		1,5		1,5		1,5		1,5		1,5	
Buildup step	ΔP [bar]											
1	0,41	0,65	0,32	0,23	0,64	0,93	1,08	1,15	0,43	0,21	0,51	0,31
2	0,77	1,20	0,77	0,68	1,54	1,91	2,51	4,80	0,31	0,26	0,45	0,58
3	1,90	2,10	1,06	1,22	1,44	1,75	5,59	6,85	0,23	0,33	0,49	0,59
4	4,29	3,29	2,38	2,00	1,66	3,59		6,77	0,32	0,30	0,55	0,64
5	3,98	3,84	3,45	2,80	3,00	3,35		7,10	0,30	0,36	0,61	0,77
6	4,23	4,11	4,02	3,65	2,78	4,28			0,50	0,44	0,67	0,72
7		4,21	1,22	5,04					0,46	0,51	0,60	0,71
8									0,58	0,48	0,71	0,81
9									0,61	0,63	0,72	0,38
10									0,43	0,67	0,62	
11									0,48	0,70	0,32	
12									0,47	0,58		
13									0,43	0,54		
14									0,32			
15									0,22			
Max ΔP	4,29	4,21	4,02	5,04	3,00	4,28	5,59	7,10	0,61	0,70	0,72	0,81

Results from table 27 imply that there is no significant correlation between gel strength and HCl concentration. Temperature, however, plays a much bigger role here.  $\Delta P$  values for 80°C samples are much lower than the ones for lower temperature samples. This may be caused by early syneresis or shrinkage of the total gel volume in the tube as it cools down. Some shrinkage has been observed when test tube is cooled down to room temperature. An example is shown in figure 31. In the upper panels of the figure 31, the initial state of gel is shown. Pictures are taken right after the test tube is taken out from the oven, and both caps are removed. The tube is then left in room temperature to cool down. Lower panels show the testing tube when temperature is reduced from 60°C to 25°C. Shrinkage is clearly visible and may be a cause for water flow between tube wall and gel. More elastic gels, however, seem to be able to block water flow without an early breakthrough. This negative shrinkage effect is most visible for hard gels at the highest temperatures.



*Figure 31: Gel shrinkage when cooled down*

A series of new 10,5 wt% HCl samples was made, but a polymer solution with different polymer concentrations were used instead of distilled water. With addition of Xanthan polymer, a more elastic gel was attempted to create. Presence of polymer had little, if any, effect on gelation time. Table 28 presents measured pressure build- up data from the test.

Table 28: Pressure extrusion results for silicate/HCl systems with Xanthan

Temperature [°C]	60					
Polymer ppm	500		750		1000	
Time [hrs]	16		16		16	
Rate [ml/min]	1,5		1,5		1,5	
Buildup step	ΔP [bar]					
1	0,22	0,73	0,31	0,05	0,18	0,08
2	0,67	0,35	0,13	0,16	0,13	0,10
3	0,58	0,31	0,09	0,18	0,01	0,15
4	0,49	0,22	0,09	0,18	0,04	0,17
5	0,89	0,22	0,14	0,23	0,15	0,24
6	0,77	0,23	0,20	0,10	0,19	0,22
7	0,45		0,34	0,15	0,17	0,46
8	0,43		0,34	0,20	0,28	0,45
9	0,46		0,29	0,21	0,34	0,43
10	0,74		0,35	0,23	0,29	0,38
11	0,58		0,42	0,26	0,29	0,28
12	0,59		0,41	0,28	0,32	0,30
13			0,30		0,30	0,47
14			0,37		0,22	0,38
15			0,36			0,26
16			0,39			
17			0,35			
18			0,28			
19			0,35			
20			0,48			
Max ΔP	0,89	0,73	0,48	0,28	0,34	0,47

By comparing the pressure buildup values from columns 4 and 5 in table 27 with table 28, it is clear, that the presence of polymer has a negative effect on gel strength in this case. Gel strength is strongly reduced. A cause for this reduction might be the structure of polymer

molecules in water and inability of sodium silicate to properly capture these molecules and create a strong network of particles. Further experiments including polymer were abandoned except for one sample with glyoxal.

### 5.3.2 Sodium silicate crosslinked with glyoxal

It was stated in literature that concentration of glyoxal has a big effect on gel strength. First, a gel consisting of 4 wt% sodium silicate concentration with different glyoxal concentrations was tested. Results from pressure extrusion tests are presented in table 29.

Table 29: Pressure extrusion results for glyoxal samples

Temperature [°C]	60							
Glyoxal wt%	2,5		3		4		6	
Time [hrs]	48		48		23		20	
Rate [ml/min]	1,5		1,5		1,5		1,5	
Buildup step	$\Delta P$ [bar]							
1	0,25	0,32	0,44	0,41	0,78	0,92	1,20	1,42
2	0,37	0,26	0,30	0,30	2,10	1,22	2,86	2,83
3	0,42	0,30	0,27	0,35	1,17	1,35	3,81	4,08
4	0,82	0,22	0,53	0,44	1,45	1,24	3,94	6,36
5	0,64	0,38	0,68	0,61	2,07	1,53	5,49	5,72
6	0,75	0,39		0,41	2,47	1,96	5,25	6,26
7	0,39	0,55		0,61	2,00	2,04	5,70	9,47
8	0,33	0,50		0,50	2,51	2,36	4,14	10,40
9	0,20	0,55		0,70	3,17	2,85		
10		0,71		0,44	2,69	2,79		
11		0,58		0,46				
Max $\Delta P$	0,82	0,71	0,68	0,70	3,17	2,85	5,70	10,40

Table 29 shows that gels are getting more rigid for systems with higher glyoxal concentrations.  $\Delta P$  value of 10,4 bar for 6 wt% glyoxal is the highest pressure drop applied during the testing of gel strength for all systems.

Samples with lower concentrations were tested at higher temperature. At 25°C, gelation time for samples with 2 and 2,5 wt% glyoxal was 315 and 53 hours respectively. It was interesting to test, whether gels with such long gelation times at room temperatures, would have sufficient strength at reservoir temperatures. Results obtained from this test are shown in table 30.

Table 30: Pressure extrusion results for low glyoxal concentrations

Temperature [°C]	80			
Glyoxal wt%	2		2,5	
Time [hrs]	14		13	
Rate [ml/min]	1,5		1,5	
Buildup step	ΔP [bar]			
1	0,13	0,13	0,46	0,30
2	0,16	0,15	0,52	0,43
3	0,17	0,10	0,22	0,42
4	0,22	0,10	0,43	0,29
5	0,19	0,18	0,10	0,29
6	0,18	0,14	0,10	0,29
7	0,18	0,15		0,35
8	0,13	0,13		0,39
9	0,23	0,12		0,40
10	0,22	0,16		0,30
11	0,22	0,12		0,41
12	0,31	0,10		0,37
13	0,22	0,15		0,37
14	0,28	0,24		0,39
15	0,21			0,46
16	0,20			
Max ΔP	0,31	0,24	0,52	0,46

As table 30 indicates, gels are much weaker compared to gels with high glyoxal concentrations. However, gel strength is comparable to HCl gels, formed at the same temperature, as shown in columns 6 and 7 in table 27. From these results, it follows that a gel with similar strength can be created by using glyoxal instead of high concentrations HCl. Gelation times, on the other hand, are very different, especially at lower temperatures.

Salinity effect is evaluated by comparing the results of pressure extrusion tests for same glyoxal and sodium silicate concentration with varying NaCl concentration. The results are presented in table 31.

Table 31: Pressure extrusion results for salinity test

Temperature [°C]	60					
NaCl wt%	—		1		0,25	
Glyoxal wt%	2,5		2,5		2,5	
Time [hrs]	48		20		20	
Rate [ml/min]	1,5		1,5		1,5	
Build- up step	$\Delta P$ [bar]					
1	0,25	0,32	0,14	0,13	0,09	0,29
2	0,37	0,26	0,16	0,11	0,22	0,21
3	0,42	0,30	0,18	0,13	0,16	0,18
4	0,82	0,22	0,20	0,16	0,17	0,23
5	0,64	0,38	0,17	0,20	0,28	0,31
6	0,75	0,39	0,15	0,18	0,27	0,25
7	0,39	0,55	0,15	0,18	0,31	0,23
8	0,33	0,50	0,17	0,18	0,22	0,24
9	0,20	0,55	0,22	0,22	0,22	0,26
10		0,71	0,25	0,23	0,25	0,26
11		0,58	0,23	0,26	0,17	0,28
12			0,18	0,29	0,19	0,13
13			0,22	0,20	0,27	
14			0,23	0,25	0,24	
15			0,22	0,19		
16			0,16	0,23		
17			0,18	0,23		
18			0,20	0,27		
19			0,16	0,20		
20				0,25		
Max $\Delta P$	0,82	0,71	0,25	0,29	0,31	0,31

Evidently, salinity, in addition of reducing gelation time, has a negative impact on gel strength.

Finally, sodium silicate concentration effect on gel strength was tested. Visually, gels with lower silicate concentrations (but higher than 1 wt%) were not identified as weaker and had a nice ringing sound. The measured pressure data is presented in table 32.

Table 32: Pressure extrusion test results for silicate concentration test

Temperature [°C]	60									
Silicate wt%	1	2	3	5	6					
Glyoxal wt%	3,5	3,5	3,5	3,5	3,5					
Time [hrs]	30	30	30	30	30					
Rate [ml/min]	1,5	1,5	1,5	1,5	1,5					
Buildup step	$\Delta P$									
1	0,15	0,24	0,14	0,26	0,22	0,33	0,47	0,38	0,23	0,15
2	0,15	0,11	0,30	0,38	0,64	0,50	0,40	0,35	0,23	0,26
3	0,14	0,15	0,70	0,37	0,76	0,55	0,35	0,35	0,32	0,28
4	0,45	0,60	0,58	0,40	0,12	0,65	0,66	0,42	0,32	0,29
5	0,43	0,56	0,39	0,55	0,74	0,69	0,19	0,43	0,38	0,33
6	0,83	0,52	0,63	0,61	0,73	0,83	0,30	0,47	0,39	0,15
7	0,72	0,42	0,58	0,80	0,80	0,88	0,42	0,46	0,54	0,24
8	1,07	0,38	0,85	0,83	0,90	1,03	0,42	0,38	0,14	0,37
9		0,35	1,34	0,60	0,73	1,24	0,33	0,26	0,27	0,38
10		0,20	1,04	0,38	1,12	0,41	0,36	0,25		0,33
11		0,34		0,32	1,44	0,62	0,27			0,35
12				0,30	1,42	0,62	0,28			0,20
13					1,05					0,16
14										0,33
Max $\Delta P$	1,07	0,60	1,34	0,83	1,44	1,24	0,66	0,47	0,54	0,38

Table 32 shows that higher silicate concentrations do not necessarily contribute to stronger gels. This could probably be explained by an assumption that for each silicate concentration, there should exist an optimal glyoxal concentration to create optimal gel strength. This assumption should be investigated further with more samples and more accurate tests.



Results from all these tests show that this method to test gel strength is quite inaccurate and should not be used as a base for gel design in a field trial. Core tests should give much more accurate results, however, core tests are more expensive and time-consuming. The purpose of gel bulk tests was to compare two different gel systems. Relative comparison results are quite precise because procedures were consistent for every test.

## 6 Conclusions and Recommendations

In this thesis, a laboratory evaluation of sodium silicate for water management purposes was carried out. The results obtained from the various experimental tests are summarized in this section and the conclusions, based on the results obtained in this work, are presented.

1. For the glyoxal as a gelling agent in bulk gelation tests the following conclusions can be stated:
  - Gelation time is reduced with increasing glyoxal concentration.
  - NaCl and CaCl<sub>2</sub> have catalyst effect on gelation time.
  - Ca<sup>2+</sup> ion concentrations higher than 1000 ppm cause precipitation of calcium silicate.
  - Temperature effects on gelation time can be described by Arrhenius equation for temperatures higher than 25°C.
  - Increased sodium silicate concentration tends to reduce gelation time, but no clear correlation is developed.
  - Equations for each scenario were developed and a general equation for gelation time as a function of all variables was derived by measured data matching to the previously derived formula.
  - Solution pH was tested for both crosslinkers. For silicate/HCl systems, the start value was the lowest value and pH increased with time. Opposite behavior was observed for silicate/glyoxal systems. PH had its maximum value right after glyoxal was mixed in the silicate solution. The pH then dropped to the minimum value and started increasing slowly until gel was formed.

2. Gel strength of sodium silicate gel systems with both crosslinkers (HCl and glyoxal) was tested. Gel strength was presented as pressure values at which the tested gel integrity to sustain applied pressure is compromised either as the injected water breakthrough or the gel being partially or totally displaced from the testing tube. These values are relative and should only be used when gels are tested under similar conditions. These conclusions were reached from gel strength measurements:
  - HCl concentration does not have a significant effect on gel strength.
  - Gel's strength is reduced as the temperature increases.
  - Addition of Xanthan polymer results in a reduction of the gel strength.
  - Gel strength can be increased by higher glyoxal concentrations.
  - An increase of silicate concentration only slightly increases gel strength when glyoxal is used as a crosslinker.
3. Gelation times found in literature for sodium silicate crosslinked with HCl were verified. The AcoustoSizer from Colloidal Dynamics was unable to measure particle size distribution for sodium silicate gels obtained with HCl. Measured particle diameter values deviated significantly from the expected ones.
4. Results from the tests, conducted in this work imply that gel properties vary significantly dependent under which conditions the gel is formed. For example, gelation times vary significantly with temperature and the gel strength can be adjusted by adjusting glyoxal concentration. Gel formed by crosslinking sodium silicate with glyoxal can be applied for zonal isolation, where gels need to have longer gelation for deep placement and high gel strength close to the borehole to withstand high pressure gradients. Additionally, near wellbore problems (casing repair, etc) can be solved by a formation of very hard, cement-like substances created with high silicate and glyoxal concentrations.

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## Appendix A

This appendix presents true compositions of all samples.

Sample number	1-1	1-2	1-3	1-4	1-5	1-6
Sample size [g]	50	50	50	50	50	50
HCl wt%	<b>8,5</b>	<b>9</b>	<b>9,5</b>	<b>10</b>	<b>10,5</b>	<b>11</b>
K40 [g]	7,1855	7,1789	7,2081	7,207	7,178	7,166
H <sub>2</sub> O [g]	38,562	38,327	38,001	37,8739	37,5104	37,358
2M HCl [g]	4,269	4,5127	4,16	5,0353	5,284	5,4949
Total	50,0165	50,0186	49,3691	50,1162	49,9724	50,0189
True K40 wt%	4,00	4,00	4,06	4,00	4,00	3,99
True HCl wt%	8,54	9,02	8,43	10,05	10,57	10,99

Sample number	2-1	2-2	2-3	2-4	2-5
Sample size [g]	50	50	50	50	50
Glyoxal 4% wt%	<b>2</b>	<b>2,5</b>	<b>3,5</b>	<b>4,5</b>	<b>6</b>
Glyoxal 40% wt%	20	25	35	45	60
K40 [g]	7,1903	7,1785	7,1863	7,1874	7,1841
H <sub>2</sub> O [g]	41,8320	30,4034	25,5362	20,3481	12,8727
Glyoxal 4% [g]	0,0000	12,5489	17,5286	22,5190	30,0326
Glyoxal 40% [g]	1,0069	0,0000	0,0000	0,0000	0,0000
Total	50,0292	50,1308	50,2511	50,0545	50,0894
True K40 wt%	4,0012	3,9866	3,9813	3,9976	3,9930
True Glyoxal 40% wt%	2,0126	2,5032	3,4882	4,4989	5,9958
True Glyoxal wt%	0,8050	1,0013	1,3953	1,7996	2,3983

Sample	3-1	3-2	3-3	3-4
Sample size [g]	50	50	50	50
Glyoxal 4% wt%	25	25	25	25
NaCl [wt%]	<b>1</b>	<b>0,5</b>	<b>0,2</b>	<b>0</b>
K40 [g]	7,1800	7,1816	7,1900	7,1785
H <sub>2</sub> O [g]	30,3083	30,3195	30,3192	30,4034
Glyoxal 4 % [g]	12,5030	12,5069	12,4959	12,5489
NaCl [g]	0,5027	0,2621	0,1002	0,0000
Total	50,4940	50,2701	50,1053	50,1308
True K40 wt%	3,9587	3,9772	3,9950	3,9866
True Glyoxal 40% wt%	2,4761	2,4879	2,4939	2,5032
True Glyoxal wt%	0,9905	0,9952	0,9976	1,0013
True NaCl wt%	0,9956	0,5214	0,2000	0,0000

Sample	4-1	4-2	4-3	4-4	4-5
Water type	Distilled	Distilled	Distilled	Tap	Distilled
Sample size [g]	50	50	50	50	50
Glyoxal 4% wt%	25	25	25	25	25
<b>CaCl<sub>2</sub> [ppm]</b>	<b>1000</b>	<b>500</b>	<b>200</b>	<b>12</b>	<b>0</b>
K40 [g]	7,1942	7,2225	7,1976	7,1923	7,1785
H <sub>2</sub> O [g]	30,4150	30,3213	30,3287	30,3160	30,4034
Glyoxal 4 % [g]	12,5098	12,5039	12,5062	12,5060	12,5489
CaCl <sub>2</sub> [g]	0,0490	0,2520	0,0110	0,0000	0,0000
Total	50,1190	50,0477	50,0325	50,0143	50,1308
True K40 wt%	3,9962	4,0177	4,0050	4,0035	3,9866
True Glyoxal 40% wt%	2,4960	2,4984	2,4996	2,5005	2,5032
True Glyoxal wt%	0,9984	0,9994	0,9998	1,0002	1,0013
True CaCl <sub>2</sub> [ppm]	977,6731	5035,1964	219,8571	0,0000	0,0000

Sample	5-1	5-2	5-3
Sample size [g]	50	50	50
4% Glyoxal [wt%]	25	25	25
<b>NaCl [wt%]</b>	<b>1</b>	<b>0,5</b>	<b>0,2</b>
<b>CaCl<sub>2</sub> [ppm]</b>	<b>0</b>	<b>200</b>	<b>500</b>
K40 [g]	7,1766	7,1875	7,1992
H <sub>2</sub> O [g]	30,1953	30,0979	29,862
Glyoxal 4 % [g]	12,5067	12,512	12,4974
NaCl [g]	0,1023	0,2606	0,5014
CaCl <sub>2</sub> [g]	0,0257	0,0115	0
Total	50,0066	50,0695	50,06
True K40 wt%	4,00	4,00	4,00
True Glyoxal 40% wt%	2,50	2,50	2,50
True Glyoxal wt %	1,00	1,00	1,00
NaCl [wt%]	0,20	0,52	1,00
CaCl <sub>2</sub> [ppm]	513,93	229,68	0,00

Sample	6-1	6-2	6-3	6-4	6-5	6-6
Water type	Distilled	tap	Distilled	Tap	Distilled	Distilled
Sample size [g]	50	50	50	50	50	50
40% Glyoxal wt%	2	2	2,5	2,5	6	0
HCl wt%	0	0	0	0	0	11
K40 [g]	7,1903	7,1909	7,1785	7,1923	7,1841	7,1660
H <sub>2</sub> O [g]	41,8320	41,8700	30,4034	30,3160	12,8727	37,3580
Glyoxal 4% [g]	0,0000		12,5489	12,5060	30,0326	0,0000
Glyoxal 40% [g]	1,0069	1,0067	0,0000	0,0000	0,0000	0,0000
HCL [g]	0,0000	0,0000	0,0000	0,0000	0,0000	5,4949
Total	50,0292	50,0676	50,1308	50,0143	50,0894	50,0189
True K40 wt%	4,0012	3,9985	3,9866	4,0035	3,9930	3,9885
True Glyoxal 40% wt%	2,0126	2,0107	2,5032	2,5005	5,9958	0,0000
True Glyoxal wt%	0,8050	0,8043	1,0013	1,0002	2,3983	0,0000
True HCl wt%	0,0000	0,0000	0,0000	0,0000	0,0000	10,9856

Sample	7-1	7-2	7-3	7-4
Water type	Distilled	Tap	Distilled	Tap
Sample size [g]	50	50	50	50
4% Glyoxal wt%	2	2	2,5	2,5
K40 [g]	7,1856	7,1770	7,1785	7,1923
H <sub>2</sub> O [g]	41,8076	41,8754	30,4034	30,3160
Glyoxal 4% [g]	0,0000	0,0000	12,5489	12,5060
Glyoxal 40% [g]	1,0064	1,0159	0,0000	
Total	49,9996	50,0683	50,1308	50,0143
True K40 wt%	4,0010	3,9907	3,9866	4,0035
True Glyoxal 40% wt%	2,0128	2,0290	2,5032	2,5005
True Glyoxal wt%	0,8051	0,8116	1,0013	1,0002

Sample	1% silicate	2% silicate	3% silicate	4% silicate	5% silicate	6% silicate
Sample size [g]	50	50	50	50	50	50
Glyoxal 40% [g]	3,5	3,5	3,5	3,5	3,5	3,5
K40 [g]	1,8061	3,5972	5,3854	7,1863	8,9965	10,7644
H <sub>2</sub> O [g]	46,4560	44,6902	42,8656	25,5362	39,3303	37,4845
Glyoxal 40% [g]	1,7520	1,7544	1,7536		1,7589	1,7553
Glyoxal 4% [g]	0,0000	0,0000	0,0000	17,5286	0,0000	0,0000
Total	50,0141	50,0418	50,0046	50,2511	50,0857	50,0042
True K40 wt%	1,0054	2,0012	2,9983	3,9813	5,0007	5,9931
True Glyoxal 40% wt%	3,5030	3,5059	3,5069	3,4882	3,5118	3,5103
True Glyoxal wt%	1,4012	1,4023	1,4028	1,3953	1,4047	1,4041

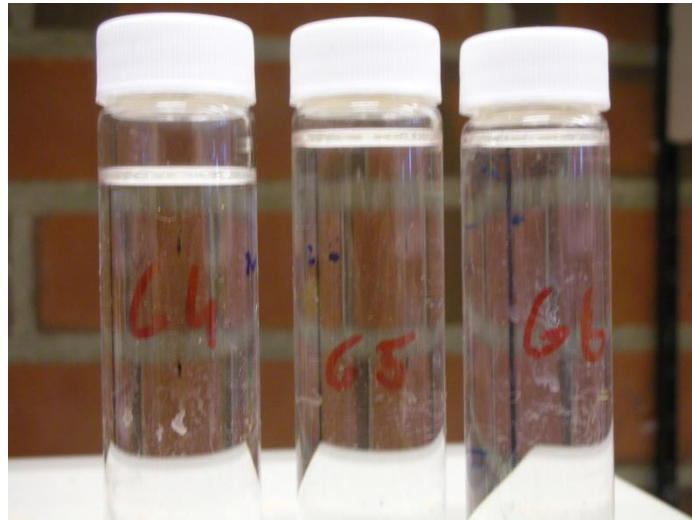
Sample	1% silicate	2% silicate	3% silicate	4% silicate	5% silicate	6% silicate
Sample size [g]	50	50	50	50	50	50
Glyoxal 40% [g]	4,5	4,5	4,5	4,5	4,5	4,5
K40 [g]	1,8110	3,5966	5,3741	7,1904	9,0010	10,7614
H <sub>2</sub> O [g]	45,9450	44,1694	42,2978	40,4987	38,9971	36,9741
Glyoxal 40% [g]	2,2541	2,2499	2,2509	2,2519	2,2549	2,2471
Total	50,0101	50,0159	49,9228	49,9410	50,2530	49,9826
True K40 wt%	1,0082	2,0020	2,9969	4,0083	4,9865	5,9940
True Glyoxal 40% wt%	4,5073	4,4984	4,5088	4,5091	4,4871	4,4958
True Glyoxal wt%	1,8029	1,7993	1,8035	1,8036	1,7948	1,7983

Sample	1% silicate	2% silicate	3% silicate	4% silicate	5% silicate	6% silicate
Sample size [g]	50	50	50	50	50	50
Glyoxal 40% [g]	6	6	6	6	6	6
K40 [g]	1,8071	3,6001	5,3671	7,1877	8,9871	10,9110
H <sub>2</sub> O [g]	45,1980	43,4410	41,5870	39,9900	37,8541	36,1748
Glyoxal 40% [g]	3,0100	2,9971	3,0250	3,0190	3,0010	2,9874
Total	50,0151	50,0382	49,9791	50,1967	49,8422	50,0732
True K40 wt%	1,0059	2,0030	2,9897	3,9864	5,0199	6,0664
True Glyoxal 40% wt%	6,0182	5,9896	6,0525	6,0143	6,0210	5,9661
True Glyoxal wt%	2,4073	2,3958	2,4210	2,4057	2,4084	2,3864

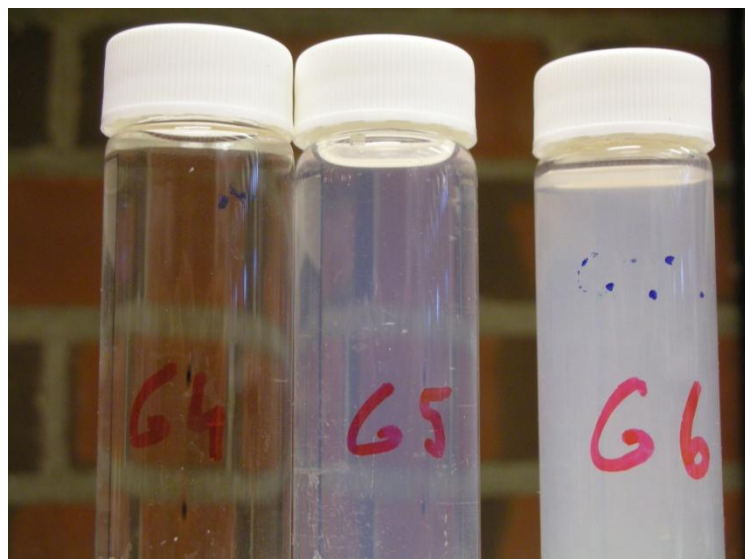
## Appendix B

This appendix presents some pictures to show differences between different gel types and stages of the gelation process.

The initial state of all samples is shown, here sodium silicate is crosslinked with glyoxal and picture is taken right after crosslinking.



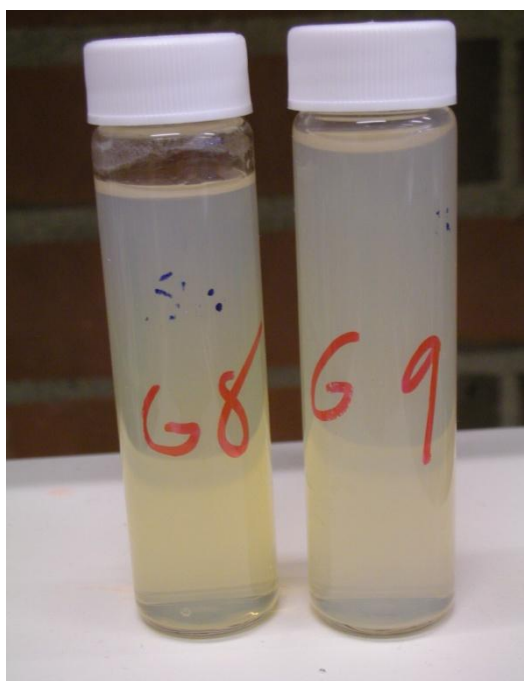
The same samples are shown below. From left, sample is still at gel code 0, in the middle, gel code 1 is reached and gel code 3 is shown on the right side.



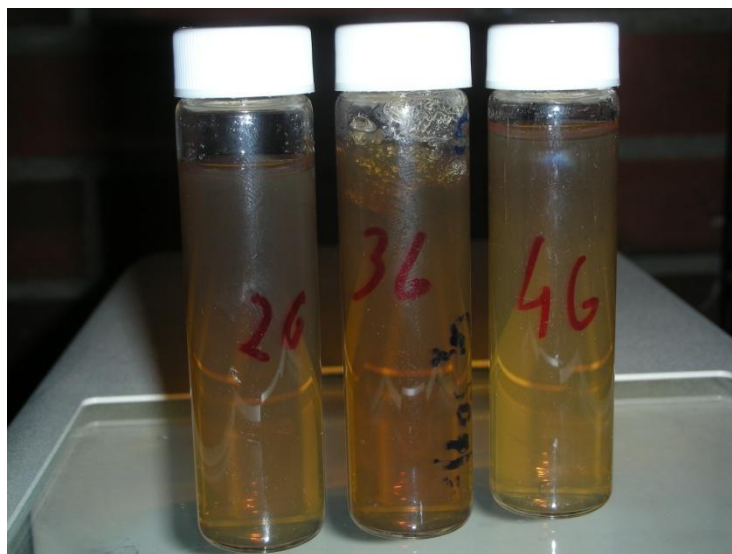
Here, samples with 2,5 wt% glyoxal are shown after forming a relatively clear gel at 80°C. Distilled water is replaced by tap water in sample on the right side of the picture.



The same concentrations as the above, but gelling took place at 25°C. The samples are much cloudier. Distilled water is replaced by tap water in sample on the right side of the picture.



Samples with high glyoxal concentrations are shown below. Concentrations are (from left to right) 4, 6 and 8 wt% glyoxal. The gelation of these samples is almost immediate (<20 min)



Below, samples with 3,5 wt% glyoxal are shown. Silicate concentration is increased (from left to right) 1-6 wt%





A better illustration of how clear the samples with low silicate concentrations are is presented below. Sample on the left side of the picture has 2 wt% silicate, the other one- 1 wt%.m Glyoxal concentration is 3,5 wt% in both samples.





Finally, two identical samples are compared. The one on the left side has gelled at room temperature, the other one at 60°C. They both were mixed at the same time. The picture is taken 20 hrs after mixing. Gelation time at 25°C is ~3hrs, at 60°C ~20 minutes.

