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Lars-Espen Kolberg. Stavanger 2013

1 ABSTRACT

This thesis on "Geopolymerization of Norite" has been a study of plugging materials for plug and abandonment operations, and the different requirements for plug and abandonment operations based on Norsok D-010 standard.

The materials studied was, ordinary Portland cement and geopolymers such as; blast furnace slag, metakaolin and Norite. The shrinkage of Portland cement and geopolymers was also looked into as a basis for the shrinkage tests.

A series of shrinkage tests were performed on the Norite cement recipe developed by Mahmoud Khalifeh, and the Portland class G cement provided by Halliburton. The results was a 3-3,5 % shrinkage in the class G cement and 0 % shrinkage in the Norite cement exposed to a pressure of 5000 psi and 87°C, the curing time was between 24 to 72 hours.

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2 INTRODUCTION

According to the plug and abandonment forum presentation by Martin Straume [1], over 2000 wells needs to be plugged and abandoned from now until 2040 on the north continental shelf. The purpose of a plug and abandonment operation is to seal the reservoirs from the surface in order to avoid leakage of hydrocarbon or other substances from the well onto the surroundings. There are several requirements for plugging and abandoning a well, where the Norsok D-010 standard are used as a guideline on the north continental shelf.

The most common plug material used today is ordinary Portland cement, but this cement is known to lose its integrity over time at high temperature and pressure. This is why the petroleum industry is looking for new types of cements to replace the ordinary Portland cement in order to mitigate with the poor properties of the Portland cement at high pressure and temperature. An alternative to Portland cement is geopolymers, which have been studied for some time in the construction business for its ability to withstand heat, and because of the low setting time. Geopolymers are complex materials and much work have gone into making the perfect recipe that are able to meet the requirements of the industry with low shrinkage and cracking mechanisms as well as low CO₂ emissions [4].

3 PLUG AND ABANDONMENT

3.1 Plug and abandonment regulations

The purpose of plug and abandonment operations is to leave a well that either have been drilled dry, stopped producing or is to be side tracked in order to increase the production from other parts of the reservoir/reservoirs. Above all, the plug and abandonment of wells on the north continental shelf should be designed with the minimum requirements of the NORSOK D-010 regulations issued by the Petroleum safety authorities in Norway [2][3]. However, other standards can be used as guidelines if the operation is proven to be equal or better than the solution recommended by the NORSOK D-010 Standard [3].

The regulations describes in detail the requirements of each of the different components in the plug and abandonment design such as the; required properties of the plugging material, length of plug and placement of the plug for different abandonment situations. The cemented plugs will work as well barrier in the well together with casing supported by cement in annulus or by itself in an open-hole section. A well barrier is defined by NORSOK D-010 as an *“envelope of one or several dependent barrier elements preventing fluids or gasses from flowing unintentionally from the formation, into another formation or to surface”* [3].

There are mainly two different types of plug and abandonment operations, they are described in the NORSOK D-010 as permanent abandonment and temporary abandonment. The permanent abandonment operation is referred to as the process of leaving a well for eternity, while the temporary abandonment operation is the process of leaving a well in a condition so that it is safe to re-enter the well at a later occasion [3].

The placement of barrier plugs in the wells is dependent on the well configuration, and a well with several side-tracks and reservoirs will require more plugs for zonal isolation compared to a well with one bore and one reservoir. The different well configurations are described with illustrations in the NORSOK D-010 [3]. An example of plug placement can be seen in fig. (3.1).

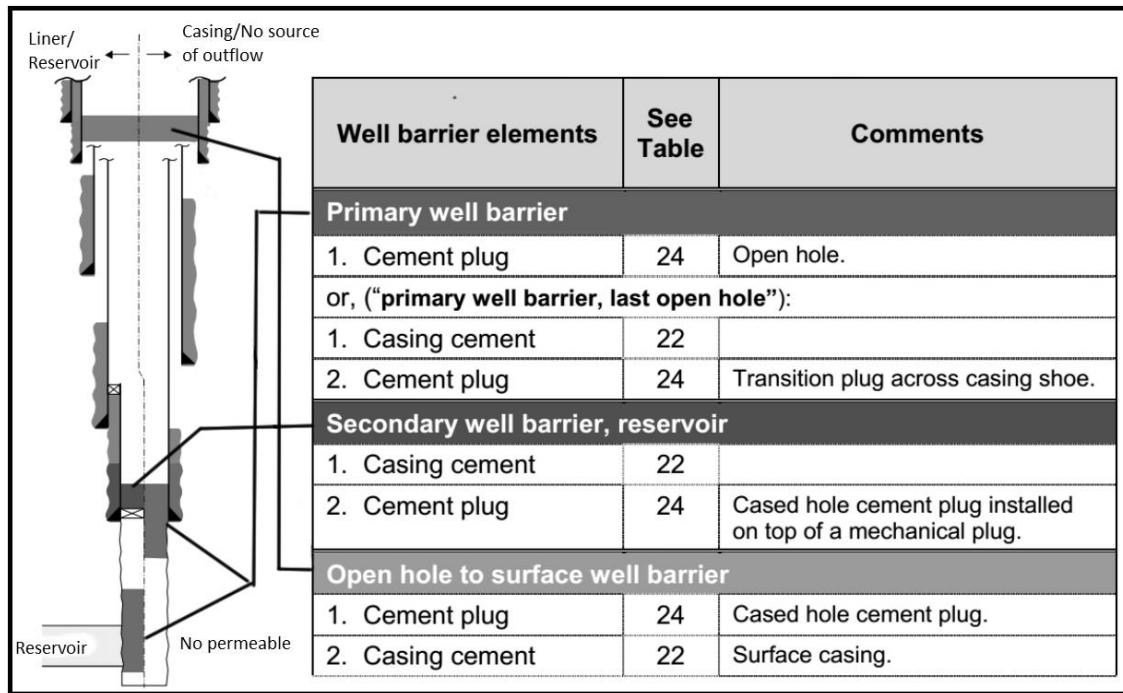


Fig. 3.1 is an example of how the layout of a plug and abandonment configuration for an open-hole completion. An abandonment configuration with liner and reservoir in the open-hole section is shown to the left of the dotted line, while an abandonment configuration for a dry open-hole section with no permeable formation is shown to the right of the dotted line.

The plug and abandonment configuration steps for an open-hole completion layout as shown to the left of the dotted line in fig. (3.1) are; cementation of a cement plug over the reservoir with a 50 m column of cement over the reservoir as the primary barrier, then installation of a mechanical plug combined with a 50 m cement column just above the liner shoe as a second barrier. The secondary barrier has to be set in a place where the casing is supported by cement in the annulus. Finally a surface plug is set in the surface cemented casing before all subsea equipment and piping above 5 meters below the surface is removed. The equipment has to be removed in order to avoid complications when fishers are trawling the area where abandoned wells are located. The right side of the figure illustrates the layout of a plug and abandonment configuration for a dry well with no permeable reservoir. The well barriers can consist of several barrier elements, such as the secondary barrier which consist of cement plug and casing cement. The barrier elements cannot by themselves prevent flow from one side to another side [3].

The requirement for plug length is 100m MD for a class G cement in a cased hole with a mechanical plug as foundation and that the plug shall extend min 50 m above any source of inflow and 50 m above the open-hole section if there is a transition between open-hole and cased hole in the area of plug placement [3]. If a mechanical plug is set in the cased-hole and tagged before the cement plug is installed, then there is no need for tagging of the cement plug.

Plug placement in cased-hole section has to be placed in a section of the cased-hole where the casing is supported by cement in the annuls, if the desired depth does not fulfill this requirement, an operation where the section of the well is modified by either a milling operation, where cement is squeezed behind the casing, or another operation where the well integrity of the plug placement zone is established. The plug shall be placed such that it covers the whole cross section of the well as seen in fig. (3.2).

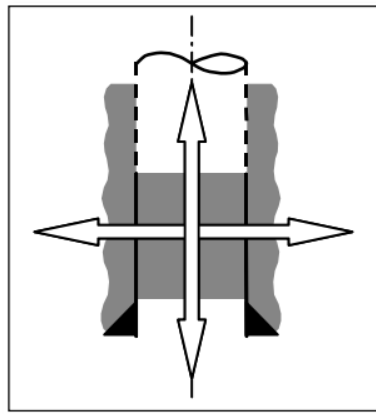


Fig. 3.2 the picture illustrates how the plug shall extend over the whole cross section of the well and how cement is covering the whole outside of the casing.

Pressure testing and tagging the depth of the plug is required after plug placement in order to verify if plug have been placed successfully in a cased hole. While tagging depth of the plug is sufficient for an open-hole plug. The method used for testing the seal of the plug is by decreasing the pressure above the plug in order to increase the differentially pressure over the plug [3].

The plugging material is the cement pumped into location in order to seal of the reservoir from the environment. The NORSOK D-010 requirements for plug material used in plug and abandonment operations are:

- a) *Impermeable*
- b) *Long term Integrity*
- c) *Non-shrinking*
- d) *Ductile - (non-brittle) – able to withstand mechanical loads/impacts.*
- e) *Resistance to different chemicals/substances (H_2S , CO_2 and hydrocarbons).*
- f) *Wetting, to ensure bonding to steel.*

The Norsok D-010 requires a 100 m cement plug, or a 50m column of cement above any source of inflow because this will most likely create a plug that is impermeable. However, there are no scientific calculations tied to these numbers. Long term integrity is considered to be the cements ability to withstand the physical and chemical conditions of the surrounding for a long time, the optimum cement would form itself to the surrounding as changes appears in form of earthquakes, corrosive chemical migration etc.

3.2 Plugging materials

The Norsok D-010 standard does not recommend any specific material for use in plug and abandonment operations, but the material should fulfil the Norsok D-010 requirements mentioned earlier in best possible way. A long term integrity test should be performed in order to verify the materials properties at well conditions, in order to identify possible future failures [3].

The most common material used for cement in plug and abandonment operations today are Ordinary Portland cement used together with different additives in order to establish the right properties required of the Norsok D-010 standard [3].

The development of new types of cements are looking to reduce emissions during production and improve the properties of the cement with the focus on shrinkage, corrosive resistance and the ability of shaping itself in relationship with changes happening in the well after the plug and abandonment operations.

One of the materials looked at in the search for new cementing materials are Geopolymer cements. This type of material can be used both in regular Portland cement as an additive or by itself as a mixture of different Geopolymer components.

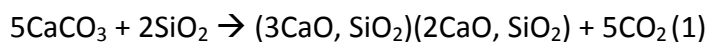
4 GEOPOLYMERS

Geopolymers are essentially long chains of aluminium silicate monomers bonded together by the process of dissolution and poly-condensation. The aluminium silicate monomers can be obtained by mixing aluminium and silicate rich materials such as fly-ash and metakaolin with an alkaline solution like for instance Sodium hydroxide (NaOH) or Potassium hydroxide (KOH), note that there are also other combinations of materials that can obtain this type of reaction [4].

The geopolymer can be used as an alternative/additive to the ordinary Portland cement in concrete and mortars for different purposes such as buildings and roads etc. geopolymer materials can also be used as thermal insulation, radioactive and toxic waste containment, low energy ceramics, and fire resistive materials [5].

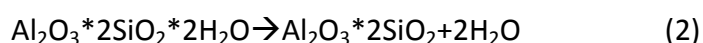
The advantages by using geopolymer cement instead of ordinary Portland cement is lower CO₂ emissions, faster setting time and less energy required in the production due to a lower calcination temperature [5].

It is in the calcination of Portland cement where the vast amount of CO₂ is produced. The Portland cement is made by heating ground limestone and clay at 1400-1500 °C. The calcination process is performed in order to get a more reactive material and thus, better binding properties. The chemical reaction of the calcination process is shown in eq. (1) [7].



The chemical reaction releases 0.55 tonnes of chemical CO₂, and additional CO₂ is released in the heating process due to the high energy required in the calcination process [7].

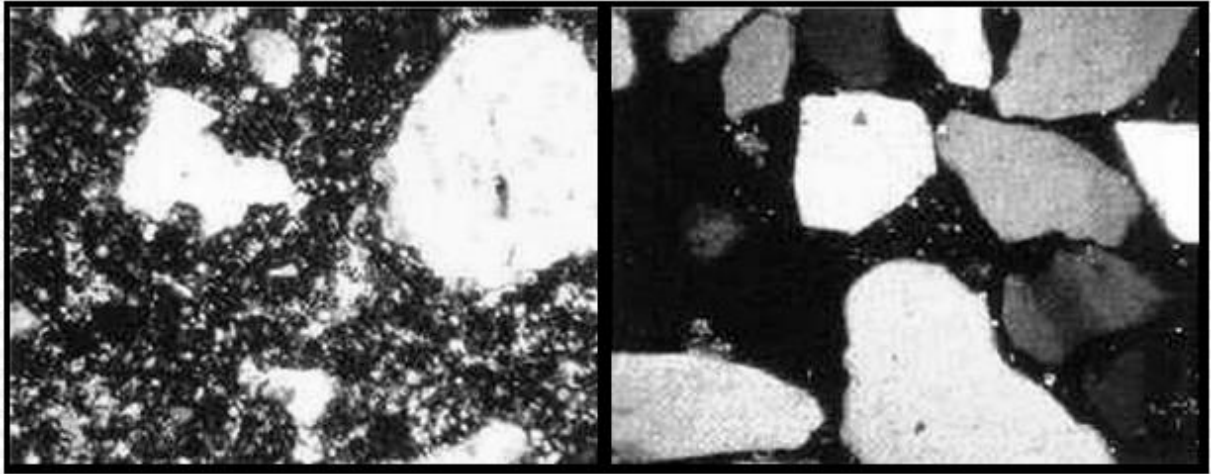
The calcination of geopolymer such as metakaolin is performed at 750°C. Metakaolin is a calcination product of the clay mineral kaolinite and the by product in the calcination process is vaporized water. The chemical reaction is shown in eq. (2) [8].



The setting time of ordinary Portland cement can be several days, but for geopolymer cement it could be lowered to hours, an example of this is the Pyrament cement product introduced by the Lone Star industries in 1988.

Pyrament is geopolymer based cement developed in collaboration with the Geopolymer Institute, and its advantages over Portland cement were that it was able to build high strength much faster. The ability to build strength in a very short time 4-6 hours made this cement attractive to the military, which used the Pyrament cement to build temporary airports during the gulf war. This type of cement was also found to be ideal for repairing roads and other constructions in a shorter amount of time compared to ordinary Portland cement [5].

Pic.(4.1) show the difference in the microstructure of plain concrete made with ordinary Portland cement (left picture) and concrete made with Pyrament cement (right picture). It can easily be seen that the Pyrament bound concrete has a much more homogenous binding compound in between the grains in the concrete than the Portland based concrete. This more coarse grained substance in the Portland based concrete is believed to be more subjective to cracks and weaknesses than the geopolymer based concrete [6].



Picture 4.1 ordinary Portland cement on the left and geopolymer concrete on the right picture [6].

Some common materials used when producing geopolymer cements are rock-forming minerals, such as metakaolin, ground granulated blast furnace slag, fly-ash, water-glass (Na_2SiO_3), quartz (SiO_2) etc.

The compressive strength of geopolymer is according to Matthew Rowles et al. [9] dependent on the Na:Al and Si:Al ratio in the cement paste. The compressive strength is increased as both Na:Al and Si:Al is increased, from this it is evident that the NaOH concentration is of great significance, this would probably also be the case for KOH, but the molar ratio of K:Al was not discussed in paper. The Na:Al concentrations was tested with molar ratios between 0.5-2, while the molar ratios of Si:Al tested was in the range between 1-3 [9].

In the research for finding better geopolymer compositions there have been differentiated between to models of alkali activated cement, namely the activation of slag (Si+Ca) and the activation of metakaolin (Si+Al), these two models are discussed in a paper published by Chao Li et al [10] on the comparison between alkali-activated slag (Si+ Ca) and metakaolin (Si+Al) cements.

They found that the metakaolin will have a high water demand because of its high surface are. This will make the make the geopolymer very sensitive to water loss if large quantities of metakaolin are used. Thus, increasing the risk of shrinkage and cracking. Even though the

properties of the metakaolin (Si+Al) was mapped in terms of chemical reactions , the reactions related to slag based materials were not mapped out in the same way due to the lack of knowledge about the reactions. On the other hand, they found that the calcium had a positive effect on the strength of the geopolymer, but an increased PH on the activating solution would result in a lower solubility [10].

5 SHRINKAGE

5.1 Shrinkage of ordinary Portland cement

Shrinkage is one of the challenges with the use of ordinary Portland cement as plugging material. The shrinkage occurs during the hydration process (chemical reactions between the cement and the water) and the drying process (evaporation of water from the surface of the cement).

If shrinkage of plugging material occurs in an oil well, the hydrocarbons can migrate from the reservoir to the environment due to the lack of bonding between plugging material and formation or because of cracks in the plug caused by shrinkage mechanisms.

When the cement reacts with water the chemical reaction between them is exothermic. The exothermic reaction is the start of the hydration process that causes the volume of the cement paste to decrease.

The hydration process can be divided into 5 stages and the first stage of the process is when cement is mixed with water, leading to a high exothermic reaction that last for a couple of minutes. The second stage of the process starts when the exothermic reaction stabilizes and is constant for a couple of hours. This stage of the hydration process is called the induction period, and it is usually during this stage that the cement is applied to its determined location. After some hours a new exothermic reaction starts within the cement, where the cement starts to set and build strength from the surface and inwards. After some time (usually before 24h) the maximum reaction is reached and the hydration processes within the cement will start to decrease, see fig. (5.1) [17] [11]. Fig (5.2) Illustrate the degree of hydration vs. time, and the development of compressive strength vs. time for Portland cement [19]. From this figure we can see as stated before that the hydration rate is highest at the beginning of the reaction and will slow down as time passes [19].

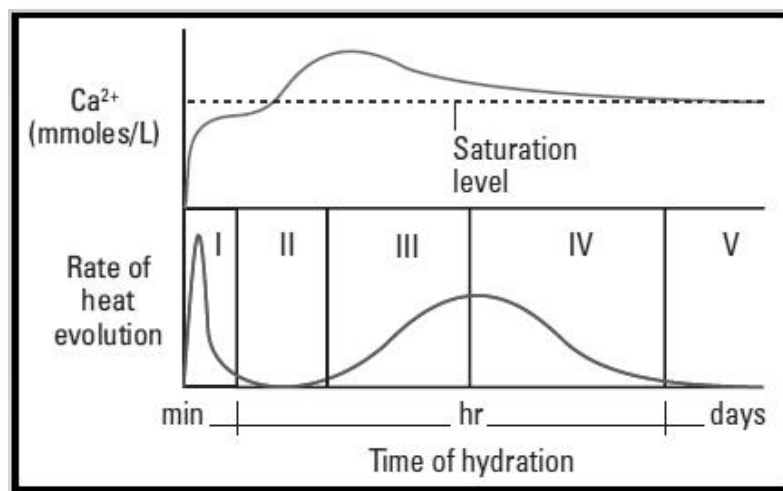


Fig. 5.1 illustrates the hydration behaviour for Portland cement [11].

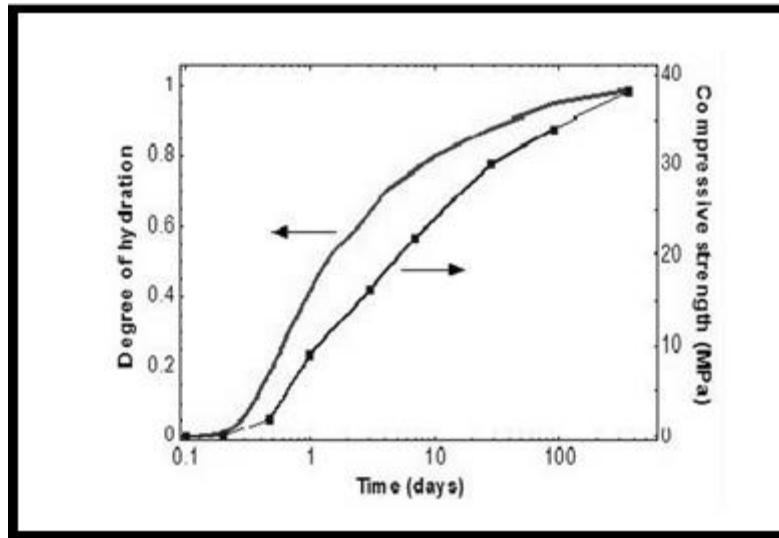


Fig. 5.2 illustrates how Portland cement builds strength over time (the curve to the right) and degree of hydration versus time (the curve to the left) [19].

The shrinkage of cement is also dependent on the air humidity during the drying process, since water evaporated from the cement will cause tension in the internal pores, resulting in collapsing pores and volume decrease of the placed cement. Drying shrinkage is not likely to occur in oil and gas wells that are filled with water because of the physical conditions required for water to evaporate, which are a surface between water and air [18] [11].

In order to develop knowledge about how and why shrinkage occur Gilbert et al. [15] differentiated the shrinkage into four different types: Plastic shrinkage, chemical shrinkage, thermal shrinkage and drying shrinkage.

Plastic Shrinkage is the state where the cement is still in a plastic state (where no strength development has been introduced) and occurs because water evaporates at the surface of the concrete. This type of shrinkage depend on relative humidity, temperature, cement slurry content and water to cement ratio. When cement content is high and water content is low the plastic shrinkage is higher compared to a concrete with high water content and low cement content. Chemical shrinkage is the shrinkage caused by chemical reactions in the cement slurry, this is shrinkage related to the hydration process in ordinary Portland cement where volume of cement and water initially is larger than when it is mixed and fully reacted. Thermal shrinkage is the shrinkage caused by an exothermic process that is initiated when cement reacts with activating solution. Drying shrinkage occurs during the drying process of the cement, and is caused by water loss due to evaporation as mentioned earlier [15].

5.1.1 Shrinkage reducing measurements for Ordinary Portland cement

Shrinkage in ordinary Portland cement is found to be related to the amount of water used in the cement slurry. One way of reducing the shrinkage of ordinary Portland cement is to reduce the water content in the slurry to get an optimum mixture with lower shrinkage

potential. When water is removed from the cement, water reducing agents can be used to keep the viscosity low in order to keep the cement workable. The water agents/reducers can keep the cement workable with 5-10% less water, but as water agents are added the strength and setting time of the cement are also affected [4] [14].

Other ways of reducing the shrinkage of cement is by the use of shrinkage reducing admixtures or latex modified cement systems. The shrinkage reducing admixtures usually consists of ethylene glycol derivatives and serves to reduce the drying shrinkage/loss of water. The mechanism behind this method is to inhibit the collapse of pores inside the cement caused by capillary pressure. The Shrinkage reducing admixture reduces the capillary pressure by decreasing the surface tension of water and tension on the pore walls in the cement [16]. The latex modified cement system will create a latex film between the hydrated cement particles which will prevent fluid loss, make the cement more durable and give a better bonding between the cement and oil/water wet surfaces. The result of using a latex modified system for reducing shrinkage of Portland cement can be seen in fig. (5.3) [11].

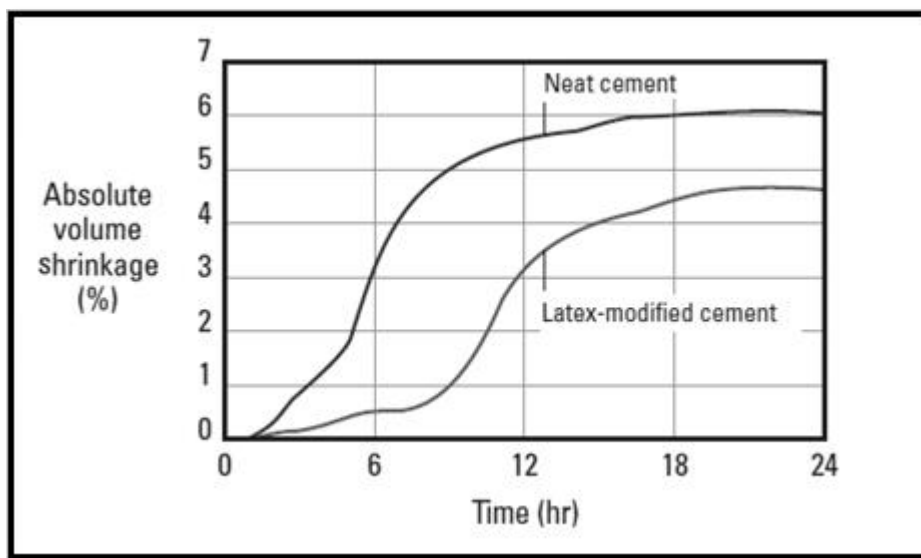


Fig. 5.3 show the shrinkage difference in using latex modified cement system compared to a regular/Neat cement system [11].

5.2 Shrinkage of geopolymer based cement

The physical properties of geopolymer based cements have not been studied as thoroughly as the Portland cement, but some work have been done by Duxon et al. [4] in order to identify the shrinkage of NaOH activated geopolymers at different temperatures and Si:Al ratios. The materials used in this study was metakaolin as geopolymer material and muscovite as an impurity for adjusting the Si:Al ratio. The experiments were also done with

pre-set plugs, where a possible shrinkage during the solidification would not be included in the results. The results from this work can be seen in fig. (5.4) [4].

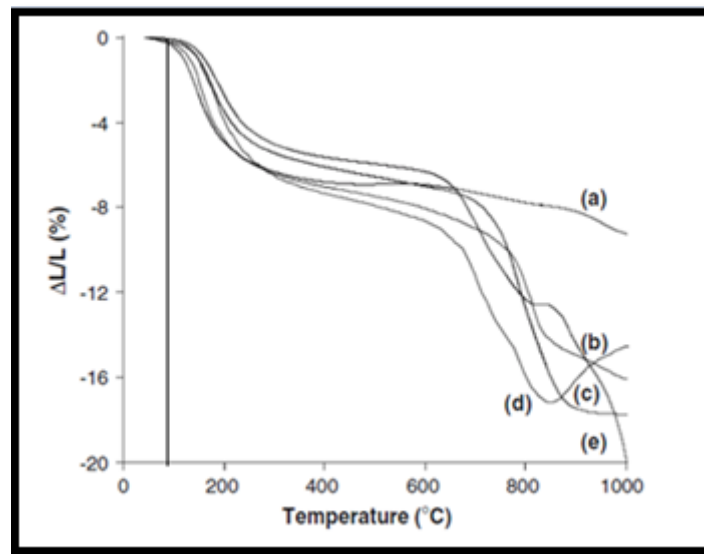


Fig. 5.4 Thermal shrinkage of Na-geopolymer with Si/Al of: (a) 1.15, (b) 1.40, (c) 1.65, (d) 1.90 and (e) 2.15 [4].

The shrinkage of the samples follows the same trend with rapid shrinkage in the temperature interval 100-300°C [12].

Another interesting study was by Carsten Kuenzel et al. [13] on drying shrinkage and cracking in metakaolin-based geopolymers. This extensive study was aimed at finding the best mixture of the different components in a geopolymer system in order to keep the drying shrinkage to a minimum. The components varied/changed was the water content, Si:Al ratio, Al:Na ratio and the influence of using Na or K based activating solution.

The results of this study by Carsten Kuenzel et al [13] was that the tests with higher water content needed more water to be removed in order to initiate shrinkage, but that the shrinkage would occur at the same water concentration of the tests. The water concentration at which the test would start to shrink was defined as the critical min water content. The water evaporated before the critical min water content would be free water, whereas removal of this water would not induce any shrinkage. Water located in the cement when the critical min water content is reached is defined as the structural water content, and it is when this water escapes the cement that shrinkage occurs according to Carsten Kuenzel et al [13].

The study on the effect of changing the Si:Al ratio from 1,15-2,15 showed an increase in structural water content by increasing the Si:Al ratio. The conclusion from these results was

that an increase in Al group density in the gel structure will decrease the amount of structural water [13].

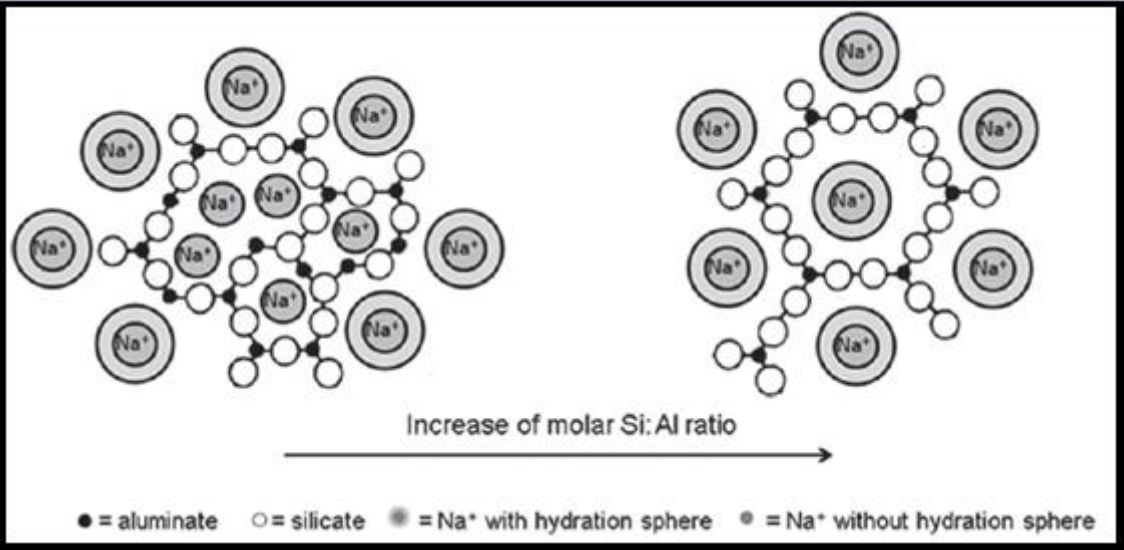


Fig. 5.5 Illustrates the difference in the structure of a low Si:Al concentration vs. a high Si:Al concentration [13].

By changing the Na:Al ratio Carsten Kuenzel et al [13] noticed that an excess amount of Na⁺ ions had a negative effect on the drying shrinkage at ambient temperature. The shrinkage is decreasing linearly with the decreasing Na⁺ ratio as seen in fig. (5.6) taken from Kuenzel et al. [13].

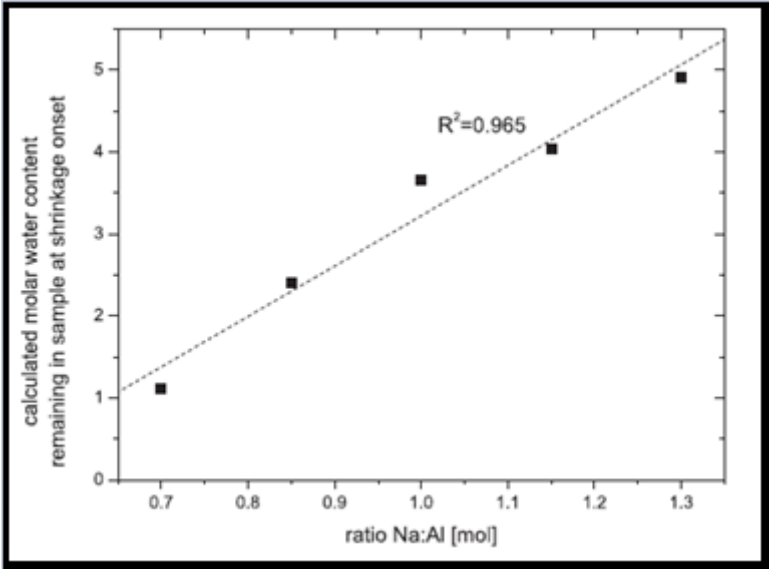


Fig. 5.6 illustrates how the ratio of Na:Al affects the critical min water content [13].

The effect of changing activation solution from NaOH to KOH resulted in lower critical min water content in the tests with KOH activated geopolymers compared to the tests with NaOH activating solution. This is believed to be because of the K⁺ ions lower charge density which will make removal of water molecules around the ions easier [13].

6 MATERIALS

6.1 Ordinary Portland cement

Ordinary Portland cement is a material that originates from limestone, it is the basic binding material commonly used in concrete, mortars etc. Portland cement is produced by heating the limestone and other various homogeneous materials to a calcining temperature of about 1450 °C. The product of this calcination is Portland cement clinker, this material is grinded into Portland cement a fine powder material that consists of approximately two thirds by mass calcium silicates, the remaining materials are aluminium, iron containing clinker phases and other compounds [20].

The Portland cement is used in well operations due to its pump-ability and due to its ability to set in water. There are several types of Portland cement and the American Petroleum Institute has divided these into class A, C, G or H. The cement used in the experiments of this thesis was Class G Dyckerhoff cement. The Dyckerhoff cement is basic well cement used by Halliburton; it is available in moderate sulphate-resistant and high sulphate-resistant grade. There are no additions other than calcium sulphate and water added to the clinker [21] [22].

6.2 Blast furnace slag

Blast furnace slag is a by-product in the production of iron ore to iron. The Iron ore is heated in a blast furnace together with coke and limestone. The melting process combines the limestone with aluminium and silicates from the ore and coke ash to form blast furnace slag as seen in fig. (6.1). The slag can be cooled in different ways to form several types of blast furnace slag; Ground granulated blast furnace slag, Air-cooled blast furnace slag, Pelletized etc.

Blast furnace slag is used as an aggregate in different types of concrete and a common objective with use of blast furnace slag is to increase the flexible and compressional strength of the material. A general chemical composition of blast furnace slag is shown in fig. (6.1) [23].

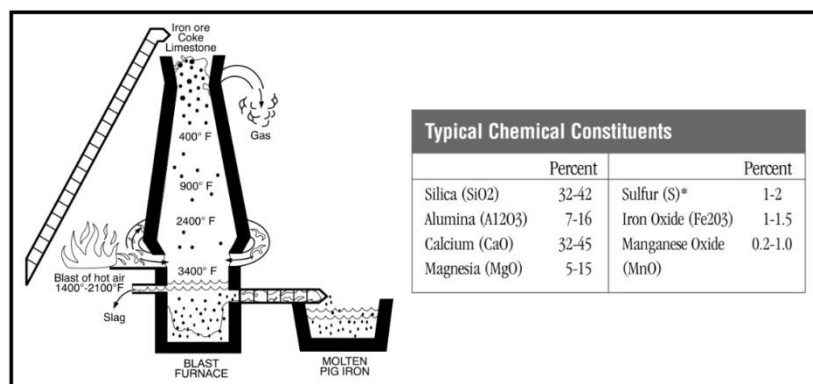
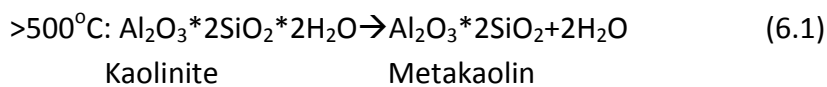


Fig. 6.1 Show the process of producing iron and slag, with the general composition of a blast furnace slag material composition in the table to the right [23].

6.3 Metakaolin

Metakaolin is a product of the clay mineral kaolinite. The main uses of metakaolin today is as a component in Portland cement and concrete to increase; compressive, flexural strength, durability, resistance to chemical attacks, and reduce; permeability, shrinkage. The high silica and alumina content makes the metakaolin interesting as a component in a geopolymer based material [24].

The process of turning kaolinite into metakaolin is called calcination. The calcination is an endothermic process where kaolinite is subjected to a large amount of heat in order to remove the hydroxyl ions and strain the bonding network. The strained bonding network is believed to cause the metakaolin to be much more reactive than the kaolinite. The calcination process is shown by eq. (6.1) [25].



It is the high reactivity that makes metakaolin suited for the use in geopolymer based materials, but this ability also requires a high water demand, thus a high risk of shrinkage and cracking if the geopolymer material is produced with a high percentage of metakaolin. The aluminium and silica composition of metakaolin ranges from 40-45% AL and 50-55% Si [25].

6.4 Norite

Norite is a rock which has similar properties to granite, but it is not as hard-wearing as the granite because of the lack of the quartz mineral. The Norite that was used in the lab work of this thesis was mined at the Titania A/S mine in Flekkefjord of Norway. The chemical composition is listed in Table (6.1) [26].

Components	%
SiO ₂	43
TiO ₂	8.2
Al ₂ O ₃	15.5
Fe ₂ O ₃	12.5
MnO	0.1
MgO	6.8
CaO	6.6
Na ₂ O	3.4
K ₂ O	0.9
P ₂ O ₅	0.3
Cr ₂ O ₃	0.03
SiO ₂	0.1
C	0.01

Table 6.1 shows the chemical composition of Norite [27].

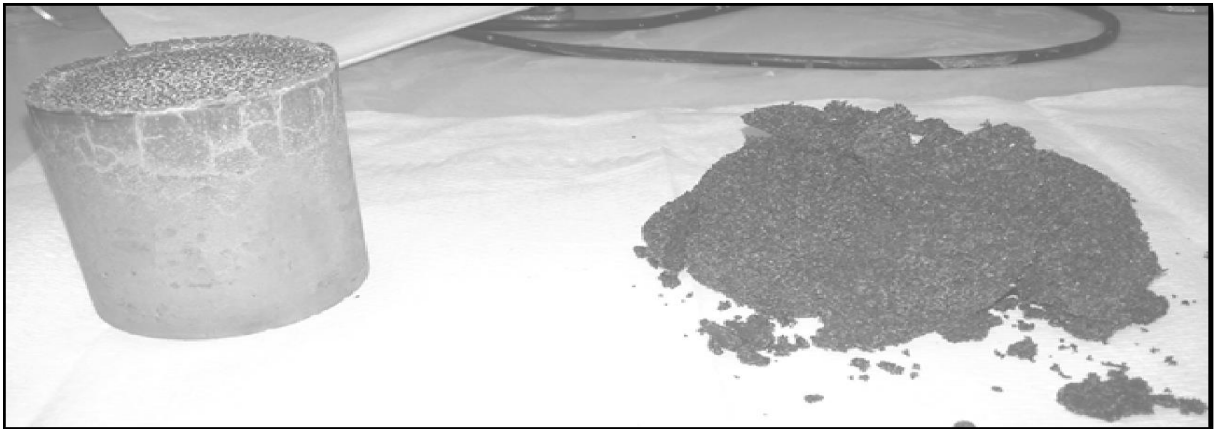
7 EXPERIMENTAL TESTS OF GEOPOLYMER IN LAB

7.1 Experimental background of the tests performed in the thesis

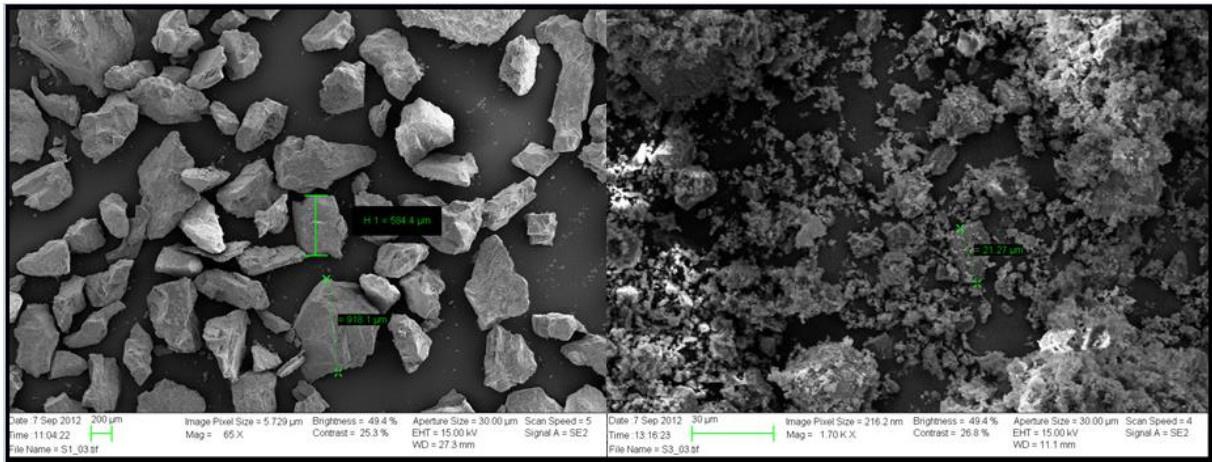
The Norite was discovered by Mahmoud Khalifeh and Helge Hodne as a suitable basis for a cheap and interesting geopolymer material for use in plug and abandonment operations. The study started with a chemical composition analysis of the Norite that revealed some silica and aluminium content which can be used in the development of a geopolymer [30]. The chemical analysis can be seen in table (6.1) [30].

Testing started with the Norite mixed with 8 M NaOH activating solution and the curing was performed in a heating cabinet set to 86°C. The tests were performed with both grinded and non-grinded Norite. The activating solution was 8 M NaOH solution because this solution was observed to give good results based on tests performed on similar materials and because of the cheaper price compared to the KOH. The observation after 4 days of curing was that the grinded material seemed to establish strength while the non-grinded material ended up being loose and unconsolidated as seen in the pic. (7.1). The reason for the different result in the tests is believed to be because the grinded Norite reacts better with the activating solution due to the higher surface area of the grinded material [30].

The particle distribution of the non-grinded Norite is about 500-1000µm, while the grinded Norite has a particle distribution of about 1-20µm. The grinded and non-grinded particle size difference can be seen in pic. (7.2).



Picture 7.1 show the difference between the grinded Norite to the left and a non-grinded Norite to the right, after being exposed to temperature of 86°C for 4 days.



Picture 7.2 Scanning electron microscope pictures with non-grinded Norite at the left and grinded Norite at the right [28].

As a result of the successful testing of Norite cement, studies were performed in order to discover additives for enhancing the physical properties of the Norite cement. The following additives were added to the Norite cement one by one to observe the physical changes of the cement; Blast furnace slag, metakaolin, water glass, $\text{Ca}(\text{OH})_2$, CaCl_2 and SiO_2 . These additives were picked because of their previous results in similar experiments and because they have been thoroughly tested and described in the Geopolymer Chemistry and Applications book by Davidovits [29] and in other papers published on Geopolymer cements [30].

Quantitative tests with different recipes based on the additives mentioned above were performed, the recipes with the best results were further studied by either ultrasonic cement analyser or unconfined compressive strength tests. Aside for good compressive strength, shrinkage was also observed and this was included in the evaluation of which recipes should be further investigated [30].

7.2 Experimental procedures

7.2.1 Sample preparation

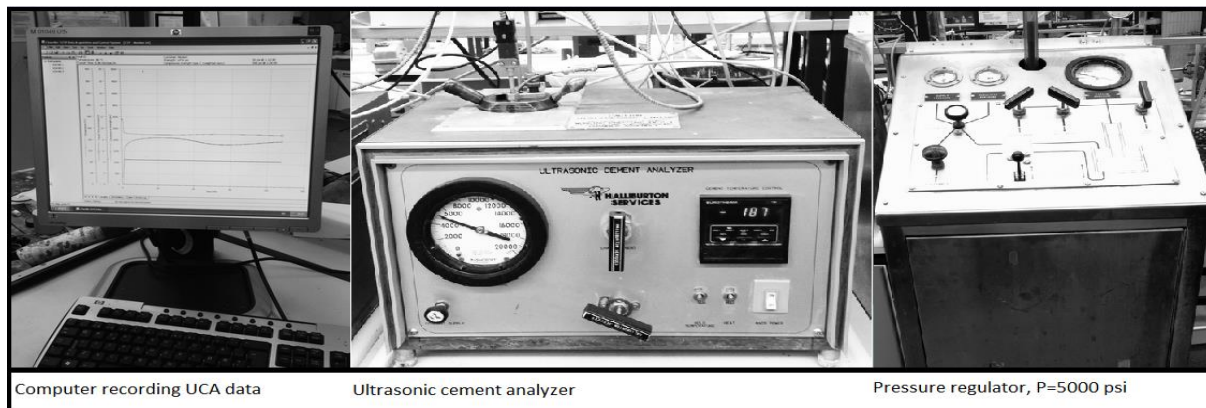
Sodium hydroxide was used as activation solution in the tests, and this was the first step in making the geopolymer material. The sodium hydroxide was mixed the day before in order to reach an equilibrium state before mixing in the other components. The concentration of the sodium hydroxide was between 8-10 Molar. The next step was to add the different solid components, where one component was added at a time and mixed with a cement mixer. The viscosity was adjusted by adding water. The final step in the sample preparation was to pour the slurry into a UCA cell and seal the cell off from the surroundings and simulate downhole conditions. Table (7.1) shows the composition for the cement samples. The measured values can be seen in table (A.1) in the appendix.

Class G cement recipe for UCA and Shrinkage tests		Norite cement recipe for shrinkage tests		Norite cement recipe 1 for UCA test 1		Norite cement recipe 2 for UCA test 2	
Cement [g]	792,0	Grinded Norite [g]	350,0	Grinded Norite [g]	200,0	Grinded Norite [g]	200
Distilled water [g]	792,0	Metakaolin [g]	175,0	Metakaolin [g]	100,0	Metakaolin [g]	100
		Blast furnace slag [g]	175,0	Blast furnace slag [g]	100,0	Blast furnace slag [g]	100
		Quartz [g]	105,0	Quartz [g]	65,0	Quartz [g]	65
		8M NaOH [g]	455,0	8M NaOH [g]	260,0	10M NaOH [g]	260
		Distilled water [g]	35,0	Distilled water [g]	20,0	Distilled water [g]	20

Table 7.1 composition of the cement samples used in the experiments.

7.2.2 Compressive strength measurement

The ultrasonic cement analyser (UCA) system is used to measure the compressive strength versus time for the different slurries at downhole conditions. The velocity of sound through the cement slurry is measured in real time and the velocity of the sound is then converted from measured time to compressive strength by the computer connected to the system. The UCA system was set to simulate a downhole pressure of 5000psi and a temperature of 88°C. The system can use different correlations dependent on what is being measured, one correlation for mud and one other for cement etc. Each test was run for approximately one week and the data collected from the test was the maximum compressive strength and the time before the cement starts to set; time before it reaches 50 psi and 500psi. The test setup is shown below in pic. (7.3).



Picture 7.3 illustrates the setup of the UCA system, where the pressure regulator keeps the pressure constant at 5000psi, and the computer records the data obtained by the UCA.

7.2.3 Shrinkage tests

The objective of this experiment was to compare how ordinary Portland cement and geopolymer based cement would shrink at reservoir conditions, with a pressure of 5000 psi and a temperature of 87°C.

Theory of the shrinkage experiment

The approach to measuring the shrinkage is to weight the mass of a system with the cement before and after exposure to a pressure of 5000 psi and temperature of 87° C for 24/72 hours. To ensure equal conditions before and after exposure, the system is pressurized at the end of the test before the weight measurement. The cell is pressurized by injecting water from the pressure pump and the increased volume of water injected is found by weighing the cylinder system before and after test. The mass of water can easily be converted into volume of shrinkage by using eq. (7.1) and assuming mass balance.

$$\text{Volume shrinkage} = \text{mass of injected water/density of water} \quad (7.1)$$

Volume of cement had to be calculated in order to calculate volume percent shrinkage of the test. The calculations required measurements of the different components in the cell due to varying volumes of each test performed. The different measurements that had to be performed were:

1. The weight of the empty system
2. The weight of the system with water at 5000 psi
3. The weight of the system with water and 3 condoms at 5000 psi
4. The weight of the system with water, 3 condoms and a pvc pipe at 5000psi
5. The weight of the 3 condoms
6. The weight of the pvc pipe
7. The weight of the system at the start of the test P=5000psi
8. The weight of the system at the end of the test P=5000 psi
9. The weight of cement
10. The density of distilled water at T=22°C

From these measurements one can calculate the internal volume the system, the total weight of the content in the system, the volume of water in the system, the volume of injected water and the volume of cement in the system. When we know the volume of cement in the system we can calculate the volume percent shrinkage as seen in eq. (7.2).

$$\text{Volume percent shrinkage} = \text{Volume of injected water} / \text{volume of cement in system} \quad (7.2)$$

Shrinkage Test procedure

The samples where mixed with a Hobart model N-50, as seen on fig. (7.1) [33]. The procedure of mixing is to pour in the materials first, and then start the mixer at mixer rate level 1 before adding the water/alkali solution into the mixture of class G cement/geopolymer cement. At mixer rate level 1 the Hobart is mixing the cement at 136 rotations per minute.

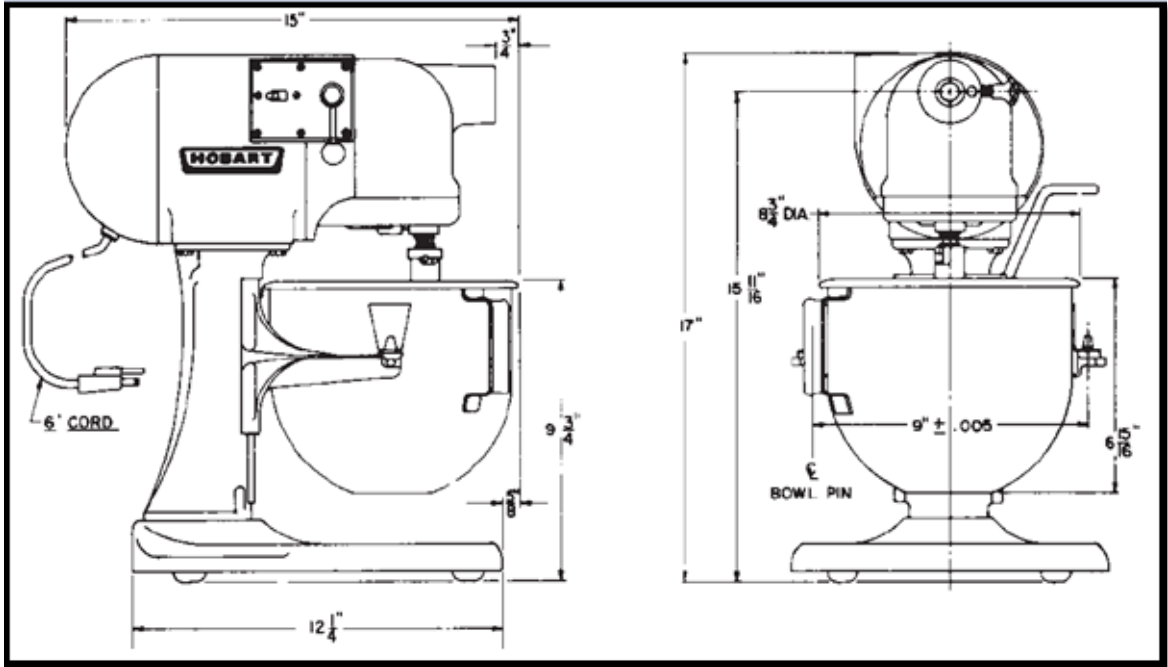


Fig. 7.1 Hobart N-50, the commercial kitchen mixer used for mixing the cement [33].

The cement is mixed for 20 minutes in order to get a uniform and air free cement, this is important in order to avoid air pockets in the system while testing for shrinkage. Next step of the procedure is to pour the cement into 3 condoms and weigh them before inserting them into a cylinder. Three condoms filled with cement will almost fill the entire volume of the cylinder; the remaining void is filled with distilled water. Fig. (7.2) illustrates the procedure of mixing, filling the condoms with cement and inserting them into the cylinder.

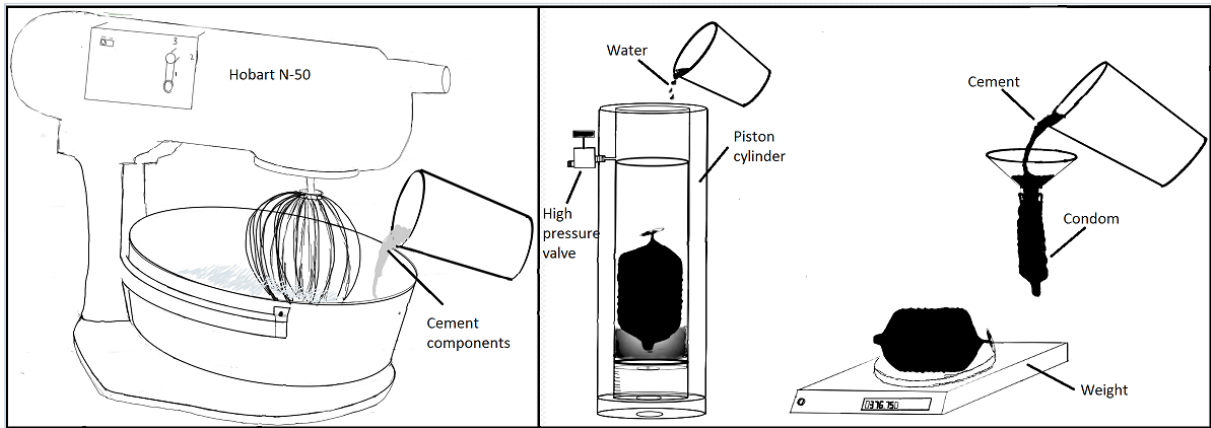


Fig. 7.2 illustrates the procedure of mixing, filling the condoms with cement and inserting them into the cylinder.

When the cylinder is closed a pressure pump is connected to the cylinder valve in order to pressurize the cylinder to 5000 psi. Then the weight of the cylinder is measured for the first time; this weight will be noted as the starting weight. When the weight has been measured the cylinder will be connected to a relief valve which will bleed of excess pressure from expansion of water and cement. When the cylinder is assembled and weighed, it will be placed inside a heat cabinet that is preheated to 87°C and left there for 24/72 hours. The procedure is illustrated in fig. (7.3).

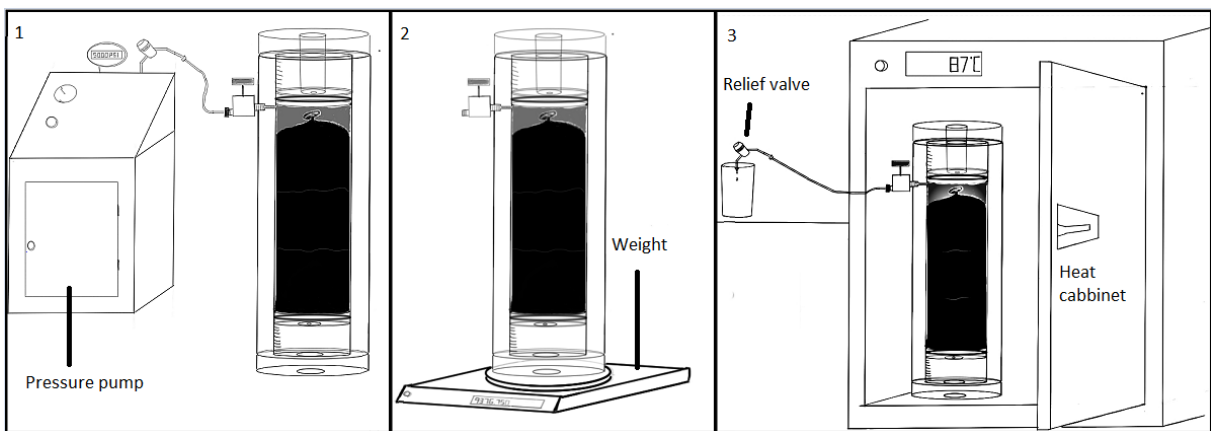


Fig. 7.3 these images show the process of; 1: Increasing the pressure of the cylinder to P=5000 psi, 2: Measuring the weight of the cylinder before exposure to T=87°C. 3: Illustrates the setup of the system when exposing the cylinder to T=87 °C.

After 24/72 hours the cylinder is withdrawn from the heat cabinet for a cool down period of 24 hours before it is pressurized to 5000psi again. The purpose of increasing the pressure is to make sure that the conditions before and after the exposure to heat are equal, temperature and pressure wise. When pressure is regulated back to 5000 psi the cylinder is weighed again, the difference between the start and end weight divided by the density of the water at room temperature is equal to the volume shrinkage as mentioned in the theory part. The procedure is illustrated in fig. (7.4). The results of the shrinkage tests are located in table (8.1).

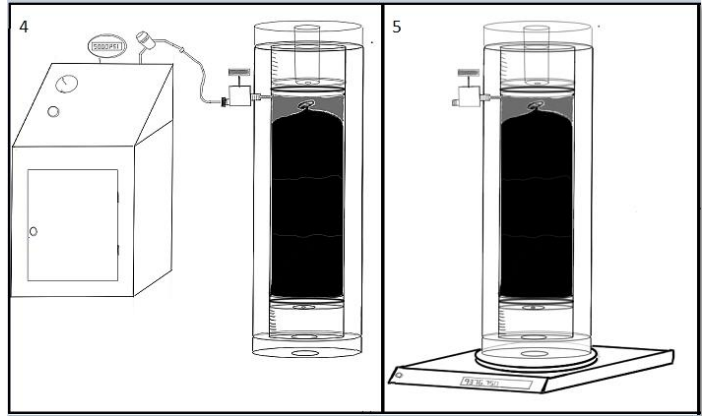


Fig 7.4 Image 4: The cylinder is pressurized at the end of the test. 5: The cylinder is weighed the last time.

The density of the cement was measured after the Hobart mixing for one test in order to compare the density of the Hobart mixed cement to the density of cement mixed by using the API standard section 5.3.4 for mixing cement and water and the API standard: section 5.4.3 atmospheric pressure conditioning method for removing air[31]. The density was measured with a density balance similar to the one in picture (7.4) according to the API standard [31], section 6.2. Picture of the density balance and atmospheric conditioning meter is shown below in pic. (7.4).



Picture 7.4 a common fluid density balance on the left and an atmospheric conditioning meter to the right in the picture [32] [34].

In order to compare the rheology of the slurries, the rheology of the slurries was measured with a rotational viscometer (shown in fig. (7.5)) according to API standard: section 11.4.1: Determination of rheological properties, and section 11.5: Determination of gel strength [30]. The results of the density measurements of class G cement are located in table (7.2), while the viscosity measurements of both class G cement and Norite cement are located in table (A.2) in the appendix.

	Measured density [g/cm ³]
Hobart N-50	1,88
Mixed according to the API standard including atmospheric pressure conditioning	1,87

Table 7.2 shows the measured density of Class G cement for both the Hobart mixing procedure and for the API standardized mixing procedure for cement.

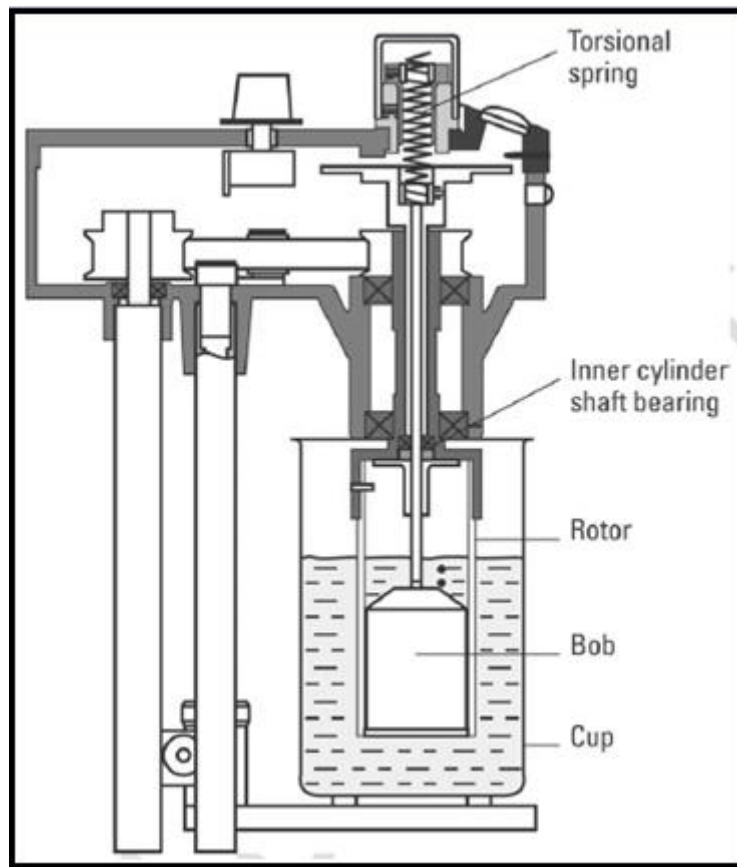


Fig. 7.5 illustration of a rotational viscometer [31].

8 RESULTS

8.1 Ultrasonic cement analyser test results

The ultrasonic cement analyser tests were performed based on results from earlier studies performed by Mahmoud Khalifeh and Helge Hodne on the cement lab at the University of Stavanger. The tests presented here have been verification tests on the compressive strength development of Norite cement. Two different recipes was tested, both of them are listed in table (7.1). The data collected from the UCA tests are presented in fig. (8.1) and (8.2).

Ultrasonic cement analyser test 1:

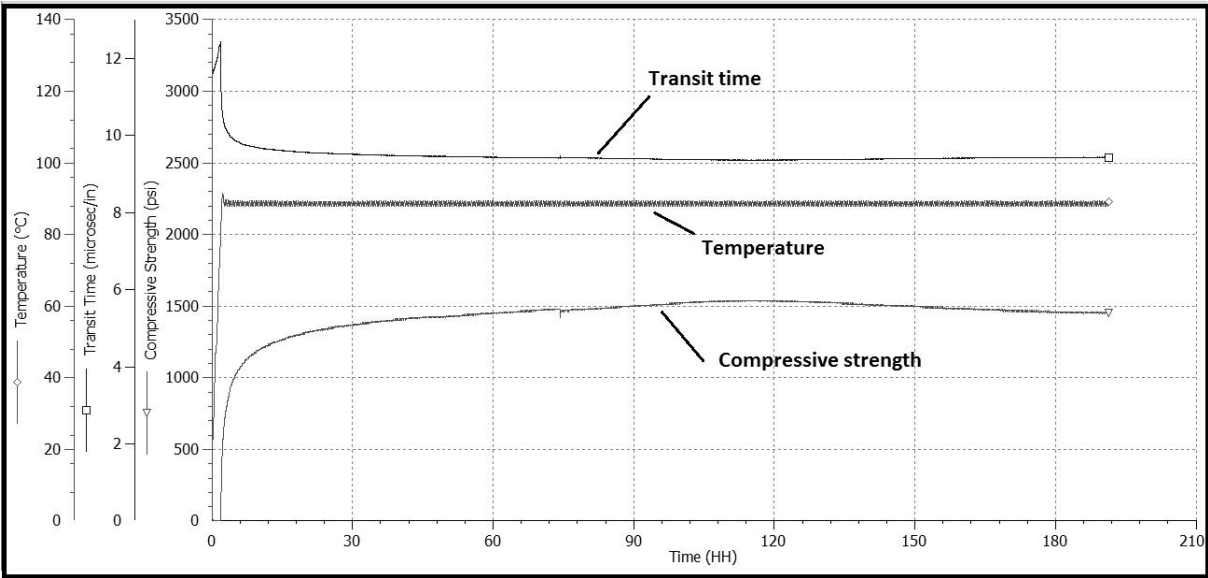


Fig. 8.1 the compressive strength development of the Norite recipe 1 cured at 87°C and 5000psi.

The compressive strength reaches 50 psi (0,35 MPa) after 1 hour and 43 minutes. The maximum compressive strength was measured to be 1544 psi (10,58 MPa) after 121 hours and 53 minutes. The experiment was stopped after 190 hours and it seemed to be stable at this point, with no significant change in compressive strength the last 20 hours of the experiment. The compressive strength after 190 hours was 1447 psi (9,98 MPa).

Ultrasonic cement analyser test 2:

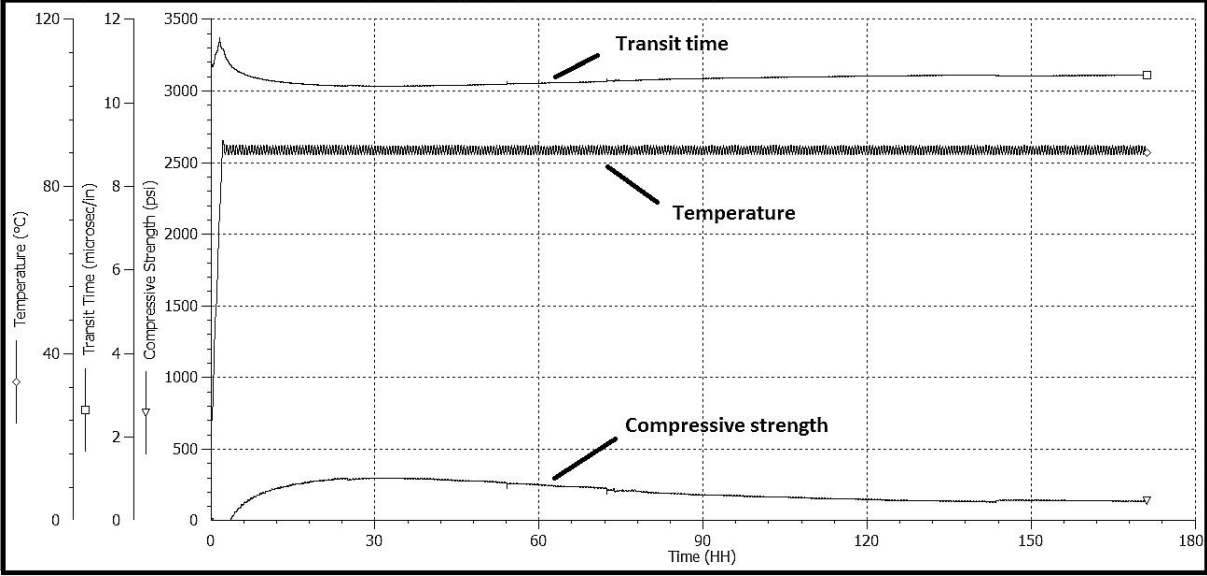


Fig. 8.2 the compressive strength development of the Norite recipe 2 cured at 87°C and 5000psi.

The compressive strength reaches 50 psi (0,35 MPa) after 4 hours and 13 minutes. The maximum compressive strength was measured to be 293 psi (2,02 MPa) after 29 hours and 43 minutes. The experiment was stopped after 171 hours and it seemed to be stable at this point, with no significant change in compressive strength the last 50 hours of the experiment. The compressive strength after 171 hours was 131 psi (0,90 MPa).

8.2 Shrinkage test results

The results from the tests of class G cement and Norite cement is shown in table [x2] below.

Cement Type	Test nr.	Weight of samples including 3 condoms [kg]	Weight of system start [kg]	Weight of system end [kg]	Weight difference, End-Start [kg]
Class G 24h	1	0,8680	13,5336	13,5491	0,0155
Norite 24h	2	0,7170	-----	-----	-----
Norite 24h	3	0,8708	-----	-----	-----
Class G 24h	4	0,9040	13,1681	13,1825	0,0144
Class G 24h	5	0,8361	13,1362	13,1515	0,0153
Norite 24h	6	0,7946	-----	-----	-----
Norite 24h	7	0,8081	12,9705	12,9703	-0,0002
Norite 72h	8	0,6904	13,0662	13,0651	-0,0011
Class G 72h	9	0,8101	13,1164	13,1307	0,0143

Table 8.1 the shrinkage for class G cement and Norite cement, exposed to 5000 psi and 87 °C.

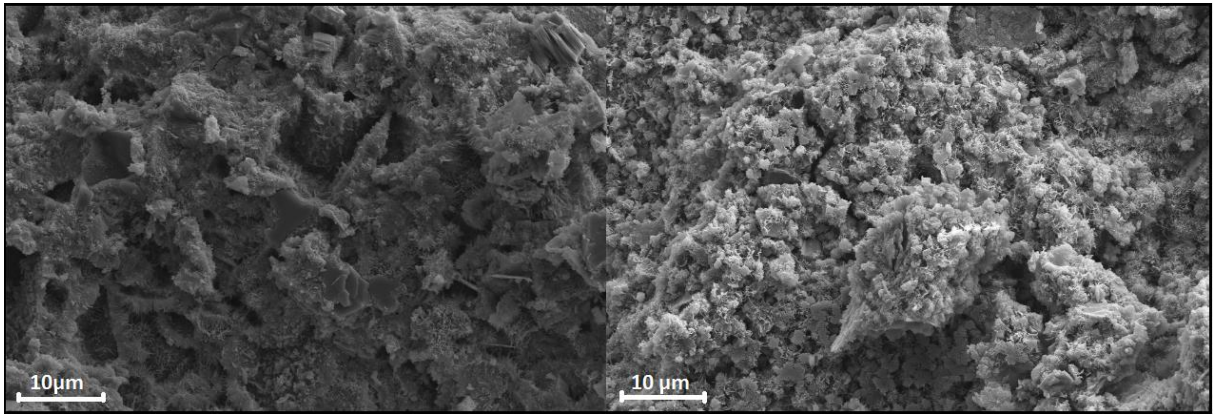
The shrinkage of the samples are presented as weight difference between starting weight and end weight, the theory is explained in the procedure part of the. Test 2 and 6 failed due to leak in the cylinder valve. Test 3 failed because the valve got stuck at the end of the test, which made it impossible to pressurise the cylinder at the end of the test. Test 1, 4, 5, 7, 8 and 9 ran as planned and the results of shrinkage can be seen on the all the way to the right in table (8.1). Two of the tests, tests 8 and 9 were exposed for 72 hours instead of 24 hours, but this did not seem to make any major impact on the shrinkage results.

Test nr.	Calculated shrinkage [V%]	Weight of the content in the cylinder [kg]	Weight of water in the system [kg]	Volume of water in the system [liter]	Volume of cement in the system [liter]	Volume of injected water due to shrinkage [liter]
4	3,0800	1,0451	0,1411	0,1414	0,4686	0,0144
5	3,5455	1,0132	0,1771	0,1775	0,4325	0,0153
8	-0,3091	0,9432	0,1648	0,1652	0,3566	-0,0011
9	3,3621	0,9934	0,0953	0,0955	0,4263	0,0143

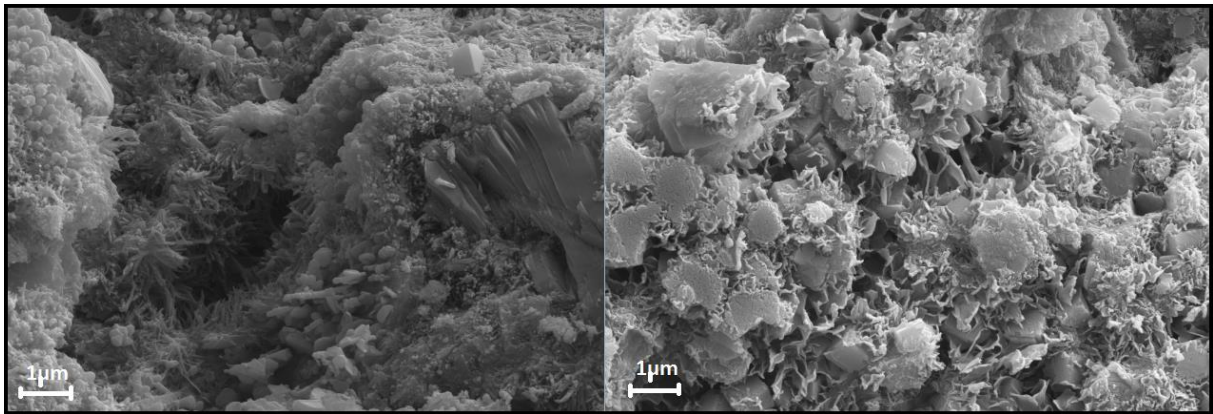
Table 8.2 shows the calculated shrinkage of test 4, 5, 8 and 9 including the volume calculations needed to obtain the volume shrinkage percent.

The volume shrinkage percent was calculated for tests 4, 5, 8 and 9 because these test had the exact same test setup, with the same cylinder and valves. This made it possible to use the same volume calculations in order to find the volume of shrinkage for the tests. The Class G cement had a volume percent shrinkage of about 3.1-3.55 % as seen in table (x3). While the Norite cement tests seemed to have zero shrinkage.

Scanned electron microscope (SEM) pictures of class G cement and Norite cement taken in cooperation with Ingunn Cecilie Oddsen at the University of Stavanger:



Picture 8.1 SEM picture of class G cement to the left and Norite cement to the right, taken after shrinkage test.



Picture 8.2 SEM picture of class G cement to the left and Norite cement to the right, taken after shrinkage test.

The above pictures show the difference in the structure of the two cements. In pic. (8.1) it can be seen that the class G cement has some crystalline particles while the Norite cement is more homogeneous. In pic. (8.2) it is possible to see the threads that binds the two materials and it seems like everything is linked together by the threads in the Norite cement, while some of the material on the right side in the class G cement picture seems to be unreacted.

9 DISCUSSION

Ultrasonic cement analyser test 1 had a much higher compressional strength than the ultrasonic cement analyser test 2. It seems strange that the increase of molar concentration from 8 M NaOH to 10 M NaOH would decrease the compressional strength from 1447 psi in test 1 to 131 psi in test 2. The reason for this is unclear, but it could be related to a failed calcination of the kaolin prior to the mixing of the test sample 2.

The Class G cement had a volume percent shrinkage of about 3-3.5 %, which correlates well to the results of K.R. Backe et al. [35] in the study of well cements. The shrinkage that occurs is likely to be a product of chemical and thermal shrinkage, while drying and plastic shrinkage can be eliminated due to the lack of a surface of which water can evaporate from. The chemical/thermal shrinkage is a consequence of hydration of which water and cement reacts as explained in the shrinkage theory part of this thesis. One observation made during the testing of the cement was that the cement samples were stuck inside the pvc pipe and difficult to remove upon cleaning the cell. This observation is interesting because even though the cement shrinks it may seem like it is still able to work as a plug; inhibiting the vertical communication in the cell.

The shrinkage of the Norite tests are more difficult to explain due to the lack of published papers on the subject of Geopolymer shrinkage, but some studies have demonstrated shrinkage in several Geopolymer compositions. However, the studies have been at atmospheric pressure and ambient temperatures. The physical conditions in these studies will give the water a surface which it can evaporate from, resulting in loss of structural water that leads to shrinkage as described by Carsten Kuenzel et al [13]. Since there was no surface between the water and air in the shrinkage tests performed in this thesis, the evaporation of water from the cement was eliminated leading to zero shrinkage for the Norite cement samples.

The viscosity of both the Norite and class G cement was also measured; the results are located in table (A.2). The viscosity of the Norite cement was too high for the viscometer to measure. This would make the Norite cement very difficult to pump in to location in a plug and abandonment operation, but it could probably be solved with different additives in order to reduce the viscosity.

10 CONCLUSION

While the Class G cement had an average shrinkage of about 3-3.5 %, the Norite cement did not experience any shrinkage in the shrinkage test setup used in this thesis. The main reason for the lack of shrinkage is believed to be because of the non-existing surface area between the water and air. In conclusion, the Norite cement will not achieve the same compressive strength as class g cement, but it does not shrink at 5000 psi and 87°C for the first 72 hours after placement. These results make the Norite cement a good candidate for further study in the search for a better alternative to the Portland class G cement for use in plug and abandonment operations.

11 FUTURE WORK

Throughout this experiment I have thought of ways to develop the testing method. One weakness of this experiment is as the shrinkage occurs the pressure will drop inside the cell due to lack of pressure support. A pressure regulator could easily be mounted to the cell instead of the relief valve in order to regulate the pressure as the content of the cell expands or shrinks. One other thing that could be interesting is to measure the weight of the system in real time and identify when shrinkage occur.

The Norite seems to build sufficient strength with zero shrinkage, but is it impermeable?

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13 APPENDIX

Components	Measured weight [gram]	Components	Measured weight [gram]
	Measured values test 1		Measured values test 6
Class G cement	792,00	Grinded Norite	350,00
Disstilled water	349,94	Metakaolin-750	175,02
		Blast furnace slag	175,00
	Measured values test 2	SiO ₂	105,02
Grinded Norite	350,03	8M NaOH	455,04
Metakaolin-750	174,98	Disstilled water	34,99
Blast furnace slag	174,98		
SiO ₂	105,05		Measured values test 7
8M NaOH	455,11	Grinded Norite	349,99
Disstilled water	35,04	Metakaolin-750	174,99
		Blast furnace slag	174,99
	Measured values test 3	SiO ₂	104,98
Class G cement	791,99	8M NaOH	455,01
Disstilled water	348,98	Disstilled water	35,00
	Measured values test 4		Measured values test 8
Class G cement	792,02	Grinded Norite	349,99
Disstilled water	349,00	Metakaolin-750	174,99
		Blast furnace slag	175,01
	Measured values test 5	SiO ₂	105,00
Class G cement	792,05	8M NaOH	455,00
Disstilled water	349,01	Disstilled water	35,01
			Measured values test 9
		Class G cement	792,04
		Distilled water	349,03

Table A.1 Measured weight of the cement components used in each shrinkage tests.

Rheological properties test				
	Class G cement		Norite cement recipe 1	
Rotational speed r/s	Ramp-up reading	Ramp-down reading	Ramp-up reading	Ramp-down reading
3	14	13	---	---
6	18	18	---	---
30	40	40	---	---
60	53	49	---	---
100	63	58	---	---
200	80	77	---	---
300	94		---	
Gel strength measurement	10 sec	10 min	10 sec	10 min
	15	20	---	---

Table A.2 Results from measuring the viscosity of class g and Norite cement after 20 min of mixing in the Hobart n-50 mixer. The Norite cement's viscosity was higher than the maximum viscosity level possible to measure with the viscometer available at the cement lab.