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And final thanks to all my friends and classmates that have encouraged me to work towards my goals, and supported me all the way!

Abstract

The purpose of this work is to investigate and develop aplite-based geopolymer as an alternative material for Portland cement. This was done by conducting a series of experiments using an Ultrasonic Cement Analysis (UCA) on different recipes. In order to get the desired results, the recipes were modified after each experiment. When the final recipe was found, several Uniaxial Compressive Strength (UCS) tests were conducted to verify the obtained results from the UCA.

The reason for wanting to develop this geopolymeric material, is to find an alternative to Portland cement for plug and abandonment operations. Portland cement is the most common sealant used for Plugging and Abandonment (P&A) operations. However, when it comes to high temperatures and corrosive environments it has its weaknesses. So if geopolymers are more resistant in these cases, and may be produced cheaper and do less impact on the environment, then this would be a good development for the industry.

After series of experiments the results suggested that a high silica/aluminum ratio was needed to develop strength. The increase of concentration of the alkali solution also improved the strength. However, a too high content of NaOH gave poor results, and might be explained by excess Na^+ ions that weakened the geopolymer framework. After modifying the recipe and removing metakaolin a recipe was developed that achieved a compressive strength of 4200 psi in the UCA, and 5700 psi by UCS tests. The results suggest that an elevated curing temperature and pressure increases the compressive strength of the mentioned geopolymer. They also indicate that a higher Solid – Liquid Ratio (SLR) will reduce the time for the slurry to set. All the experimental work was done at the University of Stavanger in the well cement lab, and the concrete lab.

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List of symbols and abbreviations

ACBFS - Air-Cooled Blast Furnace Slug
BFS - Blast Furnace Slag
$CaCO_3$ - Calcium Carbonate
$Ca(OH)_2$ - Calcium Hydroxide
CH_4 - Methane
CO_2 - Carbon dioxide
ECD - Equivalent Circulating Density
GBFS - Granulated Blast Furnace Slug
HSE - Health, Safety and Environment
H_2S - Hydrogen Sulfide
ISO - International Organization for Standardization
KOH - Potassium Hydroxide
MD - Measured Depth
mD - milli Darcy
MPa - Mega Pascal
MSc - Master of Science
Na_2CO_3 - Sodium Carbonate
Na_2O - Sodium Oxide
NaOH - Sodium Hydroxide
Na_2SiO_3 - Sodium Silicate (Water glass)
NCS - Norwegian Continental Shelf
N/A - Not available
OBM - Oil Based Mud
PSA - Petroleum Safety Authority
PWC - Perforate, Wash and Cement
P&A - Plugging and Abandonment
ROP - Rate Of Penetration
RPM - Rounds Per Minute
SEM - Scanning Electron Microscope
SiO_2 - Silica
SLR - Solid Liquid Ratio
SPF - Shoots Per Foot
UCA - Ultrasonic Cement Analysis
UCS - Uniaxial Compressive Strength
UiS - University of Stavanger
WBE - Well Barrier Element
WBM - Water Based Mud
WOC - Wait On Cement
WOT - Weight On Tool

1.0 Introduction

In the 1950s no one believed that there would be oil or gas on the Norwegian Continental Shelf (NCS), because of negative seismic surveys done earlier. However, this changed when gas was found offshore from the coast of the Netherlands in 1959. Enthusiasm grew, and the first exploration well was drilled on the NCS in 1966. It was a dry well. Several wells were drilled in the following years, and the Norwegian Oil Adventure started when Phillips Petroleum finally found oil in 1969. The Ekofisk oil field was discovered.

Now, over 40 years later it is estimated that only 40% of the petroleum resources on the NCS have been exploited (Ministry of Petroleum and Energy, 2013). Since then, multiple fields of different sizes have been discovered, leading to a high drilling activity. The platou has been reached for oil production and it has started its descent. Gas, on the other hand will keep producing at its platou level as new gas fields are developed.

As the oil and gas wells are being depleted and the reservoir pressure decreases, the wells will eventually become non profitable. These wells, in addition to wells with high water cuts or where well integrity is lost due to geological activities, are prepared for abandonment. To abandon a well the Norwegian government requires it to be properly plugged first to avoid pollution of freshwater reservoirs by cross flow from an overlying water reservoir or migration of hydrocarbons. Hydrocarbons can migrate all the way to the seabed, reach the surface and harm the environment. On the NCS there have alone been drilled 3800 development wells and 1523 exploration wells since the first exploration well was drilled back in 1966. All the exploration wells have been plugged and abandoned, while 170 of the development wells have been permanently abandoned and 800 temporarily abandoned (Khalifeh et. al., 2013). The number of wells drilled in the last century has passed several million on a worldwide basis, making Plug and Abandonment (P&A) a growing field of importance in the industry. These wells are not just for extracting oil and gas, but also for finding fresh water reservoirs, injection/disposal, testing, measurements, exploration and other industrial applications (Smith, 1993).

Some of these wells in the United States date all the way back to the early 1900s, when a well could be drilled and later abandoned without implementing any means of securing the borehole. More recent discoveries have shown that some of the ground water reservoirs used for drinking water have been contaminated by these wells. In 2005, 51% of the population used ground water as their primary drinking water supply, and thus the need for action have been recognized.

During the years, the requirements for P&A have gradually become stricter, reducing the risks of any accidents but also increasing the cost of the operations. Today P&A can easily contribute to 25% of the total well cost, and are sometimes equal or even larger than the cost of the original drilling program (Khalifeh et. al., 2013). With these increasing expenditures comes a large potential for developing new technology, methods and procedures to reduce the time and cost during P&A, which is the basis for this thesis.

1.1 Objectives

This Master thesis is written as a supplement to Mahmoud Khalifeh's work with his PhD on finding an alternative to Portland cement. Portland cement is currently the preferred sealing agent offshore. The goal is to find a geopolymer cement, which is user friendly and builds enough strength to compete with Portland cement. It should also be more resistant to higher temperatures and corrosive environments. This would allow it to be used in High Temperature and High Pressure (HTHP) wells, where cement failure is a common problem. Portland cement is relatively expensive due to the large quantity needed. Since geopolymer cement is made up of several waste products and other materials that have a low energy demand, it will be less expensive and might be a competing alternative to Portland cement in the oil and gas industry. This thesis will focus on aplite-based geopolymer cements.

This was done by testing several different additives into the geopolymer recipe, and testing the strength first by using an UCA test, to identify the strength development. The ingredients that are used will be locally available, reducing the cost as much as possible. After a successful recipe has been developed, several samples were made with this recipe, and UCS tested to confirm the strength.

If the strength found is acceptable, the recipe could be optimized with respect to other cement properties, which are needed, before starting field trails.

2.0 Plugging and abandonment

The operation of plugging and abandoning a well can be divided into three phases. The first represents the plugging and isolation of the reservoir sections. The complexity of this phase depends on several factors:

- The reservoir conditions (temperature, pressure, fluids, formation etc.).
- Type of well (orientation: vertical, inclined or horizontal).
- Number of reservoirs.
- Number of sidetracks from the mother bore.
- If the field is operated as a subsea field, from a platform or is land field.
- If the tubing needs to be pulled.

The second phase involves setting shallower barriers, the surface barrier, and removal of casing sections. The last phase is to remove the wellhead (WH) and conductor, and fill the cavity with cement (Oil & Gas UK, 2011). During these phases there are regulations that need to be followed. Removal of tubing, casing and WH is outside the scope of this thesis. This chapter will, however, focus on some regulations and well integrity issues with an emphasis on the NORSOK standards, as well as the operational steps in setting a permanent well plug.

2.1 Regulations and Well integrity

On the Norwegian continental shelf, all the oil companies need to follow the hierarchy of laws and regulations shown in Fig. 2.1. The overarching legislation in Norway is the Norwegian Constitution. Next in the hierarchy are the acts, where the Petroleum activities, working environment, the fire and explosion prevention act can be found, which is under the Petroleum Safety Authority Norway's (PSA) area of jurisdiction (The Norwegian Oil Industry Association, 2004). Another important act that should be mentioned and is relevant for P&A, is the Pollution and waste act, which regulates what can be dumped on the seabed, quantities that are acceptable to leak out etc.

Figure 2.1.: The hierarchy of laws and regulations

Another level down in the hierarchy in Fig. 2.1 is the regulations. The most important regulation of all, is the framework Health, Safety and Environment (HSE), which affects all the operations done on the NCS. The regulations do not specifically tell how to perform operations. For that guidelines and standards are needed. These are tools to better understand, interpret and give a more detailed and practical understanding of the regulations. A very important set of standards for the oil and gas industry is the NORSOK standards. Its main purpose is to: "… ensure adequate safety, value adding and cost effectiveness for petroleum industry developments and operations. Furthermore, NORSOK standards are as far as possible intended to replace oil company specifications and serve as references in the authorities' regulations" (The Norwegian Oil Industry Association, 2004). NORSOK is developed by different actors in the Norwegian petroleum industry based on international standards as the ISO standards and the API standards. PSA encourages all oil companies to use the NORSOK as a minimum requirement during their operations. At the bottom of the hierarchy the companies' own additional requirements are found. They are as strict or stricter than the guidelines and standards.

During P&A operations the NORSOK D-010 standard is a frequently used standard. Its purpose is to "focus on well integrity by defining the minimum functional and performance oriented requirements and guidelines for well design, planning and execution of well operations in Norway" (The Norwegian Oil Industry Association, 2004). In all operations it is important to maintain full well integrity, preventing any form of uncontrolled release of fluids from the well at any stage of its life cycle. Well integrity is defined as: "an application of technical, operational and organizational solution to reduce risk of uncontrolled release of formation fluids throughout the life cycle of the well". The NORSOK D-010 requires all wells to have at least one barrier between the surface and a potential source of inflow. However, if a reservoir that contains hydrocarbons and/or has flow potential, two barriers are required. Further, NORSOK D-010 defines a well barrier as an "envelope of one or several dependent barrier elements preventing fluids or gases from flowing unintentionally from the formation, into another formation or to surface" (The Norwegian Oil Industry Association, 2004). Several examples of well barrier schematics for different operations are given in this standard. The requirements when plugging a well is slightly different if the purpose is to temporarily abandon a well, or abandon it permanently.

2.1.1 Temporary abandonment

A well is said to be temporary abandoned when the well is abandoned in a fashion where it is intended and possible to be re-entered in a safe manner at a later stage. The time frame of temporary abandonment may be in the range of a couple of days to several years. The materials used for barriers during such a temporary abandonment must keep its integrity at least twice as long as the planned time frame for the abandonment.

2.1.2 Permanent abandonment

A permanently abandoned well (or well section) is a well that is determined to never be re-entered. NORSOK D-010 defines the requirements for a permanent plugged wells as follows: "Permanently plugged wells shall be abandoned with an eternal perspective, i.e. for the purpose of evaluating the effect on the well barriers installed after any foreseeable chemical and geological process has taken place" (The Norwegian Oil Industry Association, 2004).

Permanent plugging can be performed when abandoning a well, or when doing slot recovery with sidetracking. The well path beneath the sidetracking must be permanently plugged.

There also needs to be installed a permanent well barrier in the last open hole section of the well. This barrier must isolate the complete borehole. This requirement holds regardless of the pressure or flow potential as previously mentioned. (The Norwegian Oil Industry Association, 2004) The NORSOK D-010 stipulates that "Permanent well barriers shall extend across the full cross section of the well, include all annuli and seal both vertically and horizontally". Usually this requires cement logging to verify the quality of the cement job behind the casing. If there is an adequate interval with a satisfactory cement job, a permanent plug can be placed inside the casing. However, if it turns out to be poorly cemented behind the casing interval, then milling, washing and cementing is required. This procedure will be addressed in Ch. 2.3. A permanent well barrier should preferably have the following properties:

- Ability to seal:

Fluids will migrate through plugs due to differential pressure and diffusion through the connected pore channels (permeability), conduits due to defects in sett plug and between formation and plug. Rate of penetration can, however, be reduced to an acceptable rate by using good placement techniques, adequate plug heights, and using a material that has low permeability.

- Long-term integrity and chemical resistance:

The material must be able to keep its sealing properties and position over time without being degraded by pressure, temperature and chemicals (CO_2, CH_4, H_2S).

- Good wetting properties and non-shrinking:

It is important to get a proper seal between the plug and casing and/or formation, preventing any leaks at the boundaries. It is also crucial that the material does not shrink, creating flow paths for fluids, and increasing the plugs' probability to fail.

- Ductile:

To be able to withstand mechanical loads or impacts, pressure and temperature changes, the material should be ductile (Oil & Gas UK[2], 2012). If there are changes in the stratigraphic layers, a material with good ductile abilities is able to keep its sealing properties up to a certain point.

As mentioned above a well barrier/plug must ensure no leakage from the well and therefore cover the whole cross section of the borehole and seal in both vertical and horizontal directions. The ideal sealing material for well abandonment should have the following five properties:

- Readily available and easily mixed
- Be chemically non-reactive with groundwater
- Provide good bonding across the zones being sealed when properly placed
- Remain proper fluid displacement and develop adequate strength within a short period of time
- Have low permeability when set to resist the flow of fluid through the sealing material and the interface along the formation being sealed

The most common sealing material used today is Portland cement and is covered in detail in Ch. 3.3.

2.2 Positioning and length of barriers

As previously mentioned if there is a reservoir or flow potential in the well, two barriers are required. The primary barrier should then be set across or above the reservoir or point of inflow, i.e. open hole section or perforation interval. Setting the plug as close to the reservoir as possible will reduce the maximum differential pressure across it. The plug must regardless of its position be able to withstand worst-case scenarios, and an eventual casing must also be strong enough at this point (Oil & Gas UK, 2012). The secondary barrier is placed above the primary, working as a backup, yet has the same requirements.

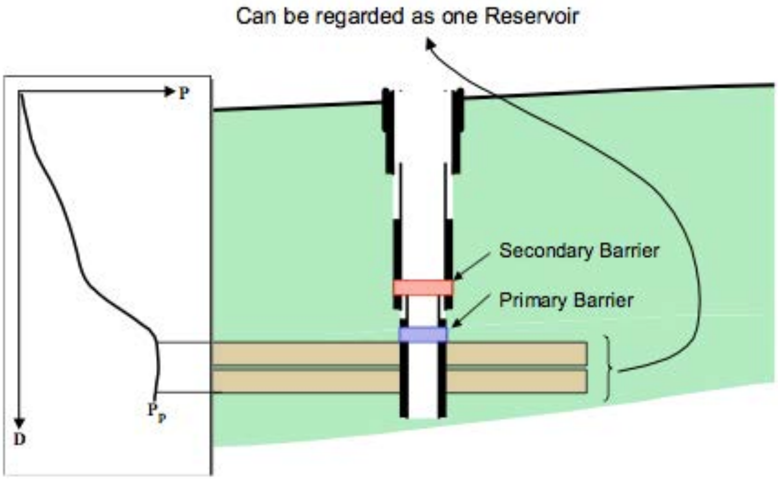

Figure 2.2.: Barriers for several reservoirs in the same pressure regime (The Norwegian Oil Industry Association, 2004)

If several reservoir layers are located in the same pressure regime, they can be considered as one reservoir, as shown Fig. 2.2 (The Norwegian Oil Industry Association, 2004). If this is not the case then each reservoir needs to have two barriers. It is, however, allowed to use the secondary barrier for one reservoir as the primary for a shallower one (See Fig. 2.3).

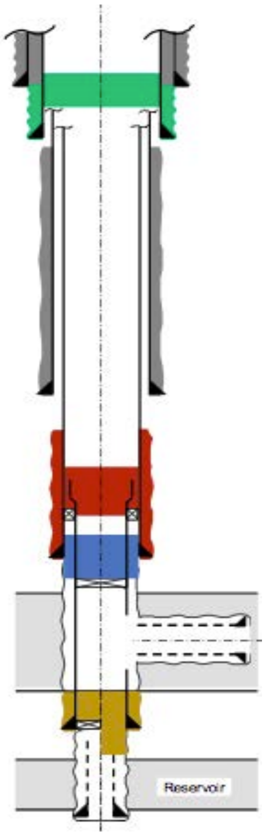

Figure 2.3: Upper barrier: surface barrier, second barrier: secondary barrier for the upper reservoir, third barrier: primary barrier for upper barrier and secondary barrier for lower reservoir, forth barrier: primary barrier for the lower reservoir (The Norwegian Oil Industry Association, 2004)

To account for contamination and ensure that the plug will seal off the whole cross-section, the firm plug length should be a minimum of 100 meters measured depth (MD). The minimum length is reduced to 50 meters MD if the plug has a mechanical plug as a foundation inside a casing. In this case the cement outside the casing must be verified by cement logging. The cement must also extend 50 meters above the source of inflow, or above the last casing shoe if the cemented area is in a transition from open hole to casing.

2.3 Setting a permanent plug

The conventional method for setting a permanent plug involves logging, section milling and underreaming before the plug can be set properly. Due to these expensive and time-consuming operations, there is a high demand to find faster and cheaper alternatives to set a permanent plug. The steps mentioned will now be presented, followed by a new tool that may make P&A operations more efficient.

2.3.1 Cement logging

The first step when looking to plug a well is to check the cement quality behind the casing of the desired well section (Nelson & Guillo, 2006). A commonly used method for cement control is acoustic logging. A sketch of how an acoustic tool works is shown in Fig. 2.4. The functioning of the tool is that it can have several senders and receivers, which transmits acoustic sound waves and records their traveling time. Each type of material and fluid have different acoustic properties affecting the waves' traveling time. By evaluating these logs, it is possible to give a prediction of the cement quality behind the casing. Based on these logs the next step in the P&A operation can be determined. If the cement is of sufficient quality in all annuli then the plug may be set inside the casing. If this is not the case, then milling is the most commonly used option.

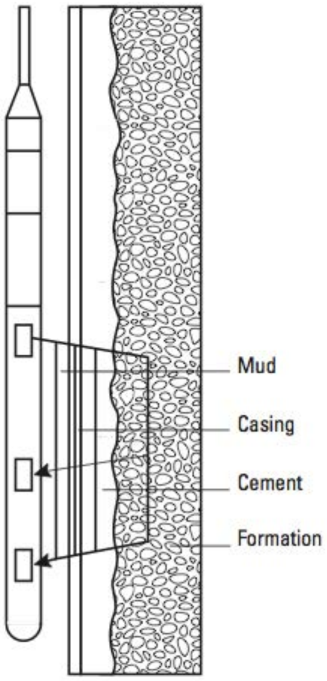

Figure 2.4: Sketch of an acoustic tool, verifying cement quality (Nelson & Guillo, 2006)

2.3.2 Milling

Milling is the operation to remove casing sections by using a milling tool or cutters to cut up the casing into small metal debris called swarfs. Fig. 2.5 shows a milling tool, while Fig. 2.6 (Ferg, et. al., 2011) shows swarf. NORSOK requires that 165 feet (50m) of the casing have to be milled before allowing a plug to be set (Ferg, et. al., 2011). A standard milling operation lasted for up to an average of 65 days per well that was abandoned (Scanlon, et. al., 2011). Baker Hughes and Conoco Phillips introduced new cutter technology, including a more impact resistant cutter material, design and applied a downhole optimization tool during a P&A campaign on the Ekofisk Whisky platform (Scanlon, et. al., 2011). The new cutters had an extended life time allowing to mill a whole section without tripping out of the hole to change milling tool, as well as increasing the rate of penetration (ROP). The downhole optimization tool sent real time data like weight on tool (WOT), torque, revolutions per minute (RPM), bending moment, vibrations, pressure and temperature, to the surface. This allows the driller to better understand what is going on down in the hole, and faster respond if any of the parameters make a change for the worse. The new tools reduced the last four wells on the P&A campaign on Whisky to an average of 46 days, which saved the operator for a lot of cost.

Figure 2.5: Milling tool used to remove casings during section milling

Figure 2.6: Metal debris, also known as swarf (Borrowed from zimoun.net)

During milling operations, large quantities of swarf must be transported to the surface to avoid packing of the tools and plugging the hole. To be able to do this, a high viscosity fluid is needed. Yet, this gives way to another concern. The high viscous fluid will increase the Equivalent Circulating Density (ECD). This might push the well pressure above fracturing pressure, leading to fractured formation and losses. To avoid this complication, a reduced ROP must be considered. When the swarf reaches the surface it is transported with the mud through the bell nipple. To prevent the swarf from damaging the screens, and to reduce the workload on the roughnecks, a swarf unit can be installed. It is installed between the bell nipple and shakers and removes the swarf from the mud before it reaches the shakers. The swarf is dumped into containers and sent onshore for processing. After the milling process is completed it is important to clean the open hole section, to ensure that there is no swarf left to interfere with tools and the operations conducted at a later stage.

2.3.3 Underreaming

After the casing is milled and the hole is cleaned, the next step in the P&A operation is underreaming the hole, i.e. increasing the hole diameter. The purpose of this is to remove any residue of the previously set cement, and to expose new formation to allow better bonding and seal properties for the next cement job. An underreamer sub from Halliburton is shown in Fig. 2.7. It contains three cutter arms that are activated by hydraulic force and adjusted to a preferred diameter. The hole is now ready for plug placement.

Figure 2.7: Halliburton Underreamer Heavy Duty Borehole Enlargement Tool (Borrowed from Halliburton, 2013)

2.3.4 Plug placement

There are several placement methods for setting a plug. Commonly used techniques involve the balanced method, the dump bailer method and the two-plug method, which will be presented in this section.

2.3.4.1 Balanced Method

A balanced plug is set by pumping down cement onto a base, as shown seen in the illustration in Fig. 2.8 (Nelson & Guillo, 2006). The base can be a bridge plug or a high viscous fluid and ensures that the plug is set at the desired location in the well. When there is an equal height of cement slurry in the annulus and inside the pipe, the string can slowly be pulled out allowing the cement to solidify. This is a quite simple method that can be used with both drill pipe or coiled tubing, and is therefore a commonly used method.

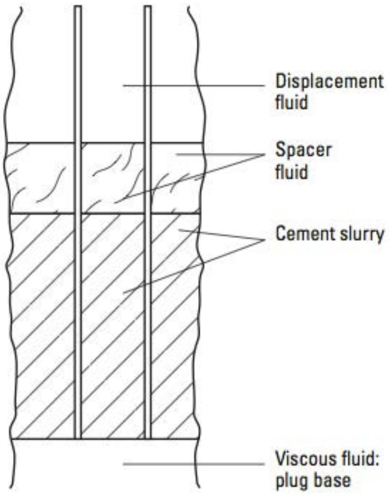

Figure 2.8: Balanced Method for plug placement (Nelson & Guillo, 2006)

2.3.4.2 Dump Bailer Method

The dump bailer method uses a vessel containing cement that is run on wireline, as shown in Fig. 2.9 (Nelson & Guillo, 2006). The vessel is run down to a permanent bridge plug placed below the desired plug interval. When contacting the bridge plug the vessel will open and dump the cement slurry upon the plug. This method allows better control of cement placement and positioning. Another advantage is that it does not require a rig to execute the operation, but it is, however, more time consuming due too small volumes that can be contained by the vessel.

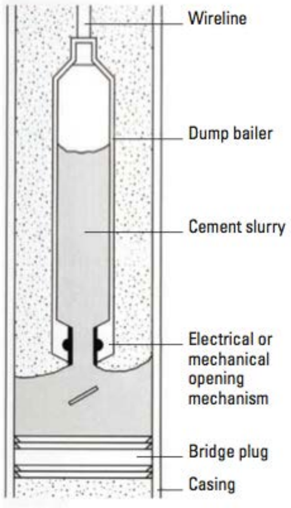

Figure 2.9: Dump Bailer Method (Nelson & Guillo, 2006)

2.3.4.3 The two-plug method

The two-plug method uses a special tool to set a cement plug at a calculated depth (Nelson & Guillo, 2006). Using this method, it can be done with a maximum of accuracy and a minimum of cement contamination, ensuring a high success rate. The tool consists of a bottomhole sub installed at the lower end of the drill pipe, an aluminum tailpipe, a bottom wiper plug, and a top wiper plug. Each wiper contains a dart or foam ball, which is essential for the use of this method.

The steps in the two-plug method are shown in Fig. 2.10 and Fig. 2.11 and are explained below:

- The cement is used to pump a plastic plug down the drill pipe to clean the walls and to separate the cement from other fluids.
- When the plug reaches the bottom of the string it is locked, pressure builds up. When this pressure increase is detected, the operator knows that the cement has reached the bottom.
- By increasing pump rate the plug breaks, allowing cement to enter the well.
- Behind the cement a second plug is pumped down with a displacing fluid. The plug stops when it reaches a certain depth, allowing the pressure to build up a second time. At this point the operator knows that the cement is placed at its desired position, and pumping stops.

- The string is pulled to the top of the desired plug height, and the remaining cement is reverse circulated out.

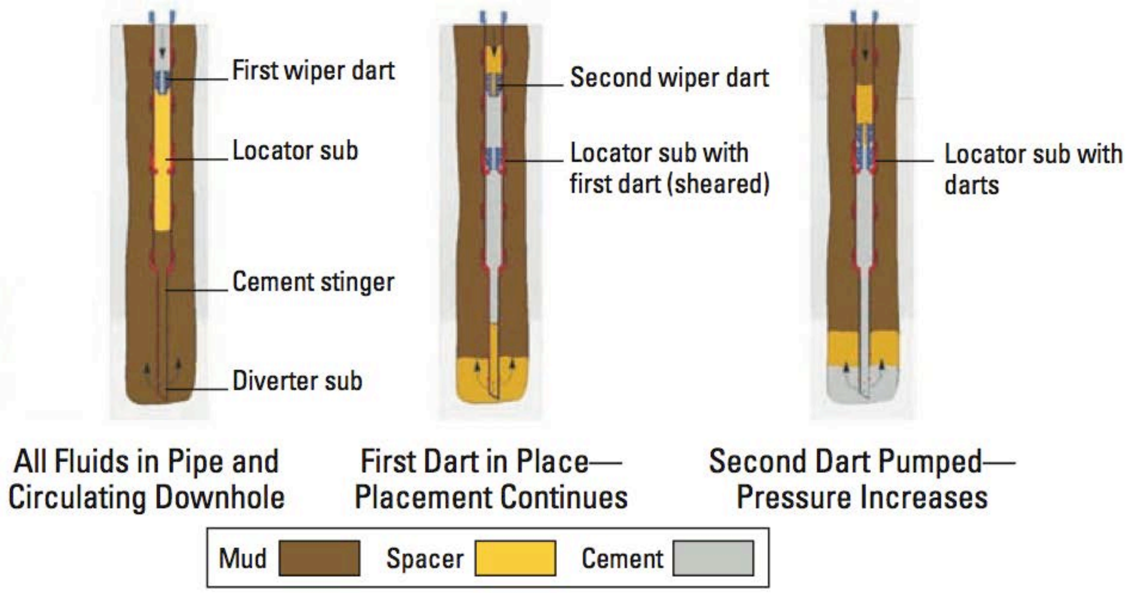

Figure 2.10: Two-plug method step 1-3 (Nelson & Guillo, 2006)

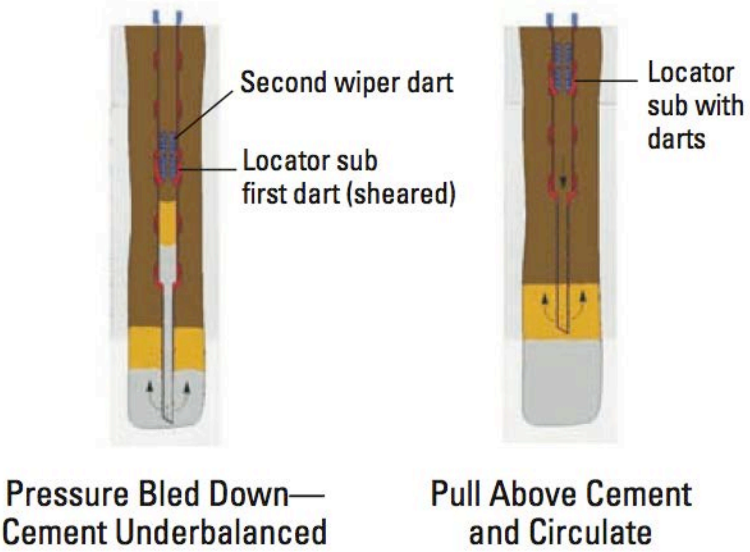

Figure 2.11: Two-plug method step 4-5 (Nelson & Guillo, 2006)

2.4 Bonding considerations of the plug

A plug's ability to seal of a well is affected by the bonding of the cement/casing interface and cement/formation interface, and the bulk cement properties. Cementing regulations are often based on strength requirements, with the assumption given that a plug has a certain strength, the bonding will also be good enough to seal the well (Nelson & Guillo, 2006). This is not always the case. Two mechanical forces are important for effective zonal isolation along the cement interface; shear bond and hydraulic bond to the wall of the hole. Shear bond mechanically supports the plug in the hole, securing its place along the borehole. Shear bond strength is equal to force divided by contact area. Hydraulic bonding blocks the migration of fluids or gas through the cement. This is often tested by applying pressure at the cement/casing interface until a leakage occurs. The hydraulic bonding is critical (Smith, 1993). A solid hydraulic bonding will usually depend on 3 main factors:

- Good cement – formation contact
- A uniform mud cake
- Removal of mud

Other factors that affect the well sealing properties are: the handling of fluids, and the cleanliness of the well before pumping in the cement slurry.

2.5 Verification

The NORSOK D-010 has several requirements for plug setting verification. The requirements vary depending on the kind off well and barrier that is being set. A short description of normal verifications and tests will be presented here. For more detailed description review Table 24 in NORSOK D-010 rev. 3.

2.5.1 Strength development

First the strength development of the cement slurry used should be tested in a pre-job test. Pre-job testing means that the conditions in the well are replicated in a lab, with the same kind of tools, cement and fluids. A perfect reconstruction is impossible, nevertheless the pre-job test will give an indication of how the cement and fluid systems will react in the well. The operation in the well should still be done with caution. After the cement is set as explained in Ch. 2.3.4 it needs time to build strength. If the cement is not allowed to build enough strength before the next operation starts, then the pressure increase due to pumping/circulation can cause serious damage. This could in worst case ruin the cement and the whole job. The pre-job test will also give an indication of the Waiting on Cement (WOC) time, which is the time needed to build strength before pumping can commence. NORSOK requires that the entire operation is planned and documented, including records from the cement operation (volumes pumped, returns during cementing etc.) (The Norwegian Oil Industry Association, 2004).

2.5.2 Position

The position of the plug should be verified by tagging, meaning touching down on the plug with a drill pipe or coiled tubing until a firm surface is seen on the surface by weight reduction. If there is a bailer connected to the string, a sample may be brought back so that the cement quality can be analyzed. (Oil & Gas UK, 2012).

2.5.3 Strength

After the position is verified, the strength and sealing properties must be checked. The most conventional method is to perform a pressure test. Strength can be tested by increasing the pressure to a minimum of 3.45 MPa (500 psi) above the calculated inflow pressure beneath the plug (i.e. from open formation or perforations). The desired pressure is achieved by pumping fluids into the well without taking any returns. In this process, it is important to not increase the pressure above the casing or cement strength.

2.5.4 Sealing

An inflow test is also needed, and the pressure is then reduced to get maximum pressure difference across the plug to check for any leaks (Oil & Gas UK, 2012). The NORSOK also requires that a cementing program shall be issued for each cement plug installation (The Norwegian Oil Industry Association, 2004).

2.6 The Perforate, Wash and Cement System

The conventional way of P&A when the cement job behind the casing is not sufficient enough is time consuming. However, a new tool has been field tested in 2011 (Ferg, et. al., 2011). This tool has the potential to greatly reduce the operation time for setting plugs. The tool is a combination of perforation guns, a wash tool and cement stinger. The tool is called a PWC system. Before this tool can be used, a cement log needs to be run, because a successful operation requires a free section without cement or collapsed formation behind the casing.

2.6.1 Tool components and function:

At the bottom of the tool string there are 50 meters with tubing conveyed perforation guns with 12 shoots per foot (SPF) and a spacing of 35 degrees, as shown in Fig. 2.12. After the guns have been fired, they are dropped into a rat hole. Located above the perforation guns is a washing tool. The washing tool is activated by dropping an activation ball, which closes the bottom of the string, and directs the flow out between two wash cups. The wash cups seal off the borehole above and below the re-directed fluid flow, and forces it into the perforations. This allows for the cleaning of the formation behind the casing without doing any milling. When the washing process is completed, another ball is dropped to deactivate and release the tool. The wash cups on the washing tool have enough contact force with the casing that it will not move and can thus be used as a base for the plug. The last component of the PWC tool is the cement stinger. Prior to the cementing commences, the well is circulated with maximum loss free flow rate, to remove any material that is left behind after the washing operation. Now the plug is ready to be set as a balanced plug.

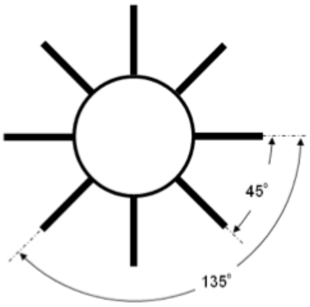

Figure 2.12: Phasing of perforating guns
(Ferg, et. al., 2011)

During the field trails the cement quality and sealing ability in the annulus were tested. This was done by drilling through the cement that was set inside the casing and conducting a cement log, which showed the quality of the cement behind the casing. The PWC tool allows a rig to set a plug in one single run, where the traditional methods need at least 3 successful runs to complete the same job. However, there are some issues with implementing this method offshore. The drill crews need to get the proper training. Procedures need to be developed. There will be some uncertainty of whether the cement in the annuli is good enough, and a risk of losses when washing through the perforations.

3.0 Fluids

In this chapter, some of the fluids that are involved during a P&A operation will be discussed, i.e. drilling fluids, preflushes/spacers and cement. The primary focus will be directed towards cement. Additives to control the behavior of cement will also be presented.

3.1 Drilling fluids

Drilling mud has the primary function to allow the operator to drill a well safe, fast and economically. This is achieved by:

- Establishing the correct well pressure to prevent collapse or fractures.
- Transporting drill cuttings to the surface
- Lubricating the string
- Cooling the drill bit
- Preventing influx of formation fluids
- Creating a mud cake to prevent loss of mud to formation
- Transmitting data via mud pulses

To be able to achieve this, the mud needs to be modified with additives, and some of these additives make the mud incompatible with cement.

Drilling fluids uses polymers to increase the viscosity to be able to transport cuttings to the surface. This, however, makes it hard to displace the mud when pumping cement, leading to fingering effects (channeling) and mixing of the fluids. Mixing cement with other fluids has the potential of changing the cement properties and risking a plug failure. An example may be the high concentration of calcium chloride and calcium hydroxide that is used in the aqueous phase in oil based mud (OBM). If this gets in contact with the mud it can accelerate the curing process, and might ruin the plug (Nelson & Guillo, 2006).

To be able to prevent mixing of cement and other fluids, several methods can be used. The two-plug method as mentioned in chapter 2.4.3.4 is a good option, another alternative is to use wash pills and/or spacers.

3.2 Preflushes/Spacers

The primary purpose for preflushes is to prevent the mixing of two fluids that are not compatible. This is done by pumping the spacer in-between the fluid that is going to be displaced and the fluid that is going to enter the well. It is usually done when changing from OBM to water based mud (WBM), or to separate mud from the cement. Preflushes should have the three following properties:

- Be compatible with both the mud and cement slurry
- Present optimal rheology and density under downhole conditions to ensure good mud displacement.
- Ability to clean solid surfaces and make it water wet to ensure good bonding for the cement.

The simplest form of preflush is fresh water, but to ensure a good mud displacement and cleaning of the walls dispersants and surfactants are usually added.

Still, when using one of these preventions to avoid contaminating the cement it is crucial that there is no fluid movement after the plug is set until it has built adequate strength.

3.3 Cement

Portland cement is widely used material all over the world. Its applications range from operations offshore as the most commonly used sealant in P&A, to all kinds of land-constructions (Nelson & Guillo, 2006). To handle the different conditions and requirements, the cement can be customized by adding different additives to adjust the properties. They will be addressed later on in this chapter.

Portland cement is categorized as a hydraulic cement. This implies that it develops strength due to hydration, involving a chemical reaction between water and cement compounds. A unique property of this type of cement that is the curing process does not only occur if the cement and water mixture is in contact with air, but also submerged in water. This property is crucial for setting cement plugs in offshore wells. Another quality with cement is that the development of strength is predictable, uniform, and relatively rapid. Its low permeability, high strength and ability to not get dissolved or harmed by water after hardening, makes it a regular choice for sealant of wells (Nelson & Guillo, 2006). However, it does not withstand high temperature and corrosive environments. There are also several cement parameters that affect the sealing properties that can go wrong such as: incorrect cement density, poor mud and filter cake removal, high permeable slurry, significant cement shrinkage etc. (Khalifeh et. al., 2013).

3.3.1 The manufacturing of cement

There are two basic methods for making the Portland cement; dry and wet method. Main minerals in Portland cement are calcium, silicon, aluminum and iron, which are provided mainly by limestone and smaller amounts of clay and sand (The Portland Cement Aassociation, 2013). In the dry method these are crushed and milled down to fine powder before being analyzed and proportioned into the right ratios. The mixture is then preheated before it is sent into a kiln, where the temperature reaches 1870℃. The temperature of the blend increases up to 1480℃, and it becomes partially molten. When these temperatures are met, calcium and silica react and forms calcium silicates. This is the primary compound of cement. The material that exits the kiln is called clinker, and is cooled down and grinded into an extremely fine powder, which is the Portland cement. The dry method is shown in Fig. 3.1 and Fig. 3.2. This method has during the last years become the main method, due to its heat efficiency. The wet method is distinguished from the dry method by the water added to the raw material before grinding, then pumping the slurry over the shakers that sorts out the oversized components to be re-grinned. The slurry is stored in large basins with agitators to keep the slurry homogenous. From the storage basins the slurry moves on to the kiln (Nelson & Guillo, 2006). An advantage with the wet method has been the control of mixing the raw material, but technology developments have also improved this for the dry method.

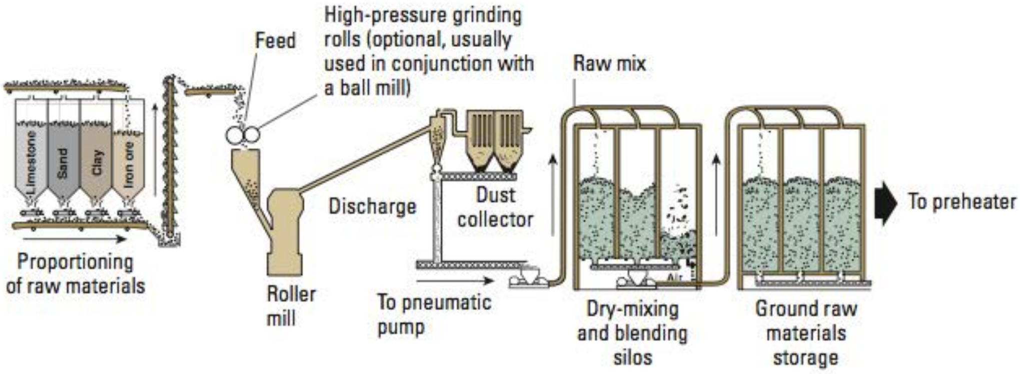

Figure 3.1: Part 1 of the dry method to create Portland cement (Nelson & Guillo, 2006)

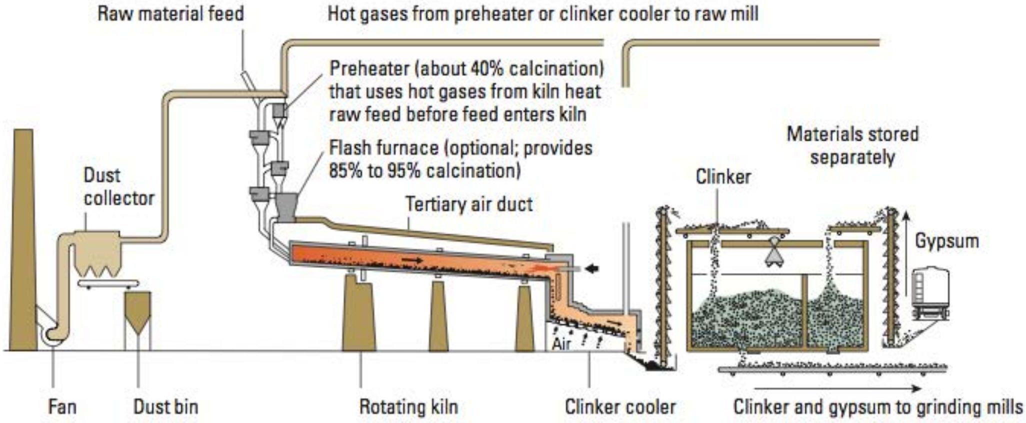

Figure 3.2: Part 2 of the dry method to create Portland cement (Nelson & Guillo, 2006)

The hydration and curing of cement is a complex process, with several chemical reactions happening simultaneously. Clinker components both dissolve and precipitate, leading to the thickening and strength build of the cement. The raw materials used to create the clinker differ from each time, which results in different kinds of oxide ratios, which again affects the hydration process differently. Nevertheless, temperature is the single most important parameter that affects the hydration process. By increasing the temperature the hydration will increase, giving a shorter setting time, which also reduces the maximum strength (Nelson & Guillo, 2006).

3.3.2 Additives to cement

Portland cement is a highly used sealing agent in oil and gas wells. The wells may vary from shallow to deep geothermal wells. Here the pressure may vary from surface pressure, up to 29 000 psi, and temperatures range from several minus to 350℃ (Nelson & Guillo, 2006). This requires different properties from the cement allowing the cement to set at the right place at the right time. It also needs to be able to keep its integrity over the defined time period of the abandonment. There are currently hundreds of additives that can help change and modify the cement properties to achieve a successful plug placement under all these different conditions. The additives can be categorized into eight main categories, which will be briefly discussed:

3.3.2.1 Accelerators

Accelerators are chemicals that speed up the strength development and also reduce the setting time of the cement. It can be used to counter out the effects of other additives that might retard the curing process. Inorganic salts work as accelerators, and chloride is the most commonly used. Different salts work as accelerators at different concentrations, e.g. NaCl works as an accelerator up to 15%, above 20% it has a retarding effect. Na_2SiO_3 (water glass), NaOH and KOH are well known accelerators. (Nelson & Guillo, 2006)

3.3.2.2 Retarders

The retarder delays the curing process. It is still unclear what mechanism that makes accelerators accelerates and retarders delay the curing process (Nelson & Guillo, 2006). But for retarders the essence in all the main theories is that salts are dissolved and react, get absorbed and prevent the hydration process. Examples of the most commonly used retarders are the sodium and calcium salts of lignosulfonic acids.

3.3.2.3 Extenders

The two main functions of an extender are to reduce the density of the cement and to reduce the amount of cement per volume. Reducing the density will reduce the hydrostatic pressure in the well during cementing. This decreases the risk of fracturing and loss, and allows the cementing operation to be performed in fewer stages. By reducing the amount of cement per volume, the total amount of cement needed is reduced, making process more economically efficient.

Extenders are divided into three groups: Water based, low-density based and gaseous based. Water based extenders are clays and other water viscosifying agents that bind more water to the cement system. Low-density extenders are based on materials that have a lower density than the cement ($3.2 g/cm^3$). Adding large amounts of this material will give the desired effect. Gaseous extenders are based on using nitrogen or air to create foamed cement with very low density.

Pozzolan might be one of the most important group of extenders. These have little or no cementitious properties, but when in contact with water react with calcium hydroxide ($Ca(OH)_2$) and form compounds that have cementitious properties. When 100kg of cement hydrates, about 22kg of free $Ca(OH)_2$ are liberated (Nelson & Guillo, 2006). $Ca(OH)_2$ has low effect on building strength, but when dissolved and removed by water that is in contact with the cement, it will lead to a reduction of the cement strength. When pozzolans are present, this will stop the escape of $Ca(OH)_2$ and create a stable and very durable compound with low permeability (0.001 mD). This in turn protects against corrosive fluids. One type of artificial pozzolan used during this work is micro silica, which is further explained in Ch. 4.1.4.

3.3.2.4 Weighting agents

To prevent a well from collapsing, or reduce the risk of fracturing, the pressure is the key parameter to control. For deeper wells, the pore pressure and collapse pressure is increased, which requires heavier fluids than for shallower wells. The mud weight during drilling of these wells can exceed 2.16 g/cm^3. The cement must therefore be of the same magnitude. One method used to increase the density of the cement would be to reduce the amount of water, since water pulls the cement slurry density down. But the maximum achievable density by reducing the water amount is 2.16 g/cm^3, so this is not always sufficient. By using this method the fluid-loss control, slurry rheology and solid settling will often change for the worse, which in some cases is unacceptable, and may lead to slurry bridging, and non-uniform slurry properties. A preferable alternative is to use weighting agents to increase the density. It is important that the weighting agents have the same particle-size distribution, have a low need for water, and must not be affected with the hydration process within the cement. They must also be compatible with the other components in the cement slurry. Common weighting agents in cement are barite, ilmenite and hematite where the densities vary from 4 – 5.3 g/cm^3 (Society of Petroleum Engineers, 2012).

3.3.2.5 Dispersants

Cement slurries have a high concentration of suspended particles and can have a solid volume fraction up to 0.7. This makes the slurries very viscous, which again can cause problems during the placement of the cement. To get the right rheology and viscosity, dispersants can be added. Some of the most commonly used dispersants are lignosulfonates and hydroxycarboxylic acids. The problem with these is that they have a powerful retarding effect as well. Polynaphtalene sulfonate is the mostly used dispersant in well cementing, but due to its toxicity to algae it is being less used in some marine environments.

3.3.2.6 Fluid-loss control agents

When a cement plug is to be set in a permeable zone under pressure, there will be a fluid flow from the cement slurry and into the formation, also known as fluid loss (Nelson & Guillo, 2006). If this rate is too high and not stopped, severe problems may be caused. The solid to liquid ratio increases, increasing the density of the slurry. With a sufficiently high density it might cause problems in pumping the cement further down. Also, the design properties of the slurry will change and may ultimately cause failure of sealing of the well. To prevent this, fluid-loss control agents are added. These agents may increase the viscosity of the aqueous phase in the cement slurry, make the filter cake on the bore wall less permeable, or both.

The most commonly used groups of fluid-loss control agents are particular (bentonite, carbonate powder, micro silica, asphaltenes), and water-soluble polymers; both natural and synthetic. The particular agents are often fine particles that infiltrate the filter cake and reduce its permeability, while the polymers both increase the viscosity and prevent the flow through the filter cake.

3.3.2.7 Lost-circulation control agents

During cementing, lost circulation may cause severe problems. This may occur in weak, high permeable or fractured zones. To avoid this, from happening lost-circulation control agents with good bridging properties are used to increase the strength of the zone and block pores. Examples of good bridging agents are gilsonite and granular coal. If the slurry enters a cavernous zone that is too big to prevent lost circulation with bridging, thixotropic cement can be used. When this slurry enters the formation, it will no longer be subjected to shear, as a result it gels and becomes self-supporting. Eventually, the thixotropic cement plugs the lost circulation.

3.3.2.8 Specialty additives

In addition to all the previous mentioned additive groups, there are still many materials that do not fit under any of these groups. Examples are anti-foaming agents, fibrous materials to increase the resistance against stresses and distribute local stresses more evenly, radio-active tracing agents to easier locate the plug, and mud decontaminants to reduce retarding of the slurry if mixed with drilling fluids. All these are gathered in the specialty additives group.

4.0 Geopolymer

Industries all over the world are experiencing growth, which leads to growing pollution. Large industries as the metal melting industry and electrical power plants produce several million tons of waste products every year (Khale & Chaudhary, 2007). These by-products are often hazardous and need to be disposed at landfills, which is expensive for the foundries, and may pollute ground waters. It would therefore be beneficial to re-use some of the by-products in other products.

A product that might do just that is the geopolymers, which is currently under great development. It is an inorganic polymer, usually lacking both hydrogen and carbon atoms. By using geopolymerization, materials that do not have any cementitious properties may react with each other and build strength. (Duxson, et. al., 2006). Joseph Davidovits first invented and developed geopolymerization in the late 1970’s. The raw materials for creating geopolymers are mainly rock forming minerals of geological origin. The geopolymers can be considered to be amorphous feldspars, but is synthesized as thermosetting organic polymers. He therefore coined the new material ”geo”polymers.

Geopolymerization is a geosynthesis that involves naturally occurring aluminum-silicates (Al – O – Si) (Khale & Chaudhary, 2007). Any pozzolanic material or source of silica and alumina, which is mixed with an alkaline solution, acts as a precursor for geopolymers. Examples of ingredients with silica and/or aluminum content that may be used in geopolymers are by-products as fly ash, micro silica, Blast Furnace Slag (BFS). Geopolymerization can be divided into separate stages as shown in Fig. 4.1 (Duxson, et. al., 2006). The first stage is when the aluminum-silicates are dissolved by alkaline hydrolysis (consuming water) from an alkaline solution e.g. sodium hydroxide and potassium hydroxide. The alkaline solution is known as the activator that triggers the geopolymerization. The dissolution of the aluminum-silicate source releases both aluminum and silicates into the solution. At high concentrations they form a gel. During the next steps reorganization, crystallization and release of water occurs. Large three-dimensional chains with aluminum-silicates that are connected with co-valent bonds in a complex and integrated network forms, and build its strength. They are structurally comparable to those that build natural rocks and they form the building blocks of geopolymers.

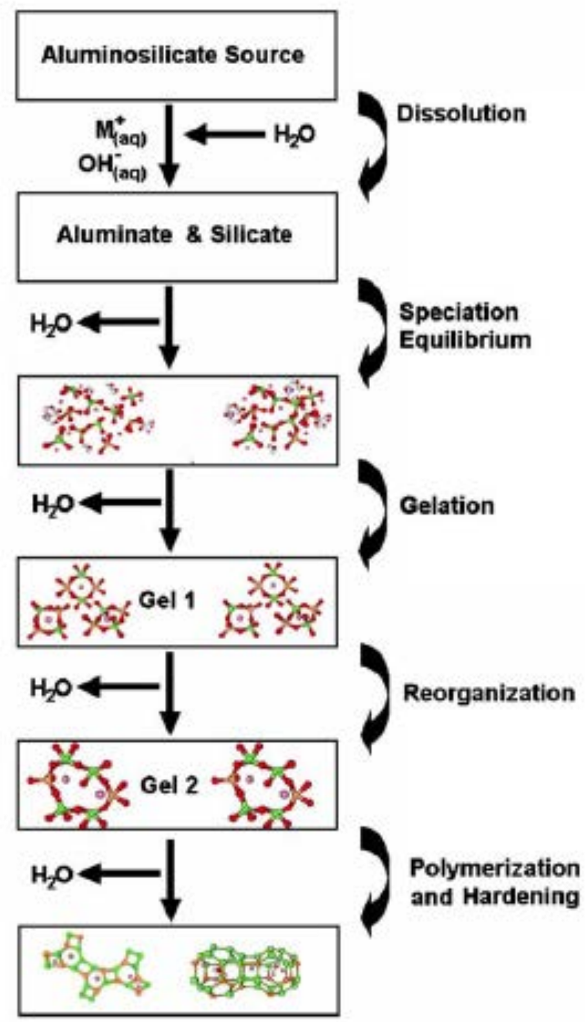

Figure 4.1: Conceptual model for geopolymerization (Borrowed from: Duxson, Fernandez-Jimenez, Provis, Lukey, van Deventer & Palomo, 2006)

The geopolymer cement is a binding system that can build strength and harden at room temperature. It reduces the carbon footprint and is more resistant to many of the durability issues that can plague conventional concretes (Davidovits, 2013). Geopolymer cement can now be used as an alternative to regular Portland cement, and is used in building roads, construction and offshore operations. There are several influencing parameters for geopolymerization:

- Temperature is an important parameter affecting the strength of the geopolymers. Several researches have shown in different experiments that an increase in temperature increases the strength and reduces the curing time. An elevated temperature favors the dissolution of the reactive species mainly, that of slag and fly ash (Khale & Chaudhary, 2007).

- Curing time is another factor that affects the total strength of geopolymers. A prolonged curing time will often increase the strength (Khale & Chaudhary, 2007). However, compressive strength may decrease if the geopolymers are exposed to an elevated temperature for a longer period. This could break the granular structure in the geopolymers leading to dehydration and shrinkage.

- The concentration of the alkali solution also plays an important role in the geoplymerization. The higher concentration of hydroxide ions in the solution the more soluble aluminum-silicates are, yielding higher strength (Khale & Chaudhary, 2007). However, when the concentration becomes too high excess alkali ions in the framework might reduce the total strength. Observations have also shown that a pH in the range of 13-14 is preferable for high strength of geopolymer cement.

- Solid-Liquid Ratio (SLR) has a similar effect on geopolymers as on cement. An increased amount of water leads to reduced compressive strength.

- Silicate/aluminum ratio is also important for compressive strength. A high content of highly soluble silicate is important to create aluminum-silicates that can create good interparticle bonding and physical strength (Khale & Chaudhary, 2007). A silicate/aluminum ratio 3.16 – 3.42 showed in experiments conducted by Khale and Chaudhary had good compressive strength.

4.1 Materials

In the experimental part the following ingredients have been used to create geopolymer cement: Blast Furnace Slag (BFS), metakaolin, aplite, micro silica, KOH, NaOH, water glass, and as a mixing agent distilled water. These will be mentioned now in more detail, to give a better understanding of why they are being used in the recipes. Where all the materials have been produced/bought can be found in the Appendix A.

4.1.1 Blast Furnace Slag

BFS is a byproduct created during the processing of iron ore into pig iron. This is done in a blast furnace by burning a fuel (charcoal or coke) to heat up air that is blasted into the furnace. Silica and aluminum then combines with limestone or dolomite and magnesia forming a molten slag with temperatures up to 1 550°C (Nelson & Guillo, 2006). Since the density of molten iron is much higher than the slag, the iron can be collected at the bottom of the furnace. BFS has normally been treated as a waste product but is in later years especially from the 1990s been used more as an additive in cement. The slag is molten when removed from the furnace. Depending on the cooling method used different slag products are formed (Federal Highway Administration, 2012). These products include Air-Cooled Blast Furnace Slag (ACBFS), foamed slag and Granulated Blast Furnace Slag (GBFS). The main composition of a typical BFS is presented in Table 4.1 (Emery, 1992).

Table 4.1: Composition of Blast Furnace Slag (Borrowed from Federal Highway Administration, 2012)

Components	Percent	
	Mean	**Range**
Calcium Oxide (CaO)	39	34-43
Silicon Dioxide (SiO_2)	36	27-38
Aluminum Oxide (Al_2O_3)	10	7-12
Magnesium Oxide (MgO)	12	7-15
Iron (FeO or Fe_2O_3)	0.5	0.2-1.6
Manganese Oxide (MnO)	0.44	0.15-0.76
Sulfur (S)	1.4	1.0-1.9

ACBFS is formed by simply allowing the molten slag to cool down to ambient temperature. This is a slow process, so the amount of ACBFS that can be handled at a furnace can limit the iron production. GBFS is created by abruptly cooling down the slag with water jets, making it glassy without crystals. The result by milling or crushing GBFS is a fine powder with cementitious properties. However, in comparison to cement that only needs water to get activated, BFS needs an activator like NaOH, KOH or Sodium Carbonate also known as Soda ash (Na_2CO_3) to be able to build strength. It can also be used as a suitable partial replacement for Portland cement or just as an additive (Nelson & Guillo, 2006). This is also one of the reasons that GBFS is becoming the primary slag handling method.

When using BFS slag as cement or mixed with Portland cement it gains some properties such as better sulfate resistance, slower diffusion of chloride and alkali ions through the cement matrix, and a lower permeability (Nelson & Guillo, 2006). The reason for the added properties is the change in the microstructure in the cement matrix. By adding 75% of BFS in the Portland cement mixture the total porosity can be reduced by up to 30%. This is due to the reduced amount of portlandite crystals, which are large crystals that creates bigger pores. In geopolymers, BFS acts as absorbents for free water, due to its high content of CaO. It also gives a higher acid resistance (Khale & Chaudhary, 2007).

4.1.2 Metakaolin

Metakaolin is the product of calcination of the clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$). This can be done by heating the clay mineral to 500 – 800 ℃. If this is done correctly the result is Metakaolin, a very pozzolanic material. During calcination the crystalline structure is changed into an amorphous structure that stores larger amounts of energy and increases their reactivity (Khale & Chaudhary, 2007). Calcination also affects the amount of aluminum and silica that are released from source materials during geopolymerization. If the temperature goes above the dehydroxylization point the kaolinite gets sintered and becomes mullite, which is dead burnt and not reactive. Kaolinite is the main mineral in kaolin clay. Its primary used in the recipe for its aluminum content, which is important to build a correct and strong geopolymer structure. The metakaolin used in the experiments was calcined in an oven at a temperature of 750°C for 6 hours and used 6 hours to cool down.

4.1.3 Aplite

Aplite is an igneous rock with quartz (SiO_2) and feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) as its dominant minerals, and is quite similar to granite in composition (SandAtlas, 2013). The full composition is presented in Table 4.2. The magma that formed the aplite had a high rate of heat loss, which results in a short crystallization time. This is the reason that it is so fine grained compared to granite. Aplite is an intrusive rock and forms often dykes and threads in other granitic bodies. To be able to use aplite in geopolymer cement the rock needs to be grounded into fine sand. It is the aluminum and silica content, and the pozzolanic properties, which make this rock a good ground component for creating geopolymer cement.

Table 4.2: Aplite composition (Harestad, 2012).

Formula	Percentage
SiO_2	83.4
Al_2O_3	8.29
Fe_2O_3	0.9
CaO	0.92
MgO	0,06
Na_2O	2.16
K_2O	2.86
Loss on ignition	0.8
Other	0.61

4.1.4 Micro silica

When coal is burned in a furnace some by-products that are non-combustible is made. Some of it is ash that remains on the bottom, therefore the term bottom ash, while the rest are elevated by the flue gases (MP BioMass, 2013). The latter is called fly ash, and can be captured by electrostatic precipitators before the flue gases reach the chimneys. Fly ash is the most commonly used additive in cements and has normally no cementitious properties alone. So, if not in presence with a cementing agent, it needs a chemical activator, which will lead to the formation of a geopolymer and strength. Fly ash has a high silica content, but contains also aluminum, iron and sulfur oxides.

Micro silica also known as silica fume is a byproduct of the silicon and ferrosilicon alloy production in electric furnaces (Federal Highway Aadministration, 2011). It is an ultrafine powder of high silica content, which is a much purer product than fly ash, with similar properties. In previous years the fume was released into the atmospheres, but after environmental requirements was imposed, the fume was collected and dumped in land fillings. This gave the economic potential to use it in other applications like additives in cement. Micro silica has been found to improve compressive strength, bond strength and abrasion resistance, with its small particles it reduces permeability. The composition of micro silica can be seen in Table 4.3.

Table 4.3: Composition of micro silica

Formula	Name	Percentage
SiO_2	Silica	Min. 95.5%
Fe_2O_3	Iron oxide	Max 0.3%
Al_2O_3	Aluminum oxide	Max 0.7%
CaO	Calcium oxide	Max 0.4%
MgO	Magnesium oxide	Max 0.5%
K_2O	Potassium oxide	Max. 1%
Na2O	Sodium oxide	Max. 0.4%

4.1.5 Potassium hydroxide and sodium hydroxide

Potassium hydroxide (KOH) and sodium hydroxide (NaOH) are alkali salts and inorganic compounds. They are often used in liquid form, and are both strong bases. Compared to NaOH, KOH is a slightly weaker base. Jawed & Skalny proved in 1978 that alkalis had an effect on the hydration process. They saw a positive effect on the early strength in setting of Portland cement, but a reduction in the long term strength. The primary alkalies in cement are sodium and potasium. These have a tendency to be unstable, and are therefore kept bellow 1% (Nelson & Guillo, 2006). To be able to activate the silica and aluminium in the recipe and create geopolymers, a strong alkali activator is needed (Khale & Chaudhary, 2007). In this case the activators used have been KOH and NaOH as well as water glass.

4.1.6 Water glass

Water glass is often known as sodium silicate with the molecular formula of Na_2SiO_3. However, the formula may vary depending on the ratio of sodium oxide (Na_2O) and silica (SiO_2) (Chemicalland21, 2013). Water glass is used in this thesis as an activator in aqueous solution, but is also available in solid form. Sodium carbonate and silicon dioxide is heated up to above 1000 ℃ in a furnace, which makes them both molten. They will now react with each other, creating water glass and release CO_2 as seen in Eq. 4.1:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \qquad (4.1)$$

This method has been used since the 19th century. When water glass dissolves in water it produces an alkaline solution, which is glassy and colorless. Sodium silicate can also be prepared directly into a liquid phase by dissolving silica sand in an aqueous solution of sodium hydroxide under high pressure. Eq. 4.2 shows the reaction that now occurs:

$$2NaOH + SiO_2 \rightarrow Na_2O{\cdot}SiO_2 + H_2O \qquad (4.2)$$

Water glass is used in many different industrial products because of its convenient source of sodium. It is used in laundry detergents, as a flocculent in water-treatment plants, and many other applications. In this thesis it was used as an activator with its alkali properties. It will react under acidic conditions and form a hard glassy gel that is useful as a bonding agent in cement.

4.1.7 Water

For all our mixtures distilled water was used. It is important for the hydration process and as a mixing agent in the slurry. In the recipes water is found in the KOH, NaOH and water glass solutions, but can be added in pure form to decrease the viscosity and to be better able to mix all the ingredients to an uniform slurry.

4.2 Why use geopolymers instead of Portland cement?

During the production of clinker to create the Portland cement the reaction shown in Eq. 4.3 occurs, when calcium carbonate is calcinated.

$$5CaCO_3 + 2SiO_2 \rightarrow (3CaO,SiO_2)(2CaO,SiO_2) + 5CO_2 \qquad (4.3)$$

This creates large amounts of CO_2, just from the process of creating clinker. In addition to these large amounts of CO_2 is also created during the combustion of the carbon-fuels to heat up the kiln. Davidovits estimates that for each ton of Portland cement 900kg of CO_2 is also created in the process. On the other hand geopolymer cement does not rely on calcium carbonate ($CaCO_3$), and therefore does not generate the same amount of CO_2 as regular Portland cement. The reduction may range all the way from 40 – 90%. The world today uses approximately 3 billion tons of Portland cement each year, which is a considerable part of the total emission of greenhouse gasses. So by developing the geopolymer cement, it would greatly reduce the impact on the environment.

Since several ingredients in the geopolymer cement can be waste products from other industries, this greatly reduces the price of this type of cement. This can have a large impact on P&A, but also all other operations that requires cement due to the large amount that is needed.

Also when it comes to energy needed to create geopolymer cement vs. Portland cement the geopolymer comes out on top. Since it uses by-products from the industry (BFS, fly ash, micro silica), this reduces the energy needed to create the cement with up to 59% (Davidovits, 2013).

Today standard Portland cement is used to immobilize toxic and radioactive metals. The cost of this is quite large, and is thus another field where geopolymers may be used with large benefits (Khale & Chaudhary, 2007). There have not been done much research on this application of geopolymers. However, the work that has been done shows that geopolymers have properties that might be far superior compared to standard Portland cement when it comes to leach rates.

5.0 The Experiment

5.1 Experimental Equipment

During this work both an Ultrasonic Cement Analyzer (UCA) and an Uniaxial Compressive Strength (UCS) tester were used to determine the strength of the different recipes.

5.1.1 Ultrasonic Cement Analyzer

A UCA from Halliburton Services was used to measure the strength of the different slurries that was mixed (Halliburton, Cementing: Innovative Cement Enhancements, 2008). The UCA sends ultrasonic sound waves through a cement sample. The sender is placed on top of the cylindrical sample that is placed inside the UCA, while the receiver is located at the bottom. The transit time to the sound waves are proportional to the compressive strength of the material. Correlations on the computer give the estimated strength at a given time.

Figure 5.1: Container that is used in the Ultrasonic Cement Analyzer

The sample is placed in a sample holder (See Fig. 5.1) and into the UCA just after being mixed. By continuously sending ultrasonic waves through the sample, gives information on curing time, maximum strength, and the early strength build up. This is important for the WOC time, since the cement needs to have certain strength before the operation can continue. The strength that is required will depend on what type of operation that is taking place. The curing time of the cement, however, needs to be customized to the well length and depth, so that the cement does not start to set before it has been properly placed. Adding retarders or accelerators can customize the setting time as mentioned in Ch. 3.3.2.1 and 3.3.2.2.

To be able to simulate the conditions that are at setting depth in the well the UCA is equipped with an internal oven that can regulate the heat. The UCA is also connected to a compressor making it possible to get a desired pressure on the sample. During these experiments a temperature of 88℃ (188℉) and a pressure of 358.5 bar (5200 psi) were used. The UCA that was used is a machine from Halliburton and can be seen in Fig. 5.2.

Figure 5.2: Halliburton: Ultrasonic Cement Analyzer

5.1.2 Uniaxial Compressive Strength

To verify the results found in the UCA, UCS tests were done on the same recipe. A Toni Technic was used to perform the UCS tests, the Toni Technic has a strength limit at 3000kN. The machine can be seen in Fig. 5.3. By doing so the strength curve found by the UCA can be confirmed. Several samples of a given recipe must be made. It is important that the top and bottom of the samples are flat. With only small uneven areas the load on the sample will not be uniform and the results will not be accurate (Technical Research Institute of Sweden). During the UCS test each sample is put under increasing axial load until it fails. This gives good mechanicle strength measurements.

Figure 5.3: Toni Technic: Uniaxial Compressive Strength machine

5.2 Mixing Procedure

The different ingredients in the recipes were weighed using an electronic weight, and mixed in the following order:

Add solids:
- Aplite
- Metakaolin
- Micro silica
- BFS

Add liquids:
- KOH or NaOH
- Water glass
- Distilled water (if needed)

Mix with a “Waring Commercial Laboratory Blender” on mixer level: High. Do so until the recipe is uniformly mixed. Use a spoon if necessary to ensure that there is no residual solids in the bowl. In recipes number: 106-110 and 113 a “Hamilton Beach Scovill” mixer was used at mixer level: Medium.

Note that some of the recipes have a short setting time, and it is therefore important that they are quickly put into the designated container after it has been mixed.

5.3 Experimental conditions

Several experiments were carried out in order to find the recipe with the highest compressive strength. An UCA was used to measure the instantaneous strength development during curing. After a UCA experiment was conducted, adjustments were made to the recipe, to improve the measured values. The obtained data from the UCA can be found in Appendix B. These data sheets contain time versus temperature, transit time and compressive strength. UCS tests were performed to verify the obtained results from the UCA for the recipe with the highest compressive strength. The data sheets for these tests are found in Appendix C.

5.3.1 The recipes

In this section all the recipes are presented and arranged into two tables. In Table 5.1 all the different recipes used in the UCA testing are gathered. The main changes between the recipes are from recipe no. 72A when micro silica first was used, from no. 94 the 4M KOH was substituted with 8M NaOH, which is marked with ^{1} in Table 5.1. Metakaolin was omitted from recipe no. 96 and the amount of alkali solution was also reduced by almost two thirds. The new BFS was introduced in recipe no. 102, which is therefore marked with ^{2}. Distilled water was only used in sample no. 68 to lower the viscosity.

The formula used to calculate Solid Liquid Ratio (SLR) can be found in Appendix A.

Table 5.1: Recipes for Ultrasonic Cement Analyzer experiments

Test no.	68	72A	72B	80	94	96	98	102
Aplite	475.7g	238.3g	239.1g	239g	237.4g	243g	244g	243.1g
Metakaolin	146g	72.5g	73g	80g	73.1g	0g	0g	0g
4M KOH	342.1g	200.8g	203.3g	236.3g	203.2g^1	73.2g^1	75.1g^1	72.8g^1
Water glass	66.95g	59.4g	58.3g	66.4g	58.3g	73.1g	74.7g	72.7g
Micro silica	0g	37.9g	37.9g	38.1g	37.7g	35.2g	34.8g	35.4g
BFS	133.1g	66.5g	66.4g	67g	66.9g	121.5g	121.6g	121.6g^2
Dist. water	30.5g	0g	0g	0g	0g	0g	0g	0g
SLR	1.71	1.60	1.59	1.40	1.59	2.73	2.67	2.75

In Table 5.2 all recipes are basically the same as no. 102. Some of them are multiplied to provide a larger slurry volume, allowing several samples from the same recipe. Recipe no. 106-110 were prepared for UCS testing. Samples no. 103, 105 and 114 were sent to an external lab in Trondheim, Norway where they were tested for porosity, permeability and durability in a corrosive environment. The results of these tests are not included in this thesis.

Table 5.2: Recipes for UCS tests and external lab

Test no.	103	105	106	107	108	109	110	114
Aplite	244.2g	488.4g	366g	244.5g	244.3g	244.5g	244.5g	366g
8M NaOH	75.5g	149.9g	112.6g	75g	74.9g	75.0g	95.9g	112.7g
Water glass	74.7g	149.8g	112.8g	75.2g	74.9g	75.3g	95.7g	112.6g
Micro silica	34.8g	69.7g	52.2g	34.9g	34.8g	34.9g	34.9g	52.2g
BFS	121.6g	243.2g	182.4g	121.7g	121.7g	121.7g	121.7g	182.4g
Cement	0g	0g	0g	0g	0g	110.3g	110.3g	0g
SLR	2.67	2.67	2.66	2.67	2.68	3.40	2.67	2.67

5.3.2 Ultrasonic Cement Analyzer results

In the following sections the results from the individual experiments will be presented with a graph where compressive strength development measured in psi is plotted against time in hours. The UCA tests were conducted at 88°C and a curing pressure of 5200 psi +/- 100 psi. To get a more detailed look at the first five experiments, the y-axis (compressive strength) has been set to a range from 0-600 psi. The last three experiments exceed these values, and therefore have a range off 0-4000 psi. To get a better comparison of all the experiments, the more detailed data sheets can be found in Appendix B.

5.4 Results

Aplite no. 68:

The first test was run as a pre-test. In Fig. 5.4 the strength development measured in psi is presented. The recipe started to build strength immediately, and had a very slow increase of strength during the curing time. 50 psi was reached after just 2 min, but the recipe had only reached a final strength of 216 psi when the test was ended after 171 hours. The strength, however, increased at a higher rate after 144 hours and until the test ended. Table 5.3 shows some key data from the graph.

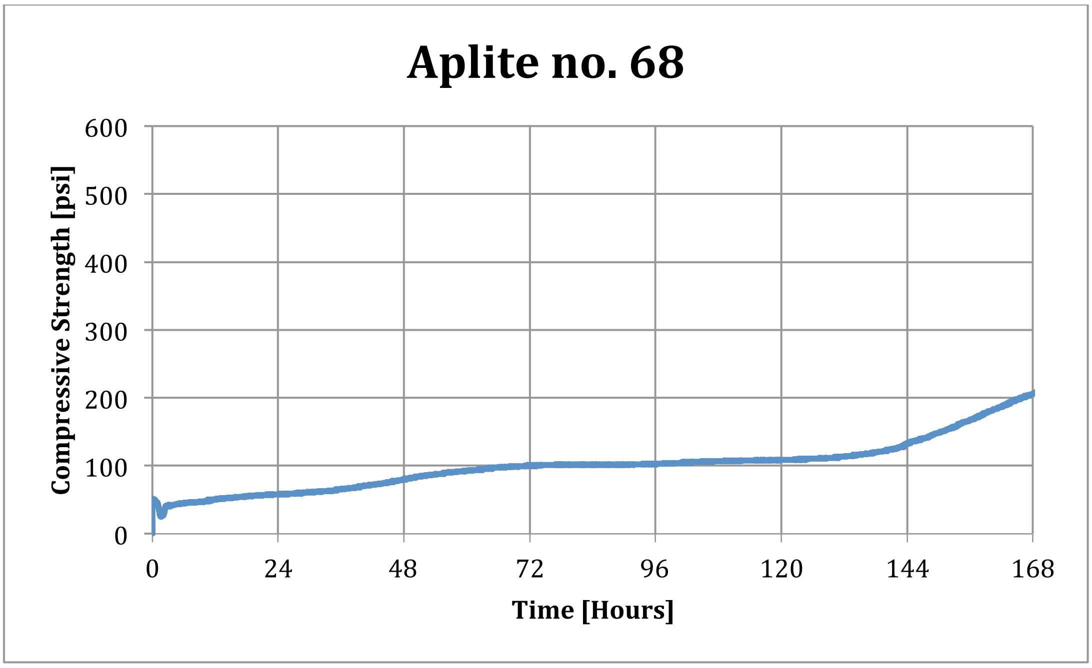

Figure 5.4: Compressive strength of aplite no. 68 measured by UCA at 88°C and 5200 psi

Table 5.3: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	216	28	216
Transit [µs/in]	14.00	13.60	12.67	13.77	12.67
Temperature [°C]	23	24	89	89	89
Time [HH:MM]	0	2min	171:15	1:55	171:15

The remaining slurry from recipe no. 68 was used to make a sample that was cured at atmospheric pressure and room temperature. A picture of the sample is shown in Fig. 5.5. The sample is facing bottom up. The top surface was much darker and harder than the rest of the sample, which might be due to oxidation. The sample was soft enough to be scratched using the fingernail. The sample broke during cutting with a diamond blade cutter, when it was being prepared for UCS test, due to its low strength, and could not be tested.

Figure 5.5: Picture of atmospheric sample of recipe no. 68

Aplite no. 72A:

Test no. 72A was the first test whereas micro silica was added to the recipe. This was done to increase the SiO_2/AlO_3 ratio, to increase the maximum strength. The strength started to build after about 2 hours as seen in Fig. 5.6. It had a rapid increase in strength and reached 50 psi after almost 3 hours. 500 psi was achieved after 27 hours. From the graph it looks like the strength was about to stabilize at about 580psi. But due to leakage in the pressure supplier the test data are not reliable after 72 hours where strength of 558 psi was reached. All the key features from the graph are listed in Table 5.4.

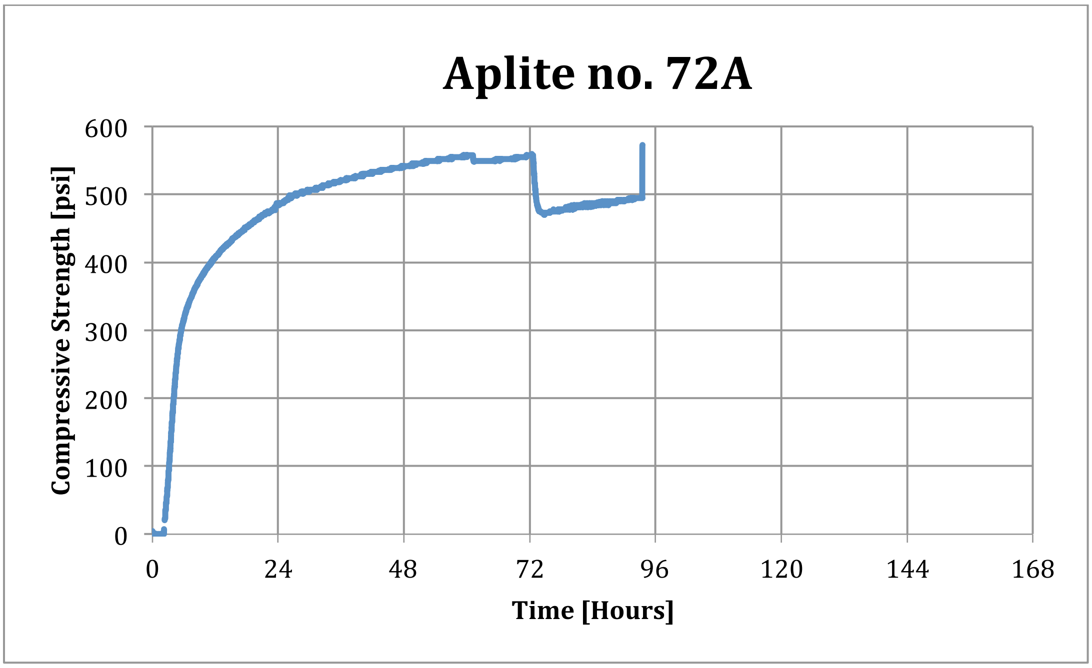

Figure 5.6: Compressive strength of aplite no. 72A measured by UCA at 88°C and 5200 psi

Table 5.4: Key features taken from the original data sheet found in Appendix B

	Onset	50psi	500psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	500	558	0	558
Transit [µs/in]	13.41	13.14	11.44	11.29	13.43	11.29
Temperature [°C]	90	89	89	89	90	89
Time [HH:MM]	2:13	2:41	27:12	72:30	2:04	72:30

Aplite no. 72B:

This test was done to confirm the results from test no. 72A, and to see the further strength development. The graph in Fig. 5.7 shows that the onset was after approximately 2 hours. It reached 50 psi in less than 3 hours. Maximum strength was 444 psi after 143 hours, but a decline in strength was observed after 144 hours. When the test ended after 167 hours the compressive strength was 302 psi and the strength was still declining. Key features from this experiment are presented in Table 5.5.

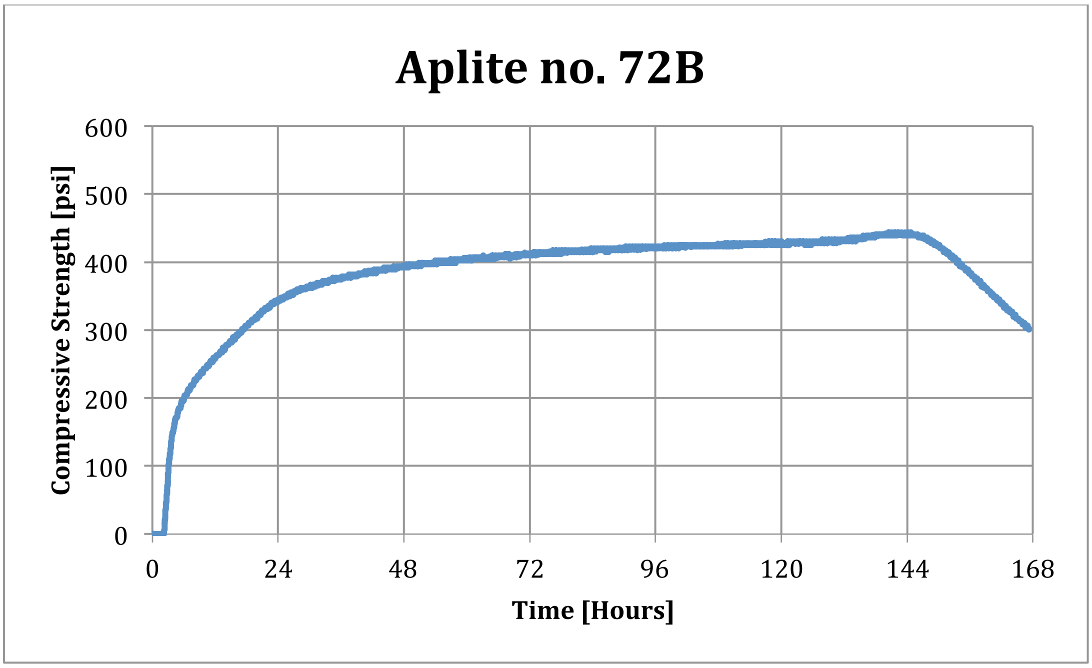

Figure 5.7: Compressive strength of aplite no. 72B measured by UCA at 88°C and 5200 psi

Table 5.5: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	444	0	302
Transit [μs/in]	13.36	13.06	11.55	13.55	11.98
Temperature [°C]	89	89	89	89	88
Time [HH:MM]	2:13	2:41	142:50	1:50	167:00

The remains of slurry no. 72B was used to make a sample that cured at atmospheric pressure and room temperature. When the sample was being cut with a diamond blade cutter before UCS testing after it had cured for 9 weeks it crumbled due to its low strength.

Aplite no. 80:

The changes made to the recipe from experiment no. 72B to no. 80 is a small increase in the amount of metakaolin, KOH and water glass, which reduced the SLR from 1.59 to 1.40.

From Fig. 5.8 it is apparent that the recipe started to build strength after 2.5 hours. 50 psi was reached after 3 hours, and a maximum strength of 388 psi after 90 hours. Afterwards, compressive strength started to decline until it reached a local minimum at 163 psi after 139 hours before increasing till the test was ended after a total of 168 hours. The final strength was 214 psi. All the key numbers are gathered in Table 5.6, and the original UCA file is found in Appendix B.

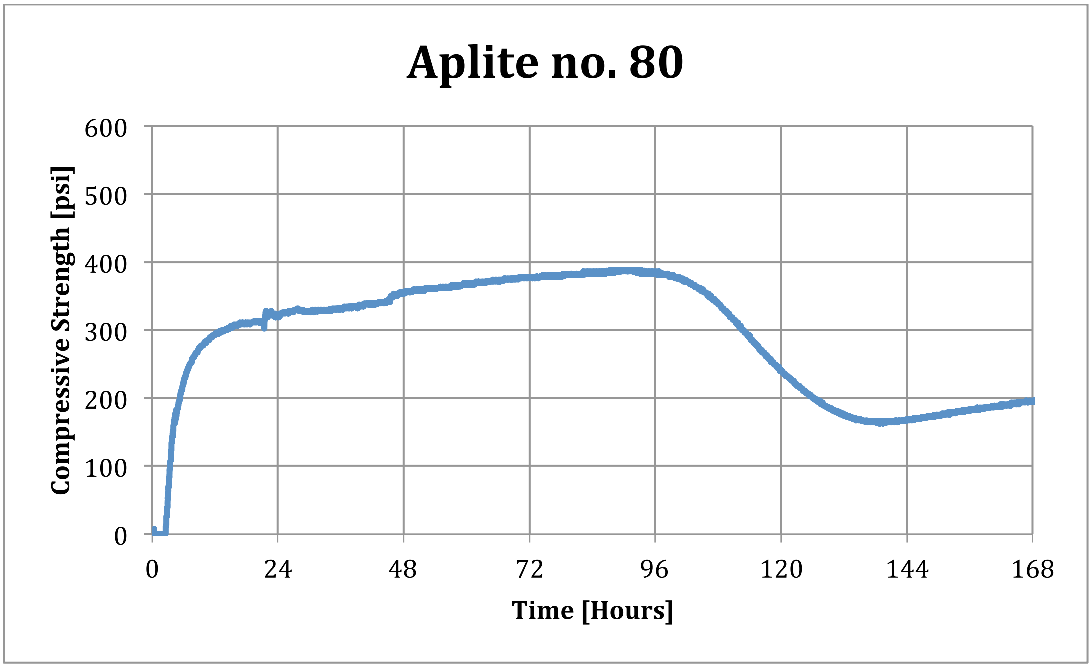

Figure 5.8: Compressive strength of aplite no. 80 measured by UCA at 88°C and 5200 psi

Table 5.6: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	Max strength	Local low	Curing temp reached	End point
Strength [psi]	0	50	388	163	0	214
Transit [µs/in]	13.57	13.24	11.79	12.63	13.85	12.42
Temperature [°C]	89	89	89	89	89	89
Time [HH:MM]	2:30	2:57	90:30	138:47	1:59	190

Aplite no. 94:

Recipe no. 94 was almost identical to no. 72A-B, with the exception that 8M NaOH replaced 4M KOH. This was done to find effect of different type of alkali solutions on strength as Khale and Chaudhary (2007) concluded in their work, that an increase in concentration of the alkali solution would help to increase the total strength of the geopolymer cement to a certain point. However, it makes the slurry less user-friendly, but the main goal was to find the recipe that builds the highest compressive strength.

The graph in Fig. 5.9 shows that the onset of recipe no. 94 was less than 2 hours. The 50 psi point was reached after 2.5 hours. The maximum strength was 390 psi, but then it declined to 46 psi. A small increase in strength is witnessed in the end. But due to a power shut down at the laboratory the test results after 56 hours are not reliable and the test was ended, with a strength of 63 psi. Key features from the original graph are found in Appendix B and are presented in Table 5.7.

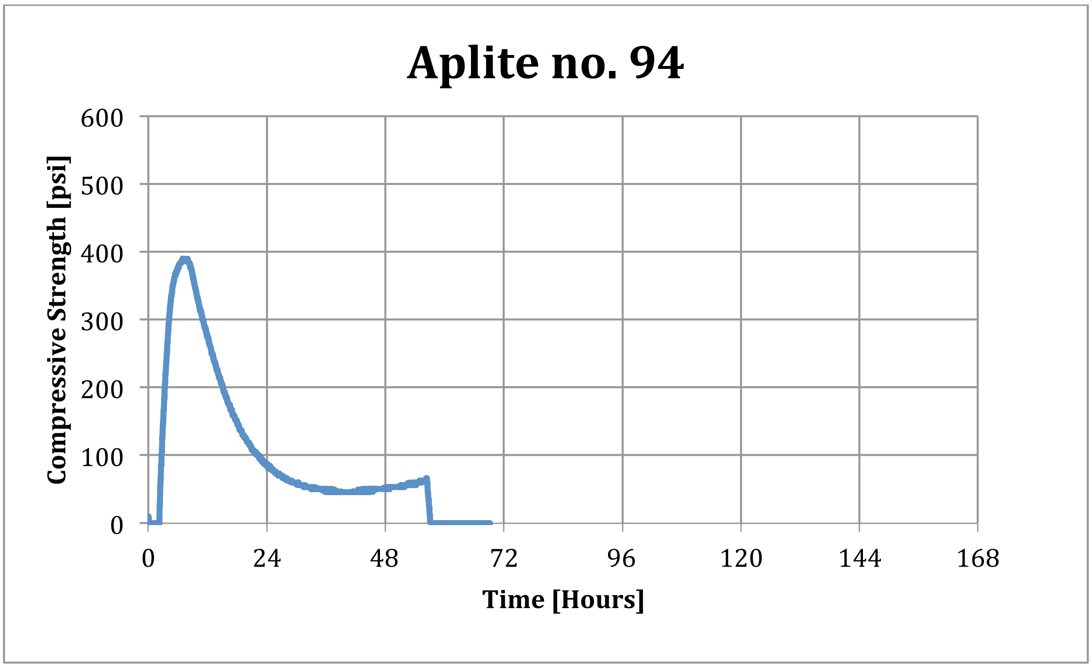

Figure 5.9: Compressive strength of aplite no. 72B measured by UCA at 88°C and 5200 psi

Table 5.7: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	Local low point	Max strength	Curing temp reached	End point
Strength [psi]	0	50	46	390	0	63
Transit [µs/in]	11.25	11.14	11.14	10.49	11.59	11.10
Temperature [°C]	89	89	89	89	89	89
Time [HH:MM]	2:13	2:25	38:20	6:55	1:50	56:00

Aplite no. 96:

With this recipe a new approach was done. Metakaolin was omitted, NaOH and water glass used had a ratio of 1:1. This implied a large reduction in the volume of NaOH in the recipe. The final change was the amount of BFS that was doubled.

Fig. 5.10 shows the compressive strength development vs. time for test no. 96. It had an onset after just 1 hour, and reached 50, 500 and 2000 psi after approximately 1 hour, 1.5 and 15 hours respectively. There were some pressure disturbances after 28 hours and pressure was lost after 103 hours and this pressure loss had a duration of about 16 hours. The graph would most likely have continued linear if it had not been for the interference. The test was ended after 120 hours and had strength of 3457 psi. Key features from the original graph are found in Appendix B and listed in Table 5.8.

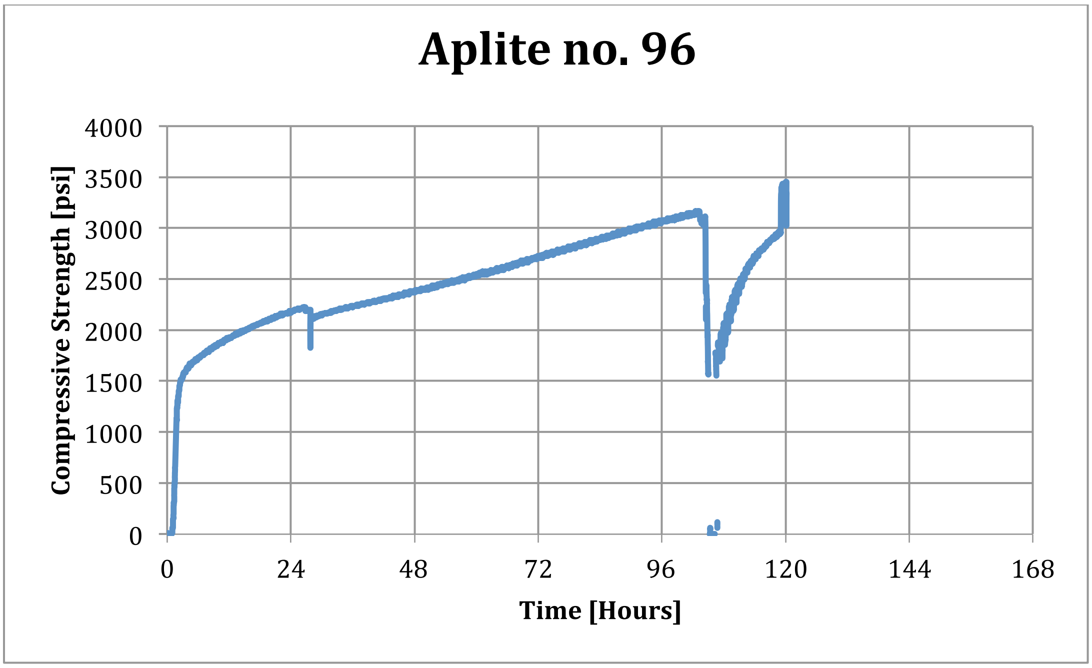

Figure 5.10: Compressive strength of aplite no. 96 measured by UCA at 88°C and 5200 psi

Table 5.8: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	500 psi	2000 psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	500	2000	3457	1307	3457
Transit [µs/in]	11.29	11.15	10.30	8.90	8.17	9.40	8.17
Temperature [°C]	50	54	69	89	89	89	89
Time [HH:MM]	0:54	1:03	1:28	14:49	120:00	2:00	120:00

Aplite no. 98:

Due to the pressure disturbance in test no. 96, an almost identical experiment was carried out to verify the results, and to see the further development of strength. The strength started to build after less than 1 hour as shown in Fig. 5.11. This sample had a rapid strength development and reached 50 psi and 500 psi after less than 1 hour. From the graph it is clear that the rate of strength development started to decrease at approximately 1400 psi. 2000 psi was achieved after 23 hours. The test was ended after 168 hours with strength of 3577 psi. Looking at the graph it seems that the strength development would stabilize at about 3800 psi. Key numbers from the original data sheet are found in Table 5.9. As mentioned earlier this test was performed in UCA no. 3 which increased its temperature faster than the UCA no. 1 and no. 2, which might be the reason for the earlier strength development.

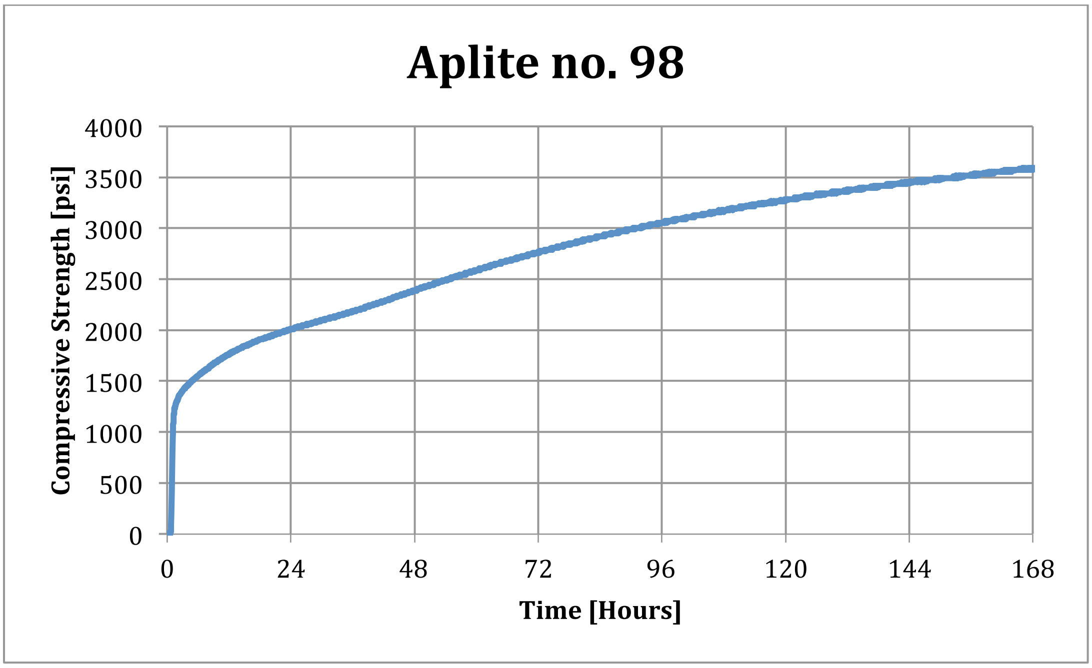

Figure 5.11: Compressive strength of aplite no. 98 measured by UCA at 88°C and 5200 psi

Table 5.9: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	500 psi	2000 psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	500	2000	3577	1046	3577
Transit [µs/in]	11.16	11.04	10.24	8.87	8.19	9.61	8.19
Temperature [°C]	66	70	82	89	89	89	89
Time [HH:MM]	0:40	0:43	0:56	23:20	168:00	1:10	168:00

Fig. 5.12 and 5.13 are Scanning Electron Microscope (SEM) images of sample no. 98 retrieved from the UCA test. Fig. 5.12 is magnified 20 000 times, while Fig. 5.13 is magnified 100 000 times. The image clearly indicates that the sample is almost amorphous, which is an indication of geopolymerization. But areas that are crystalline is also apparent.

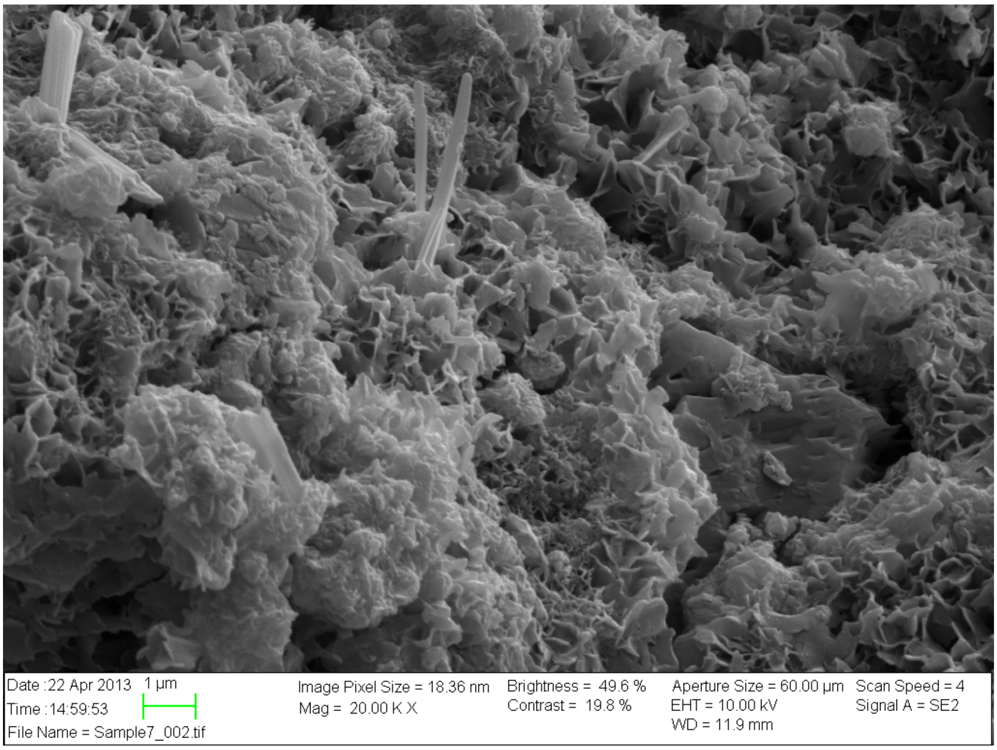

Figure 5.12: SEM picture of sample taken from test no. 98 magnified 20 000 times

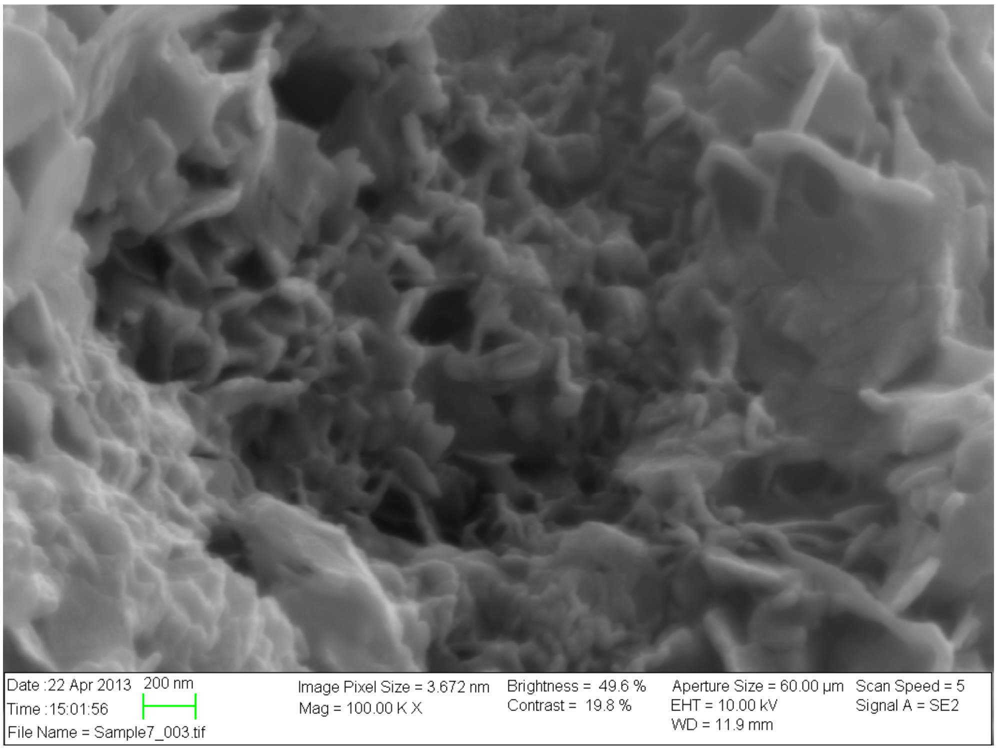

Figure 5.13: SEM picture of sample taken from test no. 98 magnified 100 000 times

Aplite no. 102:

A new BFS was introduced, and thus test no. 102 is a replica of test no. 96 and no. 98. This is done to see if the same results are possible to reproduce with the new BFS. In addition in this test, NaOH and water glass were mixed 24 hours in advance of making the recipe. This was done to see if there would be a positive effect on the compressive strength as Heah et. al. reported in their work.

Fig. 5.14 reveals the strength development of test no. 102 with compressive strength on the y-axis and time on the x-axis. The slurry started to develop strength after 33 min, and had a rapid increase similar to tests no. 96 and no. 98. 50 psi and 500 psi was registered after respectively 38 min and 50 min. At a measured strength of 1250 psi the strength development rate starts to slow down. The obtained data has almost a logarithmic appearance, and looks like it is reaching a final plateau of about 3500 psi. The test was terminated after 163 hours, and a final strength of 3160 psi was measured. All the key numbers from the original graph are tabulated in Table 5.10.

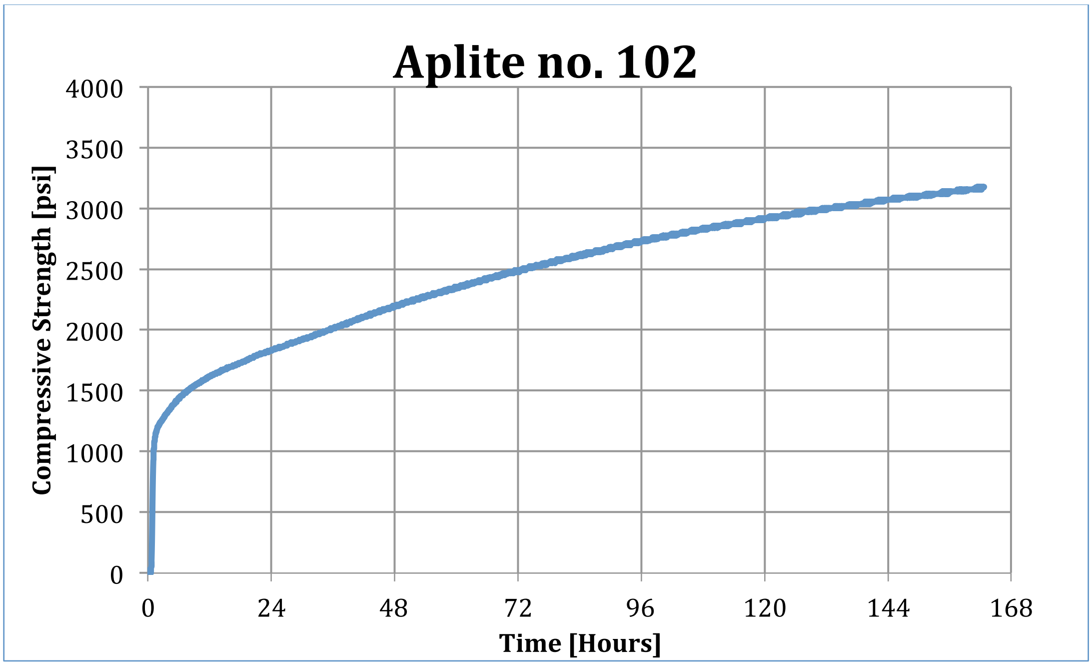

Figure 5.14: Compressive strength of aplite no. 102 measured by UCA at 88°C and 5200 psi

Table 5.10: Key features taken from the original data sheet found in Appendix B

	Onset	50 psi	500 psi	2000 psi	Max strength	Curing temp reached	End point
Strength [psi]	0	50	500	2000	3160	724	3160
Transit [µs/in]	11.24	11.09	10.32	8.89	8.28	9.99	8.28
Temperature [°C]	66	72	85	89	89	89	89
Time [HH:MM]	00:33	00:38	00:50	34:44	163:00	00:55	163:00

5.3.3 Uniaxial Compressive Strength tests

After three successful UCA test recipe no. 102 was decided to be examined with UCS apparatus. A total of 9 UCS tests were conducted in this experimental work. All the sample dimensions and results are tabulated in Table 5.11, while the original data sheets from the UCS tests are located in Appendix C. The results are converted from applied force in kN to compressive strength measured in psi. All the recipes during these tests were mixed with a "Hamilton Beach Scovill" mixer, and the ingredients are found in Table 5.2.

Table 5.11: Dimensions of samples and compressive strength from the UCS tests

Test name	Length [mm]	Diameter [mm]	Compressive strength [psi]
Aplite 1	71.3	51.6	5971
Aplite 2	81.1	52.3	5104
Aplite 3	78.6	51.2	7286
Aplite 4	85.1	51.6	4664*
Aplite 5	95.5	52.3	5520
Aplite 6	96.9	52.3	5701
Aplite 7	94.8	52.4	4316
Aplite 8	95.7	52.0	3902
Cement 1	88.9	52.3	N/A

*Note: Aplite 4 had a deep fracture before it was UCS tested, and it was through this fracture that the sample failed when 4664 psi was reached.

Aplite no. 106:

From recipe no. 106 a total of six samples were prepared, which were called "Aplite 1-6". They were molded in plastic containers at a temperature of 88℃ for six days. The samples were under pressure during their curing time in the oven. The initial pressure was 1900 psi, but due to leakage the pressure after six days was 320 psi. The complete and detailed pressure profile can be viewed in Fig. C.1 in Appendix C. After six days samples were allowed to cool down for one day at room temperature and atmospheric pressure. The samples had to be cut at the ends to ensure a smooth and flat surface before the UCS testing.

Aplite no. 107 and no. 108:

One sample was made from each of the recipes and named “Aplite 7-8”. The samples were cured at room temperature and atmospheric pressure. The main purpose was to compare them with the ones that cured under pressure and at elevated temperature. The samples cured for six days before they were cut with a diamond blade cuter. After being cut the samples was left to cure for one more day outside the plastic containers. Fig. 5.15 shows the taken photo of Aplite 7. As the pictures shows, several cracks had developed during the last day of curing. This was the case for both samples. The reason for the fractures might be that the geopolymer cement shrinks.

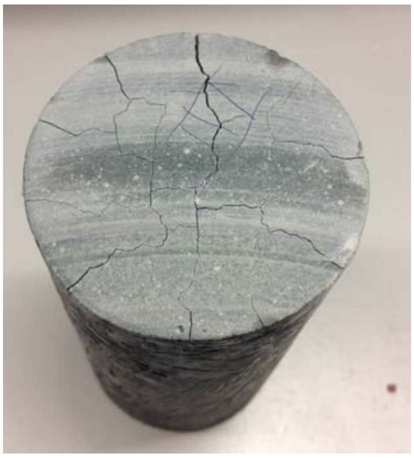

Figure 5.15 Picture of Aplite 7 showing fractures developed after last day of curing

The picture in Fig. 5.16 shows Aplite 7 after being crushed in the UCS. Small pores can be seen in the matrix, which is due to air bubbles that did not get compressed when curing under atmospheric pressure.

Figure 5.16: Sample no. 107 after UCS test

SEM images were also taken of Aplite 7-8 to look at the structure in detail. Since both samples were identical, only Aplite 7 atmospheric is presented. Fig. 5.17, 5.18 and 5.19 pictures that are magnefied by 1000, 10 000 and 50 000 times respectivly. The figures shows an almost amorphous structure indicating that geopolymerization has taken place. However, in Fig. 5.19 the arrow points at a spheric structure, which is an impurity. Several of these impurities were found on both samples.

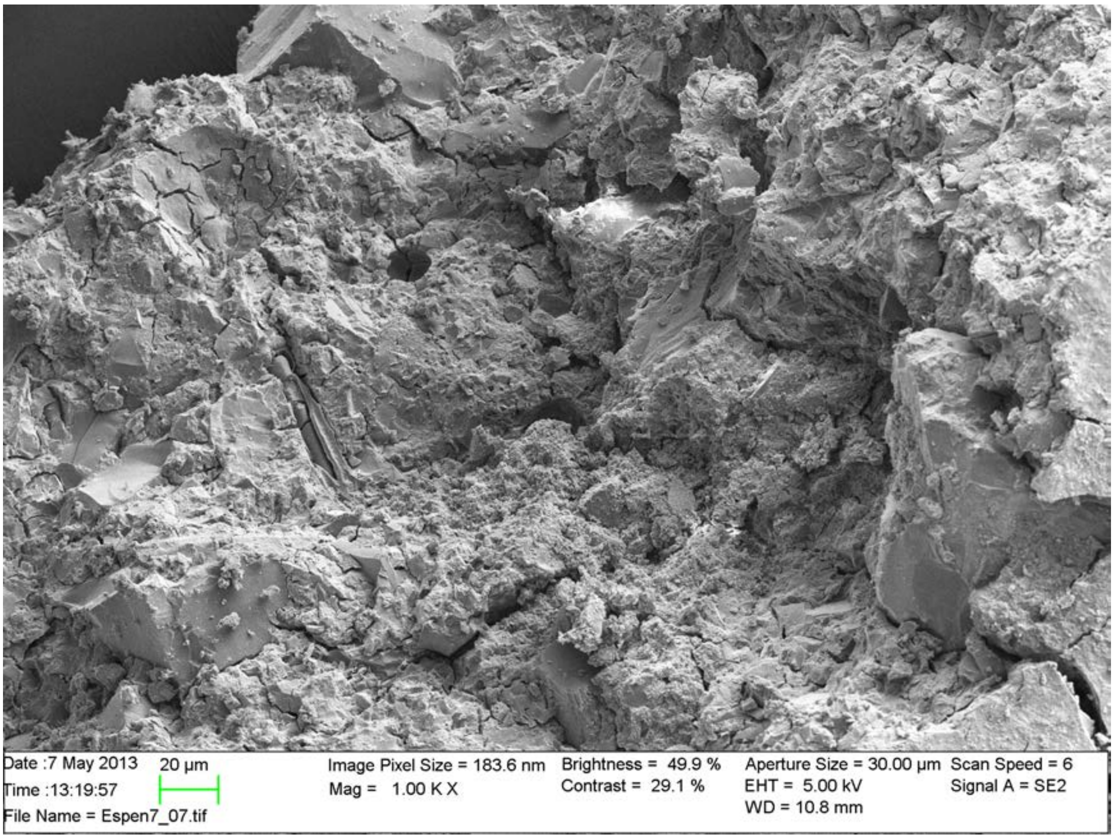

Figure 5.17: SEM picture of sample taken from Aplite 7 magnified 1000 times. The picture shows a almost amorphous structure.

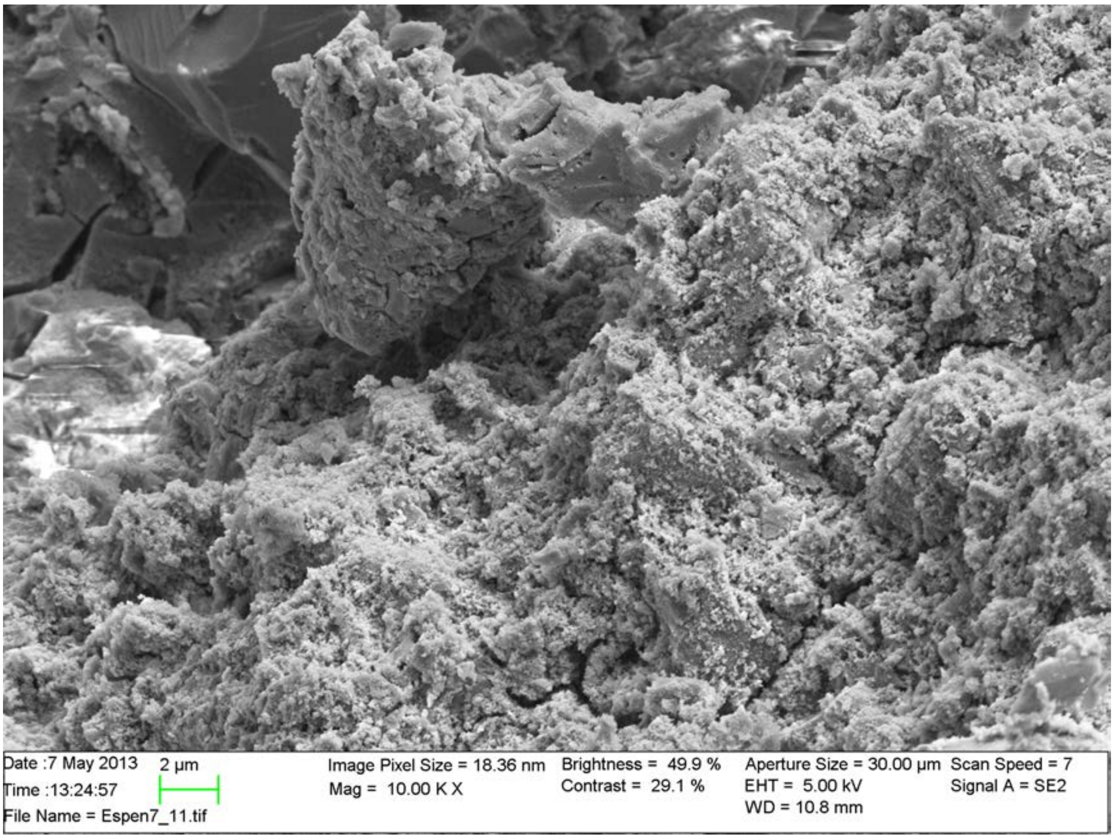

Figure 5.18: SEM picture of sample taken from Aplite 7 magnified 10 000 times. The picture shows a almost amorphous structure

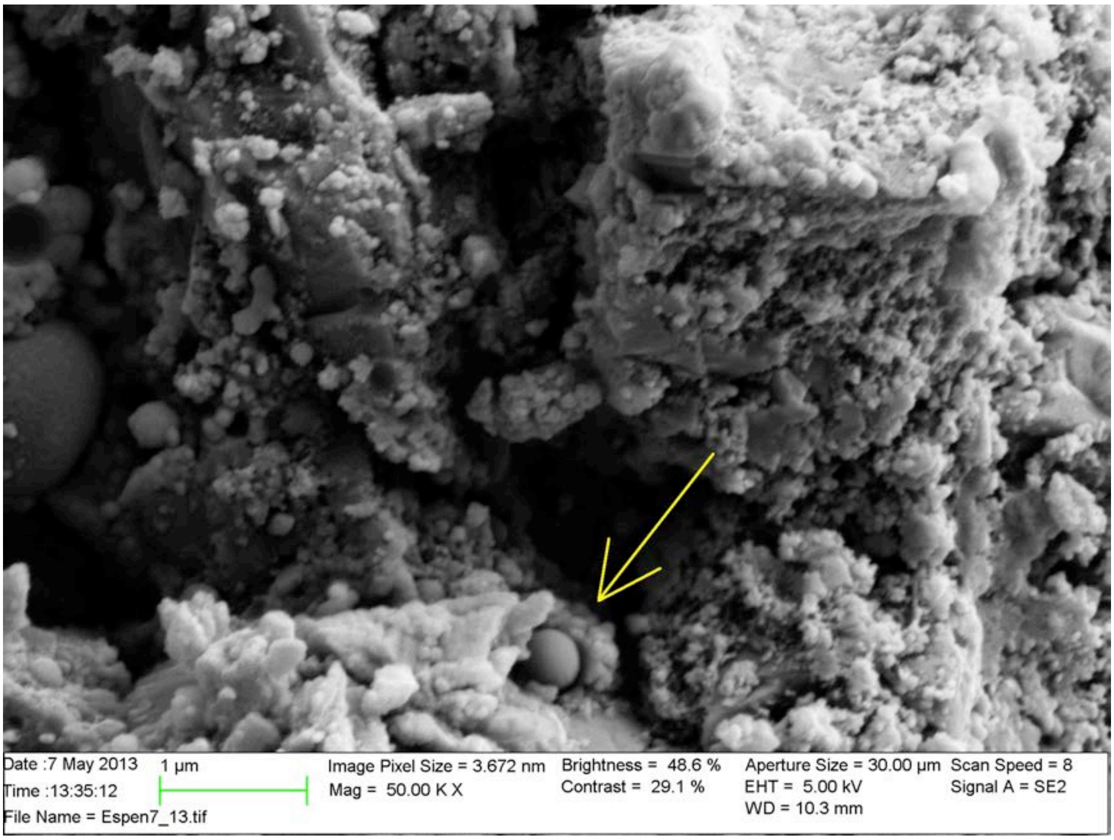

Figure 5.19: SEM picture of sample taken from Aplite 7 magnified 50 000 times. The arrow points at an impurity

Aplite no. 109:

To try to prevent the sample from developing factures 20 wt% Portland cement was added. A high SLR and the heat generated during the mixing made it set too fast to be able to move it into its plastic container.

Aplite no. 110:

To prevent the sample from setting before properly mixed and placed in its container, both the amount of NaOH and water glass was increased. The volume that was added was calculated to give the same SLR as recipe no. 108. The sample cured at room temperature and atmospheric pressure for seven days. However, technical problems occurred after the UCS tests so the data file was lost.

5.3.4 External lab

Aplite no. 103, no. 105 and no. 114:

One sample was made from each of the recipe no. 103, no. 105 and no. 114. All samples cured at room temperature and atmospheric pressure. All samples were sent to an external lab in Trondheim, Norway for further analysis of porosity, permeability and durability in corrosive environments. The results are not included in this thesis.

The sample from recipe no. 105 partly failed due to the amount of heat generated during mixing, which made the geopolymer cement set much faster than anticipated. This made it hard to fill up the plastic container before it set.

6.0 Discussion

Fig. 6.1 shows the compressive strength development for the first five UCA tests in the same plot. Test no. 72A built the highest compressive strength, but due to leakage the test was terminated early. The duplicate test, no. 72B, proved that the result from no. 72A was hard to reproduce. Test no. 68 is the only test that did not build a compressive strength to any degree of note compared to the other four experiments. This might be explained by the low ratio of SiO_2/AlO_3, which did not allow the slurry to synthesize a high amount of aluminum-silicates (Khale & Chaudhary, 2007). When micro silica was added this ratio increased, and the compressive strength reached 400-500 psi. Another effect that could explain the increased strength is the fact that micro silica has pozzolanic properties. Pozzolanic materials react with $Ca(OH)_2$, and form a stable, low permeable compound (Nelson & Guillo, 2006). $Ca(OH)_2$ would normally have been transported out of the cement due to osmosis, and reduced the strength. BFS has a large content of CaO, which can react with water and create $Ca(OH)_2$, and could therefore contribute to this effect.

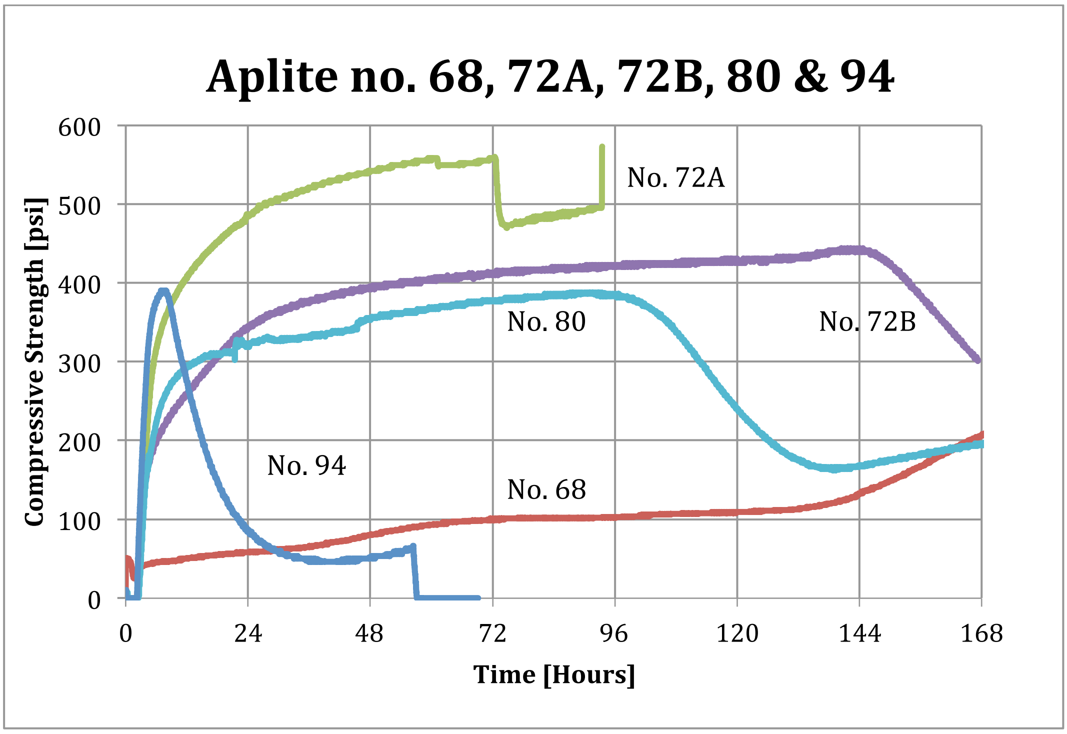

Figure 6.1: Plot that compares compressive strength development of recipe no. 68, 72A, 72B, 80 and 94

However, the strength achieved from all the tests presented in Fig. 6.1 were still lower than desired. The results show that several of the cement slurries start to lose their strength after 4-5 days. As mentioned in Ch. 4.0 Khale and Chaudhary pointed out that curing geopolymer cement for a prolonged time at an elevated temperature might break the granular structure (Khale & Chaudhary, 2007). This could then lead to dehydration, shrinkage and reduced compressive strength. The reason why no. 94 has a very strong decline might be to the fact that 4M KOH was replaced by 8M NaOH, which could have given the slurry a too high excess amount of Na^+. These ions can then replace the silica and aluminum in the structural framework leading to a reduction in the overall compressive strength (Heah, et. al., 2012). Nevertheless, none of the tests gave a sufficient compressive strength.

In Fig. 6.2 the three last UCA are compared. After removing metakaolin, reducing NaOH, while doubling the amount of BFS the compressive strength increased incredibly. The reduction of NaOH can have balanced the amount of Na^+ needed, removing the possibility for the excess ions to reduce the strength of the framework. Another key change that probably could have had an impact on the strength was the removal of metakaolin. This might have adjusted the SiO_2/AlO_3 ratio to a more beneficial ratio. The three test have almost an identical strength development, where no. 102 has just a slightly lower strength. This can be due to the new BFS that was introduced in this test, as well as the new mixing procedure.

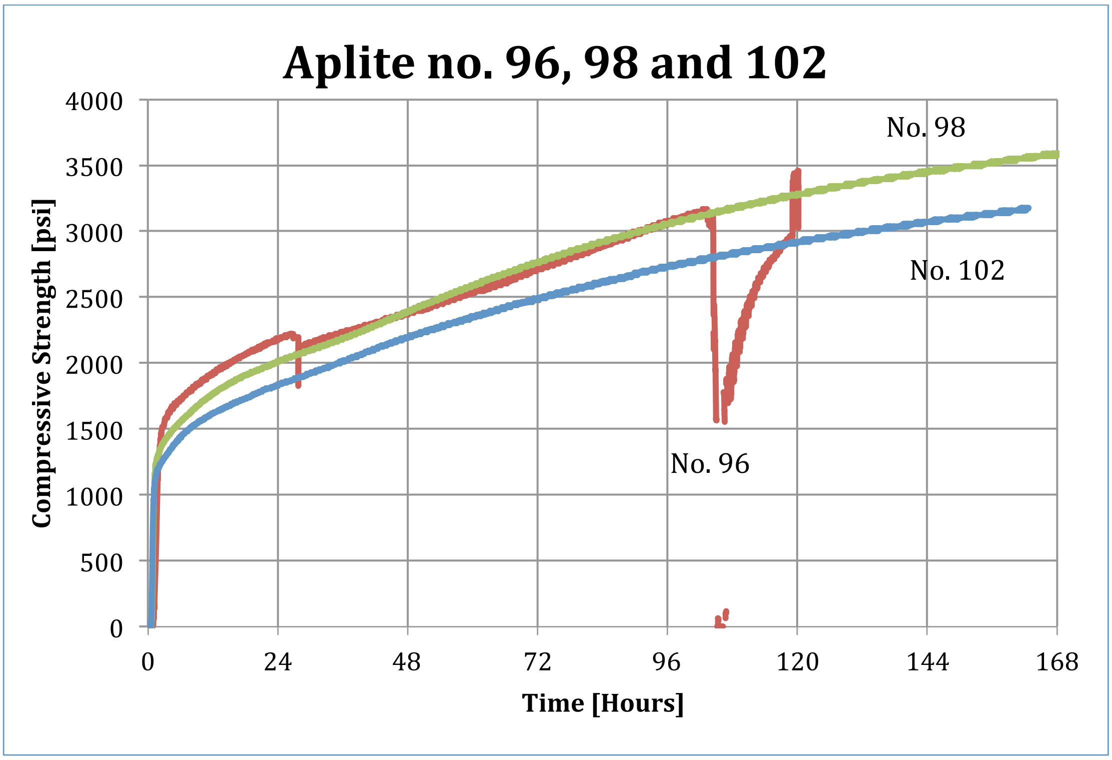

Figure 6.2: A plot comparing the compressive strength development of test no. 96, 98 and 102.

When comparing experiments no. 94 to 96 another difference comes to light. The onset time was reduced by 50% (from two to one hour). Furthermore, the onset time was reduced to approximately 30 min for test no. 98 and 102. The first change in onset can be explained by the increase in SLR from 1.6 to 2.7, but might also have to do with the increased amount of BFS in the recipe. BFS have an ability to absorb water due to its high content of CaO (Khale & Chaudhary, 2007). This might reduce the amount of free water, and also the onset time. The second change is due to the change of UCA temperature development. From two hours to only one hour to reach the designated curing temperature of 88°C. It should be kept in mind that KOH, NaOH and water glass are all accelerators, which reduces the onset time as well. It might be a good idea to add a dispergent to reduce the viscosity and retard the setting of the recipes.

The UCS test that was based on recipe no. 102 gave a much higher result than obtained from the UCA. The UCS results are most likely more reliable due to the fact that it is a mechanical test, while UCA measures the strength indirect, based on correlations. Nonetheless, It should be taken into account the fact that the samples that were UCS tested varied in length, which will affect the strength outcome of the tests. The pressure that Aplite 1-6 cured in, was much lower than the 5200 psi, which the UCA samples cured at. The reduced curing pressure should normally reduce the compressive strength, but pressure plays only a minor role to the compressive strength compared to temperature (Nelson & Guillo, 2006).

Aplite 7-8 that cured at room temperature and atmospheric pressure developed fractures during the last day when they were removed from their plastic container. This could be due to shrinkage or dehydration. The compressive strength obtained from UCA testing gave a mean compressive strength of 4100 psi. This is 1100 psi below the ones that cured in the oven, which was tested the same day as they were removed from their container. This could indicate that the curing temperature has an important role in the strength development. However, the fractures must also take some of the blame for the reduced strength. The SEM picture in Fig. 5.19 showed an impurity. This could be aplite that does not take part in the geopolymerization, or simply an impurity that originates from another substance from the lab.

6.1 Proposed further work

In this experimental work a geopolymer cement recipe based on aplite with high strength was developed. There are several properties that would be interesting to investigate. An obvious start would be to investigate if the fractures observed are due to shrinkage or not. If the geopolymer cement shrinks, then it cannot be used as a sealant in P&A. A solution might be to add small amounts of Portland cement to the recipe.

Properties like porosity, permeability and bonding would be interesting to determine, since these are key parameters for being an efficient sealant in wells.

Since the cement slurry also often is used to displace other fluids in the well, the viscosity and density will be crucial to perfect to avoid fingering, fracturing and loss. So fluid dynamic experiments could be recommended to perform.

All these parameters need to be optimized before real field trials can be conducted.

One of the goals for the geopolymer cement is to be able to perform in HTHP wells. So another parameter that should be experimented with is temperature. Will the recipe be able to handle temperatures up to 150°C, or will it decompose?

A last thing that could be recommended for further research is to try to delay the setting time of the geopolymer cement. During the experiments conducted in this thesis the slurries started to set almost instantaneously, which might have to do with the heat generated during mixing. Another factor that caused the early setting is the high SLR. It could be recommended to do a series of experiments with different SLR’s by adding water to recipe no. 102, and see if the onset time could somehow be delayed, and optimized. If not the decreased SLR gives the desired results then some retarders could be added to try to improve the onset time, and the application of this geopolymer cement.

7.0 Conclusion

The goal for this work was to investigate if an aplite-based geopolymer cement could build adequate strength and be used as a replacement for Portland cement in the oil and gas industry. Based on this work it can be concluded that geopolymer shows potential to become an good alternative for Portland cement. The compressive strength achieved from the last recipe is high enough to satisfy the NORSOK strength requirements.

During the experiments done, a recipe for an aplite-based geopolymer has been developed. The obtained result from the UCA gave an compressive strength of 4200 psi, while the UCS tests gave an average of 5700 psi. The UCA results also reveal that this strength would increase to even higher strengths, if it had more time to cure.

The series of experiments gave results that indicated that both an increased curing temperature and pressure favors a higher compressive strength. Observation showed that the effect of an increased SLR made the samples set much faster. However, it may lower the maximum compressive strength due to incomplete reaction. The experiments also suggested that the increased concentration of alkali solution increases the strength, but that a too large volume gives a negative effect. The data did reveal that by adding micro silica and removing metakaolin the compressive strength increased. SEM images reveal amorphous structure, which is an indication of geopolymers. However, crystallinity was observable, which shows incomplete reaction.

If this geopolymers cement recipe can be optimized, then it could reduce the cost for operators offshore. It would also reduce the environmental impact worldwide, by reducing the amount of CO_2 emitted to the atmosphere due to the production of Portland cement. However, there are still several parameters that need to be investigated before field trails can be done. If the geopolymer cement should be applied as a sealant in offshore wells on the NCS, especially in HTHP wells, then temperature effects and possible shrinkage problems are of greatest concern.

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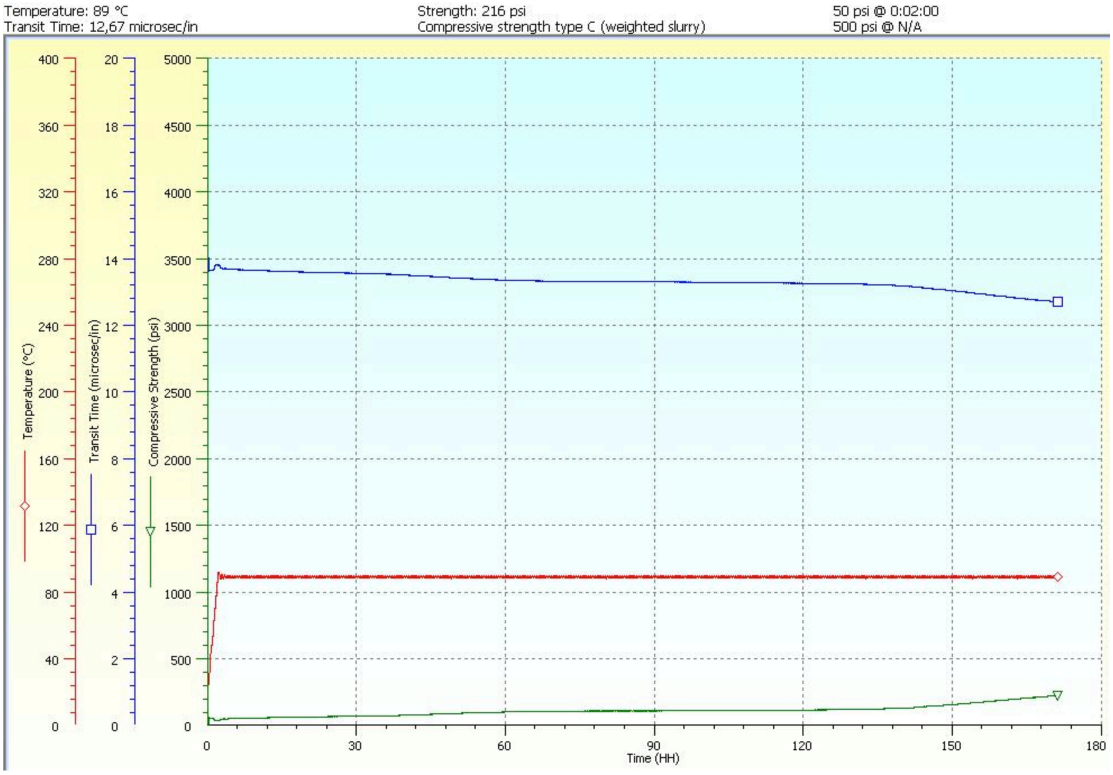
Appendix A

Eq. A1: Solid-Liquid Ratio (SLR) = $\frac{\sum Solids\ [grams]}{\sum Liquids\ [grams]}$

Table A.1: Ingredients in the different recipes and their respective producers.

Material	Producers	Location	Used in recipe no.
BFS 1	Unknown	Unknown	68, 72a, 72b, 80, 94, 96, 98
BFS 2 (Merit 5000)	Merox	Oxelösund, Sweden	102, 103, 105, 106, 107, 108, 109, 110, 114
Kaolinite	Merck	Germany	68, 72a, 72b, 80, 94
Metakaoline (MK-750)	Khalifeh, Mahmoud	Stavanger, Norway	68, 72a, 72b, 80, 94
Aplite		Finnvolldalen, Norway	All
Micro silica (Grade 955)	Elkem	Kristiansand	All except 68
KOH	Laboglass	Hinna, Norway	68, 72a, 72b, 80
NaOH	Merck	Germany	94, 96, 98, 102, 103, 105, 106, 107, 108, 109, 110, 114
Water glass	Merck	Germany	All

Appendix B

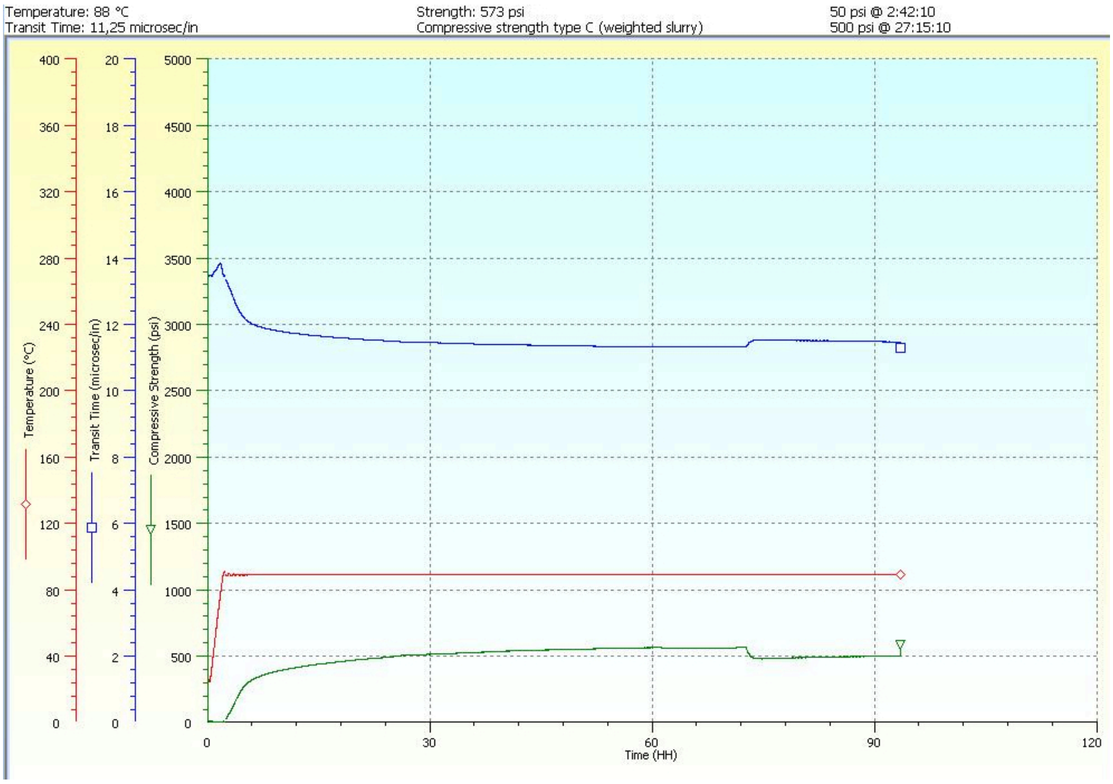


Temperature: 89 °C
Transit Time: 12,67 microsec/in

Strength: 216 psi
Compressive strength type C (weighted slurry)

50 psi @ 0:02:00
500 psi @ N/A

Figure B.1: Aplite no. 68 UCA test:
Upper curve is transit time [microsec/in]
Middle curve is temperature [°C]
Lower curve is compressive strength [psi]

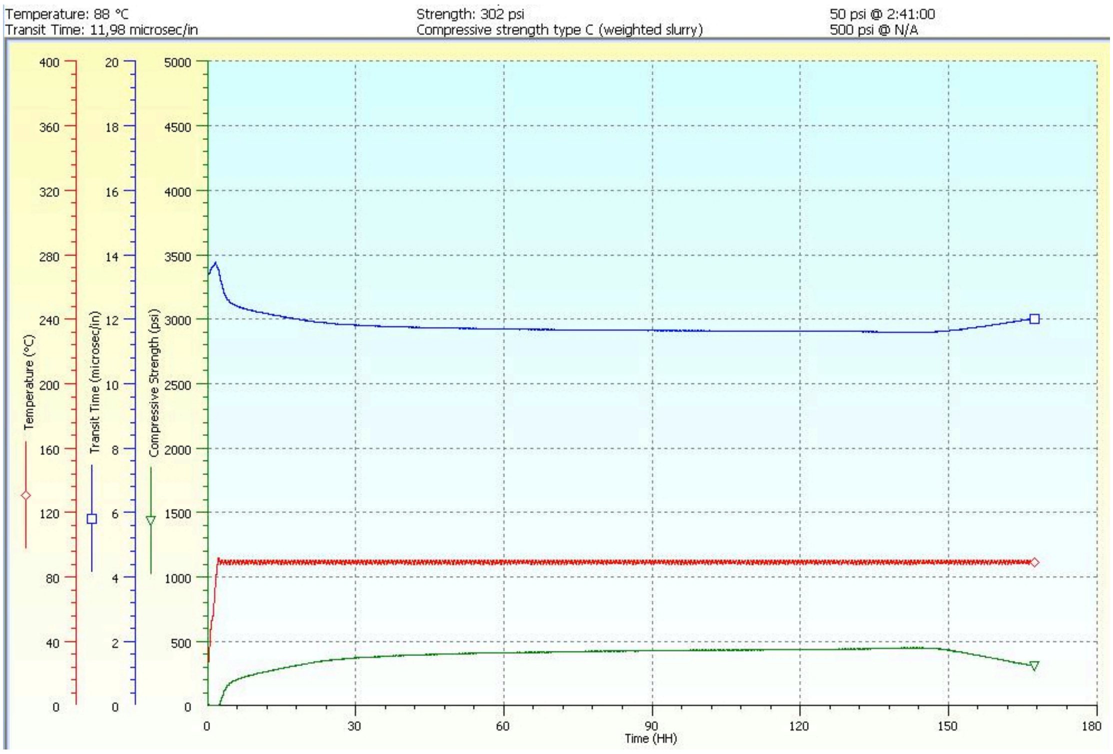


Temperature: 88 °C
Transit Time: 11,25 microsec/in

Strength: 573 psi
Compressive strength type C (weighted slurry)

50 psi @ 2:42:10
500 psi @ 27:15:10

Figure B.2: Aplite no. 72a UCA test:
The upper curve is transit time [microsec/in], the middle curve temperature [°C]
and the lower curve compressive strength [psi]

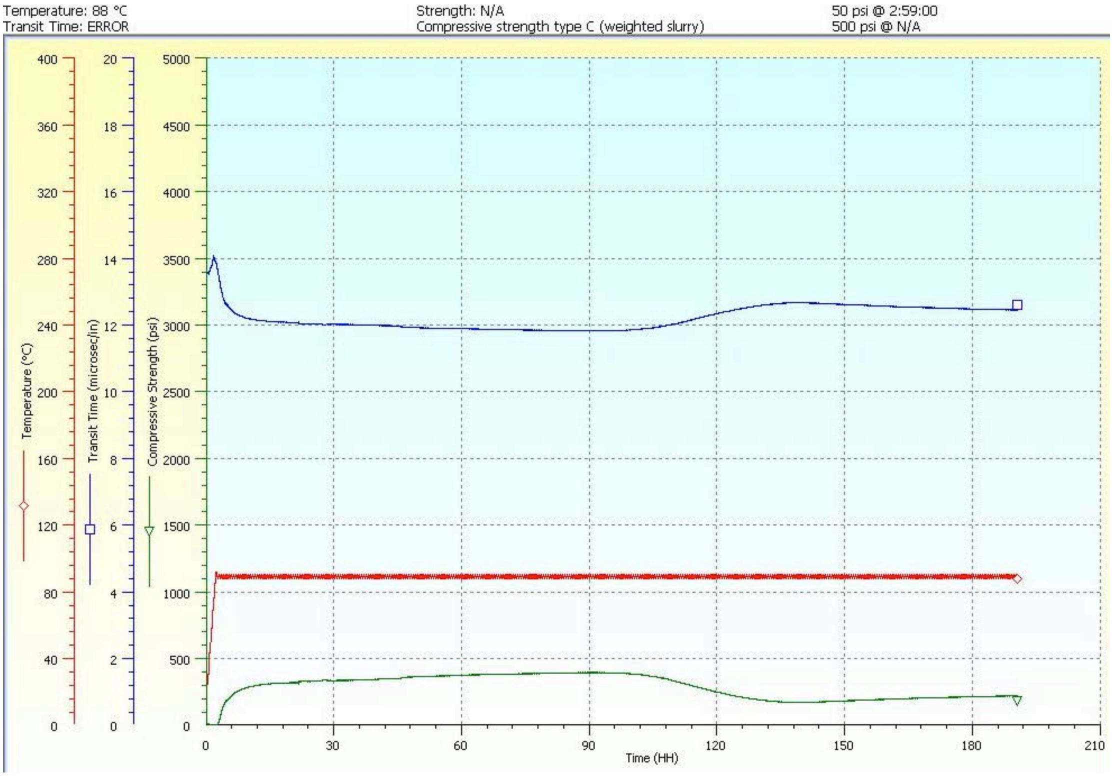


Temperature: 88 °C
Transit Time: 11,98 microsec/in

Strength: 302 psi
Compressive strength type C (weighted slurry)

50 psi @ 2:41:00
500 psi @ N/A

Figure B.3: Aplite silica no. 72b UCA test:
Upper curve transit time [microsec/in]
Middle curve temperature [°C]
Lower curve compressive strength [psi]

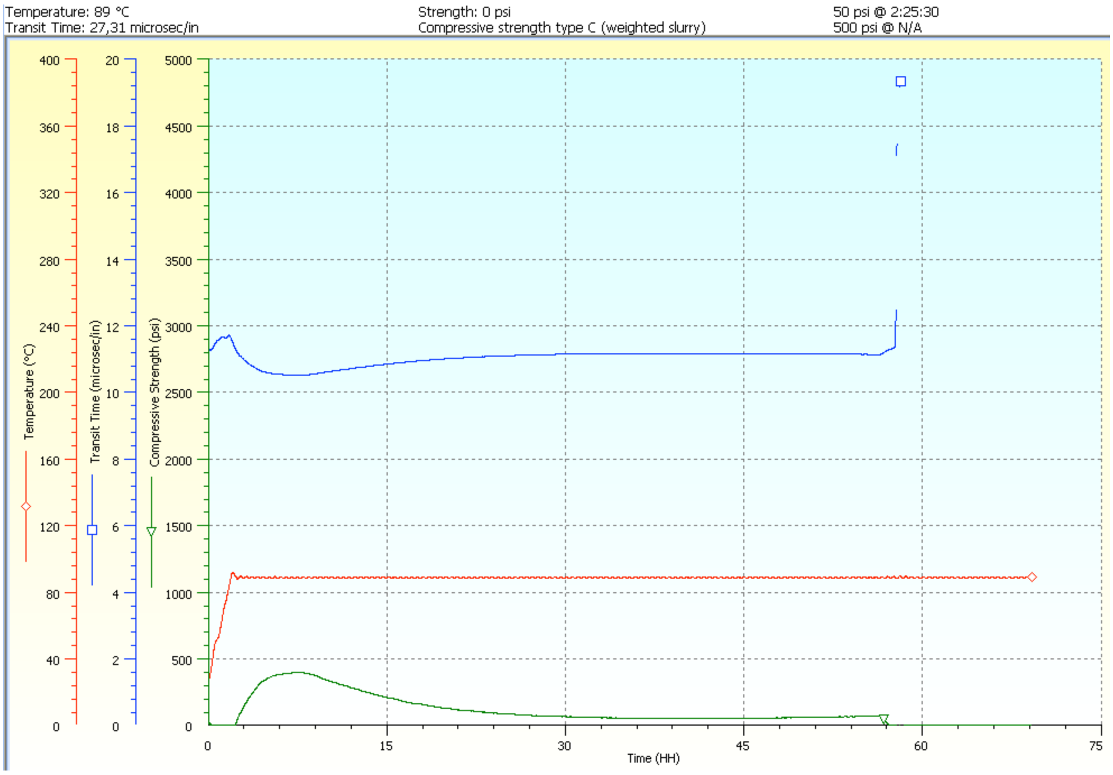


Temperature: 88 °C
Transit Time: ERROR

Strength: N/A
Compressive strength type C (weighted slurry)

50 psi @ 2:59:00
500 psi @ N/A

Figure B.4: Aplite & micro silica no. 80 UCA test:
Upper curve transit time [microsec/in]
Middle curve temperature [°C]
Lower curve compressive strength [psi]

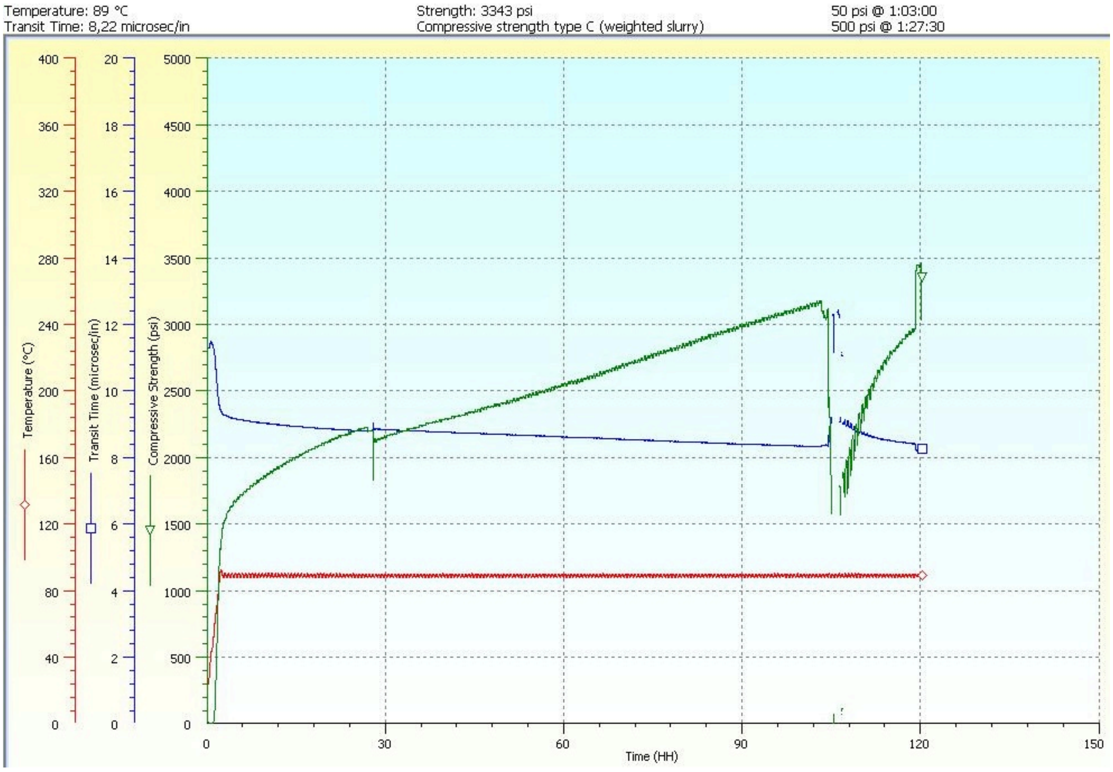


Temperature: 89 °C
Transit Time: 27,31 microsec/in

Strength: 0 psi
Compressive strength type C (weighted slurry)

50 psi @ 2:25:30
500 psi @ N/A

Figure B.5: Aplite no. 94 UCA test:
Upper curve transit time [microsec/in]
Middle curve temperature [°C]
Lower curve compressive strength [psi]

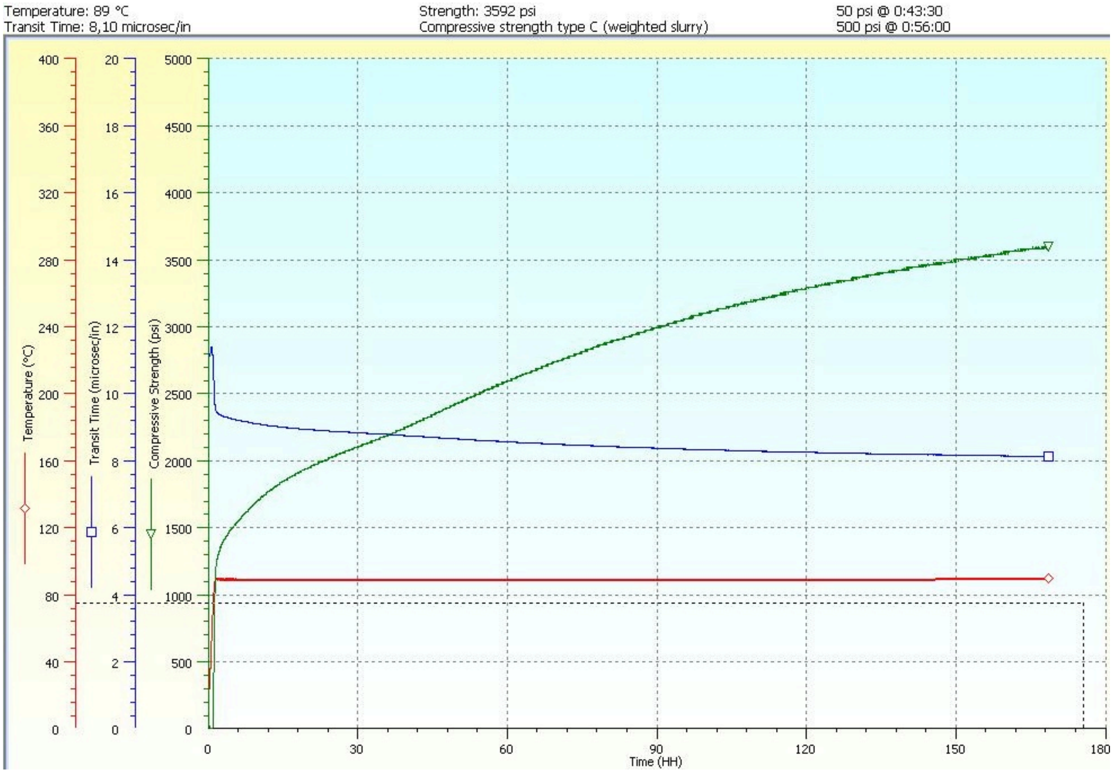


Temperature: 89 °C
Transit Time: 8,22 microsec/in

Strength: 3343 psi
Compressive strength type C (weighted slurry)

50 psi @ 1:03:00
500 psi @ 1:27:30

Figure B.6: Aplite & micro silica no. 96 UCA test:
The upper declining curve is transit time [microsec/in]
The increasing curve is compressive strength [psi]
The constant curve is the temperature [°C]

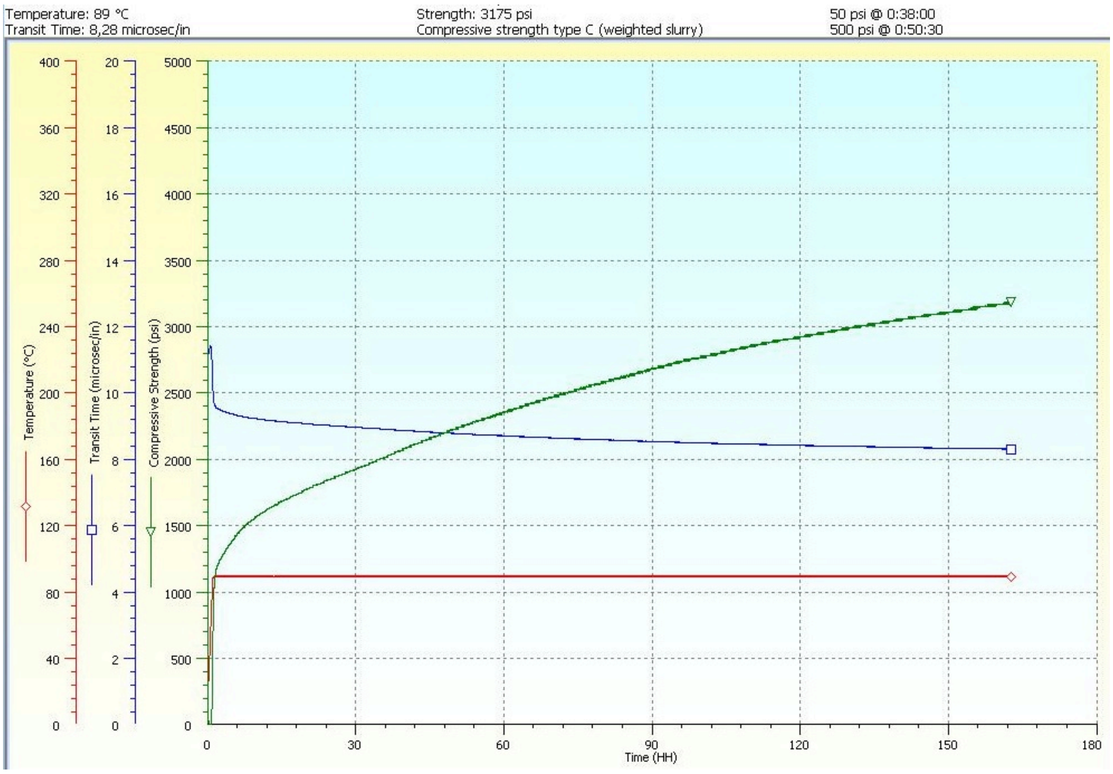


Temperature: 89 °C
Transit Time: 8,10 microsec/in

Strength: 3592 psi
Compressive strength type C (weighted slurry)

50 psi @ 0:43:30
500 psi @ 0:56:00

Figure B.7: Aplite no. 98 UCA test:
The upper declining curve is transit time [microsec/in]
The increasing curve is compressive strength [psi]
The constant curve is the temperature [°C]



Temperature: 89 °C
Transit Time: 8,28 microsec/in

Strength: 3175 psi
Compressive strength type C (weighted slurry)

50 psi @ 0:38:00
500 psi @ 0:50:30

Figure B.8: Aplite no. 102 UCA test:
The upper declining curve is transit time [microsec/in]
The increasing curve is compressive strength [psi]
The constant curve is the temperature [°C]

Appendix C

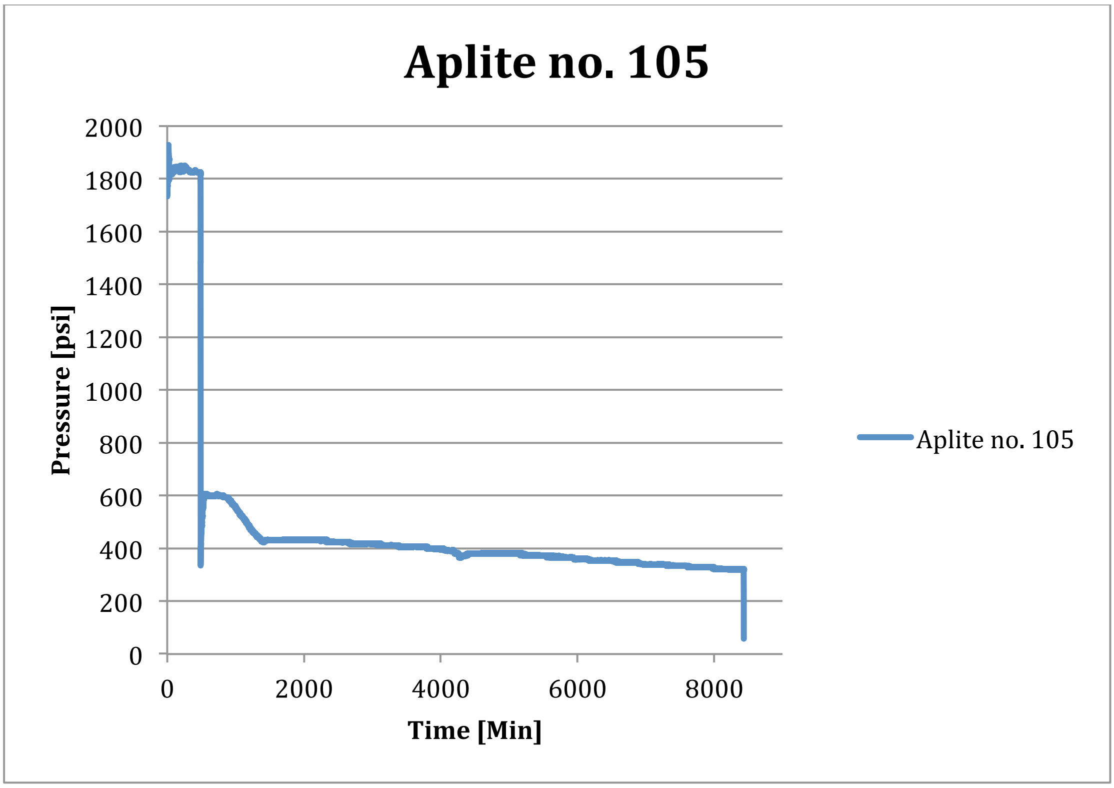
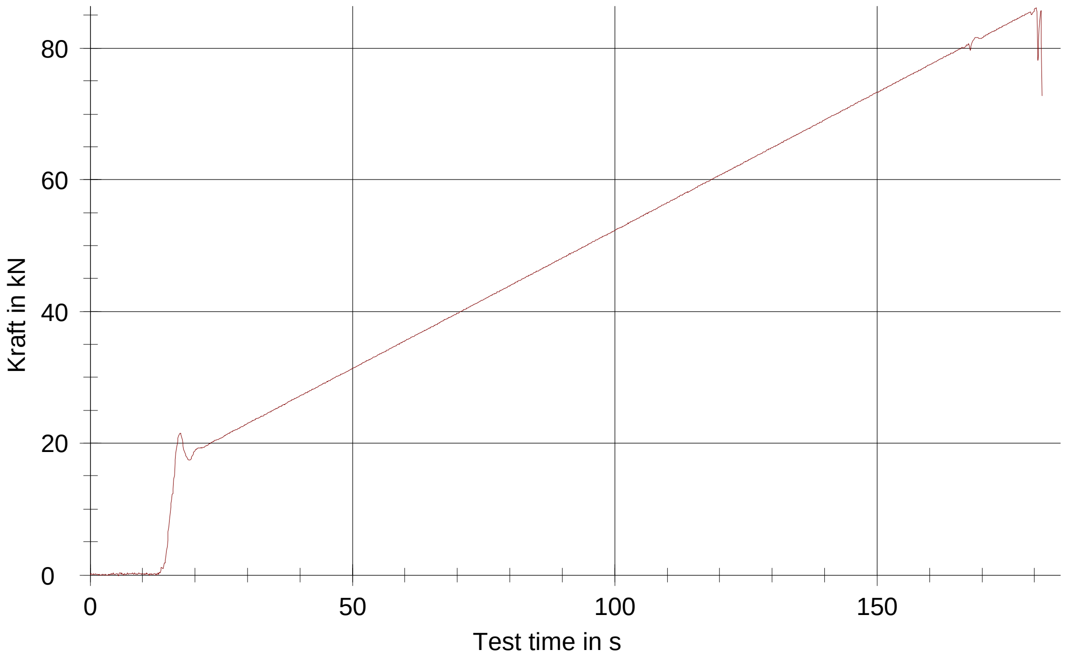


Figure C.1: Aplite no. 105 pressure profile before UCS test

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
1	aplite 1	86,10	41,18	71,3

Grafisk fremstilling:



Statistikk:

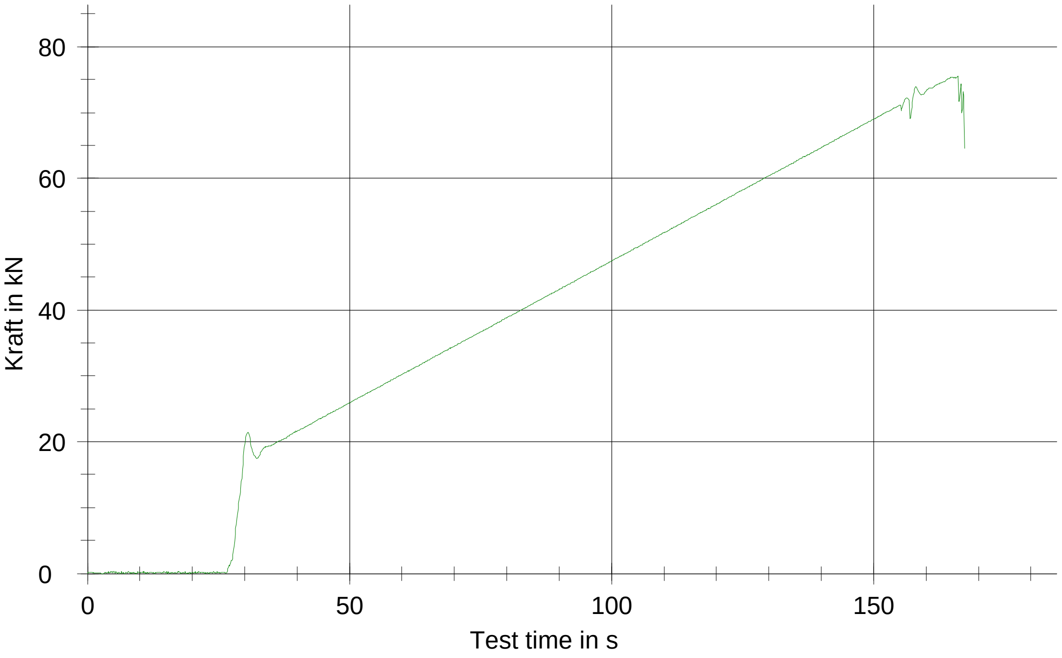
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	86,10	41,18	71,3
s	-	-	-
ν	-	-	-

Figure C.2: UCS test Aplite no. 1

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
2	aplite 2	75,61	35,19	68,1

Grafisk fremstilling:



Statistikk:

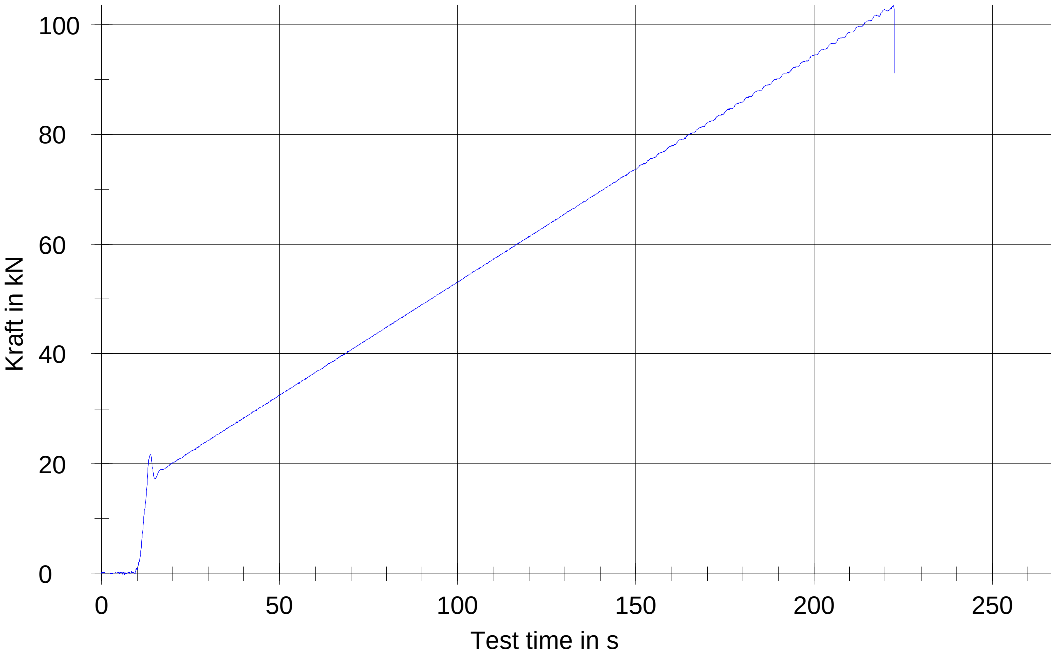
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	75,61	35,19	68,1
s	-	-	-
ν	-	-	-

Figure C.3: UCS test Aplite no. 2

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
3	aplite 3	103,44	50,24	78,6

Grafisk fremstilling:



Statistikk:

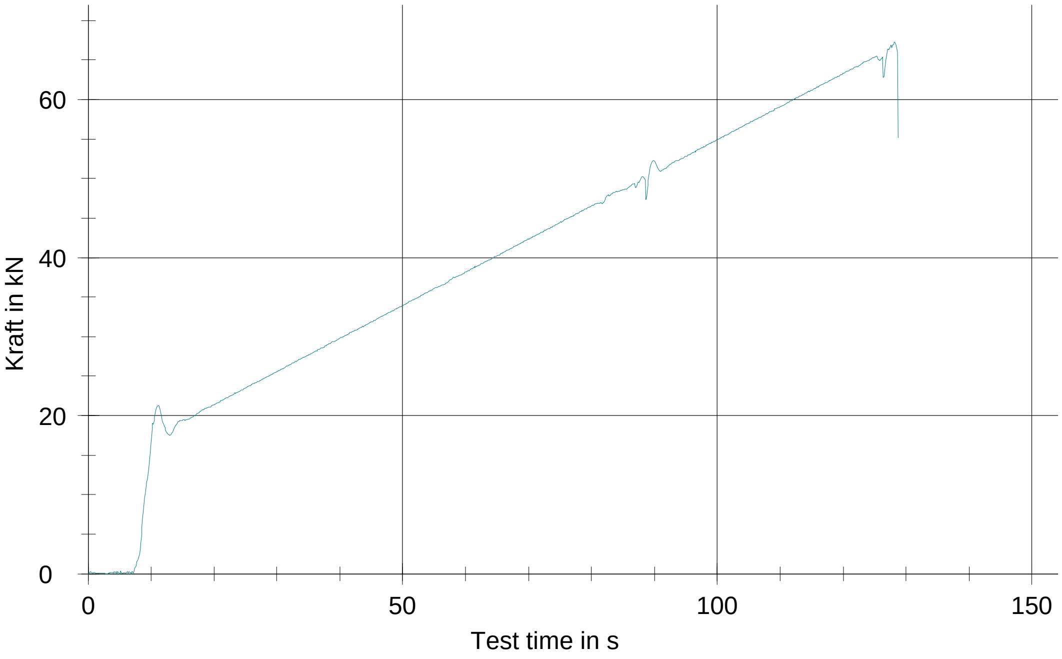
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	103,44	50,24	78,6
s	-	-	-
ν	-	-	-

Figure C.4: UCS test aplite no. 3

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
4	aplite 4	67,25	32,16	85,1

Grafisk fremstilling:



Statistikk:

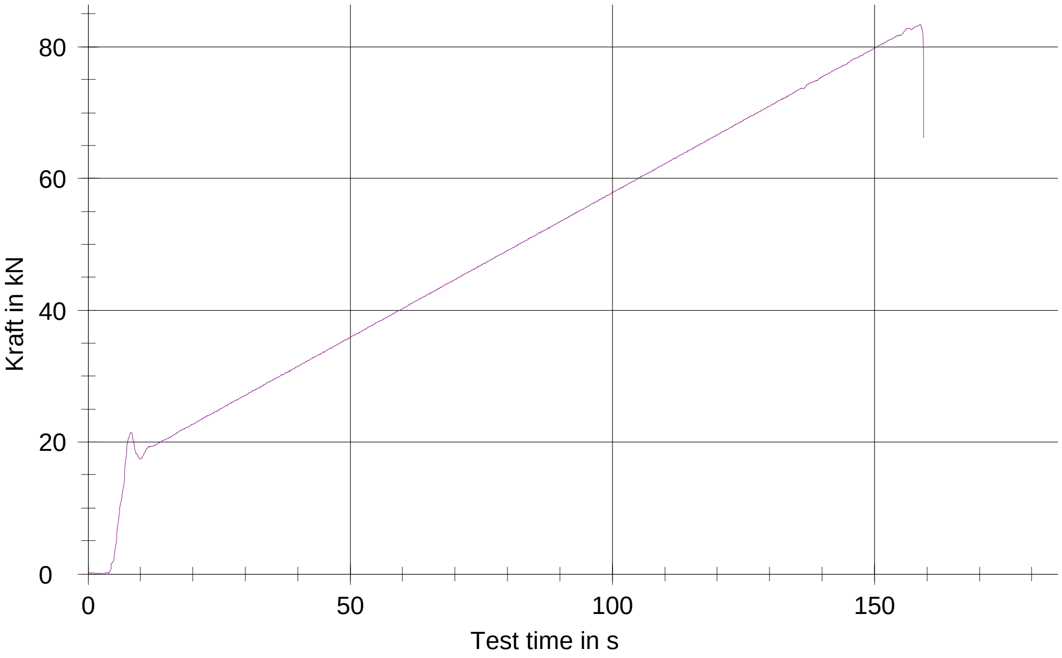
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	67,25	32,16	85,1
s	-	-	-
ν	-	-	-

Figure C.5: UCS test aplite no. 4

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
5	aplite 5	83,33	38,06	95,5

Grafisk fremstilling:



Statistikk:

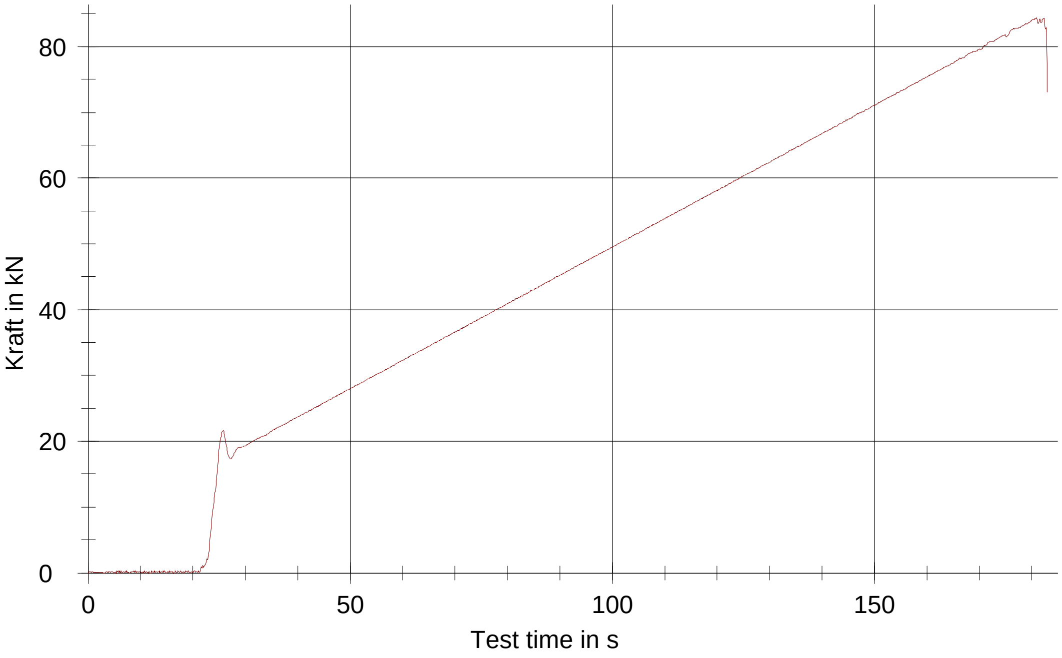
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	83,33	38,06	95,5
s	-	-	-
ν	-	-	-

Figure C.6: UCS test aplite no. 5

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
6	aplite 6	84,45	39,31	96,9

Grafisk fremstilling:



Statistikk:

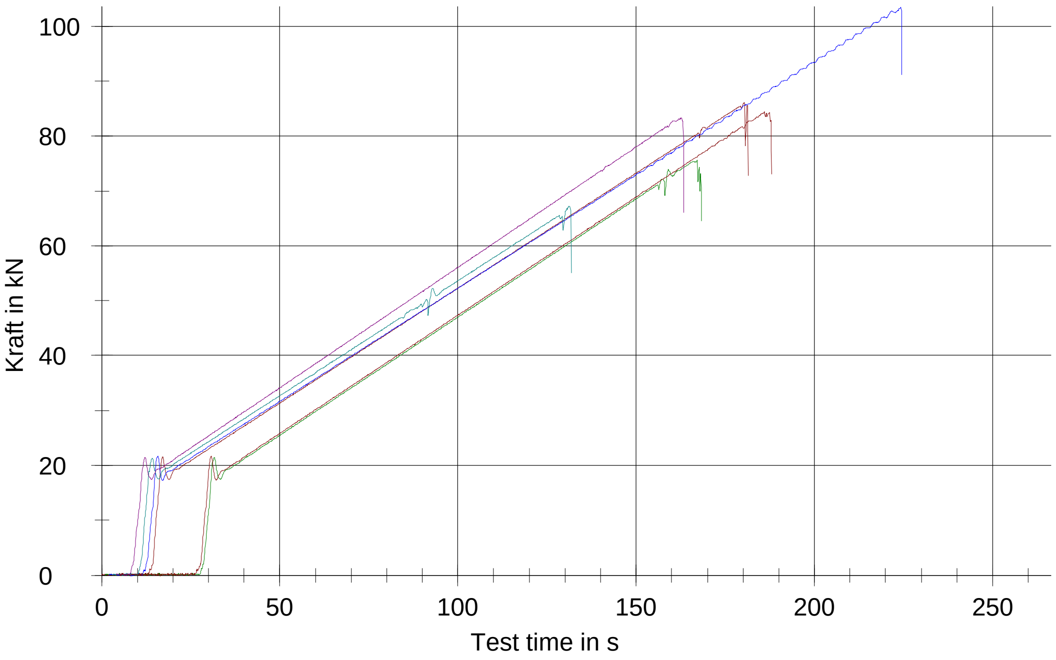
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	84,45	39,31	96,9
s	-	-	-
ν	-	-	-

Figure C.7: UCS test aplite no. 6

Resultater:

	ID	F_m	σ_m	h
Nr		kN	N/mm²	mm
1	aplite 1	86,10	41,18	71,3
2	aplite 2	75,61	35,19	68,1
3	aplite 3	103,44	50,24	78,6
4	aplite 4	67,25	32,16	85,1
5	aplite 5	83,33	38,06	95,5
6	aplite 6	84,45	39,31	96,9

Grafisk fremstilling:



Statistikk:

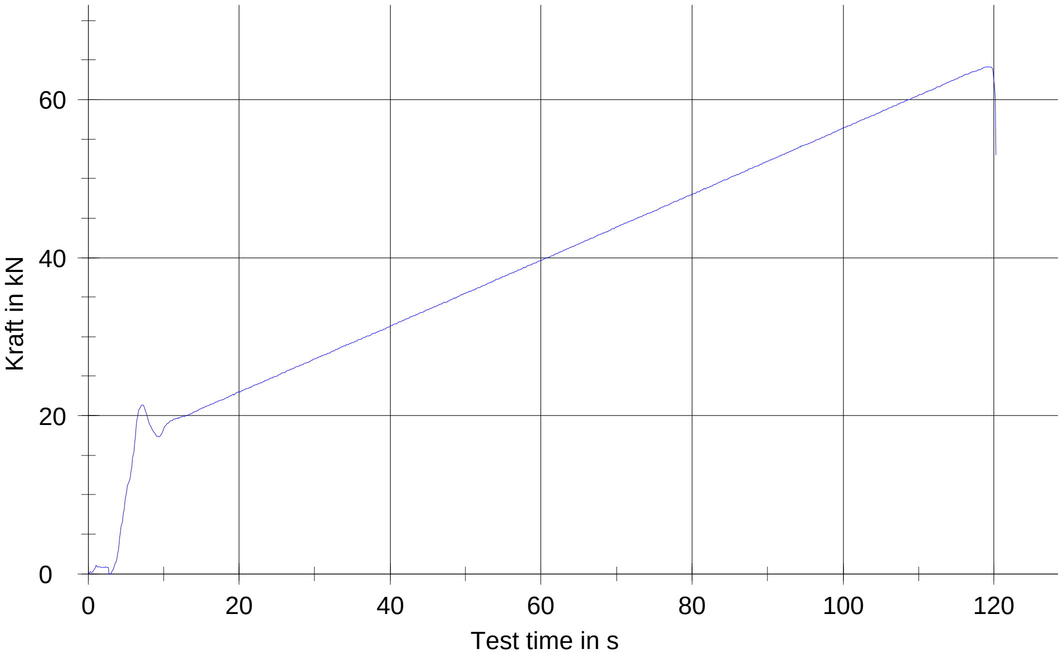
Series	F_m	σ_m	h
n = 6	kN	N/mm²	mm
$\bar{x}$	83,36	39,36	82,6
s	12,10	6,21	12,1
ν	14,51	15,77	14,64

Figure C.8: UCS test aplite no. 1-6

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
12	aplite 7	64,17	30,80	93,6

Grafisk fremstilling:



Statistikk:

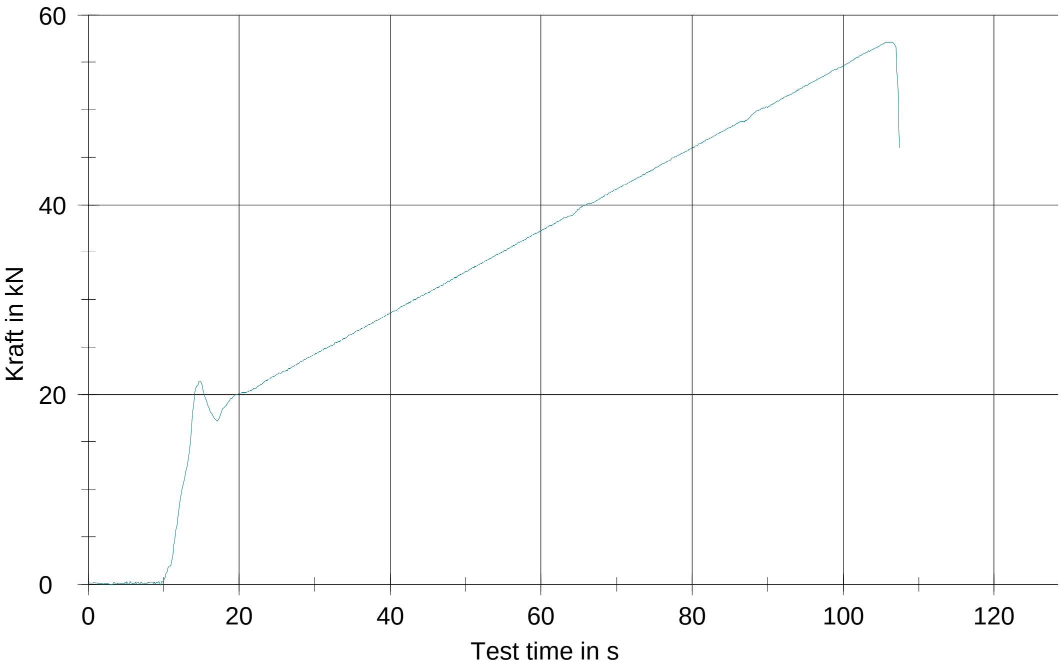
Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	64,17	30,80	93,6
s	-	-	-
ν	-	-	-

Figure C.9: UCS test aplite no. 7

Resultater:

Nr	ID	F_m kN	σ_m N/mm²	h mm
13	aplite 8	57,14	26,29	94,7

Grafisk fremstilling:



Statistikk:

Series n = 1	F_m kN	σ_m N/mm²	h mm
$\bar{x}$	57,14	26,29	94,7
s	-	-	-
ν	-	-	-

Figure C.10: UCS test aplite no. 8