GEOPOLYMERS AS ALTERNATIVE TO PORTLAND CEMENT IN P&A

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Para a minha família, pelo seu acreditar e apoio incondicional, especialmente a minha mãe que tornou possível esta aventura e para o meu pai, onde quer que ele esteja… que todos sem exceção continuem a sentir orgulho da pessoa que me tornei. Adoro-vos.

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Abstract

When oil and gas wells reach the end of their production life, they need to be permanently plugged and abandoned.

Due to the maturity of the fields in the North Sea, in the next decades many of the wells will have to be permanently plugged and abandoned therefore, Plug and Abandonment (P&A) has become a major focus in the petroleum industry.

P&A is the last phase of the life cycle of a well and hence no return of capital from it is expected. Furthermore, the responsibility of the operators for the abandoned well lasts long after the wellbore has been plugged, therefore an efficient plugging procedure will be the main goal for any permanent abandonment.

The requirements for a permanent barrier state that it must cover the entire cross-section of the wellbore, including all annuli, sealing permanently that region avoiding any fluid leakages through the barrier itself.

This thesis evaluates fly-ash based geopolymers as an alternative sealant material for establishing a cross-sectional barrier instead of the commonly used Portland cement which presents some weaknesses when exposed to well conditions, mainly high temperatures and corrosive environments.

In order to investigate the reliability of fly-ash based geopolymers, a series of experiments were conducted using fly ash-based geopolymers which were produced by the alkali-activation of fly ash. Several different recipes were prepared using different molarities and activators. Uniaxial Compressive Strength tests were performed to compare the results for each recipe and those results showed that higher concentrations of alkali solutions developed higher compressive strength.

In addition, durability tests were performed to evaluate the resistance of geopolymers in corrosive environments. In this case, a solution of 15% HCl was used and geopolymers revealed a better resistance when in contact with this corrosive substance.

The promising results showed that there is a great potential in geopolymers usage. Moreover, if geopolymers make less of an impact to the environment, geopolymers might be regarded as a good alternative for the industry.

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Nomenclature

Ag_2O – Silver oxide
Al – Aluminium
Al_2O_3 – Aluminium oxide
API – American Petroleum Institute
ASTM – American Society for Testing and Materials
BOP – Blow-Out Preventer
CaO – Calcium oxide
Cl – Chlorine
CO_2 – Carbon dioxide
DSC – Differential Scanning Calorimetry
ECD – Equivalent Circulating Density
Fe_2O_3 – Ferric oxide
H_2S – Hydrogen sulphide
HCl – Hydrochloric acid
HF – Hydrofluoric acid
HPHT – High Pressure and High Temperature
IEA – International Energy Agency
K_2O – Potassium Oxide
K_2O – Potassium oxide
K_2SiO_3 – Potassium silicate
KCl – Potassium chloride
KOH – Potassium hydroxide
mD - Milidarcy
MD – Measured depth
MgO – Magnesium oxide
MnO – Manganese oxide
NaCl – Sodium chloride
Na_2O – Sodium oxide
Na_2SiO_3 – Sodium silicate
NaOH – Sodium hydroxide
NORSOK - Norsk Sokkel (Norwegian territory)
OPC – Ordinary Portland Cement
P&A – Plug and Abandonment
P_2O_5 – Phosphorus pentoxide
Rb_2O – Rubidium oxide
Si – Silicon
SiO_2 – Silicon dioxide
SO_3 – Sulphur trioxide
SrO – Strontium oxide
TiO_2 – Titanium dioxide
UCS – Uniaxial Compressive Strength
X-mas tree – Christmas tree
XRF – X-Ray Fluorescence
ZnO – Zinc oxide
ZrO_2 – Zirconium dioxide

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1. Introduction

Significant North Sea oil and natural gas reserves were discovered in the 1960s. The earliest find of oil in the North Sea was made 40 years ago when Dansk Undergrunds Consortium (DUC) led by Maersk Oil drilled their first exploration well [1]. A few years later, also United Kingdom and Norway became oil and gas producers. Five decades passed and presently, there are more than 8.200 drilled wells in the North Sea (figure 1-A) that are either in production, injection or that have been suspended and awaiting for Plug and Abandonment (P&A).

Until a few years ago, P&A was seen as a necessary evil from the operator's point of view because it would not create any additional value or revenue for the operating companies. Therefore, plugging jobs were usually postponed as long as possible in order to minimize costs.

Normally a well's production life is about 5 to 20 year [2] because, even after enhanced oil recovery strategies have been applied, pressure starts decreasing and more and more water starts to be produced, leading to a progressive decrease in oil production. When the amount of oil extracted from the reservoir becomes non profitable to its owner, the production will cease. By this time, all wells will have to be permanently plugged and abandoned.

Figure 1-B also presents the average age of North Sea Installations. Offshoreenergy.dk records indicate that almost 600 installations in the North Sea were constructed before 1996 and have therefore reached the age where they should be considered to be decommissioned [1].
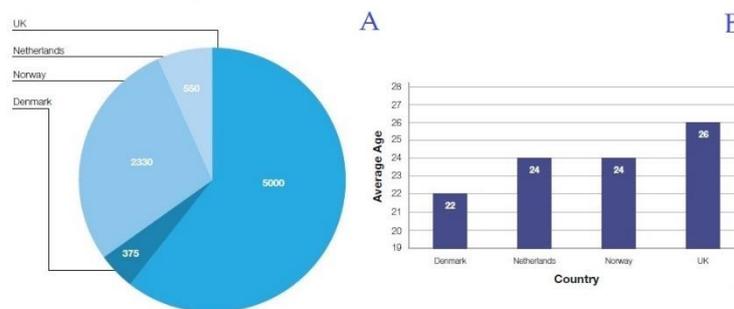
Figure 1 - Number of wells and average age of installations in the North Sea [3]

This problem has become of major concern for oil and gas industry operators because the number of wells needing to be permanently abandoned will increase rapidly for the next 20-30 years. The abandonment of these wells will be very costly and time consuming for operators, therefore the use of new technology and the upgrade of field-abandonment procedures have to be performed in order to guarantee an efficient and permanent isolation of the wells.

The life of a well comprises of numerous stages. A conventional life cycle of a well (figure 2) can be divided into five stages.
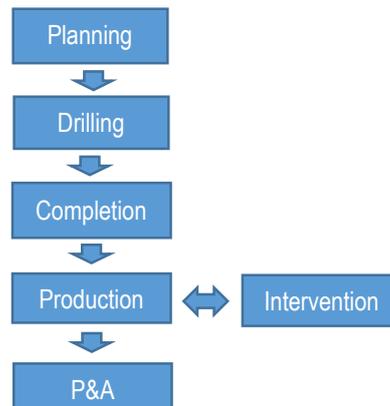
Figure 2 - Life cycle of a well

Planning – In this phase drilling engineers design and implement procedures to drill wells as safely and economically as possible. These procedures involve estimating the value of reserves, costs estimation to access reserves and type of equipment needed to reach the target. The planning is mainly based in geological surveys. These surveys are performed through sonic waves with their reflections helping geologists to identify which types of rocks, geological structures and accumulations of hydrocarbons are present below surface.

Drilling - Exploration wells (wildcat wells) need to be drilled to determine whether oil or gas is present or not in a certain area. If exploration wells show technically and commercially viable quantities of oil and gas, drilling operations can start. The main objective is to drill a hole as fast as possible without accidents.

As each section of the well is drilled, steel casing is run into the well and cemented into place to prevent the well from collapsing.

This is one of the most expensive stages in the oil and gas industry, mainly when it takes place off-shore.

Completion - After the well has been drilled it has to be completed and prepared for production. Thereby, different tools are installed inside the well to allow reservoir fluids to come out to surface in a controlled and safe way. Tools related with well control will be installed on the top of the well (upper completion) and those related with production control, will be installed on the bottom of the well (lower completion).

Production – During the production phase the main objective is to extract as much oil as possible, separating the well fluids into oil, gas and water phases. While oil and gas are produced, revenues for the operator are being generated.

Well Intervention - During the production phase several problems might occur which will lead to the need of a well intervention. Problems due to mechanical failures or even to improve reservoir recoveries can be a reason to fix the well. Operations like scale removal (salts forming in the well),

acid stimulation (carbonates), removing sand or cleaning sand screens and even perform production logging to detect water producing formations that should be sealed can be considered as intervention operations as well.

Plug and Abandonment (P&A) - When the hydrocarbon production rate is no longer economical the reservoir is abandoned and the well is sealed ensuring minimal risk to the environment.

Operations to plug the well permanently and leave it in a safe state are achieved by placing permanent barriers in the well (cement or other plugging material) in order to seal the well and avoid gas or hydrocarbons leakages to the surface.

2. Objective

Geopolymers, recently become a developing field of research for replacing Portland cement as the most widely used plugging material in plug and abandonment operations. Several studies performed by different authors about geopolymers and their applicability, presented promising results to consider them as a viable alternative to Portland cement.

In this thesis, fly ash-based geopolymers were studied as an alternative in P&A.

Samples with higher concentrations of alkali solutions were produced and presented good compressive strength results, however they showed high viscosities and short setting times needing the use of plasticizers and/or retarders to improve their workability.

Therefore, the objective of this thesis was to find an equilibrium between viscosities, setting times and relative good compressive strength results using two different activators and molarities.

Furthermore, additional experiments were conducted in order to investigate other important properties to assess if geopolymers are a viable alternative to Portland cement in P&A operations.

3. Plug and Abandonment (P&A) in general

3.1. Definition of Plug and Abandonment

In the oil and gas industry, all wells drilled either for exploration, production or injection will sometime in their life be plugged and abandoned, usually when logs determine there is insufficient hydrocarbon potential to develop the well or after production has ceased. The purpose for plugging an abandoned well is to maintain all the fluids confined permanently at the bottom of the well in perpetuity, preventing fluid leakages along the well thereby avoiding the contamination of local environment by brine, oil or gas moving upward the drilled well. To avoid this contamination, several critical intervals of the well must be plugged from the bottom hole to the surface [4].

Moreover, all the area used during drilling and well activities, has to be left behind with none "visible" traces or obstructions as if no activity had ever been conducted in that region.

A P&A operation is a complex operation that need detailed planning, thorough cost and risk estimation, and with large emphasis on safety. It consists of several phases, starting with plugging the reservoir, and ending with wellhead removal [5].

3.2. Standards

Depending on the regions where the wells are located, different rules and regulations which constitute the guidelines for proper well abandonment procedures are in place. In jurisdictions where those guidelines are not supplied by regulatory authorities, operators tend to follow their own internal standards. Most of these standards are similar since many originated in the North Sea. That region has some of the world's most stringent regulations mainly for environmental protection and because responsibilities for well integrity are enduring and any future failure must be remedied by the operators [3] [6].

Some examples of these mentioned standards and the locations where they are in place are given below:

- Denmark - A guide to hydrocarbon licenses in Denmark or API Bulletin E3 - Well Abandonment and Inactive Well Practices for U.S. Exploration and Production Operations;
- Norway - NORSOK Standard D-010 - Well Integrity in Drilling and Well operations;
- United Kingdom - OGUK OP071 - Guidelines for the suspension and abandonment of wells and guidelines on qualification of materials for the suspension and abandonment of wells.
- United States of America – API Bull E3 – Well abandonment and inactive well practices for U.S. exploration and production operations

As it was mentioned before, the different regulations in place in the North Sea have similarities thereby further considerations in this work will be based on NORSOK – D010.

3.2.1. NORSOK D-010 - Well Integrity in Drilling and Well operations

In 1993, the Norwegian petroleum safety authorities developed a specific standard to create or replace the company specifications by a specific standard. In those standards, concepts are described for developing an action to a desired level of quality.

For P&A activities, the most relevant requirements rely under NORSOK D-010.

The scope of NORSOK D-010 is to provide a standard that mainly 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 the North Sea [7].

3.3. Current situation of abandoned wells before standards

Even if these mentioned guidelines/standards cannot avoid failures, the question that arises is what is presently the current situation of the abandoned wells which were sealed, before regulatory rules or standards had defined proper sealing and abandonment procedures? This means that wells can have been constructed with poor cement jobs being accepted without any thought for well abandonment. If they are not sealed properly, they can become a significant threat to environment and remedial job to repair a well previously plugged and abandoned, will be costly and time consuming. Therefore, the quality of cementing job between the casing and formations, (figure 3) which was performed during drilling operations, will play an important role in the long-term isolation performance of the well years later, when the production is ceased [8].
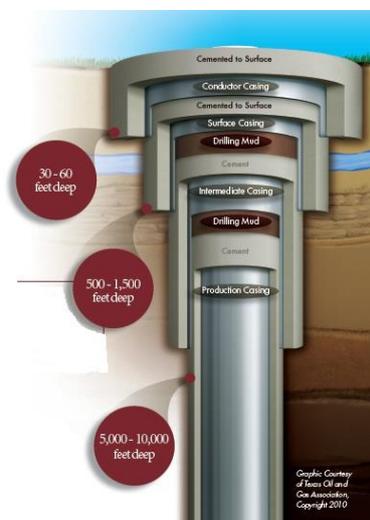
Figure 3 - Casing cement

3.4. Types of Abandonment

A well can be abandoned in two different ways: temporary or permanently.
According to NORSOK D010, a well can be abandoned in two different ways: temporary or permanently. The standard defines Temporary Abandonment and Permanent Abandonment as follows:

- Temporary Abandonment: "Well status where the well is abandoned and/or the well control equipment is removed. This is done with the further intention of resuming operations within a specified time frame (from days up to several years)".
- Permanent abandonment: "Well status where the well or part of the well is plugged and abandoned permanently with the intention of never being used or re-entered again" [8].

The focus of this thesis is permanent P&A, so unless stated temporary P&A, the term P&A refers to permanent plug and abandonment.

3.5. General operational procedure

3.5.1. Procedures before P&A

Before starting a P&A procedure, the well has to be "killed" therefore a heavy fluid is pumped into the wellbore to make the well overbalanced.

Afterwards, a logging is done in order to verify the integrity of the cement on the outside of the area where the cement plug will be set, as the plug has to extend across the full cross section of the well, including annulus, and seal both in horizontal and vertical direction [5].

3.5.2. Pulling the production tubing

In permanent abandonment operations, the production tubing/upper completion (figure 4) can be either pulled out or left in the hole but all downhole equipment (lower completion) if possible, have to be retrieved.

Removing production tubing is a delicate and time consuming operation. It needs special equipment that can handle high loads and in the case of subsea wells, semi-submersibles or jack-up rigs have to be used increasing the final costs of a P&A operation.

Usually, the normal procedure is to cut the tubing above the production packer (if not retrievable), remove the X-mas tree and install a blow-out preventer (BOP). Finally, the tubing is then pulled up the wellbore [5].

①	Conductor pipe
②	Surface casing
③	Production tubing
④	Tubing hanger
⑤	Casing hanger
⑥	Casing hanger
⑦	Annulus metal seal
⑧	Production casing
⑨	Intermediate casing
⑩	Production packer

Subsea template
Conductor housing
Wellhead housing
Christmas tree support
Subsurface safety valve
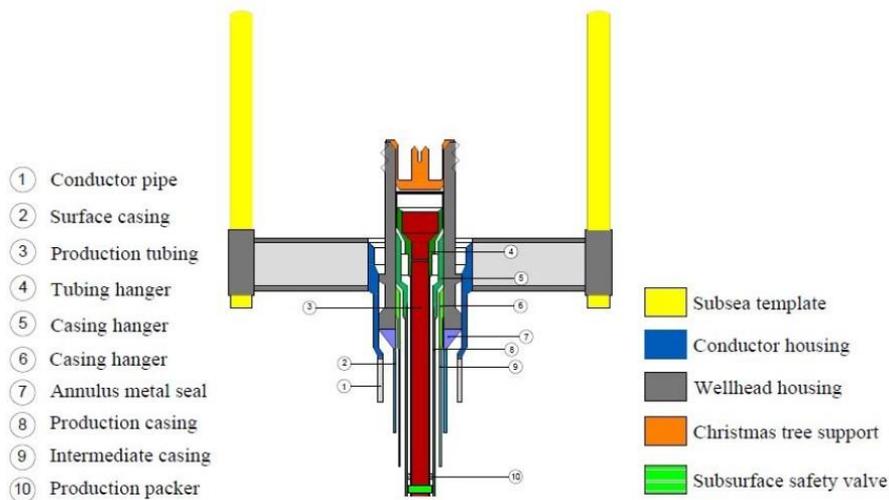
Figure 4 - Typical upper completion of a subsea well

3.5.3. Wellbore Cleanout

After the downhole well equipment has been removed, the wellbore has to be cleaned in order to remove the fill, scale, and other debris covering perforations. Then, a circulating fluid with sufficient

density to control pressure inside the well is used to clean out the wellbore and remove the unwanted material [9].

3.5.4. Establishing barriers

NORSOK D-010 states that a permanent well barrier shall extend the full cross section of the well, including all annuli and seal both vertically and horizontally as illustrated in figure 5.
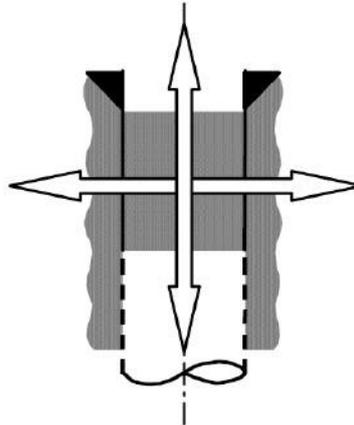
Figure 5 - Permanent Well barrier design criteria [8]

It is expected that formation fluids in presence of a possible flow path, will move from higher to lower pressure zones inside the wellbore. The properties of the formations like thickness, porosity and permeability together with the density and viscosity of the fluids will define the path between formations in response to that pressure differential [10].

Therefore, the plug has to be placed at a depth interval where the logs verified a good integrity of the existing casing cement. If the cement behind the casing is sufficient and in good conditions, the plugging operation can be initiated.

It is important to note that, for NORSOK-D010, pressure integrity of casing cement is considered as a vertical seal but not as a horizontal seal as illustrated in figure 6. Therefore, casing cement will not qualify as well barrier element across the wall.
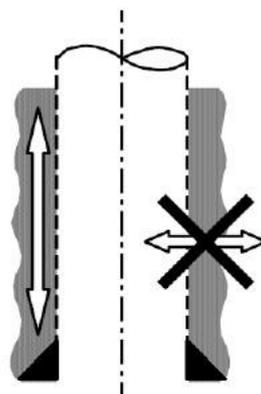
Figure 6 - Casing cement as a well barrier element [8]

Multiwall perforations are shot at different depths (Figure 7) and when tubing placed in the wellbore is perforated, cement is pumped through the tubing and circulated between the tubing and casing to achieve a wall-to-wall cement barrier at the desired depth.

Figure 7 - Perforated tubing [11]

NORSOK D-010 states that there has to be at least one permanent well barrier between the surface and a potential source of inflow, but when we are dealing with a source containing hydrocarbons, there have to be two well barriers which should be above this source of inflow meaning, above the reservoir. Cement across a section which is located through the reservoir will not count as a part of the permanent barriers because as it was mentioned before, barriers have to be installed above the reservoir [5].

The last open hole section of a wellbore shall not be abandoned permanently without installing a permanent well barrier, regardless of pressure or flow potential. In this case the complete borehole will be isolated.

If the integrity of the casing cement is not reliable (low quality or total absence) due to poor cement jobs during drilling operations, re-establish barrier elements is needed, therefore the casing and the remaining cement need to be removed and the hole prepared to be cemented again. In first place and according to NORSOK D-010, 50 meters of the casing will have to be cut and tried to pull out of the well. Often, casing removal is not easily accomplished due to factors like collapsed formation, settled particles of mud or cement. In these cases, section milling has to be performed. Section milling is a time-consuming operation in which the existing casing is milled away to provide access to the annulus using a bladed mill (figure 8), with all the metal debris (swarf) transported to the surface afterwards through a viscous milling fluid [5].

Figure 9 shows steel debris after a section milling. These debris can lead to serious problems downhole like:

- Increasing equivalent circulating density (ECD), the pressure into the well can exceed fracture pressure leading to a circulation loss. This can result in a mud level reduction in the well which can cause a kick.
- Clog pipes;
- Damage equipment like the BOP when circulated out;

Figure 8 - Five bladed mil [11]

Figure 9 - Metal debris (swarf) [11]

After the milling is completed, the hole needs to be prepared for the new cementing operation through a process called clean-out run. Finally, underreaming is carried out to increase the hole diameter. With this last procedure, any previously set cement will be removed and new formation will be exposed to allow better bonding and sealing properties for the new cement that will be placed [12].

3.5.5. Surface plug and wellhead removal

According to NORSOK D-010, after casings are pulled, the installation of a permanent well barrier (surface plug) in the last open hole section is mandatory before abandoning the well. From figure 5, it is noticeable that the barrier has to plug the whole cross section of the well like in the case of primary and secondary barriers.

After the installation of the previous barrier and in order to avoid that any parts of the well can protrude the seabed, the casing which shall be cut 5 meters below the seabed (either using explosives or cutting knives) and the wellhead have to be removed.

When this operation has been completed and all remaining downhole equipment related with drilling and well activities have been removed from the seabed as well, decommissioning of the rig will take place. In the case of subsea wells, if production boats or semi-submersibles have been used, this operation is easier to fulfil than if we are in presence of a platform. In this case, all the structure has to be dismantled with thousand tonnes of steel and concrete having to be removed from the location [5].

3.6. Well Barriers definition

Plugging activities, are related to the proper use of well barriers. NORSOK D-010 claims that a well barrier prevents unwanted fluids or gases to flow from the formation, into another formation or to surface by using a closed envelope of one or several dependent well barrier elements.
A well barrier element is defined as an object that alone cannot prevent flow from one side to the other side of itself [7].
Usually it is performed by placing a cement plug over the reservoir and up to the casing creating a safety barrier envelope with pressure integrity intact.
The volume of cement needed to set a plug is calculated based on the desired length and hole diameter (this information can be taken from the logs). Typically, some losses due to cement contamination or the use of spacers have to be taken into account [10].

3.7. Function and type of well barriers

NORSOK D-010 lists all types of well barriers and their functions in different abandonment scenarios. These types of well barriers are described in following table 1.

Table 1 - Function and type of well barriers [8]

Name	Function	Purpose
Primary well barrier.	First well barrier against flow of formation fluids to surface, or to secure a last open hole.	To isolate a potential source of inflow from surface.
Secondary well barrier, reservoir.	Back-up to the primary well barrier.	Same purpose as the primary well barrier, and applies where the potential source of inflow is also a reservoir (w/ flow potential and/ or hydrocarbons).
Well barrier between reservoirs.	To isolate reservoirs from each other.	To reduce potential for flow between reservoirs.
Open hole to surface well barrier.	To isolate an open hole from surface, which is exposed whilst plugging the well.	"Fail-safe" well barrier, where a potential source of inflow is exposed after e.g. a casing cut.
Secondary well barrier, temporary abandonment.	Second, independent well barrier in connection with drilling and well activities.	To ensure safe re-connection to a temporary abandoned well, and applies consequently only where well activities has not been concluded.

3.8. Positioning of Well Barriers

In NORSOK D-010 the positioning and the materials used as well barriers, are described as follows:

- *"Well barriers should be installed as close to the potential source of inflow as possible, covering all possible leak paths".*
- *"The primary and secondary well barriers shall be positioned at a depth where the estimated formation fracture pressure at the base of the plug is in excess of the potential internal pressure".*
- *"The materials used in well barriers shall withstand the load/environmental conditions it may be exposed to for the time the well will be abandoned".*

In figure 10, a typical well configuration before and after a P&A operation with the location of the well barrier elements is depicted. The image on the right, shows two types of plugging; with the tubing left in hole and with tubing pulled.
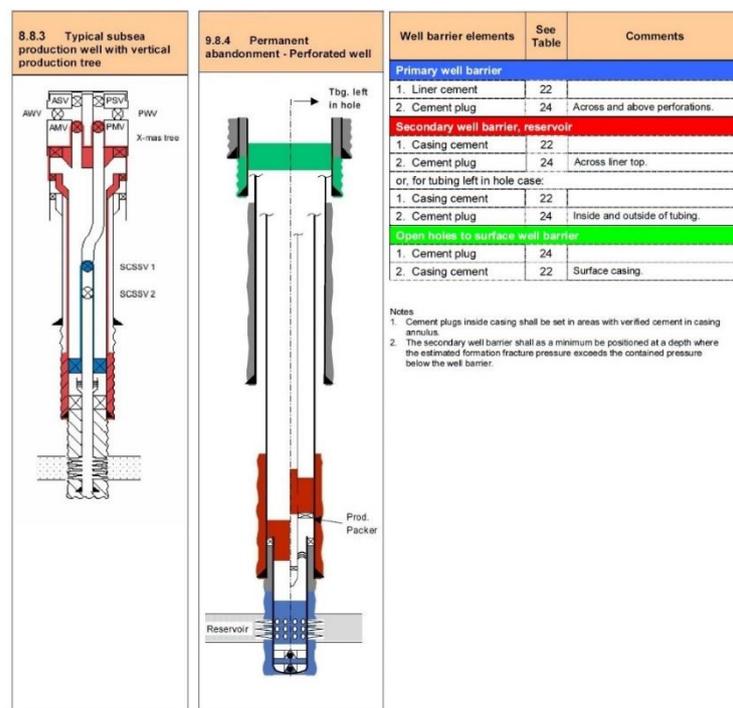
Figure 10 - Typical well schematic before and after completed P&A operation [8]

From the previous figure it is shown that three barriers have to be used. A primary well barrier, with the purpose of behaving as a first barrier against a potential source of inflow. The secondary will be a backup of the primary. The formation strength at the base of the well barriers must be able to withstand pressures from below formations.

According to acceptance criteria of a cement plug described in NORSOK D-010:

- The firm plug length shall be 100 m measured depth (MD). If a plug is set inside casing and with a mechanical plug as a foundation, the minimum length shall be 50 m MD;
- It shall extend minimum 50 m MD above any source of inflow/ leakage point;
- The open hole to surface well barrier is to permanent isolate the open hole from surface exposed after casing cut and it has to be placed as deep as possible in the surface casing and with the top minimum 50 m above the shallowest permeable zone and 5m below the seabed [13].

3.9. Full Well Abandonment vs Section Abandonment (Slot Recovery)

When a reservoir reaches the end of its economic interest but the well still has value for further operations, section abandonment is undertaken to extend a wells usable life. This kind of operation is known as slot-recovery in which the lower completion (section below the production packer) is plugged and abandoned permanently by setting required barriers and a side-track will be drilled afterwards, until reaching the desired target depth. Slot recovery is not the main focus of this thesis. Full well abandonment is performed when neither the reservoir nor the well has any future utility [7] [5].

3.10. Placement of a permanent plug

The most important aspect in P&A operations is the placement method of the plugging material. It is important to have present the definition of a cement plug. It can be defined as a volume of cement designed to fill a certain length of casing or open hole, providing at the same time a seal against vertical migration of fluid or gas [10].

If the sealing material is not properly placed the efficiency and the purpose of whole operation may be compromised therefore setting a quality cement plug in a well is dependent on good job planning and taking the specific well conditions into account [13]. The placement of the sealing material in the desired location is not straight forward. Several undesirable issues can occur like channelling or dilution of the sealing material [8].

3.11. Well Plugging Methods

Several methods for setting a plug in the wellbore are available. The chosen method depends on the wellbore conditions and regulations but in all cases the purpose is to pump cement into the well (slurry) until it reaches the desired location at a certain depth. Due to the conditions (pressure and temperature) inside the well, the cement will harden after a number of hours [10].

Presently, the three most commonly used methods are:

- Squeezing Method;
- Balanced Plug Method;
- Wire Line Dump Bailer Method;
- Two Plug Method.

3.11.1. Squeezing Method

Squeeze cementing is commonly used for plugging reservoirs. It can also be used when debris were left inside the wellbore and cement below those debris is needed, or in situations where casing leaks were detected. In these cases where the integrity of casing cement is not reliable, new cement has to be placed outside this poor cement to ensure proper sealing of that location. The placement of the cement in this method can be achieved using two different procedures that depend on how much additional pressure is needed to force cement to go down the wellbore until the desired location. In the called Braidenhead method, additional pressure at the surface is applied after the well is shut-in, through the casing valve. On the other hand, if this mentioned additional pressure is applied by using a pump, then Bullhead squeeze method is used [10]. Both methods are depicted in figure 11.

With the application of this pressure, the pumped slurry will dehydrate and form a high strength filter cake in perforations, channels, fractures or against formation. In this way, the slurry after hardening will become a physical barrier which will prevent formation fluid movement into the wellbore [8].
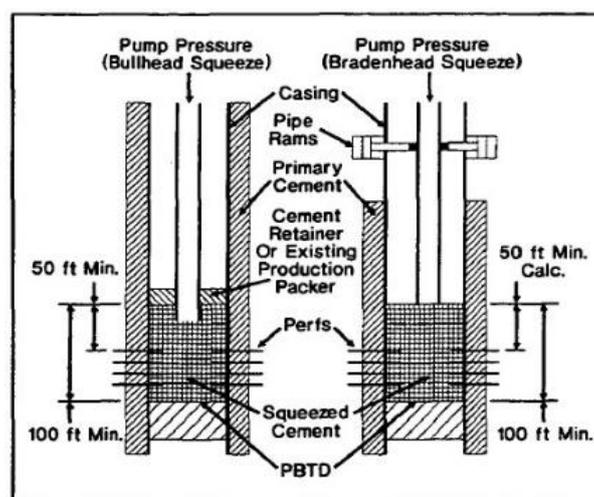
Figure 11 - Squeezing cement method [11]

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3.11.2. Balanced plug method

The balanced plug method is perhaps the most common method used for plugging in the oil and gas industry and is mainly used to place the middle plug [15] [10].

This method, as illustrated in figure 12, intends to avert the contamination of cement slurry by mud. In order to achieve that, a spacer fluid is pumped ahead and behind the slurry preventing any possible contact between the cement and the existing mud inside the well [16].

While these materials are pumped down the pipe, the mud is forced to move up the annulus space behind the casing. This procedure will end when the heights of cement slurry and spacer in the drill pipe or tubing, are the same as in the annulus.

The efficiency of this method is highly related with the control of the viscosities and densities of the different materials being used. The risk of channelling of one of the materials through the other can lead to undesired contamination of the slurry leading to an improper plugging job.
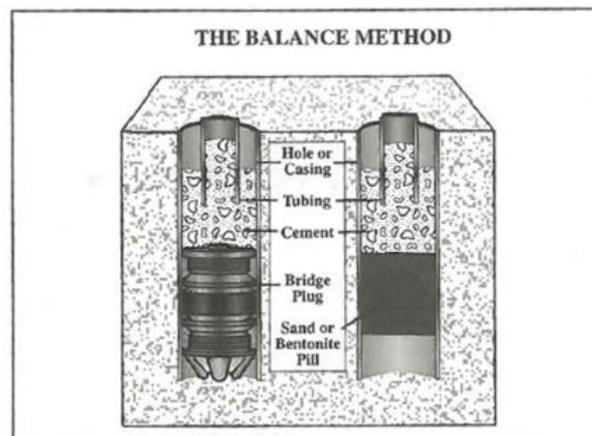
Figure 12 - Balanced plug method [8]

3.11.3. Wire Line Dump Bailer Method

If the volume of the plugs is small and accuracy of the placement location of the plug is needed then the wire line dump bailer method is the appropriate method which is described in figure 13 – A [15].

In this method, the placement of the slurry into the well is achieved by using a dump bailer on a wireline. This tool contains a measured amount of cement which is lowered into the wellbore until it reaches a previously placed bridge plug below the desired depth. With this impact, the bailer opens and the slurry is dumped. This opening can also be caused by electronic activation (figure 13 - B). The dump bailer is pulled out of the well, afterwards.

This method presents some limitations due to the volume capacity of the dump bailer, meaning that in some cases, several runs have to be performed if high volume of slurry is needed. The depth at which placement can occur is also a drawback of this method [16]

On the other hand, due to the simplicity of this method, it can be performed without the need of using a rig. Vessels or jack-up rigs can be used instead.
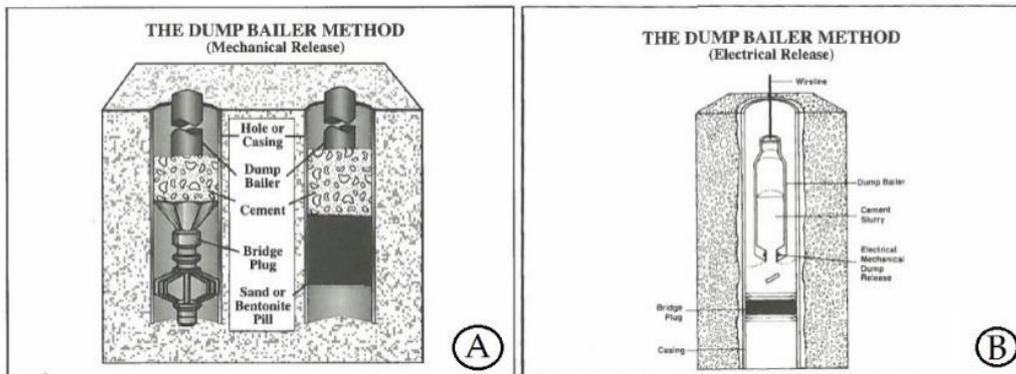
Figure 13 - Wire Line Dump Bailer Method (A) and Electrical Dump Bailer Method (B) [8]

3.11.4. Two Plug Method

The two-plug method, illustrated in figure 14, uses a special tool to set the slurry at a calculated depth avoiding at the same time any possibility of slurry contamination [17]. This mentioned tool, consists of two wiper plugs (installed at the bottom and at the top of the tool which prevent fluids to contact each other avoiding any contamination), a locator sub and a cement stinger.

The procedure consists in pumping a spacer followed by a dart (which is located inside the bottom wiper plug) with cement on top of it. The dart cleans the walls of the pipe and when it reaches the locator, it stops. With the increase of the pressure, a membrane that is located into the dart rips allowing cement to continue down the stinger. The cement is followed by the other dart (which was located inside the top wiper plug) and spacer. This second dart breaks at the locator sub and spacer keeps flowing further down. To prevent the spacer from going all the way down and mix with the cement thus contaminating it, the stinger is pulled above the cement [13].
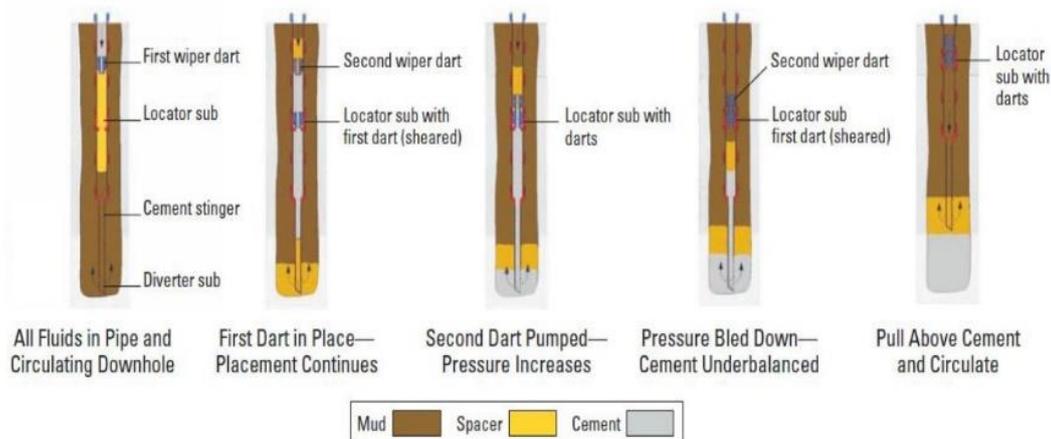
Figure 14 - Two Plug Method [16]

3.12. Verification requirements of a cement plug

NORSOK D-010 describes several verification procedures of the cement plug.

Before plugging a well, the strength of the plug must be verified through several tests on surface. The same materials have to be used and the mixture has to be cured under the same wellbore and formation conditions (pressure and temperature). This procedure is performed in order to verify if the plug will fulfil its purpose in an efficient manner.

After each permanent well barrier is set, its position or depth has to be confirmed by means of tagging. This confirmation is done by lowering down into the hole a drill pipe (which was previously measured to have it as reference) until it reaches the plug, giving the accurate position of the plug. This confirmation can also be done through the use of wireline tools. If the position of the plug is the correct, the strength or integrity of the plug can be tested afterwards performing a pressure test [13].

3.13. Materials Used in Well Abandonment

According to Dwight K. Smith [8], the ideal sealing material for plug and abandonment of wells should have the following properties:

- Readily available and easily mixed;
- Be chemically inert and nonreactive with groundwater;
- Provide good bonding across the zones being sealed when properly placed;
- Remain fluid for proper 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 at the interface along the formations being sealed.

3.13.1. Drilling fluid

It was mentioned before that the drilling fluid (mud) and the sealant have an important role in P&A operations.

Drilling fluid ensures that the well is static, meaning that no fluid is coming upward and through the slurry. Otherwise, if any movement occurs during the plug placement, the setting of the material can be inappropriate and plugging material can become contaminated. This may lead to a decrease of the compressive strength resistance and in the worst case scenario to a defective sealing.

3.13.2. Portland cement

Portland cement heretofore been the most used plugging material in P&A operations due to some properties like durability, reliability and economic factors related with the cost and availability

worldwide. Usually, cement used for cementing operations in the oil industry is composed by neat cement, sand, water and aggregates.

In P&A, the selection of a cement composition is related with the well depth, formation temperatures, formation properties, and wellbore mud properties. Typically, class A, C, G, or H (API Spec 10A) cements are used in well plugging operations [11]. Additional information about API Classification for oil and well cements is provided in table 2.

Some additives can be added as well into the mixture, in order to improve the properties of the slurry. Setting times can be changed by adding retarders (sodium chloride, sugars or cellulose) to provide enough time to pump the cement to the desired depth, or accelerators (calcium or sodium chloride) if is desirable for the slurry to harden quickly. Dispersants can be added in order to reduce the water content of the slurries reducing the permeability and therefore, increasing compressive strength.

Table 2 - API Oil Well Cement [17]

		Usable Range of API Oil Well Cement			
	Appropriate Well Depth (m)	**Type**			
Grade		Common	Medium Sulfate Resistance	High Sulfate Resistance	Remarks
A	0~1830	√	—	—	Common cement
B	0~1830	—	√	√	Sulfate-resisting cement
C	0~1830	√	√	√	High-early-strength cement
D	1830~3050	—	√	√	Medium-temperature medium-pressure conditions
E	3050~4270	—	√	√	High-temperature high-pressure conditions
F	3050~4880	—	√	√	Superhigh-temperature high-pressure conditions
G	0~2440	—	√	√	Basic oil well cement
H	0~2440	—	√	√	Basic oil well cement

Note: "√" means having this type of cement while "—" means not having this type of cement.
The cements of grades G & H are basic oil well cements, can be used under conditions of greater well depth and higher temperature when they are used with curing accelerator or retarding agent, and are the commonly used cements at present.

3.14. Plugging material requirements

NORSOK-D010 also describes the functional properties of a permanent well barrier as follows:

- Impermeable
- Long term integrity.
- Non-shrinking.
- Ductile (non-brittle) – able to withstand mechanical loads/impact.
- Resistant to different chemicals/ substances (H_2S, CO_2 and hydrocarbons).
- Good wetting, to ensure bonding to steel.

Steel tubular cannot be considered as a barrier element unless it is supported by a plugging material (with the properties mentioned before) that is placed on the inside and outside ensuring no leakages through the interfaces of both materials.

3.15. Reasons for plug cement failures

Failures in plugging procedures are normally due to four main reasons [8]:

- Interaction between the fluid system in the well and the cement slurry used in plugging;
- Insufficient pre-job preparation;
- Improper placement techniques;
- Displacement mechanics.

One critical factor in P&A operations is the cement setting process. The way how cement plug interacts at the interface with the wellbore fluid in place while plugging job is taking place is one reason of major concern. If drilling fluid is in the wellbore it can interfere with the correct placement of the cement plug due to the density differential between the two liquids. If density of the cement plug is higher than the one of the drilling fluid, cement slurry may drain through it instead of displacing it. There are several ways to solve this problem. Usually, a bridge plug, bentonite or reactive silicate "pill" is used.
Bridge plug (figure 15) is a mechanical device placed into the well bore to provide a solid foundation to the cement slurry.
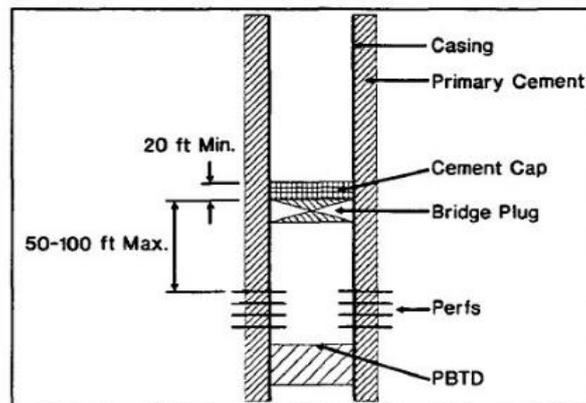
Figure 15 - Permanent bridge plug [11]

A bentonite or silicate pill will react with the fluid in place or with the pumped cement in order to form a viscous or stiff gel. This gel formation will avert the drainage of the cement through the fluid providing a plug placement at the desired location.
Another method to solve drilling fluid and cement incompatibility is through correct application of spacers. These spacers can be composed of surfactants or chemicals. Surfactants promote a water-wet surface and chemicals will react with the filter cake to improve cement bonding. It is vital for an effective plug and placement procedure to correctly estimate the necessary volume of spacer being applied. In that case an incomplete mud removal due to an inadequate cement/mud separation which could lead to the contamination and loss of mechanical properties of the plug can be avoided [8].

Another reason that can lead to a cement plug fail is the change of down-hole conditions.

It is widely known that the extraction of hydrocarbons from the reservoir and enhanced oil recovery processes will change conditions like pressure, temperature and total stress inside the reservoir. The equilibrium inside the reservoir can be reached after the well has been plugged. If those conditions were not estimated properly, the plug sealing capacity can become dramatically affected because of cement integrity failure or cement-rock de-bonding.

Finally, changes of tectonic stresses due to formation displacements can also lead to fracture set cement [8] [6].

All the previously described plug cement failures are depicted in figure 16.
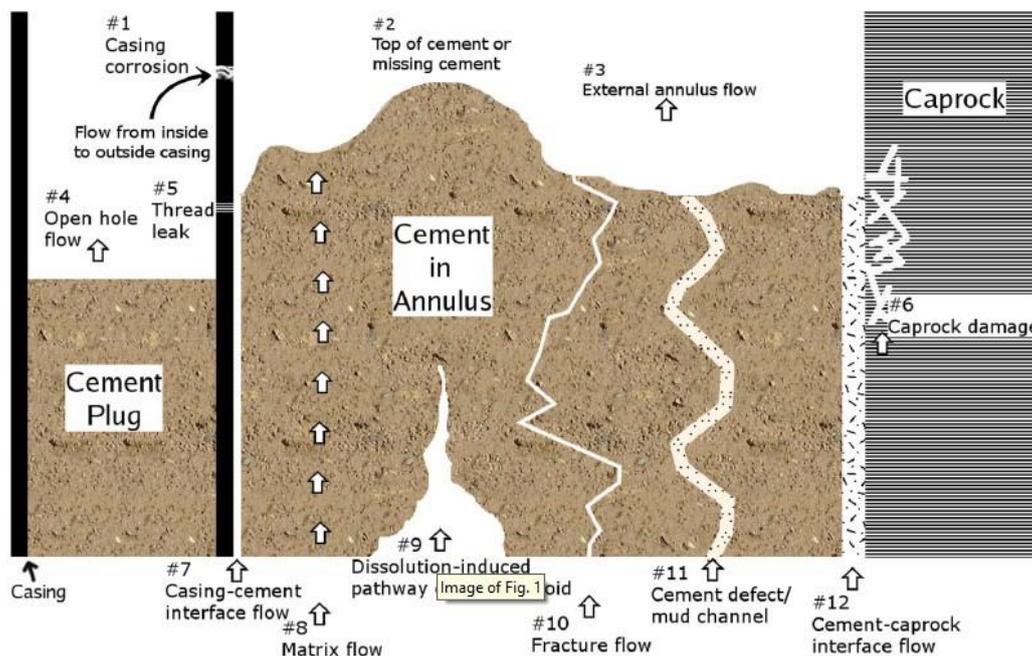
Figure 16 - Reasons for plug cement failures [19]

3.16. Requirements for cement slurry and set cement

The main goal of cementing operations, is to pump cement slurry to a desired location that can be at more than several thousand meters depth of the surface. Temperature and pressure inside the well, will affect the properties of the slurry thus changing the properties of the set cement.

A perfect cement job is achieved when a good set cement is obtained after a cementing operation. The quality of this material is dependent on its good adhesion with the other surfaces present in the wellbore (casing and wall of the formation), the consolidation strength and the good isolation of oil and gas (no channelling and no leakages).

In order to guarantee the permanency of these features in perpetuity, the cementing design should meet the following requirements:

- Minimum support strength – the compressive strength of the set cement has to be able to withstand all forces exerted by the movement of the formations;
- Increased thermal stability – When the set cement is placed in a location of the well where the temperature is higher than 110ºC, a phenomenon known as strength retrogression of set cement may occur. Some additives, like silica sand, may be added to mitigate this occurrence;
- Enhance corrosion resistance – Additives can be used to reduce corrosion of certain types of cement used in cementing operations.

During cement design, important properties that can influence dramatically the mentioned requirements have to be considered. These properties are related with the slurry from which the cement material will form and are described below:

1. Rheological property of cement slurry;
2. Cement slurry density;
3. Thickening time of cement slurry;
4. Cement slurry filter loss;
5. Free water content of cement slurry (bleeding of cement slurry);
6. Compressive strength of set cement;
7. Set cement permeability. [18]

3.16.1 Rheological property of cement slurry

Regarding P&A operations, the study of slurry rheology is important to design and execute an efficient well plugging procedure. The characterization of some important properties will help the operator to predict the behaviour of the slurry in downhole conditions. Mixability, pumpability (pump capacity and time to pump the slurry to the desired depth), density and temperature effect when placing the cement in the hole, are some of those mentioned properties.

However, a complete and accurate characterization of the cement slurry rheological behaviour is not easy to be achieved because it is dependent on many different factors. Some of these factors are:

- Water-to-cement ratio;
- Specific surface of the powder, and more precisely the size and the shape of cement grains;
- Chemical composition of the cement and the relative distribution of the components at the surface of the grains;
- Presence of additives, and mixing and testing procedures. [16]

Rheology is one method for material characterization. The flow and deformation of materials in response to applied stresses is related to properties like the molecular weight and molecular weight distribution.

To describe the flow of any fluid, equations of conservation of mass, momentum and energy are commonly used. These equations relate the deformation of the fluid (strain) to the imposed forces (stress) using the relation between the shear stress tensor (τ) and the shear rate tensor (Υ).

From a theoretical stand point, we can consider a case of a fluid which is contained between two parallel plates of equal area of which one is moving with a velocity V (figure 17).

The shear stress represents the force per unit area which causes the fluid to flow or shearing, which means the speed at which the intermediate layers move with respect to each other.
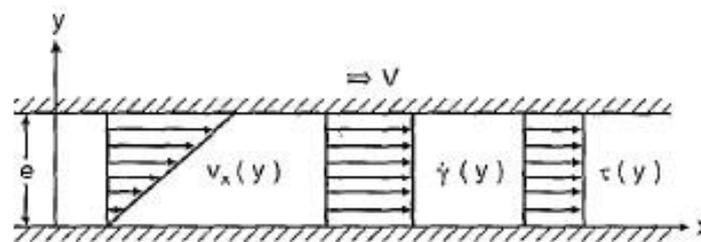
Figure 17 - Flow between parallel plates (upper plate is moving at velocity V [16]

In this case, we can conclude that the shear rate (Υ) is equivalent to the velocity gradient, since

$$\frac{d}{dy}\left(\frac{dx}{dt}\right) = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{d\Upsilon}{dt}, \ \ where \ \Upsilon \ is \ the \ strain.$$

In the previous given example, the shear rate is uniform, therefore equal to the velocity of the moving plate divided by the distance between the plates (e). The shear rate describes the shearing of the liquid.

The force necessary to move one of the plates at a given velocity V is dependent on the internal friction of the fluid. The value of this friction is determined by a fluid property called viscosity. This property is defined by the ratio between the shear stress to the shear rate.

$$\eta = \frac{\tau}{\gamma}$$

From this definition of viscosity, it is easily concluded that for high viscosity liquids, meaning with high internal friction, the amount of force required to induce its movement will be higher.

The shape of the curve or rheogram (a diagram on which shear-stress or viscosity is plotted as a function of the shear-rate) of the fluid gives the operator an idea about the behaviour of the fluid based in previously studied models. These models are divided into two groups: Newtonian and non-Newtonian fluid based models.

Common fluids, usually are included into the Newtonian group. In these cases, a relation between shear-rates and viscosity is very clear (shear stress is proportional to the rate of shear). Characterization of the behaviour of these fluids is straight forward and theoretically a single measurement of shear stress at one shear rate is enough because the rheogram of the fluid is a straight line of slope (η) passing through the origin.

Cement slurries are not included in the previous group, because cement slurries show a time-dependent behaviour which means that the viscosities of these fluids are not only dependent on the shear-rate but also on the past shear story. This time dependency is due to the following factors. One of these factors is physical interactions between cement particles in suspension during a period of time which can change its structure (and therefore the rheology). Additionally, the continuous chemical reactions may change the properties of the cement with time.

The structure of fluid is affected by the fluid deformation, thereby in order to reach an equilibrium structure a shear-rate has to be applied for a sufficient period of time. At that moment the corresponding shear-stress can be obtained through the viscometer. During this period of time, the structure builds up or breaks down; depending on if the previously applied shear-rate was higher or lower than the current rate until it reaches an asymptotic value. This phenomenon is known as thixotropy and is described in figure 18 [16].
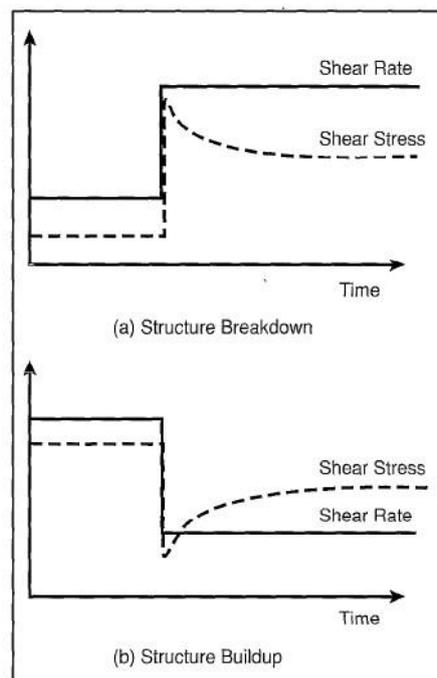
Figure 18 - Time dependent response of a thixotropic fluid to a step change in shear rate [16]

Time-independent models were studied in the past to describe the behaviour of different fluids. Each one of these rheological models has a mathematical expression for the shear stress or the viscosity as a function of the shear-rate (figure 19).

Commonly, non-Newtonian fluids are divided into two groups regarding the trend of viscosity related to the shear rate. If viscosity decreases when shear rate increases, the fluid is called shear-thinning. On the other hand, if viscosity increases when shear rate increases, then we are in presence of a shear-thickening fluid [16].
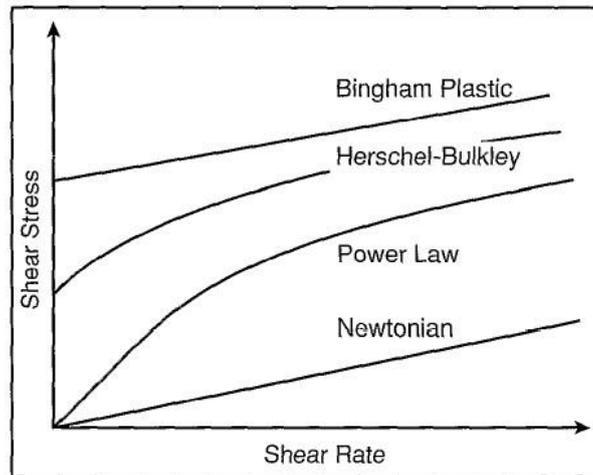
Figure 19 - Examples of flow curves used in the petroleum industry [16]

It has been shown that cement slurries, are usually included in the shear thinning group of non-Newtonian fluids and the most commonly used models to describe the rheological properties of these slurries are the Bingham Plastic and the Power Law models [15]. The main difference between these two models, is that in the case of Bingham Plastic model (equation 1), a minimum stress is required in order for the fluid to flow. This minimum stress is called yield stress (τ_y) and in oil and gas industry this stress is relevant because it interferes with the power required by the pump to start flooding the system, when pumping fluids into the well. If the obtained rheogram is fairly a straight line (Bingham Plastic model), extrapolating this line to a shear rate equal to 0 rpm, the corresponding shear stress value will be the yield stress.

Bingham plastic model assumes that above the yield stress, the shear stress is linearly related to the shear rate.

The Power law model, can be described as according to equation 2 on which "k" represents the consistency index and "n" the degree of non-Newtonian behaviour of the fluid. For shear-thinning fluids, these dimensionless parameter is always smaller than 1.

In many cases, Power Law model can be plotted on a log-log plot. In this way, the $\tau - \gamma$ relationship of the power-law model is linear.

Another model similar with Bingham plastic model with shear thinning behaviour is Herschel-Bulkley (equation 3). In this model, the yield stress is also a property which is needed to be taken into account when a rheological study of a slurry is performed.

Similarly as in Power Law model, in this case the rheogram is also curved.

In all previous cases, the corresponding viscosity measured at any particular shear rate (apparent viscosity - η') decreases from infinity at zero shear rate to the plastic viscosity (μ_p) at infinite shear rate [16].

$$\tau = \tau_y + \mu_P \times \gamma \qquad (1)$$

$$\tau = k \times \gamma^n \qquad (2)$$

$$\tau = \tau_y + k \times \gamma \qquad (3)$$

3.16.2. Cement slurry density

Cement slurry density has to be higher than the density of the drilling fluid in the well. However it has to be lower enough in order not to exert a higher pressure than the formation pressure which could lead to formation break and a kick.

The density of the slurry affects the flowability of the slurry and the strength of set cement as well.

3.16.3. Thickening time of cement slurry

From the moment that all the materials needed to produce the cement are mixed, the cement slurry starts thickening due to the continuous hydration of the cement. The period of time, from the moment when the mixture is ready until the flowability of the produced material is lost, is known as thickening time or workability. This period of time is of major importance because it has to be long enough to ensure the pumping of cement slurry to the desired location in the well.

The thickening time can be evaluated during the design of the cement through the use of a pressurized consistometer which can simulate the conditions of pressure and temperature that the slurry will find inside the well [18].

3.16.4. Cement slurry filter loss

Filter loss of cement slurry is related with the loss of the free water content in the cement slurry. This free water is released from the slurry and infiltrates into the formation through the borehole wall leaving the solid components behind. This aspect has to be controlled in the cement design because if the slurry loses water in excess, it will lead to a rapid thickening time, reducing the flowability of cement slurry. In this situation, the time to a slurry to be pumped until the desired depth or location can be seriously diminished endangering the efficiency of the cementing job [18].

3.16.5. Free water content of cement slurry (bleeding of cement slurry)

During slurry placement into the wellbore under pressure, fluid loss occurs.

Bleeding of cement slurry is a typical event which occurs during the curing of a cement slurry and is related with the release of free-water from the slurry, leading to a continuous water phase formation. Two problems can arise, if this bleeding is not controlled. The possible formation of a continuous water channel on the top of the cement inside the annulus and an increase of the density of the slurry. In the first case, this can modify the predicted setting time of the slurry thereby affecting the efficiency of the sealing [18]. In the second case, changes in the density of the slurry can cause cementing failures due to excessive increases in slurry viscosity during placemen. In such cases, fluid loss agents are commonly used to control water loss of the slurries to retain the liquid phase in the pumped systems. Example of a fluid loss agent can be a carbohydrate compound selected from the group of the water-soluble polysaccharides [20].

3.16.6. Compressive strength of set cement

The force that a set cement can withstand is one of the most important features of the set cement. The set cement has to be able to resist the pressures exerted inside the well, before rupture and without losing its mechanical integrity.

As a reference, Wan Renpu [18] claims that *"At least a compressive strength of 3.5 MPa should be achieved by set cement during an effective time in order to conduct the operations of putting the well into production."*

3.16.7. Set cement permeability

One of the main purposes of a well barrier is to avoid gas or hydrocarbons leakages to the surface. Therefore the permeability of the set cement has to be low to the full extent in order to those leakages not occur. According to the literature [21], the acceptable values of permeability are less than 0.10 mD.

3.17. Corrosion resistance

Presently, the use of acids is widely used as a method to stimulate or improve production in cases where formation has low permeability. The possibility of the sealing material inside the well to be in contact with corrosive substances is likely reasonable to occur leading to the deterioration of sealing material endangering the integrity and compressive strength of well barriers. Therefore, chemical resistance is a necessary property when cementing oil and gas wells.

3.17.1 Brief description of acid stimulation

This low permeability can be either due to the presence of debris like scale and rust which can restrict the flow in the well or due to natural low permeability of the formation.

In the first case, an acid treatment known as acid washing is performed and the purpose is to clean the tubular and wellbore. In these cases, mixtures containing HCl are used.

In the second case, when the formation is composed of rocks that dissolve in contact with an acid, such as carbonate, limestone or sandstone, then a technique known as acidizing may be required. This procedure consists of pumping acid down the well. The acid will go down the tubing, entering into the perforations and contacting the formation. The pressure exerted by the continuous pumping process will force the acid into the formation dissolving sediments and mud solids that are inhibiting the permeability of the rock, enlarging the pore spaces, producing highly conductive channels (wormholes) which will provide a path for the oil or gas to enter the well through the perforations.

There are two different methods to perform this type of acid treatment which differ in the pressure that is applied during the pumping of the mixture. If the acidic mixture is pumped with a pressure below the formation fracturing pressure we are in presence of a matrix acidizing method (figure 20 - A). On the other hand, if the acidic mixture is pumped with a pressure above the formation fracturing pressure leading to cracking or fracturing of the formation, the method is known as fracturing acidizing (figure 20 - B). The choice of one of the methods depends on formation permeability.
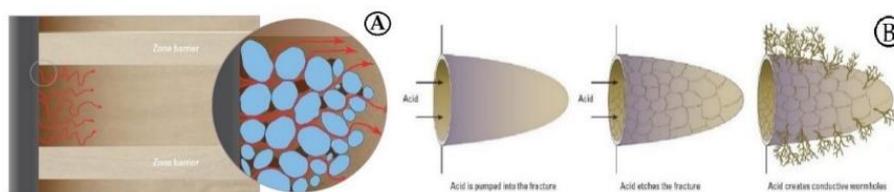
Figure 20 - Matrix stimulation (A) and acid fracturing (B) [22]

There are many types of acid which can be used in well stimulation jobs. Hydrochloric, hydrofluoric, acetic, formic, sulfamic and fluoboric acids are some examples of those acids.

The most commonly used in the oil and gas industry in carbonate or limestone formations is hydrochloric acid.

According to literature, the used HCl concentrations are within the range of 7.5% and 28% with the most common being 15%.

In sandstone or shale formations, hydrofluoric acid (HF) is more efficient instead. It can be used in combination with HCl, if some carbonate minerals are present in the sandstone formation.

After an acid job is completed, a process called backflush is performed in order to remove the acid and sediments from the reservoir [22] [23] [24].

3. Geopolymers as an alternative to Portland cement in P&A

It is widely known that, the most important ingredient in the conventional concrete is the Portland cement, however, the production of cement not only emits large amounts of carbon dioxide to the atmosphere but also requires high energy and natural resources consumption. Nevertheless the need of this material will increase for the next decades in order to meet infrastructure developments. However, the question that arises is: how modern societies will deal with this situation?

Alternative binders to obtain concrete, have to be found and investigated in order to mitigate the problems mentioned before [25] [26].

Particularly in the oil and gas industry, Portland cement due to its low cost, easy availability, relative reliability through time (permeability and durability properties) made it the most commonly used material in cementing and P&A operations. Nevertheless, it presents some limitations related with shrinkage, permeability (allowing possible gas influxes), mechanical instability at high pressure and high temperature (HPHT) conditions, integrity when exposed to corrosive environments, low ductility and long-term durability concerns [27].

Deciding the best sealing material in P&A operations is not straightforward and it will differ depending on the particular characteristics of each well. Mechanical properties of the sealing material depend on downhole conditions before and after permanent plugging.

Currently, companies are developing and investigating new cement formulations with high performance or even cements based in new materials in order to perform an effective and efficient zonal isolation during the entire life of the well. Therefore, some studies have been performed in order to investigate alternative materials for P&A operations, with better chemical and mechanical characteristics to withstand the conditions mentioned before.

Several different types of material have been studied and one of those is the geopolymers, which according to several studies, present chemical and physical characteristics that makes it a viable alternative to Portland cement as permanent barrier in P&A. Moreover, geopolymers have the additional advantage of significantly reduced Greenhouse emissions.

3.1. Definition of Geopolymer

In 1978, Joseph Davidovits found that a chemical reaction between an alkaline liquid with silicon (Si) and aluminium (Al) present in a source material of geological origin would produce binders as a product of the reaction. Because of the geological origin of the source material and type of chemical reaction (polymerization), Davidovits named this type of binder "Geopolymer".

In his studies, other by-product materials such as fly ash and rice husk ash were used as well.

The chemical composition of the geopolymer material is similar to natural zeolitic materials, but the microstructure is amorphous. The polymerization process involves a substantially fast chemical

reaction under alkaline conditions on silicon (Si) - aluminium (Al) minerals, that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [28].

The main difference in the performance of these materials when compared with Portland cement is due to their chemical structure and activation mechanism.

Portland cement is composed of Calcium Hydroxide and Calcium Silicate Hydrate where as geopolymers are based on aluminosilicate gel [29].

A comparison of Portland cement and geopolymers is described in figure 21.

Portland Cement Slurry

$CaO+SiO_2$

⬇ 1450 C Calcination

Clinker phase

⬇ Hydration

$C-S-H + Ca(OH)_2$

Geopolymer Slurry

$Al_2O_3+SiO_2$

⬇ 50 to 100 C
+ Alkali activating solution

-Si-O-Al-O-

⬇ Polycondensation

Aluminosilicate gel
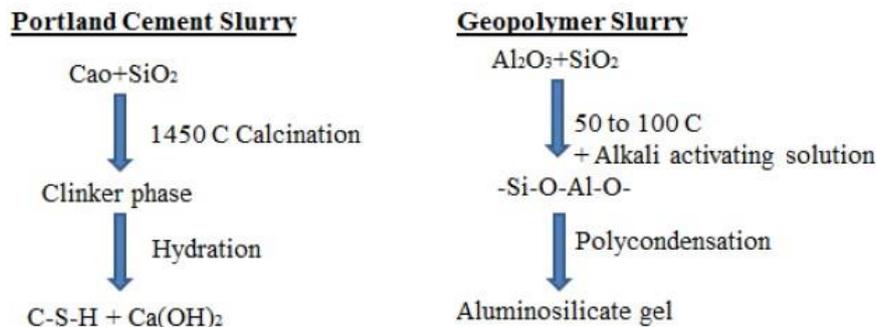
Figure 21 - Comparison of Portland cement slurry and geopolymeric slurry [29]

3.2. Constituents of Geopolymer

3.2.1. Source Materials

A source material is a material which is used as a binder, instead of Portland cement or other hydraulic cement paste, to produce cement.

In order for a material to be eligible as a source material for geopolymers based on alumina-silicate has to be rich in Si and Al.

There are many different materials from different sources that can be suitable for production of geopolymers since they have in their chemical composition mostly Si and Al in amorphous form. In the last years, several researchers have been investigating different minerals (like kaolinite, clays, etc.) and industrial by-product materials with promising results. Some of these by-product materials can be for instance, fly ash, silica fume, slag and calcined kaolin.

Which source material shall be used to produce geopolymers depends not only on the type of application but also on the availability and cost of that particular source material.

3.2.1.1. Fly ash

Fly ash is the residue of coal ash, created during the combustion of coal in electrical power plants. During incineration, the coal that is not incinerated can be collected in form of dust either from the bottom of the boiler (bottom ash) or from the flue (fly ash). This process is presented in figure 22.
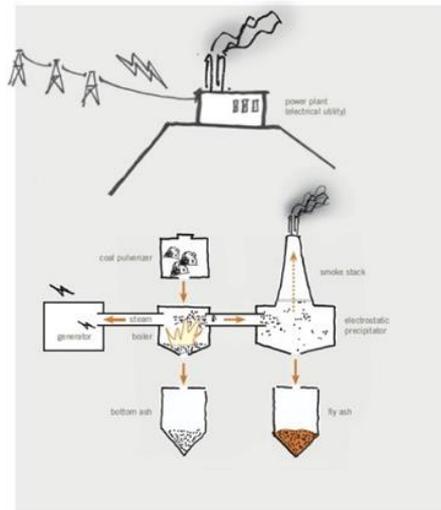
Figure 22 - Coal fuelled power plant process [25]

Large quantities of coal power plants fly ash are presently generated around the world and as the need for power increases, the volume of produced fly ash will increase as well.

When fly ash and other coal combustion residues are produced, they have two possible fates: recycling or disposal.

Some of those quantities are reused as cement additive and other applications but most of the fly ash produced is not effectively used, and a large part of it has to be disposed in disposal sites like landfills, abandoned mines and quarries.

The components of fly ash can vary considerably, depending on the properties of the coal being burned. Nevertheless, there are some common substances to all fly ash, like substantial amounts of silicon dioxide (SiO_2) and calcium oxide (CaO). The two most common types of fly ash are differentiated by the American Society for Testing and Materials (ASTM) and several scientific articles, as either class C or class F. According to ASTM, the main difference between these classes is the amount of calcium, silica, alumina and iron present in the ash. Fly ash class F, typically presents an amount of CaO under ten percent by weight. On the other hand, class C fly ash has a CaO content higher than the previous one and therefore is also known as high calcium fly ash.

Class F fly ash has been used typically to partially replace Portland cement in concrete because it is superior to Class C in mitigating both sulphate and alkali–silica damage.

Due to the presence of high contents of calcium in the composition of class C fly ash, cement can be produced without any Portland cement, only mixing to the mixture enough water to hydrate and harden [25] [26].

In the production of ordinary Portland cement (OPC), carbon dioxide (CO_2) emissions are generated by carbonate oxidation in the cement clinker production process. According to "Trends in global CO_2 emissions: 2014 Report", *"cement clinker, the largest of non-combustion sources of CO_2 from industrial manufacturing, contributed to about 4.8% of the total global emissions in 2013.*

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Fuel combustion emissions of CO_2 related to cement production are of approximately the same level, so, in total, cement production accounts for roughly 9.5% of global CO_2 emissions". Thereby the idea of substituting cement by fly-ash is commonly presented as a means to reduce carbon footprint. However, this idea is only correct if the production of fly ash is not taken into account because as stated by International Energy Agency (IEA) regarding 2012, coal combustion in coal-fired power plants which is the source of fly-ash, were responsible for 28% of CO_2 emissions from fossil-fuel combustion.

It has been shown that, to manufacture one ton of OPC, one ton of CO_2 is released due to the coal combustion but on the other hand, to produce one ton of fly ash, around twenty to thirty tons of CO_2 will be generated by the burning of coal [25].

3.2.1.2. Microsilica

Like fly ash, microsilica is a by-product of the industrial manufacture of ferrosilicon and metallic silicon in high-temperature electric arc furnaces.

It can be defined as a mineral admixture composed of very fine solid glassy spheres of SiO_2. Most of the particles are less than 1 micron in diameter, generally 50 to 100 times finer than average cement or fly ash particles.

Microsilica belongs to the class of siliceous and aluminous materials also known as pozzolans which is a kind of material that in presence of water react with calcium hydroxide to form compounds possessing cementitious properties providing a more uniform distribution and a greater volume of hydration products. Additionally as it was mentioned before, because microsilica is composed by very small particles, when added to a cement mixture (filler) decreases the average size of pores in the paste leading to a considerable improvement of strength and durability of cement [30].

3.2.1.3. Alkaline Liquids

It was found that with alkaline liquids having soluble silicate (either sodium or potassium silicate) the polymerisation process is more efficient due to the high rate of chemical reactions. Therefore, a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate respectively have been the most common alkaline solutions used in geopolymerization.

The silicon and aluminium of the source material reacting with the alkaline liquid, forms the geopolymer paste that binds the aggregates and other unreacted materials.

Silicates are most suitable as alkaline activators because they contain dissolved and partially polymerized silicon, which reacts easily, incorporating into the reaction products, and significantly contributing to improving specimens characteristics.

As complementary information, soluble silicates are prepared by fusing sodium or potassium carbonate with sand or by heating sodium or potassium hydroxide with sand under pressure. These solutions are very soluble in water, but the glassy solid dissolves slowly, even in boiling water. They present adhesive properties and are fire resistant [31].

3.3. Geopolymers properties

There are several different factors which can influence the mechanical and chemical properties of geopolymers, such as:

- Curing temperature;
- Curing time;
- Type of alkaline liquid;
- Molar composition of the oxides (concentration);
- Amount of CaO, K_2O and the molar Si-to-Al ratio in the source material;
- Liquid to solid ratio (L/S);
- Water/Solids ratio (W/S);
- Alkali-to-silicate ratio (A/S);

Curing temperature and curing time do not only affect the compressive strength of the geopolymer but also the setting time. During the curing process, energy in form of heat is provided in order for polymerization/hardening to occur. When the curing temperature increases, polymerization becomes more rapid leading to a decrease of the setting time of the cement.

Both the previously mentioned factors change the mechanical properties of the geopolymer and the ratios will play an important role in the rheology of the slurries as well, and for P&A operations this is an important matter.

According to several studies, high concentrations of oxides will tend to increase the viscosity of the slurry and the strength of the geopolymer cement up to a certain concentration limit on which a lower rate of polymer formation is produced resulting to a decrease of developed strength [32].

Regarding the ratios present into the mix designs, they will also affect the viscosity of the slurries, setting time and the properties of the hardened cement obtained from that particular mix design. This is the case because they relate the amount by weight between the liquid and solid contents of the mixture.

High water content in the mixture, decreases the stability and delays the thickening and the setting time of the suspension, which is not compatible with the well cementing at different temperatures. Furthermore, it affects the density of the slurry, which is not compatible with well cementing where the density of the suspension is imposed by the pore and fracture pressure of the formation [21]. The expressions and ranges for these ratios (for well cementing purposes) are presented below:

$$S/A = \frac{alkali\ silicate\ solution}{alkali\ solution}, \qquad with\ 0{,}4 \leq S/A \leq 2{,}0$$

$$L/S = \frac{alkali\ solution + alkali\ silicate\ solution + water}{fly\ ash}, \qquad with\ 0{,}35 \leq L/S \leq 0{,}52$$

$$W/S = \frac{water\ in\ alkali\ sol. + water\ in\ alkali\ silicate\ sol. + water}{fly\ ash + solid\ contents\ in\ alkali\ and\ alkali\ silicate\ sol.}, \qquad with\ W/S = \pm\ 0{,}35$$

The molar Si-to-Al ratio in the source material can be adjusted in order to control the setting properties of the slurries. As it was mentioned before, in P&A operations, the setting time of the slurry is a crucial factor because the operator has to evaluate if the pump is capable to pump the slurry to the desired location or depth before it sets, in a certain period of time.

According to literature [33], generally, *"increases in Al_2O_3, tend to accelerate the setting of geopolymers while addition of SiO_2 inhibits the setting. Nevertheless, increased SiO_2 content tends to produce microstructures with low porosity and hence enhance the strength of geopolymers"*.

However, based in several experiments and measurements performed in this mentioned investigation, the authors claim that an increase in either alumina or silica, accelerate the setting with an optimal SiO_2/Al_2O_3 ratio in the range 3.20–3.70. Moreover, the authors also reported that *"Decreasing of the SiO_2/Al_2O_3 ratio (or increasing Al_2O_3) favours higher strengths reaching a maximum at around SiO_2/Al_2O_3 ratio 3.50 and remains constant thereafter."*

These trends are depicted in the following figure 23.
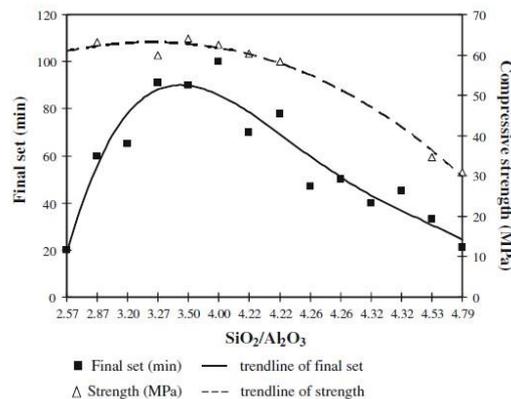
Figure 23 - Final setting times and compressive strength with respect to SiO_2/Al_2O_3 ratio [33]

It can be observed that to produce geopolymers with longest setting time and reasonably high strengths the SiO_2/Al_2O_3 ratio has to be within the range 3.20-3.70.

3.4. Manufacturing geopolymers

A highly simplified reaction mechanism for geopolymerization is presented in figure 24 and it describes schematically the main processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate.
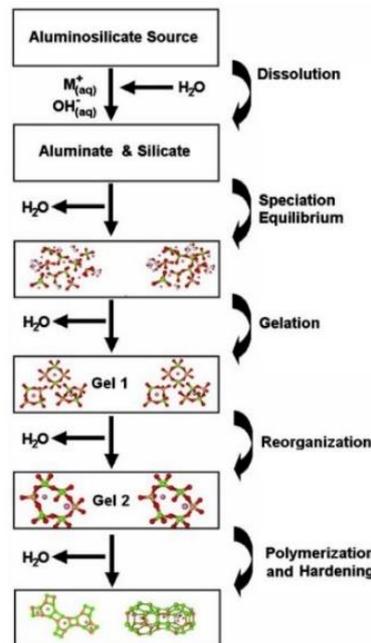
Figure 24 - Conceptual model for geopolymerization [34]

Generally, this reaction mechanism can be divided in three different stages. Dissolution, condensation and setting.

Initially, the dissolution of Si and Al atoms of the solid aluminosilicate present in the source material by alkaline hydrolysis (action of hydroxide ions) produces aluminate and silicate species. In this stage water is consumed due to alkaline hydrolysis.

Afterwards, species released during dissolution are incorporated into the aqueous phase which may already contain silicate present in the activating solution. The mixture of all these species (silicate, aluminate and aluminosilicate) will reach the "speciation equilibria". This chemical "speciation" equilibrium means that the equilibrium of the mixture will be reached, not because of total amounts of each individual species present in the solution but because of the concentration of each one of those individual species [35].

Because we are in presence of solutions with high pH, the mentioned dissolution of aluminosilicates is fast, leading to the formation of a supersaturated aluminosilicate solution and as a consequence the oligomers form large networks by condensation (reorganization of structures). Often, these networks are noticeable due to a gel formation. At this time, the water which was consumed during dissolution is released.

The system keeps evolving while the connectivity of the gel network increases generating a three-dimensional aluminosilicate network (setting or polymerization) [34] [36].

The properties of geopolymeric cement depend on geopolymerization which needs energy to occur. This energy can be provided by ambient temperature or heat from an oven. In this case, the geopolymerization is faster and according to several articles, better compressive strength development is achieved.

4. Experimental conditions

The aim of this experimental program was to study different materials, which could present an equilibrium between viscosities, setting times, relative good compressive strength results and good resistance to hydrochloric acid, in order to be used in P&A.

To conduct the experiments several test specimens were produced. Four geopolymeric mixtures, using two different concentrations of alkali solutions and two different silicates, were used. A mixture based in Portland cement class G, was also used in order to support as a reference, the results obtained from the tests with the geopolymers.

In addition, a physical characterization of the raw materials was also performed.

Afterwards, some of the properties and features described in the previous chapters, which are considered requirements for an efficient sealing material in order to be applied in cementing operations, were investigated and are discriminated below:

- Rheology of the slurries;
- Viscosities of the slurries;
- Setting time of the slurries;
- Densities of the slurries;
- Chemical and physical stability at high temperatures;
- Mass loss;
- Bulk shrinkage;
- Compressive strength;
- Resistance to HCl.

Equipment and procedures are described in this chapter. Obtained results are presented in chapter 5 and comparison and discussion of results are performed in chapter 6.

4.1. Equipment

4.1.1 Viscometer

In this work, the rheological studies were performed using a coaxial cylinder viscometer FANN model 35 SA (figure 25). The slurry is confined between two concentric cylinders with different radius such as (R2 > R1) (Figure 26). One of these cylinders rotates at a certain velocity. In this model, the outer sleeve can be rotated at six different rotational speeds (3, 6, 100, 200, 300 and 600rpm).

In this model, the slurry, contained in a large recipient was sheared between the outer sleeve (rotor) and the inner cylinder (bob) which is attached to a torque measuring device. The torque required to rotate the bob is measured by the viscometer.

By changing speeds, several viscosity ranges were measured.

Figure 25 - Cylindrical viscometer FANN S35SA
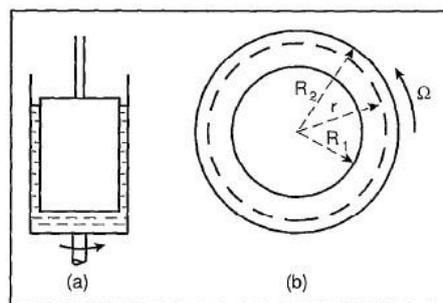
Figure 26 - Schematic representation of a cylindrical viscometer [16]

The readings were obtained following the procedure described in API Spec 10 (1988). The mentioned procedure begins by shearing the fluid at the highest rotational speed for one minute before recording the corresponding torque reading. Then, the rotational speed was decreased to the next lower rotational velocity down to the minimum, obtaining the corresponding readings after 20 seconds of rotation at each shear rate.

The equations and constants provided by the manufacturer in the instructions manual were used in order to calculate the viscosities at different rotational velocities, taking into account the rotor-bob combination used in this work.

Those equations are presented below:

$$Shear\ rate(sec^{-1})\ \rightarrow\ \gamma = K_3 \times N$$
$$Shear\ stress\ (dynes/cm^2)\ \rightarrow\ \tau = K_1 \times K_2 \times \theta$$

And for the R1-B1-F1 combination the following constants were provided:

K1 - Torsion constant, dyne-cm/degree deflection (386);

K2 - Shear stress constant for the effective bob surface, cm^3 (0.01323);

K3 - Shear rate constant, sec^{-1} per rpm (1.7023);

N - Rate of revolution of the outer cylinder (3, 6, 100, 200, 300 and 600rpm)

θ - Fann viscometer reading

4.1.2. X-ray Fluorescence (XRF)

An X-ray fluorescence (XRF) spectrometer Rigaku Supermini200 (figure 27) was used in the experimental work in order to make a chemical composition analysis and determination of elemental concentration by weight of the fly-ash and micro silica.

This analysis is based in the behaviour of the atoms of the sample when they interact with the irradiated X-radiation.

When an intense X-ray beam illuminates a sample, some of the energy is scattered and measured by a detector. The rest of the energy is also absorbed within the sample in a manner that depends on the chemical composition of the sample. The type of atoms present in the sample will define the spectrum of wavelengths (fluorescence) of the scattered X-rays [37].

Figure 27 - X-ray fluorescence (XRF) spectrometer

4.1.3 Dynamic Light Scattering Analyser (DLS)

The particle size distribution of the fly ash and micro silica was provided by a Beckman Coulter DelsaMax Pro light scattering analyser (figure 29).

In this kind of equipment, the illumination of the sample is performed with a laser beam, resulting in light scattering that is detected by a sensitive photon counting module. Afterwards, a correlator is used, to translate the pattern of the light scattering intensity fluctuations to a measure of diffusion speed, thereby providing a value for molecule or particle size [38].

A general schematic of a DLS is described in the figure below.
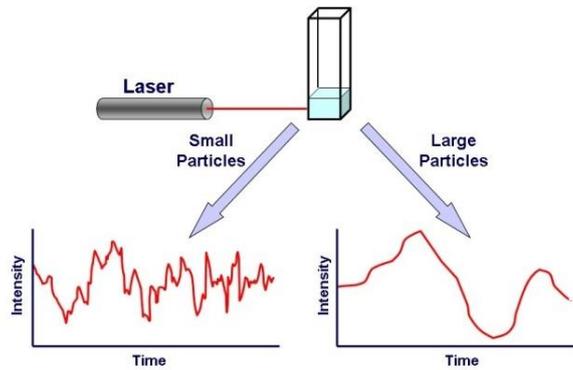
Figure 28 - General schematic of DLS [38]

A controlled solution was previously used in order to verify if the machine was calibrated. Afterwards, a solution with each of the diluted powders was prepared and from each of those solutions a sample with the particles in suspension was taken in order to be analysed.

Figure 29 - DelsaMax Pro light scattering analyser

4.1.4 Differential Scanning Calorimetry (DSC)

It was necessary to acquire some information about characteristic properties of the raw materials and the produced geopolymeric materials when they are subjected to high temperatures inside the well. A technique known as differential scanning calorimetry was used to study the chemical stability (exothermic and endothermic events) and eventual thermal transitions while samples are heated with increasing the temperature.

DSC measures the difference, as a function of temperature, in the amount of heat required to increase the temperature of a sample and a reference when the sample undergoes a physical transformation.

For this study, a Mettler Toledo DSC822e was used and is presented in figure 30.

Figure 30 - Mettler Toledo DSC822e

This technique looks for effects due to heat related with phase transitions and chemical reactions as a function of temperature. The heat flow to the sample and a reference (inert material) at the same temperature is compared. This heat flow is equivalent to the enthalpy changes.

The heat flow difference between the sample and the reference can be either positive or negative which means that we are in presence of an endothermic or an exothermic process respectively.

Endothermic process occurs when the transition absorbs energy, therefore heat flow to the sample is higher when compared to that of the reference. In the case of an exothermic process, the opposite occurs meaning that we are in presence of a transition which releases energy. Therefore heat flow to the sample is lower when compared to that of the reference [39].

The type of phase transitions depends on the kind of material and the heat flow produced by this. For instance, if we are in presence of crystalline polymers a melting transition (the polymer chains fall out of their crystal structures, and become a disordered liquid) is to be expected. On the other hand, amorphous polymers (polymers whose chains are not arranged in ordered crystals) tend to go through a glass transition which means from a hard and relatively brittle "glassy" state into a molten or rubber-like state [40].

4.1.5 Uniaxial Compressive Strength

The strength of the samples was investigated using a uniaxial compressive strength test (UCS). To avoid errors in the conduct of research three control samples of each mixture, were tested for each of the curing periods, to eliminate the possibility of accidental phenomena affecting the final results of the performance under compression. The compressive strength test was performed on a Lloyd instrument LR 50 K (figure 31), with a piston speed of 10 mm/min and preload 10N.

Figure 31 - Lloyd instrument LR 50 K

4.1.6. Vicat apparatus

When cement is mixed with water, hydration reaction begins and hydrates start to be formed. During this process, the slurry will gradually change from liquid state to solid state. This phenomenon of solidification is known as hardening process of cement slurry and is a key parameter for downhole applications. For P&A purposes, thickening time is an important property which indicates application of these slurries in downhole conditions and its pumpability.

The hardening process is defined by the thickening or setting time of the slurry.

Due to the absence of a pressurized consistometer in the university facilities, setting times of the slurries were investigated using a vicat apparatus (figure 32).

The initial and final setting times of the produced slurries, were determined taking the slurries out of the oven in intervals of 10 min after the mixture has been prepared.

The equipment can be described as a frame which has a movable rod with a cap at one end and in the other two different needles can be attached. One of the needles has a cross sectional area of 1 mm^2 that is used to determine the initial setting time. The second has a metal attachment and is used to determine the final setting time (figure 33). A graduated scale gives the depth of penetration into the sample.

Figure 32 - Vicat apparatus

Figure 33 - Different needles used in Vicat test

The procedure to determine the initial and final setting times is relatively simple and is described in the standard EN 196-3. Initial setting time is defined as the period elapsing between the time when the liquid solution is added to the powder and the time at which the first needle fails to pierce the sample to a depth of 4±1mm from the bottom of the mould. Final setting time is the period elapsing between the time when the liquid solution is added to the powder and the time at which the second needle makes an impression on the sample while the metal attachment fails to make it (figure 34). The final setting time can also be associated with the complete loss of plasticity of the cement paste.

Figure 34 – Initial and final setting time tests

This type of analysis is of major importance because it predicts the period of time on which a slurry has to be pumped until it reaches its final position inside the well. When the initial setting time of the cement is reached, it has to be placed already at the desired location, to start setting until the hardening process is concluded, with the final setting time.

4.2. Materials

4.2.1. Fly ash

Fly ash used in this study as source material to prepare the geopolymer pastes was a low-calcium (ASTM class F) dry fly ash supplied by Bioenergy & Thermal Power Plant (Esbjergværket), Esbjerg as shown in figure 35. The chemical composition of fly ash, obtained through XRF, is presented in table 3 and according to the data provided by Emineral a/s (certified company according to EN 450, which sells the fly ash from Danish power plants) the density was 2.3 g/cm^3.

Figure 35 - Low-calcium (ASTM class F) dry fly ash

Table 3 - Chemical composition of fly ash (%mass)

MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	K$_2$O	CaO	TiO$_2$
2,5207	28,6278	51,8957	0,8490	1,4781	2,2813	4,7877	1,3102
MnO	Fe$_2$O$_3$	ZnO	Rb$_2$O	SrO	ZrO$_2$	Ag$_2$O	
0,0702	5,7616	0,0262	0,0113	0,2575	0,0565	0,0661	

The particle size distribution, obtained by the DLS for the dry fly ash used in this work, is presented in figure 36.
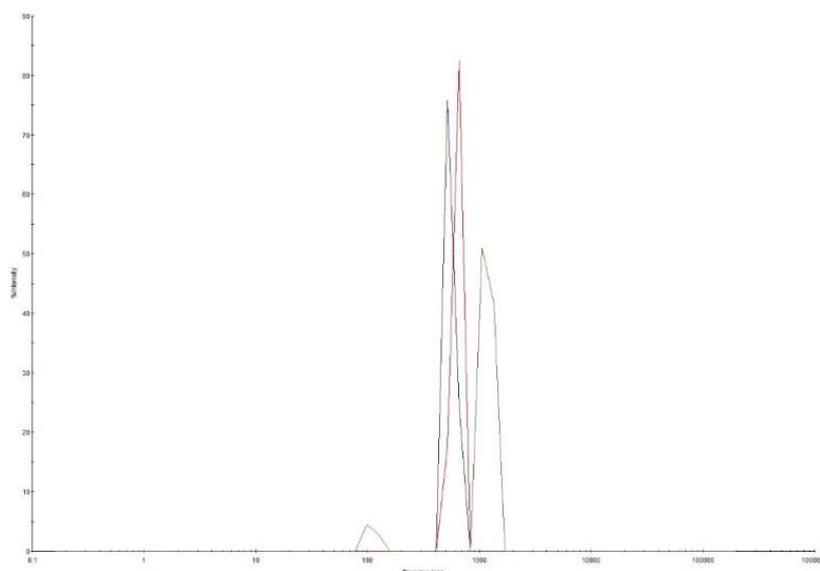
Figure 36 - Particle size distribution of fly ash

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The previous figure shows that the particles diameter is around 2400nm which is in accordance with the test results provided by the Emineral a/s (table 4). In those tests, particle size was tested on a 0,045 mm sieve and expressed as the mass proportion in percent of the ash retained when sieved.

The test results of the batches of March (when the fly ash used in this work was acquired), are presented below.

Table 4 - Particle size test results

Flyveaske type: B4 / B5 / perlefiller		
Particel size > 0,045 mm		Densitet kg/m3
Date of test:	%	EN450-1
23/03/2016	13,1	
21/03/2016	10,2	
20/03/2016	8,1	
18/03/2016	8,2	
17/03/2016	12,4	2300
17/03/2016	12,6	
16/03/2016	14,7	
16/03/2016	9,2	
15/03/2016	13,7	
15/03/2016	9,0	

Additional information about this by-product was kindly provided by Emineral a/s and is presented in Appendix.

4.2.2. Microsilica

Microsilica Grade 940-U used in this study was supplied by Elkem, Norway. The chemical composition of microsilica obtained through XRF, is presented in table 5.

Table 5 - Chemical composition of micro silica (%mass)

Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	Fe_2O_3	ZnO
0,6718	97,2610	0,2767	0,0485	1,1324	0,3225	0,2415	0,0456

The particle size distribution of microsilica was also investigated and the results obtained are presented in figure 37. As expected, the particles size of this material was smaller than the one obtained from fly ash. In this case, DLS gave a particle diameter equal to 831nm.
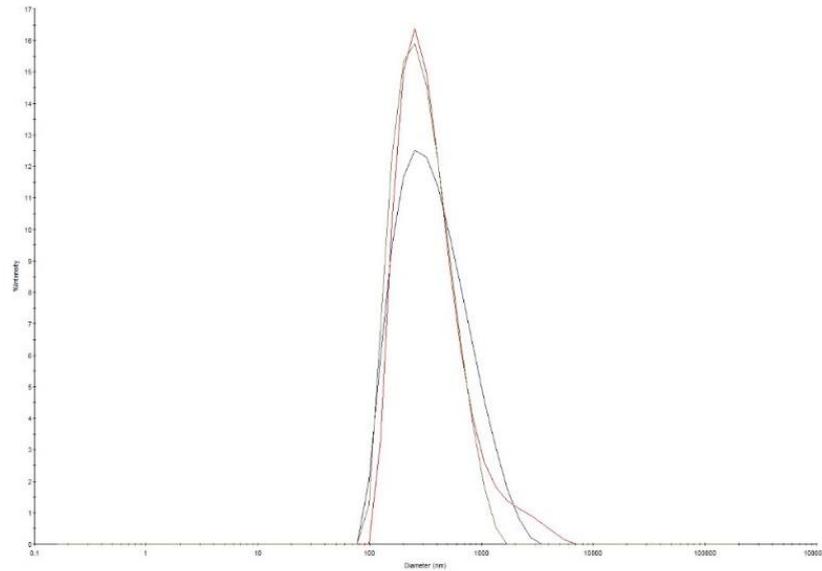
Figure 37 - Particle size distribution of micro silica

Additional information about this material can be found in Appendix.

4.2.3. Activating alkali liquids

Two types of alkali-silicate solutions were used in this study. One consisted of Na_2SiO_3 and NaOH solutions and another consisted of K_2SiO_3 and KOH solutions. A total of 4 mixtures with molarities ranging from 6M to 8M were created to study how different concentrations of KOH and NaOH influenced the compressive strength.

The Na-based activator was composed of a sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solutions. NaOH solution was prepared with a concentration of 6.0M and 8.0M using NaOH pellets of 99% purity supplied by Merck KGaA and distilled water. The Na_2SiO_3 (type 44) solution was supplied by Bollerup Jensen A/S with a specific gravity of 1.44 and a modulus ratio (Ms) equal to 2.0 (where Ms = SiO_2/ Na_2O, Na_2O = 12.80% and SiO_2 = 25.60%).

The K-based activator was composed of a potassium hydroxide (KOH) and potassium silicate (K_2SiO_3) solutions. KOH solution was prepared with a concentration of 6.0M and 8.0M using KOH pellets of 85% purity supplied by Merck KGaA and distilled water. The K_2SiO_3 (type 4009) solution was supplied by Bollerup Jensen A/S with a specific gravity of 1.38 and a modulus ratio (Ms) equal to 2 (where Ms = SiO_2/K_2O, K_2O = 13.2% and SiO_2 = 26.2%).

Additional information about these silicates is presented in Appendix.

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4.3. Mixing procedure and casting

NaOH pellets and distilled water were mixed with a magnetic stirrer until all the pellets were completely dissolved. Afterwards the silicate solution (Na_2SiO_3) was mixed together with the previous alkali NaOH solution. This alkali-silicate solution was then left for 24 h before use, to dissipate heat released from the exothermic reaction (alkali solution) in order to not affect the setting of the geopolymer. The same procedure was followed for K-based activators.

The aim of this work was to perform a comparison between two geopolymeric cements with different concentrations being activated with two different activators and providing at the same time reasonable viscosities and setting times, which would enable them to be used in P&A operations. Because the focus was not the study of those mentioned properties by using additives to improve them (like plasticizers or retarders, respectively) it was decided to use a high L/S ratio near the recommended limit. Therefore, the alkali liquid to fly ash (L/S) ratio by weight was fixed at 0.50 and the alkali silicate to alkali solution ratio (S/A) by weight of 0.80 was used for all mixtures.

To provide a reference, on all tests conducted in this work, for the results obtained with the geopolymeric mixtures, a mixture based in Portland cement Class G, was also prepared, respecting the same liquid-to-solid ratio used in the previous mixtures.

In table 6 the mixing proportions and ratios of all the slurries are depicted.

Table 6 - Mixing proportions and ratios of the mixtures

| | Portland Class G (gr) | Fly ash (gr) | 30% Micro silica (gr) | M concent. | KOH sol (gr) | | K2SiO3 sol (0,394 w/w) | NaOH sol (gr) | | Na2SiO3 sol (0,384 w/w) | Distilled water (gr) | S/A | L/S | W/S |
					KOH pellets	Distilled water		NaOH pellets	Distilled water					
MIX I	-	350	150	6M	35,08	103,92	111,2	-	-	-		0,80	0,50	0,30
MIX II	-	350	150	8M	43,14	95,86	111,2	-	-	-		0,80	0,50	0,28
MIX III	-	350	150	6M	-	-	-	26,95	112,05	111,2		0,80	0,50	0,32
MIX IV	-	350	150	8M	-	-	-	33,75	105,25	111,2		0,80	0,50	0,30
MIX V	500	-	-	-	-	-	-	-	-	-	250	-	0,50	0,50

In table 7, the SiO_2/Al_2O ratios for both solutions which use two different types of alkali activators are presented.

Table 7 - SiO$_2$/Al$_2$O ratio of geopolymeric mixtures

MIX I and II		MIX III and IV	
XRF analysis		XRF analysis	
% mass of Al_2O_3 in Fly ash:	28,60%	% mass of Al_2O_3 in Fly ash:	28,60%
% mass of SiO_2 in Fly ash:	51,90%	% mass of SiO_2 in Fly ash:	51,90%
% mass of Al_2O_3 in M.silica:	0,67%	% mass of Al_2O_3 in M.silica:	0,67%
% mass of SiO_2 in M.silica:	97,30%	% mass of SiO_2 in M.silica:	97,30%
Contents in the silicate solution (gr)		Contents in the silicate solution (gr)	
% mass of SiO_2 in K_2SiO_3:	26,20%	% mass of SiO_2 in Na_2SiO_3:	25,60%
Contents in the slurry (gr)		Contents in the slurry (gr)	
Al_2O_3	101,1	Al_2O_3	101,1
SiO_2	356,7	SiO_2	356,1
Ratio		Ratio	
SiO_2/Al_2O_3 =	3,53	SiO_2/Al_2O_3 =	3,52

All pastes were mixed in two different stages. To prepare the Na- and K-based geopolymer paste in first place, the alkaline activators in the form of solution were added to the fly ash and mixed in a Waring LB20EG (figure 38) blender for 15 seconds at a medium rotational speed followed by other 35 seconds at a high rotational speed. Afterwards, the paste was drained into a five liter bucket of a Kenwood Major mixer (figure 39) where it was mixed at a medium rotational speed for 10 minutes.

Figure 38 - Waring LB20EG

Figure 39 - Kenwood Major mixer

The fresh geopolymer pastes for the present study, were then cast into polypropylene containers with a diameter of 2.5 cm and a height of 12 cm. The samples were labelled and subjected to heat curing afterwards. In this regard, samples were placed into an oven at 90ºC (figure 40) and cured for 1, 3, 5 and 7 days.

The specimen names, were composed of four terms. Each of these terms gave information about some aspect of the sample which is described as follows: The first term refers to the sample number. The second term refers to the number of days of curing. The third term refers to the concentration and finally the last term refers to type of activator where 'K' refers to K- based activator and 'N' refers to Na- based activator. In the case of Portland cement class G, only 'G' is referred together with the number of the sample and number of days of curing.

Figure 40 - Heat curing

4.4. Specimens preparation

At the end of heat curing period, samples were taken from the oven and stored until being cool. Afterwards, they were demoulded and cut with a diamond saw to a height of 5 cm and to obtain flat surfaces for compressive strength testing. The samples were then left in the laboratory at ambient temperature until the day of testing.

All samples were weighed and measured, to determine the mass loss and shrinkage of geopolymer pastes after exposed to respective elevated temperature during a certain period of time.

For UCS testing, three samples for each number of days of curing were tested in order to obtain a better reliability in measurements.

In this work and due to oil well stimulation, it seemed to be pertinent to investigate as well, the integrity maintenance and compressive strength changes of the produced cement after being in contact with HCl. Therefore, three samples with 7 days of curing of mixture II, IV and V were immersed into an acid solution with 15% HCl. All the samples were weighed before being immersed into the acid. After 7, 14 and 21 days the samples were removed from the acid solution, dried and weighed again in order to evaluate mass loss. Later these samples were subjected to a UCS testing in order to evaluate their compressive strength.

5. Test results

5.1. Rheological studies of the mixtures

5.1.1. MIX I

In table 8, are presented the shear stresses (τ) obtained for each shear rate (Υ) and the calculated apparent viscosities (η'), yield stress and viscosity as well, of the slurry of mix I.

Table 8 - Rheology of mixture I

MIX I					
KOH Concentration	**6M**				
RPM	3	6	100	200	300
readings (θ)	**16**	**21**	**104**	**181**	**254**
τ (Pa)	8,17	10,72	53,11	92,43	129,71
Υ (sec^{-1})	5,11	10,21	170,23	340,46	510,69
η'	1,60	1,05	0,31	0,27	0,25
Yield stress (τ_y)			8,95		
$\eta=\Delta\tau/\Delta\Upsilon$ (cP)			**241**		
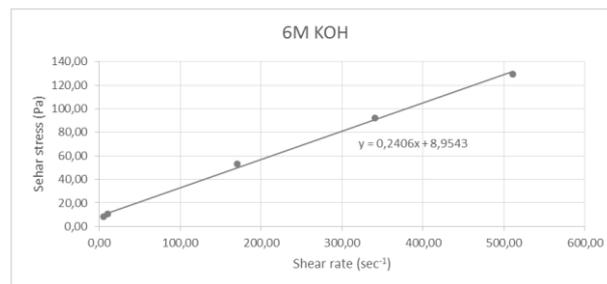
Figure 41 - Rheogram of mixture I
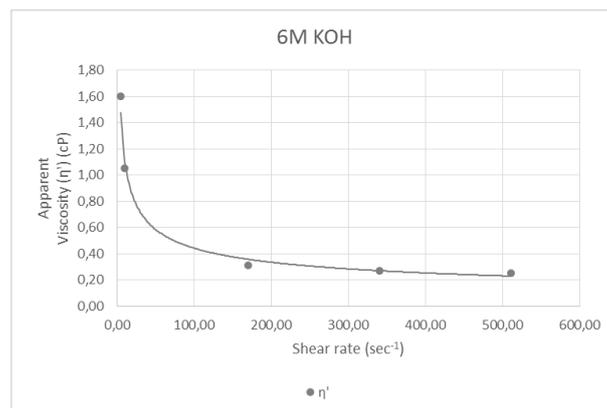
Figure 42 - Relation between viscosity and the shear rate

Initial setting time:	43 minutes after liquid solution was mixed with the powder
Final setting time:	19 minutes after initial setting time

5.1.2. MIX II

In table 9, are presented the shear stresses (τ) obtained for each shear rate (Υ) and the calculated apparent viscosities (η'), yield stress and viscosity as well, of the slurry of mix II.

Table 9 - Rheology of mixture II

MIX II					
KOH Concentration	**8M**				
RPM	3	6	100	200	300
readings (θ)	**12**	**18**	**113**	**205**	**294**
τ (Pa)	6,13	9,19	57,71	104,69	150,14
Υ (sec^{-1})	5,11	10,21	170,23	340,46	510,69
η'	1,20	0,90	0,34	0,31	0,29
Yield stress (τ_y)			6,60		
η=Δτ/ΔΥ (cP)			**284**		
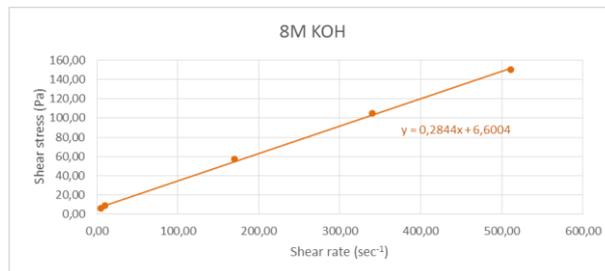
Figure 43 - Rheogram of mixture II
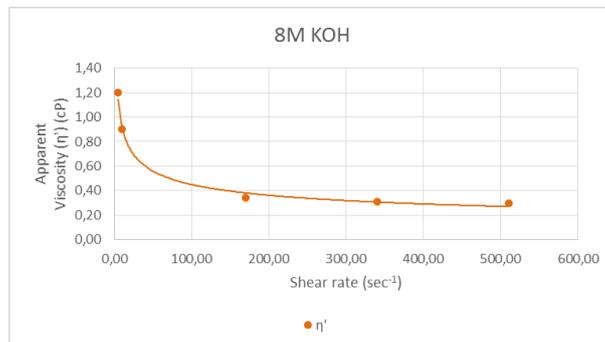
Figure 44 - Relation between viscosity and the shear rate

Initial setting time:	53 minutes after liquid solution was mixed with the powder
Final setting time:	10 minutes after initial setting time

5.1.3. MIX III

In table 10, are presented the shear stresses (τ) obtained for each shear rate (Υ) and the calculated apparent viscosities (η'), yield stress and viscosity as well, of the slurry of mix III.

Table 10 - Rheology of mixture III

MIX III					
NaOH Concentration	**6M**				
RPM	3	6	100	200	300
readings (θ)	**42**	**54**	**222**	*	*
τ (Pa)	21,45	27,58	113,37	-	-
Υ (sec^{-1})	5,11	**10,21**	170,23	-	-
η'	4,20	2,70	0,67	-	-
Yield stress (τ_y)		20,30			
$\eta=\Delta\tau/\Delta\Upsilon$ (cP)		**547**			
* - reading out of range					
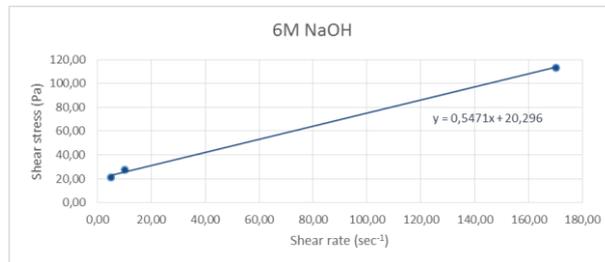
Figure 45 - Rheogram of mixture III
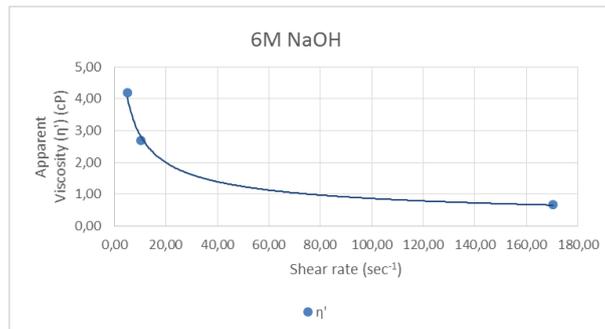
Figure 46 - Relation between viscosity and the shear rate

Initial setting time:	78 minutes after liquid solution was mixed with the powder
Final setting time:	55 minutes after initial setting time

5.1.4. MIX IV

In table 11, are presented the shear stresses (τ) obtained for each shear rate (Υ) and the calculated apparent viscosities (η'), yield stress and viscosity as well, of the slurry of mix IV.

Table 11 - Rheology of mixture IV

MIX IV					
NaOH Concentration	8M				
RPM	3	6	100	200	300
readings (θ)	31	43	272	*	*
τ (Pa)	15,83	21,96	138,90	-	-
Υ (sec^{-1})	5,11	10,21	170,23	-	-
η'	3,10	2,15	0,82	-	-
Yield stress (τ$_y$)		13,22			
η=Δτ/ΔΥ (cP)		739			

* - reading out of range
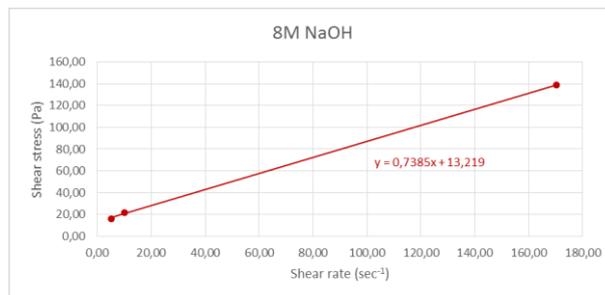
Figure 47 - Rheogram of mixture IV
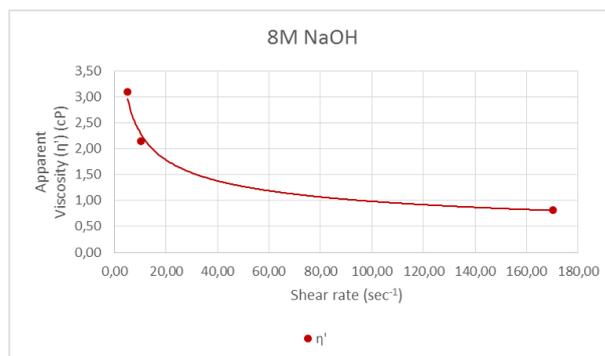
Figure 48 - Relation between viscosity and the shear rate

Initial setting time:	63 minutes after liquid solution was mixed with the powder
Final setting time:	45 minutes after initial setting time

5.1.5. MIX V

In table 12, are presented the shear stresses (τ) obtained for each shear rate (Υ) and the calculated apparent viscosities (η') of the slurry of mix V.

Table 12 - Rheology of mixture V

MIX V						
OPC Class G						
RPM	3	6	100	200	300	600
readings (θ)	10,00	16,00	58,00	74,00	83,00	110,00
τ (Pa)	5,11	8,17	29,62	37,79	42,39	56,17
Υ (sec⁻¹)	5,11	10,21	170,23	340,46	510,69	1021,38
η'	1,00	0,80	0,17	0,11	0,08	0,05
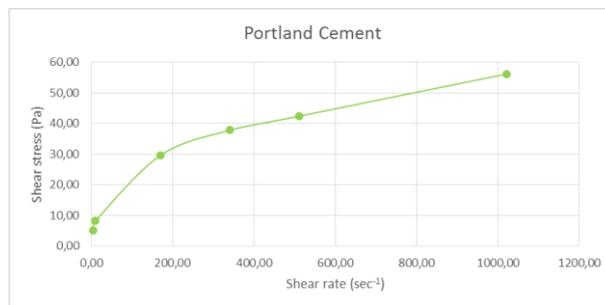
Figure 49 - Rheogram of mixture V
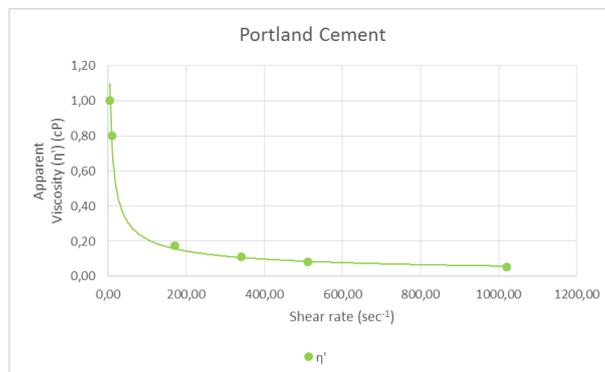
Figure 50 - Relation between viscosity and the shear rate

As it was mentioned before, when in presence of a Power-Law model, the $\tau - \gamma$ relationship is linear on a log-log plot. Therefore the parameters "*n*" and "*k*" of the mathematical expression of this model can be estimated directly from the dial readings [41], as follows:

$$n = \frac{\log \theta_{600} - \log \theta_{300}}{\log w_{600} - \log w_{300}} = 3,32 \times log \frac{\theta_{600}}{\theta_{300}}$$

$$k = \frac{\tau}{\gamma^n} \times K_1 \times K_2 = \frac{\theta_{600}}{1022^n} \times K_1 \times K_2$$

K_1 and K_2 are parameters provided by the manufacturer of the viscometer and previously described in 4.1.1.

With the readings obtained from the viscometer and the given parameters K_1 and K_2, the mathematical expression is obtained as described below:

$$n = 3{,}32 \times log\frac{110}{83} = 0{,}406$$

$$k = \frac{110}{1022^{0{,}406}} \times 386 \times 0{,}01323 \times 0{,}10 = 3{,}37 Pa.\,s^{0{,}406}$$

$$\tau = k \times \gamma^n \rightarrow \tau = 3{,}37 \times \gamma^{0{,}406}$$

With this mathematical expression, shear stresses can be obtained for all the shear rates. Like in the previous cases, apparent viscosities and the viscosity of the slurry can be calculated as well.

τ (Pa)	6,53	8,66	27,13	35,95	42,38	56,15
Υ (sec^{-1})	5,11	10,21	170,23	340,46	510,69	1021,38
η'	1,28	0,85	0,16	0,11	0,08	0,05
Yield stress (τ$_y$)			0			
η=Δτ/ΔΥ (cP)			**52**			

With these values, apparent viscosities can be found and a linear diagram can be sketched. The viscosity of the fluid can be obtained as before, by the slope of the line.
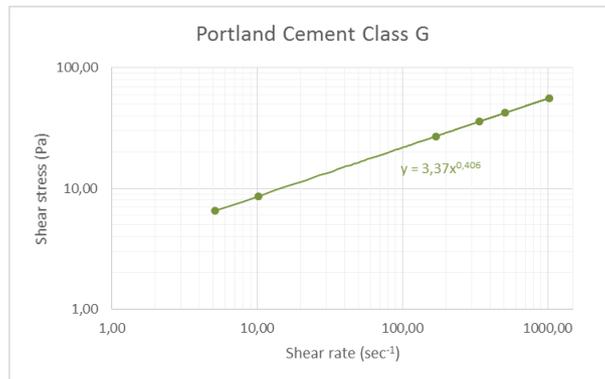
Figure 51 – Linear log-log plot of the rheogram of mixture V

Initial setting time:	160 minutes after liquid solution was mixed with the powder
Final setting time:	40 minutes after initial setting time

5.2. Mass loss due to water evaporation

In order to investigate mass loss of the specimens, weight differences before and after curing period were measured. The following tables show the mass loss, by percentage, obtained from those measurements.

Table 13 - Mass loss due to water evaporation of K-based activated mixtures

MIX I	6M KOH				MIX II	8M KOH			
Days of curing	Sample	weight (gr)	Weight after curing	Mass loss (%)	Days of curing	Sample	weight (gr)	Weight after curing	Mass loss (%)
1	S116K	81,97	80,03	2,37	1	S118K	83,89	81,60	2,73
	S216K	82,79	80,87	2,32		S218K	84,13	81,80	2,77
	S316K	82,92	81,00	2,32		S318K	84,67	82,35	2,74
3	S136K	82,48	79,54	3,56	3	S138K	84,21	81,05	3,75
	S236K	82,95	79,62	4,01		S238K	84,13	80,72	4,05
	S336K	82,78	79,31	4,19		S338K	83,52	80,15	4,03
5	S156K	83,41	79,28	4,95	5	S158K	84,19	79,45	5,63
	S256K	83,92	79,43	5,35		S258K	86	81,28	5,49
	S356K	83,02	79,91	3,75		S358K	84,68	80,18	5,31
7	S176K	83,04	7,65	7,65	7	S178K	84,56	79,25	6,28
	S276K	82,27	3,72	3,72		S278K	83,86	79,04	5,75
	S376K	82,88	3,99	3,99		S378K	84,58	80,16	5,23
	S476K	83,3	4,11	4,11		S478K	84,17	78,98	6,17
	S576K	82,58	5,01	5,01		S578K	84,01	78,59	6,45
	S676K	82,35	4,01	4,01		S678K	83,09	79,20	4,68
	S776K	82,92	5,00	5,00		S778K	85,01	78,86	7,23

Table 14 - Mass loss due to water evaporation of Na-based activated mixtures

MIX III	6M NaOH				MIX IV	8M NaOH			
Days of curing	Sample	weight (gr)	Weight after curing	Mass loss (%)	Days of curing	Sample	weight (gr)	Weight after curing	Mass loss (%)
1	S116N	83,76	82,24	1,81	1	S118N	84,56	83,67	1,05
	S216N	83,87	82,54	1,59		S218N	84,45	83,76	0,82
	S316N	84,95	83,36	1,87		S318N	84,06	83,28	0,93
3	S136N	83,32	80,48	3,41	3	S138N	84,38	78,80	6,61
	S236N	83,77	78,02	6,86		S238N	84,2	79,57	5,50
	S336N	83,58	81,08	2,99		S338N	83,97	80,58	4,04
5	S156N	82,45	77,73	5,72	5	S158N	84,6	76,81	9,21
	S256N	83,87	79,16	5,62		S258N	84,57	77,02	8,93
	S356N	83,62	80,11	4,20		S358N	84,61	74,98	11,38
7	S176N	83,23	76,01	8,67	7	S178N	85,06	72,44	14,84
	S276N	83,64	76,25	8,84		S278N	84,53	75,53	10,65
	S376N	84,18	76,05	9,66		S378N	85,75	73,51	14,27
	S476N	83,81	73,17	12,70		S478N	84,26	72,88	13,51
	S576N	83,44	72,20	13,47		S578N	84,9	72,29	14,85
	S676N	84,07	77,48	7,84		S678N	84,19	71,50	15,07
	S776N	84,4	78,02	7,56		S778N	84,2	70,70	16,03

Table 15 - Mass loss due to water evaporation of OPC mixture

MIX V	OPC class G			
Days of curing	Sample	weight (gr)	Weight after curing	Mass loss (%)
1	S11G	70,94	69,92	1,44
	S21G	72,40	70,56	2,54
	S31G	69,86	69,59	0,39
3	S13G	69,37	69,00	0,53
	S23G	72,34	69,17	4,38
	S33G	71,99	69,93	2,86
5	S15G	73,74	70,43	4,49
	S25G	71,70	69,49	3,08
	S35G	71,71	70,17	2,15
7	S17G	71,46	69,17	3,20
	S27G	71,35	68,95	3,36
	S37G	71,96	69,74	3,09

5.3. Bulk shrinkage

To investigate the shrinkage of the specimens, the differences in the diameters of the specimens after curing period, were measured. The following tables show the difference, by percentage, obtained from those measurements.

Table 16 - Diameter differences in mixture I after curing

MIX I	6M KOH				
Days of curing	Sample	Ø of the container (mm)	Ø of sample after curing (mm)	Ø difference (mm)	Average (%)
1	S116K	2,573	2,573	0,000	
	S216K	2,573	2,573	0,000	0,00%
	S316K	2,573	2,573	0,000	
3	S136K	2,573	2,573	0,000	
	S236K	2,573	2,573	0,000	0,00%
	S336K	2,573	2,573	0,000	
5	S156K	2,573	2,562	0,011	
	S256K	2,573	2,565	0,008	0,35%
	S356K	2,573	2,565	0,008	
7	S176K	2,573	2,530	0,043	
	S276K	2,573	2,559	0,014	
	S376K	2,573	2,573	0,000	
	S476K	2,573	2,573	0,013	0,65%
	S576K	2,573	2,556	0,017	
	S676K	2,573	2,558	0,015	
	S776K	2,573	2,558	0,015	

Table 17 - Diameter differences in mixture II after curing

MIX II   8M KOH

Days of curing	Sample	Ø of the container (mm)	Ø of sample after curing (mm)	Ø difference (mm)	Average (%)
1	S118K	2,573	2,573	0,000	
	S218K	2,573	2,573	0,000	0,00%
	S318K	2,573	2,573	0,000	
3	S138K	2,573	2,573	0,000	
	S238K	2,573	2,573	0,000	0,00%
	S338K	2,573	2,573	0,000	
5	S158K	2,573	2,560	0,013	
	S258K	2,573	2,566	0,007	0,26%
	S358K	2,573	2,573	0,000	
7	S178K	2,573	2,559	0,014	
	S278K	2,573	2,570	0,003	
	S378K	2,573	2,573	0,000	
	S478K	2,573	2,546	0,027	0,58%
	S578K	2,573	2,549	0,024	
	S678K	2,573	2,573	0,000	
	S778K	2,573	2,537	0,036	

Table 18 - Diameter differences in mixture III after curing

MIX III   6M NaOH

Days of curing	Sample	Ø of the container (mm)	Ø of sample after curing (mm)	Ø difference (mm)	Average (%)
1	S116N	2,573	2,573	0,000	
	S216N	2,573	2,573	0,000	0,00%
	S316N	2,573	2,573	0,000	
3	S136N	2,573	2,573	0,000	
	S236N	2,573	2,552	0,021	0,27%
	S336N	2,573	2,573	0,000	
5	S156N	2,573	2,547	0,026	
	S256N	2,573	2,561	0,012	0,54%
	S356N	2,573	2,569	0,004	
7	S176N	2,573	2,526	0,047	
	S276N	2,573	2,513	0,060	
	S376N	2,573	2,496	0,077	
	S476N	2,573	2,443	0,130	2,95%
	S576N	2,573	2,435	0,138	
	S676N	2,573	2,540	0,033	
	S776N	2,573	2,526	0,047	

Table 19 - Diameter differences in mixture IV after curing

MIX IV   8M NaOH

Days of curing	Sample	Ø of the container (mm)	Ø of sample after curing (mm)	Ø difference (mm)	Average (%)
1	S118N	2,573	2,573	0,000	0,00%
	S218N	2,573	2,573	0,000	
	S318N	2,573	2,573	0,000	
3	S138N	2,573	2,566	0,007	0,09%
	S238N	2,573	2,573	0,000	
	S338N	2,573	2,573	0,000	
5	S158N	2,573	2,491	0,082	3,58%
	S258N	2,573	2,506	0,067	
	S358N	2,573	2,446	0,127	
7	S178N	2,573	2,425	0,148	5,62%
	S278N	2,573	2,466	0,107	
	S378N	2,573	2,428	0,145	
	S478N	2,573	2,435	0,138	
	S578N	2,573	2,419	0,154	
	S678N	2,573	2,411	0,162	
	S778N	2,573	2,414	0,159	

In the samples produced with Portland cement class G, were not noticed any differences in the diameters, before and after curing process.

5.4. Uniaxial Compressive Strength results

Uniaxial compressive strength tests were performed in order to investigate developed compressive strength of all specimens. The obtained results are presented in the following tables and diagrams.

Table 20 - Compressive strength results of K-based activated mixtures

MIX I 6M KOH				MIX II 8M KOH			
Days of curing	Sample	Compressive strength (Mpa)	Young's Modulus (Mpa)	Days of curing	Sample	Compressive strength (Mpa)	Young's Modulus (Mpa)
1	S116K	13,48	1199,51	1	S118K	13,21	1197,14
	S216K	16,70	1570,26		S218K	16,98	1743,93
	S316K	16,02	1376,57		S318K	17,65	1293,51
3	S136K	16,38	1829,99	3	S138K	17,93	2416,83
	S236K	17,68	2158,83		S238K	19,25	2477,95
	S336K	16,24	1740,39		S338K	15,65	2164,69
5	S156K	16,35	2114,99	5	S158K	22,13	3119,35
	S256K	20,67	2541,83		S258K	18,11	1679,23
	S356K	13,37	1592,53		S358K	17,36	-
7	S176K	18,22	2601,55	7	S178K	26,19	4318,65
	S276K	14,89	1636,17		S278K	18,22	2395,04
	S376K	19,53	1952,40		S378K	25,20	3274,04
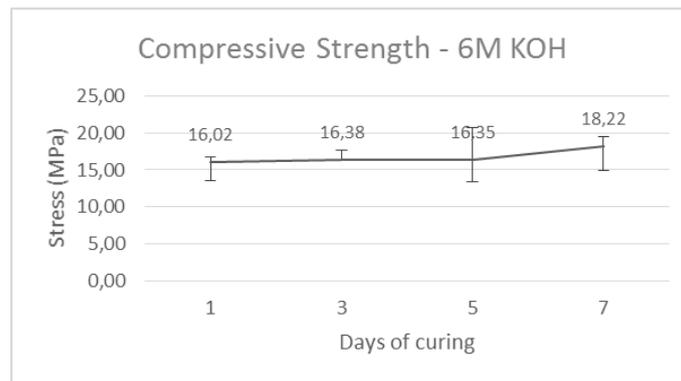
Figure 52 - Compressive strength results of mix I
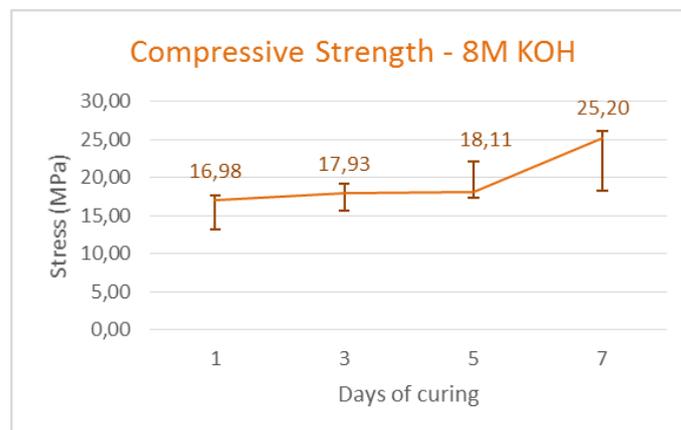
Figure 53 - Compressive strength results of mix II

Table 21 - Compressive strength results of Na-based activated mixtures

MIX III	6M NaOH			MIX IV	8M NaOH		
Days of curing	Sample	Compressive strength (Mpa)	Young's Modulus (Mpa)	Days of curing	Sample	Compressive strength (Mpa)	Young's Modulus (Mpa)
1	S116N	9,38	744,46	1	S118N	13,82	648,37
	S216N	8,87	773,30		S218N	13,17	806,03
	S316N	10,39	861,01		S318N	11,39	638,49
3	S136N	13,28	1153,26	3	S138N	12,83	1242,94
	S236N	15,69	1631,74		S238N	12,81	1062,15
	S336N	9,18	821,97		S338N	9,86	792,70
5	S156N	16,04	1759,59	5	S158N	30,14	3940,65
	S256N	15,96	1584,24		S258N	26,26	3357,58
	S356N	12,43	1253,51		S358N	27,72	3566,45
7	S176N	13,30	1145,33	7	S178N	35,40	4794,18
	S276N	23,39	2578,54		S278N	24,33	2528,98
	S376N	18,00	2164,90		S378N	24,55	5086,12
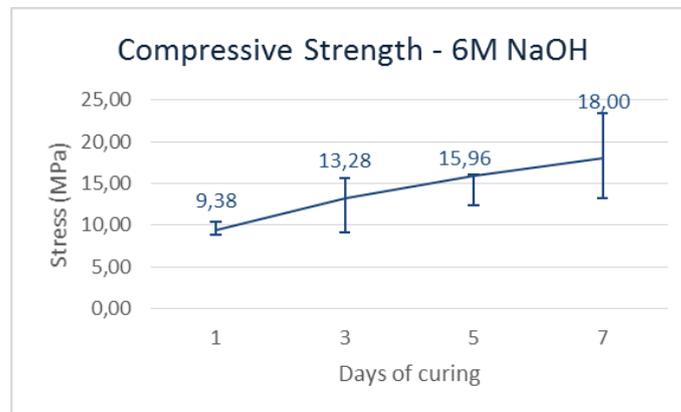
Figure 54 - Compressive strength results of mix III
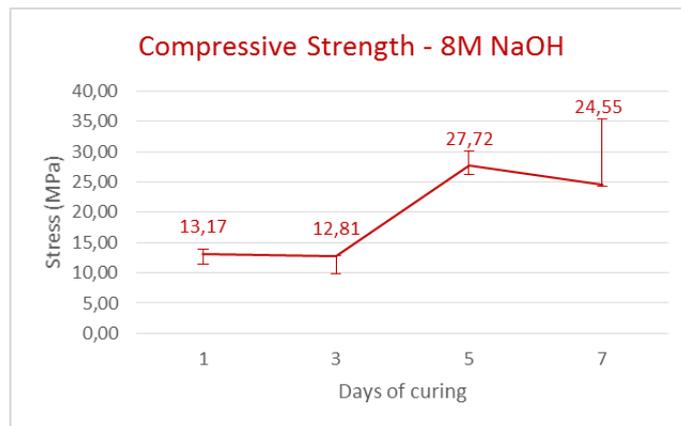
Figure 55 - Compressive strength results of mix IV

Table 22 - Compressive strength results of Portland Cement Class G

MIX V	OPC class G		
Days of curing	Sample	Compressive strength (Mpa)	Young's Modulus (Mpa)
1	S11G	14,58	1355,28
	S21G	26,16	3065,45
	S31G	18,34	2717,85
3	S13G	33,05	5080,62
	S23G	25,21	4012,45
	S33G	18,02	3997,63
5	S15G	25,02	3486,48
	S25G	31,68	4621,79
	S35G	28,77	4610,66
7	S17G	22,38	3895,70
	S27G	22,61	4146,95
	S37G	31,82	4881,86
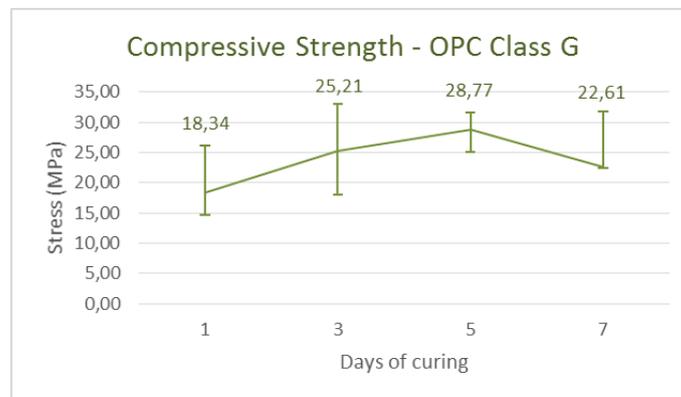
Figure 56 - Compressive strength results of mix V

5.5. Resistance to hydrochloric acid attack

To simulate a scenario where geopolymers are exposed to conditions of acidity due to the presence of HCl (used in acid stimulation in the oil and gas industry) and to study its negative effects, specimens were immersed in 15% solution of hydrochloric acid.

These tests were conducted on geopolymer samples produced from mix II, IV and V and having cure times of 7 days (figure 57). Samples were then left immersed for 21 days into the acidic solution and measurements and compressive tests performed on the 7th, 14th and 21st day, using one sample of each of the mentioned mixtures.
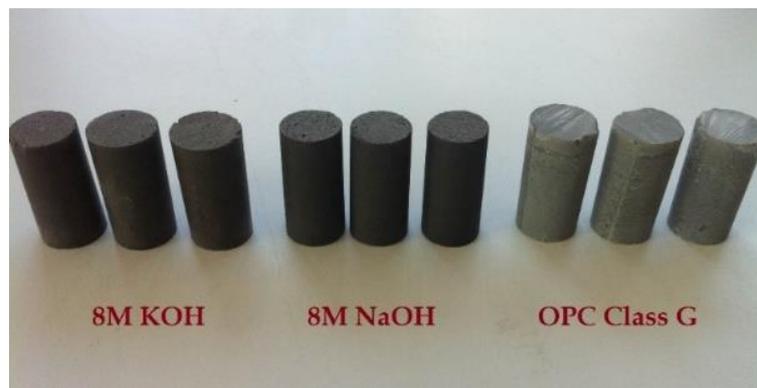
Figure 57 – Samples before being immersed in the HCl solution

Once samples were immersed in acid (pH=1.17) no further adjustment to pH was made during the test.

Samples were removed from the acid solutions after the designated days and were left in ambient temperature drying for 3 hours.

Compressive strength values of the geopolymeric specimens used in this test, were compared with the compressive strength values obtained in the regular compressive strength tests performed previously. In the case of OPC, a control sample was produced, exactly in the same day of the ones used in this test. The compressive strength test was then performed at the same time of the ones removed from the acid solution, in order to be used as a reference.

The acid resistance was evaluated on mass loss and in the change of compressive strength. The obtained results are presented in the following tables 23 and 24.

Table 23 – Percentage weight loss after acid attack

Sample	Age of acid immersion (days)	Type of acid	Weight of samples after 7 days of curing and before acid immersion (gr)	Weight of samples after acid immersion (gr)	Percentage weight loss (%)
S478K	7		39,19	37,06	5,44%
S578K	14	HCl (15%)	38,98	36,47	6,44%
S678K	21		38,82	36,14	6,90%
S478N	7		38,28	38,01	0,71%
S578N	14	HCl (15%)	38,43	37,86	1,48%
S678N	21		38,08	37,21	2,28%
S47G	7		52,71	49,65	5,81%
S57G	14	HCl (15%)	52,50	49,32	6,06%
S67G	21		52,43	48,83	6,87%

Table 24 – Percentage loss of compressive strength after acid attack

Sample	Age of acid immersion (days)	Type of acid	Obtained range of compressive strength after 7 days of curing and before acid immersion (MPa)	Compressive strength after acid immersion (Mpa)	Percentage loss of compressive strength (%)
S478K	7			12,68	5,44%
S578K	14	HCl (15%)	[18,22;26,19]	13,83	6,44%
S678K	21			12,60	6,90%
S478N	7			31,03	0,00%
S578N	14	HCl (15%)	[24,33;35,40]	20,73	1,48%
S678N	21			18,85	2,28%

Sample	Age of acid immersion (days)	Type of acid	Compressive strength of control samples (MPa)	Compressive strength after acid immersion (Mpa)	Percentage loss of compressive strength (%)
S47G	7		42,99	16,88	60,74%
S57G	14	HCl (15%)	37,29	17,60	52,79%
S67G	21		36,21	14,82	59,08%

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6. Discussion and comparison of results

6.1. Differential Scanning Calorimetry
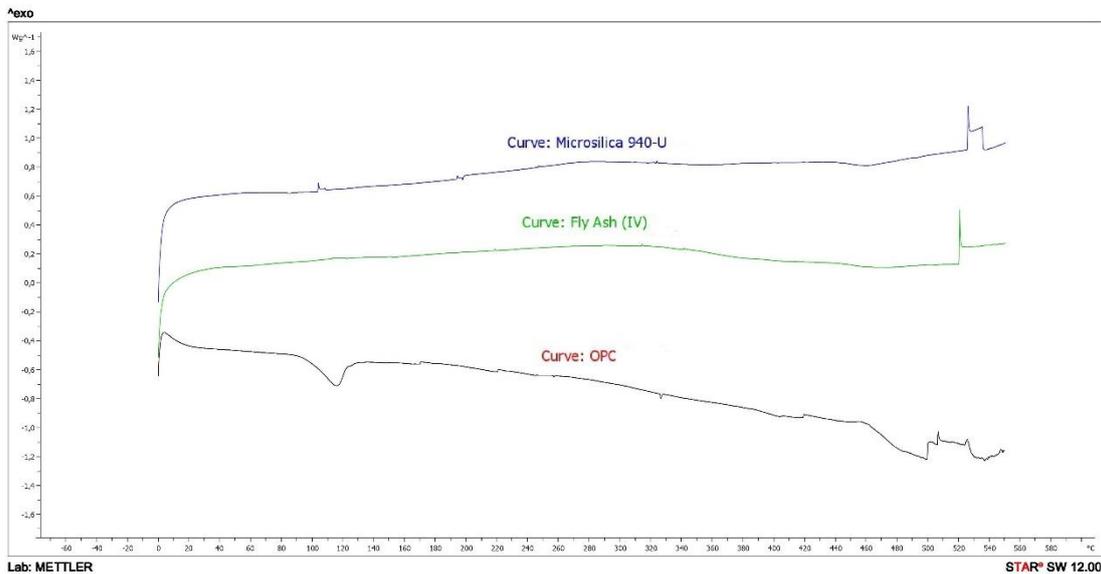
Figure 58 - Results of DSC of raw materials
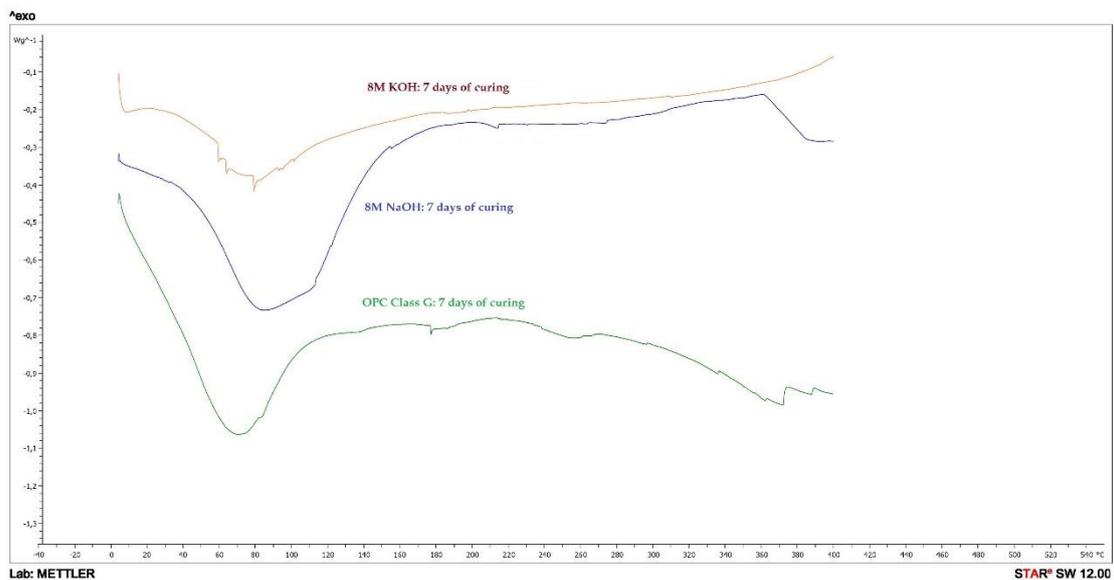
Figure 59 – Results of DSC of produced materials

The various dry powders used in the mixtures were examined with DSC in order to provide some possible peaks which could corroborate expected peaks formed in the hydrated cements caused by the sample undergoing physical transitions or chemical reactions.

In figure 58, a combined DSC thermogram of the individual powders is presented. Microsilica and fly ash present smooth thermograms with no signs of reactions or phase transitions with increasing the temperature. On the other hand, Portland cement, shows a lower temperature endothermic

peak (100–120 ºC) which can be attributed to free or adsorbed volatilized water being liberated at 100 ºC. However none of them presented any phase transition within the used range of temperatures.

Endothermic peaks on the curves above 500 ºC are meaningless and probably are due to some kind of anomaly in the measurement done by the equipment.

Regarding the cement materials (figure 59), one sample with 7 days of curing of mix II, mix IV and mix V were subjected to this test.

All of them showed an endothermic peak at the earlier temperatures of the test which also in this case is related to the release and evaporation of the remaining water from the pores of the samples at temperatures around 100 ºC.

In both geopolymeric curves (mix II and IV), no peaks were observed which means no signs of reactions or hypothetical phase transitions.

The curve related with the Portland cement, follows the same pattern of the previous ones except above 380ºC, where some exothermic peaks on DSC curve are observed, probably caused by residual carbon oxidation.

This instability can be due to a phenomenon called as strength retrogression experienced by Portland cement when exposed to high temperatures. This is one of the drawbacks associated with the use of this material in P&A. When this reduction in strength at high temperatures occurs, it is common to lead to an increase in porosity and permeability as well. In these cases, the sealant material becomes accessible by corrosive fluid present in the formation [19].

The absence of peaks and phase transitions in all the curves are due to the absence of hydrates in the crystalline form because we are in presence of amorphous materials.

6.2. Rheological studies of the slurries
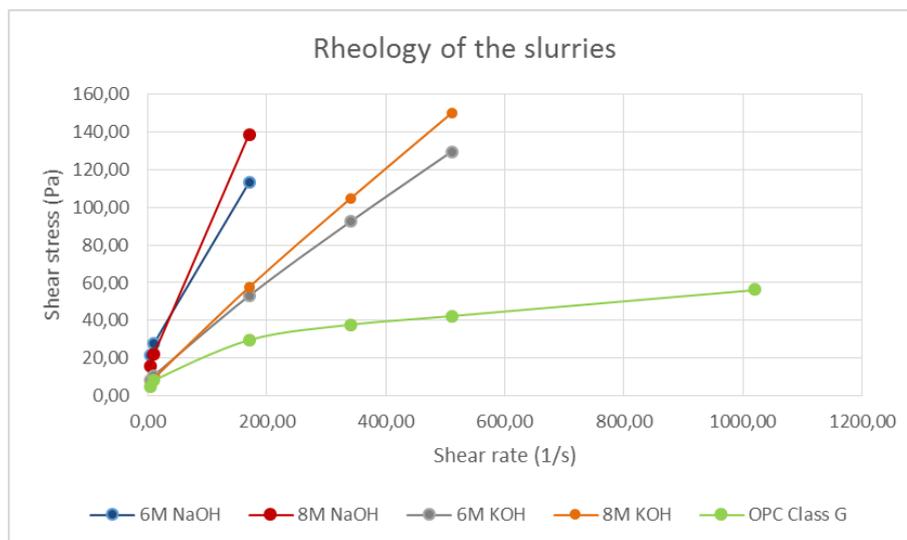
Figure 60 - Rheograms of cement and geopolymeric slurries

Figure 60 illustrates the measured shear stress of the geopolymer slurries and Portland cement class G slurry as a function of the shear rate.

It can be seen that geopolymer slurries have a high value of shear stress in comparison to OPC slurry and regarding geopolymeric slurries. Mixtures using higher molarities also presented higher shear stresses when compared with the ones with lower molarities, leading later, to higher viscosity values (figure 60).

Rheological behaviour of all the slurries shows a non-Newtonian like viscosity behaviour. Furthermore, from the previous chapter, it was shown that in all cases, viscosity decreases when shear rate increases, which means that we are in presence of shear-thinning fluids.

All the geopolymeric slurries fit in the Bingham Plastic model whereas OPC behaved like a Power Law fluid.
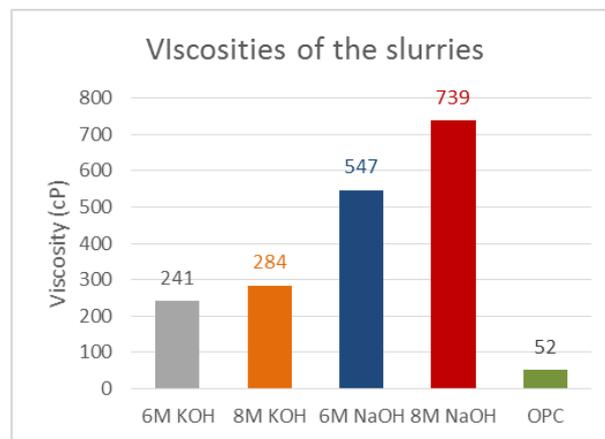
Figure 61 – Viscosities of the slurries

In the previous figure 61, it is noticeable that in general, the Na-containing slurries produced higher viscosities than the K-containing slurries.

Viscosity for Na-containing solutions is up to 2.5 times higher than the ones with K-containing solutions for the same molarities.

The OPC revealed a much lower viscosity, when compared to the other slurries.

It is reported in literature [21], that a pumpable fluid in the oilfield industry has a rheology less than 300 cP, which means that in this work and from obtained results, it can be assumed that K-based and OPC mixtures could be elected, from a rheological point of view, as potential mixtures to be used in P&A.

On the other hand, for practical operations, the viscosity of Na-based mixtures would need to be adjusted using a superplasticizer.

Slurries with high viscosity will affect the pumpability, limiting pump rate and therefore the placeability of the material during well cementing operations.

The reduction of the viscosity allows the geopolymeric suspension to be pumped with less friction pressure and utilizing less pump horsepower. If used as a displacement fluid to remove the drilling mud from the wellbore, density and rheological properties of the geopolymer suspension have to be selected and controlled to provide optimum displacement regime [42].
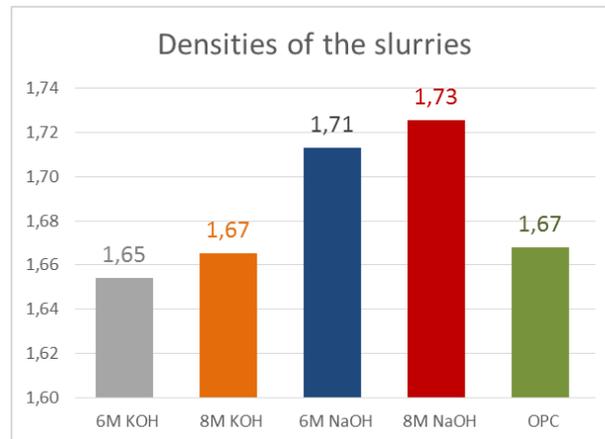
Figure 62 - Densities of the slurries

In figure 62, the measured densities of all the slurries are presented as well. The density of the geopolymeric slurries was measured to be within the range of 1.65 to 1.73 g/cm^3 at ambient pressure and temperature. The density of the Portland cement Class G slurry was determined to be 1.67 g/cm^3 at the same conditions.

Except mixture I (6M KOH), all the other geopolymeric slurries demonstrated higher values of density with respect to measured slurry density of OPC.

In literature [21], it is suggested that for oil field industry the density of the suspension of said geopolymeric slurry compositions varies between 1 g/cm^3 and 2.5 g/cm^3 and more preferably between 1.2 g/cm^3 and 1.8 g/cm^3, which is in accordance with the values obtained for all the mixtures tested in this work.

Control of the densities of the slurries is a factor of major importance in order to avoid formation damage. The density of the slurry should not allow fluid invasion of the wellbore from the formation, and at the same time it should not exert excessive hydrostatic pressure causing fluid loss of the slurries to the formation. All the problems that can arise from it were explained before, in the topics 3.16.2 to 3.16.5.

Additionally, in cases on which the drilling mud has to be displaced and removed from the wellbore by the slurry, density of it has also to be controlled.

6.3. Setting time of the slurries

Figure 63 indicates thickening test results for mixtures at temperature of 90ºC for the slurries of this study. In this figure, the lighter color in each mixture, represents the period of time between initial and final setting times.
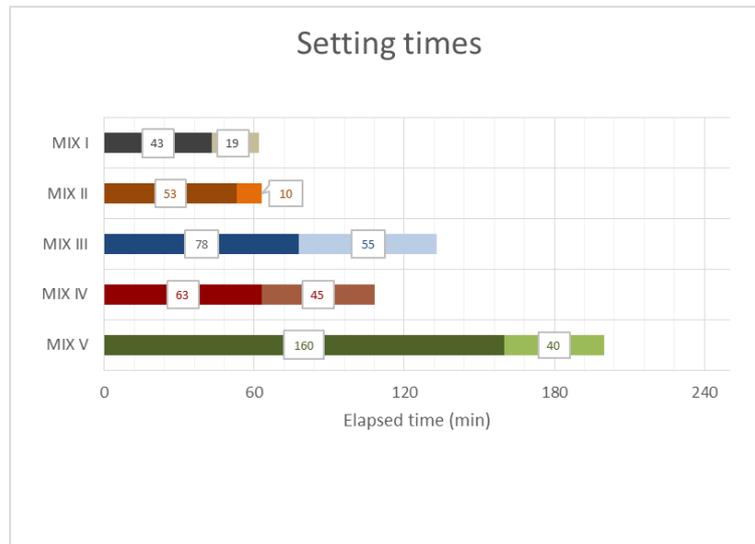
Figure 63 - Setting times of the slurries

From all the slurries tested, the one which presented a longer setting time was OPC (mix V). Regarding geopolymeric slurries, mix I and II (K- based) revealed significantly shorter setting times when compared with mix III and IV (Na- based).

Based only, on the results of this test, apparently OPC, mix III and IV seem to have acceptable thickening time without using any additive, which means that are suitable to be pumped and used as a sealing material in P&A. On the other hand, mix I and II need a retarder, to increase the initial and final setting times.

It is important to refer that thickening times are dependent on downhole conditions and depth of the location where the material has to set. For larger depths, longer setting times are required because the period of time that the material needs to be pumped to reach the desired location of placement, will be longer.

6.4. Mass loss due to water evaporation

Samples were weighed after they were casted just before curing started. Weight change of the samples was determined after predicted curing periods in order to evaluate mass loss. Results of weight changes for all samples are presented in figure 64, in percentages.
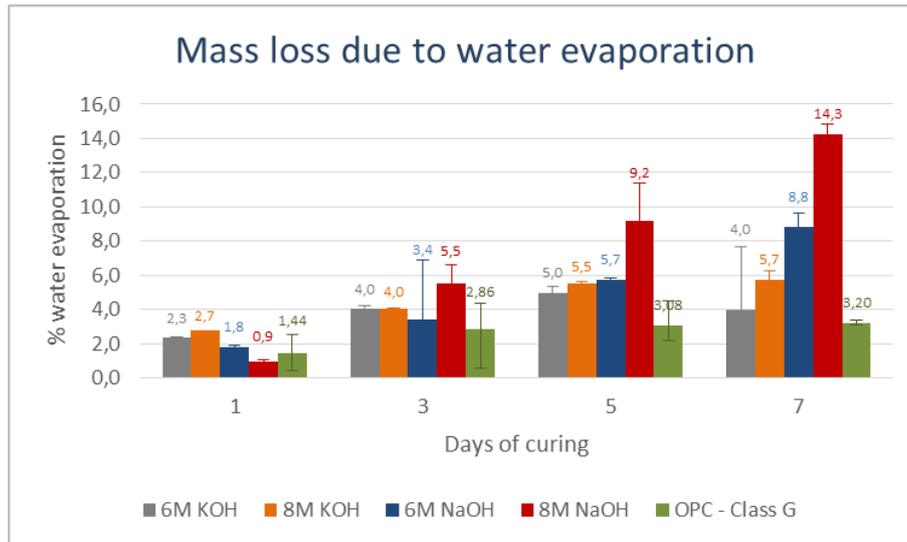
Figure 64 - Water evaporation of cement and geopolymeric slurries

The decrease in weight is attributed to the loss of evaporable water in the geopolymer due to heating during curing period.

From the previous diagram, it is clear that OPC tends to loose less water than geopolymers during all test period leading to a smaller mass loss.

Regarding geopolymeric specimens, weight loss is remarkably sharper in Na-based geopolymers starting from day 3, while in the same period, K-based geopolymers showed a steady mass loss.

6.5. Bulk shrinkage
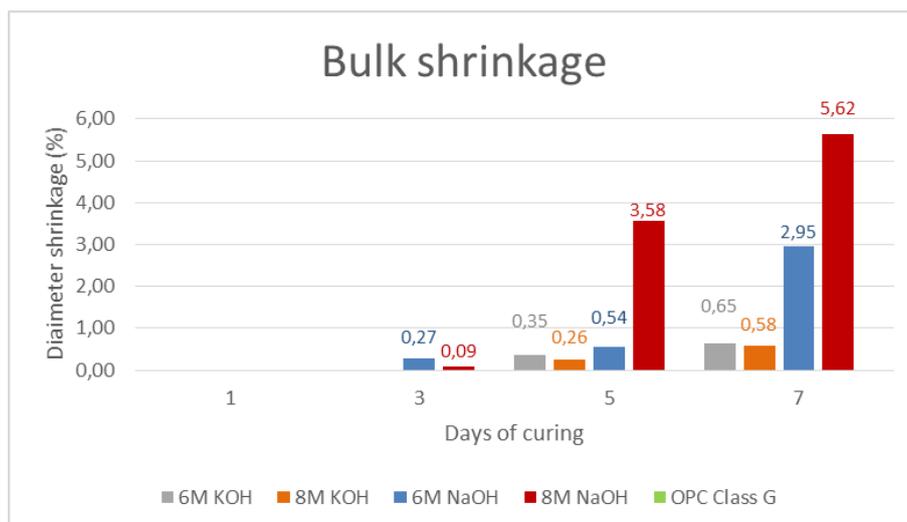
Figure 65 - Bulk shrinkage of cement and geopolymeric slurries

After curing, some of the specimens exhibited some signs of a slight expansion in the longitudinal direction, but a reduction of diameter in some of those, was the phenomenon which was clearly noticed during the experiments. This situation is related with shrinkage of the material, probably caused by mass loss due to water evaporation when subjected to elevated temperature, which is in accordance with figure 64. To have a rough idea about the percentage of shrinkage, the diameters before and after curing, were compared.

It can be seen from figure 65, that shrinkage started to be noteworthy on the 3rd day, increasing until the 7th day of curing.

From observations, the percentage of shrinkage was much higher in Na-activated geopolymers than in the ones produced with K-activators. The maximum bulk shrinkage was reached for the geopolymer slurry prepared with 8M NaOH, after 7 days of curing with a value of 5.62% of diameter reduction when compared with the initial one.

In these measurements, shrinkage in OPC materials was not noticed.

Shrinkage, results in a change in the cement's stress state, which can potentially lead to plastic deformation of not only the cement, but also the casing and formation, or de-bonding at either the casing or formation interfaces [19].

Therefore, shrinkage of the material, is a concern for plugging materials or materials used for casing cement, because it can cause an incomplete annular zone isolation.

When a leakage path is already present due to cement shrinkage, gaps along interfaces (e.g. sealing material/casing, casing/cement or cement/rock), chemical and mechanical alteration can increase leakage risks.

6.6. Uniaxial Compressive Strength results
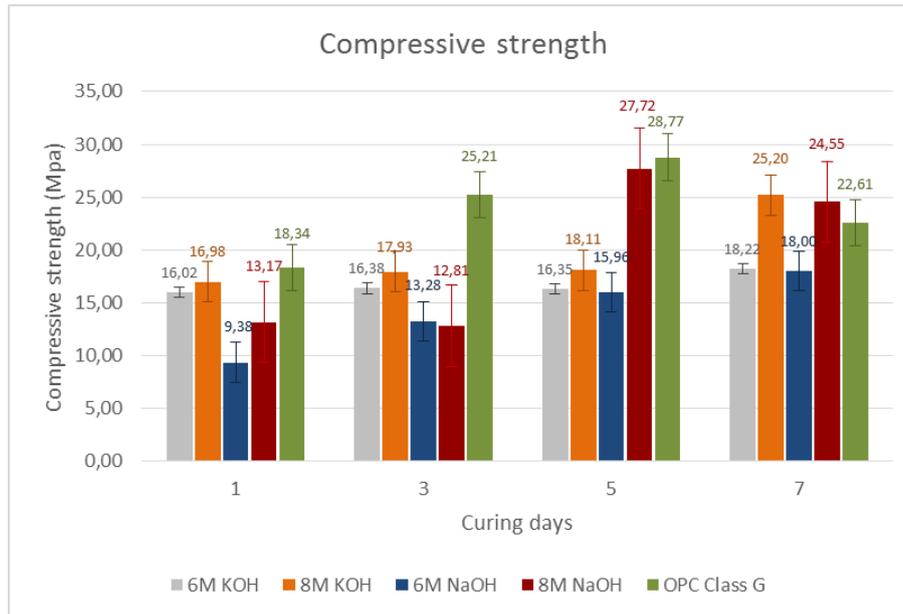
Figure 66 - Compressive strength results

The UCS test was performed to evaluate the compressive strength development of the geopolymers.

Figure 66 shows the results of the compressive strength measurements at different time intervals of 1, 3, 5 and 7 days.

From the obtained results, we can conclude that when the concentration of KOH and NaOH solution into the activating solution was increased, there was a better performance of the specimens in the compressive strength test.

Compressive strength for the geopolymers produced with KOH concentration showed that the strength development progresses with time reaching the maximum value on curing age of 7 days. The K-activated geopolymers showed higher compressive strength compared to the Na-activated geopolymers in the earlier days of testing (1 and 3 days of curing). On the 5th day of curing, a sudden increase of the compressive strength was observed in Na-activated geopolymer with 8M concentration. On the 7th day, it decreased and became similar in comparison to results obtained for geopolymer with the same concentration but produced with K-activator. In this case it also presented a sudden increase in the compressive strength but, in the last day.

The same happened with the geopolymers produced with 6M concentration of activator. On the 5th and last day of tests, they revealed identical values for UCS.

Apparently, K-based geopolymers develop more compressive strength at the earlier days of curing while in the case of Na-based geopolymers are developed later. However, after 7 days of curing, both type of geopolymers, presented similar values for the compressive strength in both concentrations.

OPC described an increasing trend of compressive strength values until the 5th day of curing, however it started decreasing that trend at the 7th day when it demonstrated lower values of compressive strength when compared with the ones showed by geopolymers with 8M concentration.

In the European Patent Specification number EP1887065B1 [21], values obtained from compressive strength tests of geopolymeric materials performed by the inventors between 9 MPa and 19 MPa are reported. According to them, the obtained results exhibited good compressive strengths meaning that those materials would be very useful in oilfield applications. The results obtained from the tests performed in this work, are well above those reported values.

Regarding the elastic material capacity, geopolymers in general, showed lower values of Young's modulus than the ones showed by OPC. The ability of a material of being elastic is an advantage. If the material has the capacity to deform when a load is applied to it and then, when the load is removed, returns to its original shape, that is a very useful feature of the sealing material. It can help avoiding fractures in the material, caused by internal stresses owning to the rock formation.

Once again it is important to underline the importance of the compressive strength on any sealing material. The capacity it has to resist when subjected to mechanical stresses induced by natural variations in subsurface conditions due to tectonic stresses or even seismicity, can affect largely its efficiency. Strain-induced fractures in the sealing material, caused by excessive mechanical stresses can lead to a leak pathway formation endangering the purpose of the plug.

6.7. Resistance to hydrochloric acid attack

In all geopolymeric samples, the cohesion of the material was maintained and did not reveal any noticeable change in color or surface degradation. Specimens were seen to remain structurally intact with no visible cracks after its drying, but at the same time, the material turned softer than it was before the acid attack. This softness, which was noticed during the compressive strength tests, indicates a deterioration of the material which tends to increase with time but could not be easily differentiated through visual inspection.

In the case of Portland cement, this deterioration is caused by calcium oxide, which is one of the oxides present in the materials. When in presence of corrosive substances, calcium is easily attacked to form the salt of the calcium and is leached out, causing a strength loss of the material. This reaction, is described below:

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \text{ [43]}$$
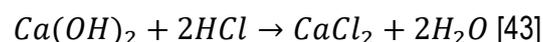
The reaction essentially causes leaching of Ca(OH)$_2$ from the set cement. After leaching out of Ca(OH)$_2$, C-S-H and ettringite (product formed after dissolution of calcium hydroxide and calcium

aluminate hydrate) start to decompose, with release of Ca^{2+} to counteract the loss in $Ca(OH)_2$ and the set cement starts to disintegrate accelerating the dissolution [43].

However, based on literature [36] and in the results obtained previously, this mentioned deterioration is more severe and fast in Portland cement because the geopolymer cement structure makes endosmosis (rate of fluid transport through the cement) happen slowly due to the presence of potassium silicate or sodium silicate into the structure. These components play a prevention role with regards to the penetration of the acid.

Nguyen et al [36], describe the process of geopolymers acid resistance following the next steps:

Step 1: Attachment of the acid proton to the lone electron pair of the siloxane oxygen:
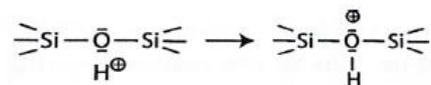
Cleavage is ruled by the relative susceptibility of the siloxo oxygen Si-O-Si against proton attack, not by the cleavage of the sialate bond Si-O-Al, due to its protection by the metallic cations (Na, K). The oxygen of the Si-O-Al sialte bond is attacked only after leaching of the protecting cation has occurred.

Step 2: Subsequent reactions leading to the scission and re-formation of siloxane/siloxo bonds, decomposition of the oxonium complex with the formation of a silanol unit Si-OH and formation of a silicon-anion Si-X bond (X is chloride):
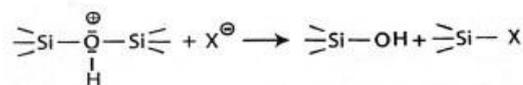
The destruction of geopolymeric backbone is limited to the effective amount of anion chloride present in the solution.

Furthermore, they also claim, that during this process, sodium chloride (NaCl) resulting from the reaction:

$$NaOH + HCl \rightarrow NaCl + H_2O \text{ [36]}$$
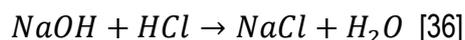
In the case of using geopolymers produced with K-based activator, potassium chloride will be formed as the previous case:

$$KOH + HCl \rightarrow KCl + H_2O$$
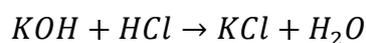
In both cases, sodium and potassium chlorides are considered remainders from geopolymerization [36] .

The formation of these chlorides prove the resistance of geopolymeric materials, because NaCl and KCl are products of the neutral between NaOH/KOH and HCl.

From the conclusion made by the investigators, it can be assumed that the concentration of the alkali solution (KOH or NaOH) weakens the corrosive effect of HCl being a factor of major importance for the resistivity of the geopolymers, in corrosive environments with presence of HCl.

In the case of OPC, a visual physical change was noted as revealed by their grey to yellowish brown color. Additionally, OPC samples also exhibited a formation of a tight layer of sludge on the surface of the sample, leading to a deposition of material at the bottom of the sample. The extent of alteration and the relative width of the layers depend on the duration, the specific reaction conditions, and the initial cement composition [19].

The mentioned physical changes are shown in figures 67, 68, 69 and 70.
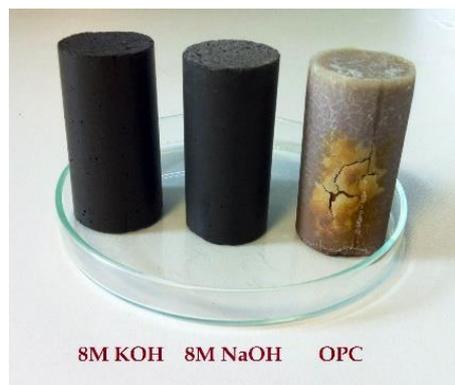
Figure 67 - Samples after being immersed for 7 days
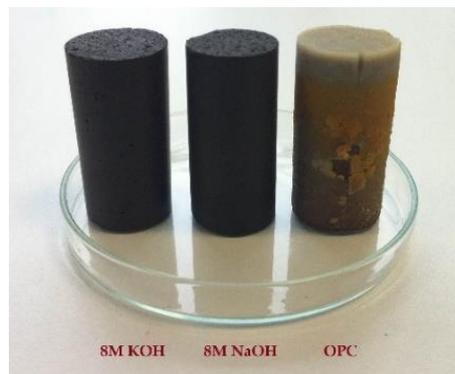
Figure 68 - Samples after being immersed for 14 days
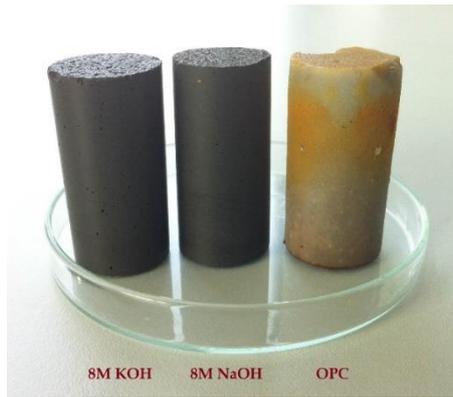
Figure 69 - Samples after being immersed for 21 days

Figure 70 - Tight layer of sludge on the surface of OPC

According to the literature [19], the mentioned layer which is located at the cement interface with the acid (figure 71), is also known as residual amorphous silicate zone. This is a by-product of restructuring of calcium-free C-S-H (calcium silicate hydrate - crystal structure in cement paste) phases with dissolved sodium and aluminium to form an amorphous aluminosilicate.

Figure 71 - Residual amorphous silicate zone

Weight change of the acid treated samples was determined after immersion period. It is important to note that initial weights of samples were measured just before the acid immersion.
Results of the weight changes for the tested specimens are presented in figure 72.
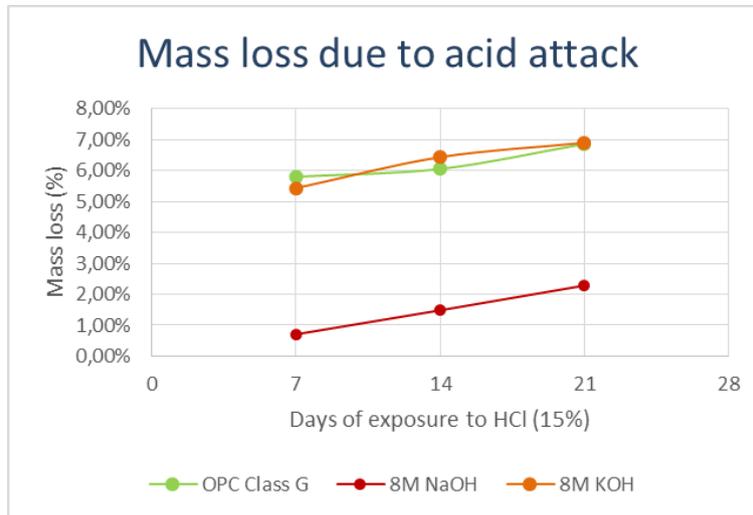
Figure 72 - Mass loss due to HCl attack

It is noticeable that, after exposure to HCl, all the specimens exhibited mass loss.
The loss of weight was observed to be lower in geopolymer using Na- based activator than in the one produced with the K-based activator. Geopolymer produced with K-based activator showed a similar mass loss when compared with OPC with values within the range of 5,5% to 7% mass loss. Regarding compressive strength loss, it was observed that the percentage loss of compressive strength of all geopolymer cement mixes are considerably lower than that of OPC cement mixture at all ages of HCl exposure (figure 73).
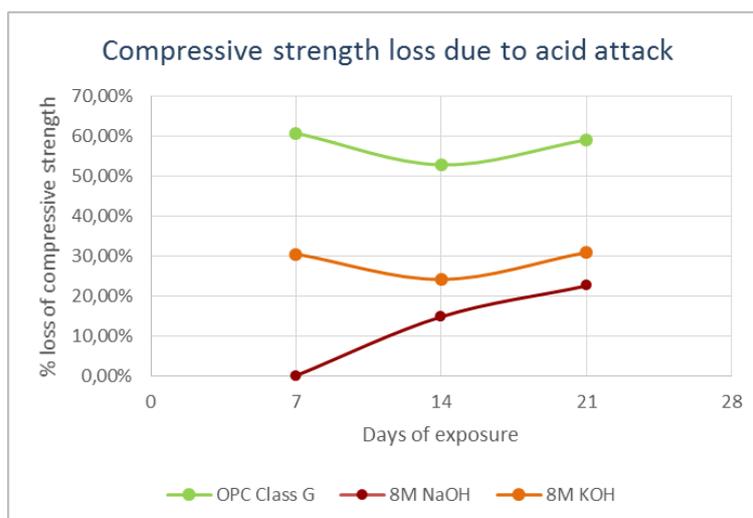
Figure 73 - Compressive strength loss during HCl immersion

At the earlier days of the test, Na- based geopolymeric specimens did not present significant loss in the compressive strength results when compared with the ones produced with K- based activator. However, at the end of the test, both of them presented similar values of compressive strength loss. In addition, it was observed that the percentage loss of compressive strength of all geopolymeric materials, are considerably lower than that of OPC at all ages of acid exposure. For instance, in the last day of the test, loss of compressive strength of OPC was almost double the loss of compressive strength of geopolymer cement.

During UCS tests, all the samples were fractured in brittle conditions.

It is important to note that, for each designated testing day, only one sample of each mixture was tested. Though, all the previous result of this topic, can present a lack of accuracy.

7. Proposed further work

In this work four different mixtures were developed and compared with the most commonly used material in P&A. The strength developed by those materials are promising and likely to be used in P&A operations. Even though, several more samples using the same mixtures should be produced and tested again, in order to verify the obtained results in the present tests.

However, due to the absence in our university facilities of a pressurized consistometer, curing period was done at ambient pressure. The effect of pressure, during the curing, on the properties developed by the specimens, should be investigated in order to have a better approximation of real well conditions. For instance, the porosity of the specimens would be reduced, leading to a less permeable material, which is one important attribute for a sealing material in P&A.

Nevertheless, other important properties have to be investigated further in order to consider this kind of material as a viable alternative to Portland cement. Some of those properties would be the density, shrinkage, porosity and permeability of the set geopolymeric material and bonding conditions with rock formation and with casing steel. The degree of contamination of these materials at the interface with the other type of fluids that can be found inside the well and how the performance of the sealing material can be affected should be investigated as well.

Due to lack of time and laboratory equipment limitations, these properties could not be investigated in detail.

After these properties have been studied in detail and if the results from laboratory tests keep showing promising results for oil and gas applications, field demonstration tests should be performed.

For economic and environmental reasons, the above mentioned properties should be further researched in order to select geopolymers as a real alternative to Portland cement in P&A.

8. Conclusions

On the basis of the obtained results, the following conclusions can be drawn.

- If the energy provided is great enough, the properties or compressive strength of concrete are increased.
- Moreover, the current knowledge shows that, the influence of alkali solutions molarity, liquid-to-solid ratio, alkali silicate-to-alkali solution ratio are also essential for achieving the optimum strength of geopolymer.
- Geopolymers exhibited superior hardness and chemical stability when compared to OPC.
- Geopolymers also revealed a better resistance elastic deformation.
- The K-containing systems showed lower viscosity compared to the Na-containing systems but both of them showed a non-Newtonian like viscosity behaviour.
- Like in this work, geopolymers are referenced as short thickening time materials. This is one of the obstacles which have to be overcome in order to these materials to be considered as viable for applications in oil and gas wells. A proper mix design has to be found (often with the addition of retarders which can be used to lengthen the setting time) in order to provide acceptable thickening times to the mixture. By doing this, the slurries can be pumpable in downhole conditions, without compromising other important properties for oil field applications, like the compressive strength.
- Geopolymers developed reasonable compressive strength which can be even more improved depending on the purpose and kind of application.
- The results confirmed that geopolymeric materials are highly resistant to HCl acid in terms of a very low mass loss and compressive strength loss when compared to conventional concrete foreseeing better durability in aggressive environments.
- The results found in these experiments indicate that there is a potential to use fly ash-based geopolymers as an alternative cementing material for plug and abandonment. Unfortunately, due to lack of research on application of these materials in oil wells, these materials are not presently well received in the industry. Further research is needed on this subject before the geopolymers can be applied in real cases.

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APPENDIX

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PRODUKTDATABLAD

FLYDENDE KALIVANDGLAS (KALIUMSILIKAT)
TYPE 4009

$^{\circ}$Be	=	40	+/- 0,4
K_2O %	=	13,2	+/- 0,2
SiO_2 %	=	26,2	+/- 0,5
Tørstof %	=	39,4	+/- 1,0
GV*	=	2,00	+/- 0,05
MV*	=	3,14	+/- 0,1
Visk. m. Pas/20 °C	=	100 - 120	
Vf.	=	1,38	

*MV (Mol-Verhältnis = mol forhold), GV (Gewicht-Verhältnis = vægt forhold).
 Forholdet mellem $K_2O:SiO_2$

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PRODUKTDATABLAD

FLYDENDE NATRONVANDGLAS (NATRIUMSILIKAT)
TYPE L 44

$^{\circ}$Be	=	44	
Na_2O %	=	12,80	+/- 0,5
SiO_2 %	=	25,60	+/- 1,0
Tørstof	=	38,40	+/- 1,5
GV*	=	2,0	+/- 0,1
MV*	=	2,1	+/- 0,1
Vf. (vægtfylde)	=	1,44	+/- 0,01

*MV (Mol-Verhältnis = mol forhold), GV (Gewicht-Verhältnis = vægt forhold)
 Forholdet mellem $Na_2O:SiO_2$

Kaliumsilikat	Revideret d.: 13.07.2015
	Erstatter d.: 20.01.2014
	Initialer: MBK

SIKKERHEDSDATABLAD

1 Identifikation af stoffet/blandingen og af selskabet/virksomheden

1.1 Produktidentifikator.

PR-nummer: 1951693
REACH-reg.nr.   01-2119456888-17-xxxx
Handelsnavn: Kaliumsilikat, vandig opløsning – Kalivandglas; type 4009

1.2 Relevante identificerede anvendelser for stoffet eller blandingen samt anvendelser, der frarådes.

Anvendelser: Råmateriale til bl.a. brandhæmmende, bindemidler, blegning, maling og andre industrielle formål.

Branche: Industrien.

Frarådede anvendelser: Ingen kendte

1.3 Nærmere oplysninger om leverandøren af sikkerhedsdatabladet.

Leverandør: **Bollerup Jensen A/S**
                     Bindesbølvej 16 – 20, Ådum, 6880 Tarm
                     Telefon: 9737 6033; Fax: 9737 6268
                     E-mail: info@bollerup-jensen.dk

1.4 Nødtelefon.
Kontakt: Giftlinien: 82 12 12 12. Lægen kan få råd om behandling fra giftinformationen på Bispebjerg Hospital.

               Leverandøren 97 37 60 33 (mandag–torsdag: 8-16 og fredag: 8-15)

2 Fareidentifikation

2.1 Klassificering af stoffet eller blandingen.
CLP-klassificering: Produktet er klassificeret i henhold til Europa-parlamentets og rådets forordning (EF) Nr. 1272/2008 samt CEES (Center Européen d'Etude des Silicates) Soluble Silicates June 2014. Skin Irrit. 2 og Eye Irrit. 2

Væsentligste skadevirkninger: Kan fremkalde irritation af øjet og virke irriterende på huden, ved længere tids påvirkning.

2.2 Mærkningselementer.   Produktet er mærknings pligtig. MR 3,1

CLP-klassificering
Signalord: Advarsel

Piktogram:

H-sætninger: H315; Forårsager hudirritation.
               H319; Forårsager alvorlig øjenirritation.

P-sætninger: P262 (Må ikke komme i kontakt med øjne, hud eller tøj).
               P280 (Bær beskyttelseshandsker/beskyttelsestøj/øjenbeskyttelse/ansigtsbeskyttelse).
               P303+P361+P353 (VED KONTAKT MED HUDEN(eller håret): Tilsmudset tøj tages straks af/ fjernes. Skyl/brus huden med vand).
               P305+P351+P338 (VED KONTAKT MED ØJNENE: Skyl forsigtigt med vand i flere minutter. Fjern eventuelle kontaktlinser, hvis det kan gøre let. Fortsæt skylning).
               P314 (Søg lægehjælp ved ubehag).

2.3 Andre farer.   Produktet opfylder ikke kriterierne for PBT eller vPvB.
                              Ingen særlig risiko ved anvendelse efter leverandørens anvisninger.

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3 Sammensætning af/oplysning om indholdsstoffer

3.1 Stoffer / 3.2 Blandinger

CAS-nr.	Stofnavn	Klassificering	w/w %	Note
1312-76-1	Kaliumsilikat	Ikke klassificeret af leverandøren (MR >3,2)	30 - 50	

4 Førstehjælpsforanstaltninger

4.1 Beskrivelse af førstehjælpsforanstaltninger

Generelle råd:	Ved ubehag, søg læge og medbring etiketten eller dette Sikkerhedsdatablad. Lægen kan få råd om behandling fra Giftlinjen. Produktet er alkalisk.
Indånding:	Intet særligt. Produktet er ikke flygtigt. Ved ubehag søg frisk luft.
Indtagelse:	Skyl munden grundigt og drik meget vand. Fremkald ikke opkastning.
Hud:	Vask huden med lunken vand.
Øjne:	Skyl straks med vand (helst fra øjenskyller) i mindst 15 min. Spil øjet godt op. Fjern eventuelle kontaktlinser.

4.2 Vigtige symptomer og virkninger, både akutte og forsinkede

Ubehag kan forekomme ved indtagelse. Stænk i øjnene kan give irritation

4.3 Angivelse af om øjeblikkelig lægehjælp og særlig behandling er nødvendig

Søg læge ved vedvarende ubehag/irritation og medbring dette Sikkerhedsdatablad.

5 Brandbekæmpelse

5.1 Slukningsmidler:

Egnede slukningsmidler:	Produktet er ikke umiddelbart antændeligt. Brand slukkes med vandtåge, pulver, skum, kulsyre.
Uegnede slukningsmidler:	Vandstråle, da det kan sprede branden.

5.2 Særlige farer i forbindelse med stoffet eller blandingen:

Produktet er alkalisk og reagerer med syrer (opløsninger af bl.a. phosphor-, salpeter-, salt- og svovlsyre og konc. flussyre).

5.3 Anvisninger for brandmandskab:

Brug passende personlig beskyttelse i tilfælde af brand (handsker, briller og åndedrætsværn).
Undgå indånding af dampe og røggasser – søg frisk luft.
Hvis det kan gøres uden fare, fjernes beholdere fra det brandtruede område.

6 Forholdsregler over for udslip ved uheld

6.1 Personlige sikkerhedsforanstaltninger, personlige værnemidler og nødprocedurer

For ikke-indsatspersonel:	Brug handsker og briller ved risiko for stænk i øjnene. Anvend samme typer værnemidler som nævnt i punkt 8.
For indsatspersonel:	Brug handsker og briller ved risiko for stænk i øjnene. Anvend samme typer værnemidler som nævnt i punkt 8.

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6.2 Miljøbeskyttelsesforanstaltninger

Forhindre at større spild løber ud i afløb og kloak.

6.3 Metoder og udstyr til inddæmning og oprensning

Større spild inddæmmes og opsamles med sand, kattegrus eller andet absorberende materialer og overføres til egnede affaldsbeholdere. Evt. nødstopsanlæg til kloak aktiveres.
Små mængder spild, kan spules bort med vand.
Vask under alle omstændigheder det forurenede område grundigt med vand, for at hindre glideulykker.

6.4 Henvisning til andre punkter

Punkt   1 for kontaktoplysninger ved uheld/ulykke.
Punkt   8 for typer af værnemidler.
Punkt 13 for bortskaffelse.

7 Håndtering og opbevaring

7.1 Forholdsregler for sikker håndtering:

Generelle råd: Der er ingen farlige dampe over produktet, hvorfor udsugning ikke er nødvendig.
Undgå at spise og drikke, når der arbejdes med produktet. Sørg for god hygiejne.
Der skal være adgang til rindende vand og øjenskyller.
Se punkt 8 for oplysninger om forholdsregler ved brug og personlige værnemidler.

7.2 Betingelser for sikker opbevaring, herunder eventuel uforenelighed:

Generelle råd: Produktet opbevares bedst i originalemballage eller tilsvarende materiale (polyethylen, rustfrit stål og stål), tæt lukket og tørt. Opbevares frostfrit, bedst ved temp. 15-60°C.

Uegnet emballage materiale: brug aldrig galvaniserede emballager, emballager af letmetaller, glas eller emballager som er fremstillet af zink, tin, aluminium eller deres legeringer.
Bør opbevares forsvarligt ikke sammen med syre, utilgængeligt for børn og ikke sammen med levnedsmidler, foderstoffer, lægemidler og lign.

7.3 Særlige anvendelser: Ingen.

8 Eksponeringskontrol/personlige værnemidler

8.1 Kontrolparametre

Grænseværdier for
Indholdsstoffer i pkt. 3:

Indholdsstof	grænseværdi	anmærkning
Kaliumsilikat	2 mg/m^3 (15 minTWA) (påvirkningsgrænse, analogt med kaliumhydroxid)	

Anmærkninger:

Retsgrundlag: At-vejledning C.0.1, 2007, Grænseværdier for stoffer og materialer.
Målemetoder: Overholdelse af de angivne grænseværdier kan kontrolleres ved arbejdshygiejniske målinger.

DNEL-værdier: langtidsvirkning, general: via huden: 1,49 mg/kg
                                                   via åndedrætsorganerne: 5,61 mg/m^3
                       langtidsvirkning, lokal: via huden: ingen data
                                                   via åndedrætsorganerne: ingen data

PNEC-værdier: vandmiljøet – fersk vand: 7,5 mg/l
                       vandmiljøet – sø vand: 1,0 mg/l
                       diskontinuerlig udledning til vand: 7,5 mg/l
                       slam: 348,0 mg/l

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8.2 Eksponeringskontrol

Egnede foranstaltninger til   Undgå at få produktet på huden og i øjnene. Der skal være adgang til rindende vand og
Eksponeringskontrol: øjenskyller. Vask hænderne før pauser, ved toiletbesøg og efter endt arbejde.

Personlige værnemidler:
  Øjenværn: Brug beskyttelsesbriller ved risiko for stænk i øjnene.
  Hudbeskyttelse: Brug handsker af gummi, nitril eller lignende som er alkali eller kemikalie resistente.
                               Gennembrudstid >480 minutter og index 6.
  Åndedrætsværn: Ikke påkrævet ved normal anvendelse. I tilfælde af dannelse af aerosoler og utilstrækkelig
                               ventilation, anvend passende åndedrætsværn med halvmaske og filter til aerosoler
                               (P2-filter).

9 Fysiske – Kemiske egenskaber

9.1 Oplysninger om grundlæggende fysiske og kemiske egenskaber.

Egenskaber:

Udseende:	Flydende
Farve:	farveløs
Lugt:	lugtløs
Lugttærskel:	Ingen data
pH-værdi (koncentreret):	13
pH-værdi (brugsopløsning):	Ingen data
Smeltepunkt/frysepunkt:	ca. -3°C
Begyndelseskogepunkt og	
Kogepunktsinterval:	ca. 100°C
Flammepunkt:	Ingen data
Antændelighed	
(fast stof, luftart):	Produktet er ikke brandbart
Øvre/nedre antændelses-	
eller eksplosionsgrænser:	Ingen data
Damptryk:	Ingen data
Dampmassefylde:	Ingen data
Relativ massefylde (vf.):	1,38 g/ml
Opløselighed:	Opløselig
Fordelingskoefficient	
n-octanol/vand:	Ingen data
Selvantændelsestemperatur:	Ingen data
Dekomponeringstemperatur:	Ingen data
Viskositet:	105-115 mPas
Eksplosive egenskaber:	Ingen data
Oxiderende egenskaber:	Ingen data

9.2 Andre oplysninger   Ingen relevante

10 Stabilitet og reaktivitet

10.1 Reaktivitet   Se 10.5
                              Produktet danner varme ved tilsætning af syrer.
                              Produktet danner brint (ved kontakt med de metaller omtalt i 10.5) der blandet med luft,
                              kan danne en eksplosiv blanding.

10.2 Kemisk stabilitet   Produktet er stabilt ved anvendelse efter leverandørens anvisninger.

10.3 Risiko for farlige reaktioner
                              Kan være eksplosivt ved kontakt med nævnte metaller (se 10.5) blandet med luft.

10.4 Forhold, der skal undgås
                              Produktet bør ikke udsættes for varme (over 60°C) samt frost.

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10.5 Materialer, der skal undgås

Reagerer med galvaniserede metaller, aluminium og andre letmetaller samt legeringer deraf f.eks. tin og zink med dannelse af brint som kan danne eksplosive blandinger med luft. Reagerer med syrer ved dannelse af varme. Ætser glasoverflader.

10.6 Farlige nedbrydningsprodukter

Ingen kendte.

11 Toksikologiske oplysninger

11.1 Oplysninger om toksikologiske virkninger

Akut toksicitet — Alle symptomer er pga. den høje basiske pH-værdi.

· Oral (Indtagelse): — Kan give ubehag. LD50(rotte) >5000 mg/kg (legemsvægt)

· Dermal (Hudkontakt): — Kan virke irriterende. LD50 (rotte) >5000 mg/kg (legemsvægt).

· Indånding: — Kan virke irriterende på næsens slimhinder og luftvejene. LC50 (rotte) > 2,06 g/m^3.

Hudætsning/-irritation: — Kan virke irriterende på huden ved længere tids påvirkning. Det er ikke påvist, at produktet er ætsende, på trods af høj pH, (på tilsvarende produkter).

Alvorlig øjenskade/øjenirritation:

Stænk i øjnene kan fremkalde irritation af øjet.

Sensibilisering / Respiratorisk sensibilisering eller hudsensibilisering:

Produktet mistænkes ikke for at være sensibiliserende.

Mutagenicitet / Kimcellemutagenicitet:

Produktet er ikke mutagent.

Kræftfremkaldende egenskaber: Produktet mistænkes ikke for at være kræftfremkaldende.

Reproduktionstoksicitet: — Produktet mistænkes ikke for at være reproduktionsskadeligt.

Andre toksikologiske virkninger: STOT – Enkelt eksponering: — ikke klassificeret (støv vil irritere næse, hals og luftveje)
STOT – Gentagen eksponering: ikke klassificeret (NOAEL oral (rotte) 159 mg/kg)

Aspirationsfare: — Ingen data.

12 Miljøoplysninger

12.1 Toksicitet — Undgå at udlede spild og rester til miljøet.

-Akut toksicitet: — Fisk (Leuciscus idus) LC50(48h) > 146 mg/l.
Hvirvelløse vanddyr (Daphnia magna) EC50(24h) > 146 mg/l

-Kronisk toksicitet: — Alger (Scenedesmus subspicatus) EC50 (72h, biomasse) 207 mg/l.
Alger (Scenedesmus subspicatus) EC50 (72h, vækstrate) > 345,4 mg/l.
Bakterier (Pseudomonas putida) EC0 (18h) > 10000 mg/l (pH 7,6-7,8),
 svarende til > 3480 mg aktiv prøve/l.
Bakterier (Pseudomonas putida) EC0 (18h) > 1000 mg/l (pH>9),
 svarende til > 348 mg aktiv prøve/l.
Bakterier EC0 (30 minutter, hæmning, ilt) 3454 mg/l

12.2 Persistens og nedbrydelighed

Produktet er let nedbrydeligt i vandmiljø.

12.3 Bioakkumuleringspotentiale

Ikke bioakkumulerende.

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12.4 Mobilitet i jord

Ikke relevant

12.5 Resultater af PBT- og vPvB-vurdering

Produktet opfylder ikke kriterierne for PBT og vPvB.

12.6 Andre negative virkninger

Produktet vil lokalt ændre pH i vandmiljøet, ved udledning af høje koncentrationer.

13 Forhold vedrørende bortskaffelse

13.1 Metoder til affaldsbehandling

Produktet er ikke farligt affald i henhold til Affaldsbekendtgørelsen.
Det anbefales at større spild og affald, bortskaffes via den kommunale affaldsordning med nedstående specifikationer (Kemikalieaffaldsgruppe og affaldsfraktion).
Mindre spild og affald bortskaffes via dagrenovationen.

Affaldsgrupper: (Større spild)	Kemikalieaffaldsgruppe: X Affaldsfraktion: 04.32 EAK-kode: afhængig af branche og anvendelse, (f.eks. 06 02 99; andet affald, ikke andetsteds specificeret).
Absorptionsmiddel/klude forurenet med produktet:	Kemikalieaffaldsgruppe: Z Affaldsfraktion: 05.99 EAK-kode:15 02 03; absorptionsmidler, filtermaterialer, aftørringsklude og beskyttelsesdragter, bortset fra affald tilhørende under 15 02 02.

14 Transportoplysninger

ADR/RID (vej/jernbane)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
    (UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -
    Tunnelrestriktionskode -
14.5 Miljøfarer -

  Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

ADN (indre vandvej)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
    (UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -
14.5 Miljøfarer -
    Miljøfare i tankskibe -

  Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

IMDG (søtransport)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
    (UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -
14.5 Miljøfarer -
    IMDG Code segregation group -

  Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

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ICAO/IATA (lufttransport)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
    (UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -

Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

14.6 Særlige forsigtighedsregler for brugeren
           Ingen

14.7 Bulktransport i henhold til bilag II i MARPOL 73/78 og IBC-koden
           Ingen

Supplerende informationer: Produktet er ikke omfattet af reglerne om farligt gods.

15 Oplysninger om regulering

Anden regulering: Ingen kendte.

Særlige forhold: Ingen kendte.

15.1 Særlige bestemmelser/særlig lovgivning for stoffet eller blandingen med hensyn til sikkerhed, sundhed og miljø

Særlige bestemmelser   Brugeren bør have kendskab til dette Sikkerhedsdatablad.

Tilladelser   Ingen tilladelser nødvendige

VOC   Ikke omfattet

15.2 Kemikaliesikkerhedsvurdering   Der er udført kemikaliesikkerhedsvurdering/eksponeringsscenarie, der kan rekvireres, ved anmodning.

16 Andre oplysninger

Anvendte kilder: Europa-Parlamentets og Rådets forordning (EF) nr. 1272/2008, om klassificering, mærkning og emballering
           af stoffer og blandinger.

           CEES (Centre Européen d'Etude des Silicates) june 2014

           Bekendtgørelse om særlige pligter for fremstillere, leverandører og importører mv. af stoffer og materialer
           efter lov om arbejdsmiljø nr. 559/2002 + forordning 1907/2006/EF

           Miljøstyrelsens bekendtgørelse om affald nr. 1309 af 18. december 2012

           Justitsministeriets bekendtgørelse om transport af farligt gods ADR 2011 og IMDG 2010

           AT-bekendtgørelse om grænseværdier for stoffer og materialer nr. 507 af 17. maj 2011
           (ændret ved nr. 1134 af 1. december 2011)

Øvrige oplysninger: Information gælder kun det omtalte produkt, og er ikke nødvendigvis gældende, hvis produktet anvendes sammen med andre produkter eller indgår i en kemisk proces.
Informationen er efter vor bedste overbevisning korrekt og komplet og er givet i god tro, men uden garanti.
Det forbliver brugerens eget ansvar at sikre sig, at informationerne er korrekt og komplet til hans specielle brug af produktet. Dvs. at brugeren udfører egne test for at sikre, at produktet opfører sig som brugeren ønsker.
Dette Sikkerhedsdatablad er udarbejdet på baggrund af de oplysninger, leverandøren har kunnet levere om produktet ved udarbejdelsen (datablade og lignende).

Uddannelse: Ingen særlige krav til uddannelse.

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Anvendelsesområder: Industrielle anvendelsesmuligheder: Kemikalie- og andre industrier – rå materiale.

Metode til klassificering: Testdata (brobygningsprincip)

H-sætninger nævnt i punkt 3:

Der er foretaget ændringer i følgende punkter: Fjerne DPD klassificering

Forkortelser:

CLP	Classification, labelling and Packaging
STOT	Specific Target Organ Toxicity
PNEC	Predicted No Effect Concentration
DNEL	Derived No Effect Level
TWA	tidsvægtet gennemsnit
LD50	Lethal Dose/dødlig dosis 50%
LC50	Lethal Concentration/dødlig koncentration 50%
EC50	Effect Concentration/effektiv koncentration 50%
EC0	Effect Concentration/effektiv konsentration 0%
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
PBT	Persistente, Bioakkumulerende og Toksiske
vPvB	very Persistente, very Bioakkumulerende
VOC	Volatile Organic Compound/flygtige organiske forbindelser
EAK	Europæiske AffaldsKatalog
H-sætning	Hazard/fare-sætning
P-sætning	Precaution/sikkerheds-sætning

BollerupJensen

SIKKERHEDSDATABLAD

1 Identifikation af stoffet/blandingen og af selskabet/virksomheden

1.1 Produktidentifikator.

PR-nummer: 1709418
REACH-reg.nr. 01-2119448725-31-xxxx
Handelsnavn: Natriumsilikat (Natronvandglas); type (alkalisk) 44; 46; 48; 50

1.2 Relevante identificerede anvendelser for stoffet eller blandingen samt anvendelser, der frarådes.

Anvendelser:
Kemikalieindustrien – rå materiale.
Cellulose- og papirindustrien – basis kemikalier. Vaskemiddel industrien – rå materiale.
Kan desuden anvendes til behandling af bl.a. fugtige vægge, utætte krukker, potter og lignende.

Branche: Industrien.

Frarådede anvendelser: Ingen kendte

1.3 Nærmere oplysninger om leverandøren af sikkerhedsdatabladet.

Leverandør:
Bollerup Jensen A/S
Bindesbølvej 16 – 20, Ådum, 6880 Tarm
Telefon: 9737 6033; Fax: 9737 6268
E-mail: info@bollerup-jensen.dk

1.4 Nødtelefon.
Kontakt:
Giftlinien: 82 12 12 12. Lægen kan få råd om behandling fra giftinformationen på Bispebjerg Hospital.
Leverandøren: 97 37 60 33 (mandag–torsdag: 8-16 og fredag: 8-15)

2 Fareidentifikation

2.1 Klassificering af stoffet eller blandingen.
CLP-klassificering:
Produktet er klassificeret i henhold til Europa-parlamentets og rådets forordning (EF) Nr. 1272/2008 samt CEES (Center Européen d'Etude des Silicates) Soluble Silicates June 2014.
Skin Irrit. 2 og Eye Dam. 1

Væsentligste skadevirkninger:
Kan fremkalde skade på øjet og virke irriterende på huden.

2.2 Mærkningselementer.
Produktet er mærknings pligtig. MR 2,1
CLP-klassificering
Signalord: Fare

Piktogram:

H-sætninger:
H315; Forårsager hudirritation.
H318; Forårsager alvorlig øjenskade.

P-sætninger:
P262 (Må ikke komme i kontakt med øjne, hud eller tøj).
P280 (Bær beskyttelseshandsker/beskyttelsestøj/øjenbeskyttelse/ansigtsbeskyttelse).
P303+P361+P353 (VED KONTAKT MED HUDEN (eller håret): Tilsmudset tøj tages straks af/ fjernes. Skyl/brus huden med vand).
P305+P351+P338 (VED KONTAKT MED ØJNENE: Skyl forsigtigt med vand i flere minutter. fjern eventuelle kontaktlinser, hvis det kan gøre let. Fortsæt skylning).
P314 (Søg lægehjælp ved ubehag).

2.3 Andre farer.
Produktet opfylder ikke kriterierne for PBT eller vPvB.
Ingen særlig risiko ved anvendelse efter leverandørens anvisninger.

Side **1** af **8**

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3 Sammensætning af/oplysning om indholdsstoffer

3.1 Stoffer / 3.2 Blandinger

CAS-nr.	Stofnavn	Klassificering	w/w %	Note
1344-09-8	Natriumsilikat	Skin Irrit. 2,H315	30 - 50	
		Eye Dam. 1, H318		
		STOT SE 3, H335		

4 Førstehjælpsforanstaltninger

4.1 Beskrivelse af førstehjælpsforanstaltninger

Generelle råd:	Ved ubehag, søg læge og medbring etiketten eller dette Sikkerhedsdatablad. Lægen kan få råd om behandling fra Giftlinjen. Produkter er alkalisk.
Indånding:	Intet særligt. Produktet er ikke flygtigt. Ved ubehag søg frisk luft.
Indtagelse:	Skyl munden grundigt og drik meget vand. Fremkald ikke opkastning.
Hud:	Vask huden med lunken vand.
Øjne:	Skyl straks med vand (helst fra øjenskyller) i mindst 15 min. Spil øjet godt op. Fjern eventuelle kontaktlinser.

4.2 Vigtige symptomer og virkninger, både akutte og forsinkede

Ubehag kan forekomme ved indtagelse. Stænk i øjnene kan give irritation

4.3 Angivelse af om øjeblikkelig lægehjælp og særlig behandling er nødvendig

Søg læge ved vedvarende ubehag/irritation og medbring dette Sikkerhedsdatablad.

5 Brandbekæmpelse

5.1 Slukningsmidler:

Egnede slukningsmidler:	Produktet er ikke umiddelbart antændeligt. Brand slukkes med vandtåge, pulver, skum, kulsyre.
Uegnede slukningsmidler:	Vandstråle, da det kan sprede branden.

5.2 Særlige farer i forbindelse med stoffet eller blandingen:

Produktet er alkalisk og reagerer med syrer (opløsninger af bl.a. phosphor-, salpeter-, salt- og svovlsyre og konc. flussyre).

5.3 Anvisninger for brandmandskab:

Brug passende personlig beskyttelse i tilfælde af brand (handsker, briller og åndedrætsværn).
Undgå indånding af dampe og røggasser – søg frisk luft.
Hvis det kan gøres uden fare, fjernes beholdere fra det brandtruede område.

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6 Forholdsregler over for udslip ved uheld

6.1 Personlige sikkerhedsforanstaltninger, personlige værnemidler og nødprocedurer

For ikke-indsatspersonel: Brug handsker og briller ved risiko for stænk i øjnene.
Anvend samme typer værnemidler som nævnt i punkt 8.

For indsatspersonel: Brug handsker og briller ved risiko for stænk i øjnene.
Anvend samme typer værnemidler som nævnt i punkt 8.

6.2 Miljøbeskyttelsesforanstaltninger

Forhindre at større spild løber ud i afløb og kloak.

6.3 Metoder og udstyr til inddæmning og oprensning

Større spild inddæmmes og opsamles med sand, kattegrus eller andet absorberende materialer og overføres til egnede affaldsbeholdere. Evt. nødstopsanlæg til kloak aktiveres.
Små mængder spild, kan spules bort med vand.
Vask under alle omstændigheder det forurenede område grundigt med vand, for at hindre glideulykker.

6.4 Henvisning til andre punkter

Punkt   1 for kontaktoplysninger ved uheld/ulykke.
Punkt   8 for typer af værnemidler.
Punkt 13 for bortskaffelse.

7 Håndtering og opbevaring

7.1 Forholdsregler for sikker håndtering:

Generelle råd: Der er ingen farlige dampe over produktet, hvorfor udsugning ikke er nødvendig.
Undgå at spise og drikke, når der arbejdes med produktet. Sørg for god hygiejne.
Der skal være adgang til rindende vand og øjenskyller.
Se punkt 8 for oplysninger om forholdsregler ved brug og personlige værnemidler.

7.2 Betingelser for sikker opbevaring, herunder eventuel uforenelighed:

Generelle råd: Produktet opbevares bedst i originalemballage eller tilsvarende materiale (polyethylen, rustfrit stål og stål), tæt lukket og tørt. Opbevares frostfrit, bedst ved temp. 15-60°C.
Uegnet emballage materiale: brug aldrig galvaniserede emballager, emballager af letmetaller, glas eller emballager som er fremstillet af zink, tin, aluminium eller deres legeringer.
Bør opbevares forsvarligt ikke sammen med syre, utilgængeligt for børn og ikke sammen med levnedsmidler, foderstoffer, lægemidler og lign.

7.3 Særlige anvendelser: Ingen.

8 Eksponeringskontrol/personlige værnemidler

8.1 Kontrolparametre

Grænseværdier for Indholdsstoffer i pkt. 3:

Indholdsstof	grænseværdi	anmærkning
Natriumsilikat, Kiselsyre, natriumsalt	2 mg/m^3 (15 min TWA) (Påvirkningsgrænse, anbefalet analogt med natriumhydroxid)	

Anmærkninger:

Retsgrundlag: At-vejledning C.0.1, 2007, Grænseværdier for stoffer og materialer.
Målemetoder: Overholdelse af de angivne grænseværdier kan kontrolleres ved arbejdshygiejniske målinger.

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DNEL-værdier:

Arbejdstagere:

langtidsvirkning, general:	via huden:	1,59 mg/kg
	via åndedrætsorganerne:	5,61 mg/m^3
langtidsvirkning, lokal:	via huden:	ingen data
	via åndedrætsorganerne:	ingen data

Forbrugere:

langtidsvirkning, general:	via huden:	0,80 mg/kg
	via åndedrætsorganerne:	1,38 mg/m^3
	via indtagelse:	0,80 mg/kg
langtidsvirkning, lokal:	via huden:	ingen data
	via åndedrætsorganerne:	ingen data

PNEC-værdier:

vandmiljøet – fersk vand:	7,5 mg/l
vandmiljøet – sø vand:	1,0 mg/l
diskontinuerlig udledning til vand:	7,5 mg/l
slam:	348,0 mg/l

8.2 Eksponeringskontrol

Egnede foranstaltninger til
Eksponeringskontrol: Undgå at få produktet på huden og i øjnene. Der skal være adgang til rindende vand og øjenskyller. Vask hænderne før pauser, ved toiletbesøg og efter endt arbejde.

Personlige værnemidler:
Øjenværn: Brug beskyttelsesbriller ved risiko for stænk i øjnene.
Hudbeskyttelse: Brug handsker af gummi, nitril eller lignende som er alkali eller kemikalie resistente. Gennembrudstid >480 minutter og index 6.
Åndedrætsværn: Ikke påkrævet ved normal anvendelse. I tilfælde af dannelse af aerosoler og utilstrækkelig ventilation, anvend passende åndedrætsværn med halvmaske og filter til aerosoler (P2-filter).

9 Fysiske – Kemiske egenskaber

9.1 Oplysninger om grundlæggende fysiske og kemiske egenskaber.

Egenskaber:

Udseende:	Flydende
Farve:	farveløs
Lugt:	lugtløs
Lugttærskel:	Ingen data
pH-værdi (koncentreret):	14
pH-værdi (brugsopløsning):	Ingen data
Smeltepunkt/frysepunkt:	ca. -3°C
Begyndelseskogepunkt og Kogepunktsinterval:	ca. 100°C
Flammepunkt:	Ingen data
Antændelighed (fast stof, luftart):	Produktet er ikke brandbart
Øvre/nedre antændelses- eller eksplosionsgrænser:	Ingen data
Damptryk:	Ingen data
Dampmassefylde:	Ingen data
Relativ massefylde (vf.):	1,44 – 1,53 g/ml
Opløselighed:	Opløselig
Fordelingskoefficient n-octanol/vand:	Ingen data
Selvantændelsestemperatur:	Ingen data
Dekomponeringstemperatur:	Ingen data
Viskositet:	Ingen data
Eksplosive egenskaber:	Ingen data
Oxiderende egenskaber:	Ingen data

9.2 Andre oplysninger

Ingen relevante

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10 Stabilitet og reaktivitet

10.1 Reaktivitet
Se 10.3 og10.5
Produktet danner varme ved tilsætning af syrer.
Produktet danner brint (ved kontakt med de metaller omtalt i 10.5) der blandet med luft,
kan danne en eksplosiv blanding.

10.2 Kemisk stabilitet
Produktet er stabilt ved anvendelse efter leverandørens anvisninger.

10.3 Risiko for farlige reaktioner
Kan være eksplosivt ved kontakt med nævnte metaller (se 10.5) blandet med luft.
Kan reagere med sukkerrester og danne kulmonooxid.

10.4 Forhold, der skal undgås
Produktet bør ikke udsættes for varme (over 60°C) samt frost.

10.5 Materialer, der skal undgås
Reagerer med galvaniserede metaller, aluminium og andre letmetaller samt legeringer
deraf f.eks. tin og zink med dannelse af brint som kan danne eksplosive blandinger med luft.
Reagerer med syrer ved dannelse af varme. Ætser glasoverflader.

10.6 Farlige nedbrydningsprodukter
Ingen kendte.

11 Toksikologiske oplysninger

11.1 Oplysninger om toksikologiske virkninger

Akut toksicitet   Alle symptomer er pga. den høje pH-værdi.

· Oral (Indtagelse):   Kan give ubehag. LD50(rotte) 3400 mg/kg (legemsvægt)

· Dermal (Hudkontakt):   Kan virke irriterende. LD50 (rotte) >5000 mg/kg (legemsvægt).

· Indånding: Kan virke irriterende på næsens slimhinder og luftvejene.
LC50 (rotte) >2,06 g/m^3.

Hudætsning/-irritation: Kan virke irriterende på huden ved længere tids påvirkning.
Det er ikke påvist, at produktet er ætsende, på trods af høj pH,
(test udført på tilsvarende produkter).

Alvorlig øjenskade/øjenirritation:
Stænk i øjnene kan fremkalde alvorlig irritation af øjet. Risiko for alvorlig øjenskade.

Sensibilisering / Respiratorisk sensibilisering eller hudsensibilisering:
Produktet mistænkes ikke for at være sensibiliserende.

Mutagenicitet / Kimcellemutagenicitet:
Produktet er ikke mutagent.

Kræftfremkaldende egenskaber:
Produktet mistænkes ikke for at være kræftfremkaldende.

Reproduktionstoksicitet: Produktet mistænkes ikke for at være reproduktionsskadeligt.

Andre toksikologiske virkninger: STOT – Enkelt eksponering: ikke klassificeret
STOT – Gentagen eksponering: ikke klassificeret; NOAEL oral (rotte) > 159 mg/kg
legemsvægt/dag
Aspirationsfare: Ikke klassificeret.

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12 Miljøoplysninger

12.1 Toksicitet Undgå at udlede spild og rester til miljøet.

  -Akut toksicitet: Fisk (Brachydanio rerio) LC50(96h) 1108 mg/l.

  -Kronisk toksicitet: Hvirvelløse dyr (Daphnia magna) EC50 (48h) 1700 mg/l.

12.2 Persistens og nedbrydelighed
Produktet er let nedbrydeligt i vandmiljø.

12.3 Bioakkumuleringspotentiale
Ikke bioakkumulerende.

12.4 Mobilitet i jord

Ikke relevant

12.5 Resultater af PBT- og vPvB-vurdering
Produktet opfylder ikke kriterierne for PBT og vPvB.

12.6 Andre negative virkninger
Produktet vil lokalt ændre pH i vandmiljøet, ved udledning af høje koncentrationer.

13 Forhold vedrørende bortskaffelse

13.1 Metoder til affaldsbehandling
Produktet er ikke farligt affald i henhold til Affaldsbekendtgørelsen.
Det anbefales at større spild og affald, bortskaffes via den kommunale affaldsordning med nedstående specifikationer (Kemikalieaffaldsgruppe og affaldsfraktion).
Mindre spild og affald bortskaffes via dagrenovationen.

Affaldsgrupper: (Større spild)	Kemikalieaffaldsgruppe: X Affaldsfraktion: 04.32 EAK-kode: afhængig af branche og anvendelse, (f.eks. 06 02 99; andet affald, ikke andetsteds specificeret).
Absorptionsmiddel/klude forurenet med produktet:	Kemikalieaffaldsgruppe: Z Affaldsfraktion: 05.99 EAK-kode:15 02 03; absorptionsmidler, filtermaterialer, aftørringsklude og beskyttelsesdragter, bortset fra affald tilhørende under 15 02 02.

14 Transportoplysninger

ADR/RID (vej/jernbane)
14.1 UN-nummer   -
14.2 UN-forsendelsesbetegnelse   -
     (UN proper shipping name)   -
14.3 Transportfareklasse(r)   -
14.4 Emballagegruppe   -
     Tunnelrestriktionskode   -
14.5 Miljøfarer   -

  Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

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ADN (indre vandvej)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
　(UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -
14.5 Miljøfarer -
　Miljøfare i tankskibe -

　Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

IMDG (søtransport)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
　(UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -
14.5 Miljøfarer -
　IMDG Code segregation group -

　Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

ICAO/IATA (lufttransport)
14.1 UN-nummer -
14.2 UN-forsendelsesbetegnelse -
　(UN proper shipping name) -
14.3 Transportfareklasse(r) -
14.4 Emballagegruppe -

　Supplerende informationer   Produktet er ikke omfattet af reglerne om farligt gods.

14.6 Særlige forsigtighedsregler for brugeren
　　　　　　　　　　　Ingen

14.7 Bulktransport i henhold til bilag II i MARPOL 73/78 og IBC-koden
　　　　　　　　　　　Ingen

Supplerende informationer: Produktet er ikke omfattet af reglerne om farligt gods.

15 Oplysninger om regulering

Anden regulering: Ingen kendte.

Særlige forhold: Ingen kendte.

15.1 Særlige bestemmelser/særlig lovgivning for stoffet eller blandingen med hensyn til sikkerhed, sundhed og miljø

　Særlige bestemmelser   Brugeren bør have kendskab til dette Sikkerhedsdatablad.

　Tilladelser   Ingen tilladelser nødvendige

　VOC   Ikke omfattet

15.2 Kemikaliesikkerhedsvurdering   Der er udført kemikaliesikkerhedsvurdering/eksponeringsscenarie, der
　　　　　　　　　　　kan rekvireres, ved anmodning.
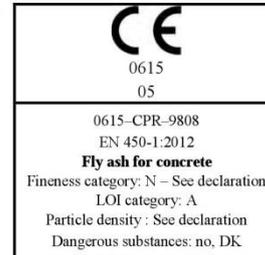
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16 Andre oplysninger

Anvendte kilder:

Europa-Parlamentets og Rådets forordning (EF) nr. 1272/2008, om klassificering, mærkning og emballering
  af stoffer og blandinger.

CEES (Centre Européen d'Etude des Silicates) june 2011

Bekendtgørelse om særlige pligter for fremstillere, leverandører og importører mv. af stoffer og materialer
  efter lov om arbejdsmiljø nr. 559/2002 + forordning 1907/2006/EF

Miljøstyrelsens bekendtgørelse om affald nr. 1309 af 18. december 2012

Justitsministeriets bekendtgørelse om transport af farligt gods ADR 2011 og IMDG 2010

AT-bekendtgørelse om grænseværdier for stoffer og materialer nr. 507 af 17. maj 2011
  (ændret ved nr. 1134 af 1. december 2011)

Øvrige oplysninger:

Information gælder kun det omtalte produkt, og er ikke nødvendigvis gældende, hvis produktet
anvendes sammen med andre produkter eller indgår i en kemisk proces.
Informationen er efter vor bedste overbevisning korrekt og komplet og er givet i god tro, men uden
garanti.
Det forbliver brugerens eget ansvar at sikre sig, at informationerne er korrekt og komplet til hans
specielle brug af produktet. Dvs. at brugeren udfører egne test for at sikre, at produktet opfører sig
som brugeren ønsker.
Dette sikkerhedsdatablad er udarbejdet på baggrund af de oplysninger, leverandøren
har kunnet levere om produktet ved udarbejdelsen (datablade og lignende).

Uddannelse:

Ingen særlige krav til uddannelse.

Anvendelsesområder:

Industrielle anvendelsesmuligheder: Kemikalie- og andre industrier – rå materiale.

Metode til klassificering:

Testdata (brobygningsprincip)

med vand, (kun hvis personen er ved bevidsthed)).

**H-sætninger nævnt
I punkt 3:**

H315 (Forårsager hudirritation).
H318 (Forårsager alvorlig øjenskade).
H335 Kan forårsage irritation af luftvejene).

**Der er foretaget ændringer
i følgende punkter:**

Fjerne DPD klassificering.

Forkortelser:

CLP	Classification, labelling and Packaging
STOT	Specific Target Organ Toxicity
PNEC	Predicted No Effect Concentration
DNEL	Derived No Effect Level
TWA	tidsvægtet gennemsnit
LD50	Lethal Dose/dødlig dosis 50%
LC50	Lethal Concentration/dødlig koncentration 50%
EC50	Effect Concentration/effektiv koncentration 50%
EC0	Effect Concentration/effektiv konsentration 0%
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
PBT	Persistente, Bioakkumulerende og Toksiske
vPvB	very Persistente, very Bioakkumulerende
VOC	Volatile Organic Compound/flygtige organiske forbindelser
EAK	Europæiske AffaldsKatalog
H-sætning	Hazard/fare-sætning
P-sætning	Precaution/sikkerheds-sætning

Emineral a/s

Nr. 0615-CPR-9808/02

Date: 01.07 2013

Declaration of performance

1. Identification code of the product : Fly ash for concrete according to EN 450-1
2. Identification of the construction product: **Type B4**
3. Intended use of the construction product: Addition for production of concrete conforming to EN 206-1 and for use in mortar and grouts
4. Name and contact address of the manufacturer: Emineral a/s. Nefovej 50. 9310 Vodskov
5. System or systems of assessment and verification of performance: System 1+
6. The notified product certification body Bureau Veritas Certification Denmark 0615 has prepared the certificate of constancy of performance based on determination of the product type on the basis of type testing (including sampling), the initial inspection of the manufacturing plant and of factory production control; the continuous surveillance, assessment and evaluation of factory production control and audit-testing of samples taken before placing the product on the market.

7. Declared Performance

		CE
		0615
		05

```
0615–CPR–9808
EN 450-1:2012
Fly ash for concrete
Fineness category: N – See declaration
LOI category: A
Particle density : See declaration
Dangerous substances: no, DK
```

Essential characteristic		Performance	Harmonised technical specification
Loss on ignition [1]		< 4,0 (4,0)	
Chloride		< 0,02 (0,02)	
Sulphate content (SO_3)		$\leq$ 3,0 (3,5)	
Free CaO		$\leq$ 1,5 (1,6)	
Calcium oxide (CaO)		$\leq$ 10,0 (11,0)	
Fineness		$\leq$ 40 (45)	
Declared value [2]		deviation ± 10 % points	EN 450-1:2012
Aktivity index	28 days	$\geq$ 75 (70) %	
	90 days	$\geq$ 85 (80) %	
Soundness		$\leq$ 10 (10,0) mm	
Particle density		2300 kg/m3± 200 (± 225) kg/m³	
Reaktive silicon dioxide		$\geq$ 25	
Sum of contents of silicon dioxide, aluminium oxide and iron oxides		$\geq$70 (65)	
Total content of alkalis (Na_2O_{ekv})		$\leq$ 5,0 (5,5)	
Magnesium oxide (MgO)		$\leq$4,0	
Total phosphate (P_2O_5)		$\leq$ 5 %	
Soluble phosphate(P_2O_5)		$\leq$ 100 mg/kg (110) mg/kg	
Initial setting time		$\leq$ 100 % test cement x 2	
Durability		Given	
Release of dangerous substances and emissions of radioactivity		safe according certificate 931-322-8	

Notes:
[1] Determined with direct measuring on LECO or ELTRA equipment. [2] Value will be supplied upon request

8. The performance of the product identified in points 1 and 2 is in conformity with the declared performance in point 7.

This declaration of performance is issued under the sole responsibility of the manufacturer identified in point 4.

Signed for and on behalf of the manufacturer by:

Emineral a/s

Peter Lundquist
Quality coordinator

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EN 450-1
BUREAU VERITAS
Certification Denmark A/S
Cert. no. 0615-CPR-9808

BUREAU VERITAS
1828
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Emineral a/s

Nr. 0615-CPR-9808/03   **Date: 01.07 2013**

Declaration of performance

1. Identification code of the product : Fly ash for concrete according to EN 450-1
2. Identification of the construction product: **Type B5**
3. Intended use of the construction product: Addition for production of concrete conforming to EN 206-1 and for use in mortar and grouts
4. Name and contact address of the manufacturer: Emineral a/s. Nefovej 50. 9310 Vodskov
5. System or systems of assessment and verification of performance: System 1+
6. The notified product certification body Bureau Veritas Certification Denmark 0615 has prepared the certificate of constancy of performance based on determination of the product type on the basis of type testing (including sampling), the initial inspection of the manufacturing plant and of factory production control; the continuous surveillance, assessment and evaluation of factory production control and audit-testing of samples taken before placing the product on the market.

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0615–CPR–9808
EN 450-1:2012
Fly ash for concrete
Fineness category: N – See declaration
LOI category: A
Particle density : See declaration
Dangerous substances: no, DK

7. Declared Performance

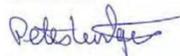| Essential characteristic		Performance	Harmonised technical specification
Loss on ignition[1]		< 5,0 (7,0)	
Chloride		< 0,02 (0,02)	
Sulphate content (SO_3)		≤ 3,0 (3,5)	
Free CaO		≤ 1,5 (1,6)	
Calcium oxide (CaO)		≤ 10,0 (11,0)	
Fineness		≤ 40 (45)	
Declared value [2]		deviation ± 10 % points	
Aktivity index	28 days	≥ 75 (70) %	EN 450-1:2012
	90 days	≥ 85 (80) %	
Soundness		≤ 10 (10,0) mm	
Particle density		2300 kg/m3± 200 (± 225) kg/m³	
Reaktive silicon dioxide		≥ 25	
Sum of contents of silicon dioxide, aluminium oxide and iron oxides		≥70 (65)	
Total content of alkalis (Na_2O_{ekv})		≤ 5,0 (5,5)	
Magnesium oxide (MgO)		≤4,0	
Total phosphate (P_2O_5)		≤ 5 %	
Soluble phosphate(P_2O_5)		≤ 100 mg/kg (110) mg/kg	
Initial setting time		≤ 100 % test cement x 2	
Durability		Given	
Release of dangerous substances and emissions of radioactivity		safe according certificate 931-322-8	

Notes:
[1] Determined with direct measuring on LECO or ELTRA equipment. [2] Value will be supplied upon request

8. The performance of the product identified in points 1 and 2 is in conformity with the declared performance in point 7.

This declaration of performance is issued under the sole responsibility of the manufacturer identified in point 4.

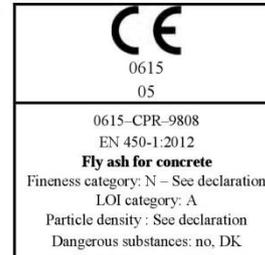Signed for and on behalf of the manufacturer by:

Emineral a/s

Peter Lundquist
Quality coordinator

EN 450-1
BUREAU VERITAS
Certification Denmark A/S
Cert. no. 0615-CPR-9808

BUREAU VERITAS
1828

*E*mineral a/s

Nr. 0615-CPR-9808/04 **Date: 01.07 2013**

Declaration of performance

1. Identification code of the product : Fly ash for concrete according to EN 450-1
2. Identification of the construction product: **Type Perlefiller**
3. Intended use of the construction product: Addition for production of concrete conforming to EN 206-1 and for use in mortar and grouts
4. Name and contact address of the manufacturer: Emineral a/s. Nefovej 50. 9310 Vodskov
5. System or systems of assessment and verification of performance: System 1+
6. The notified product certification body Bureau Veritas Certification Denmark 0615 has prepared the certificate of constancy of performance based on determination of the product type on the basis of type testing (including sampling), the initial inspection of the manufacturing plant and of factory production control; the continuous surveillance, assessment and evaluation of factory production control and audit-testing of samples taken before placing the product on the market.

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0615–CPR–9808
EN 450-1:2012
Fly ash for concrete
Fineness category: N – See declaration
LOI category: A
Particle density : See declaration
Dangerous substances: no, DK

7. Declared Performance

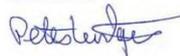| Essential characteristic		Performance	Harmonised technical specification
Loss on ignition[1]		< 9,0 (11,0)	
Chloride		< 0,10 (0,10)	
Sulphate content (SO_3)		$\leq$ 3,0 (3,5)	
Free CaO		$\leq$ 1,5 (1,6)	
Calcium oxide (CaO)		$\leq$ 10,0 (11,0)	
Fineness		$\leq$ 40 (45)	
Declared value [2]		deviation $\pm$ 10 % points	
Aktivity index	28 days	$\geq$ 75 (70) %	EN 450-1:2012
	90 days	$\geq$ 85 (80) %	
Soundness		$\leq$ 10 (10,0) mm	
Particle density		2300 kg/m3$\pm$ 200 ($\pm$ 225) kg/m³	
Reaktive silicon dioxide		$\geq$ 25	
Sum of contents of silicon dioxide, aluminium oxide and iron oxides		$\geq$70 (65)	
Total content of alkalis (Na_2O_{ekv})		$\leq$ 5,0 (5,5)	
Magnesium oxide (MgO)		$\leq$4,0	
Total phosphate (P_2O_5)		$\leq$ 5 %	
Soluble phosphate(P_2O_5)		$\leq$ 100 mg/kg (110) mg/kg	
Initial setting time		$\leq$ 100 % test cement x 2	
Durability		Given	
Release of dangerous substances and emissions of radioactivity		safe according certificate 931-322-8	

Notes:
[1] Determined with direct measuring on LECO or ELTRA equipment. [2] Value will be supplied upon request
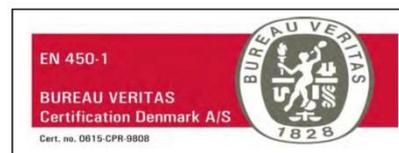
8. The performance of the product identified in points 1 and 2 is in conformity with the declared performance in point 7.

This declaration of performance is issued under the sole responsibility of the manufacturer identified in point 4.

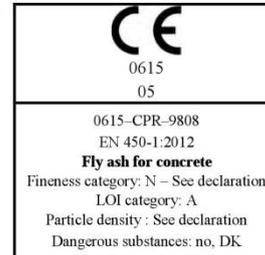Signed for and on behalf of the manufacturer by:

Emineral a/s

Peter Lundquist
Quality coordinator

EN 450-1
BUREAU VERITAS
Certification Denmark A/S
Cert. no. 0615-CPR-9808

BUREAU VERITAS
1828

Emineral a/s

Declaration of performance

Date: 01.07 2013

Nr. 01

1. Unique identification code of the product type:
Fly ash for bituminous mixtures according to EN 13043
2. Type, batch or serial number allowing identification of the construction product:
Asfaltfiller
3. Intended use of the construction product, in accordance with the applicable harmonized technical specification, as foreseen by the manufacturer:
Fly ash for bituminous mixtures and surface treatment for roads and other trafficked areas
4. Name, registered trade name or registered trade mark and contact address of the manufacturer:
Emineral a/s Nefovej 50 9310 Vodskov
5. Where applicable, name and contact address of the authorized representative:
Not Applicable
6. System or systems of assessment and verification of constancy of performance of the construction product:
System 4
7. Declared performance

CE
Emineral a/s Nefovej 50 9310 Vodskov 08
EN 13043 Fly ash Aggregates for bituminous mixtures and surface treatment for roads and other trafficked areas
LOI. 1 % - 7 % Density 2280 kg/m3 + 100 kg/m3 Fineness - see declaration*

Essential characteristic	Harmonized technical specification	Performance	Supplementary declaration
Loss on ignition (1)	EN 196-2	Variation maks. 6 %	1,0 - 7,0 %
Fineness 2,0 mm sieve	EN 933-10	100 %	
Fineness 0,125 mm sieve		Min. 85 %	2)
Fineness 0,063 mm sieve		Min. 70 %	(2)
Water content	1097-5	$\leq$ 1 %	$\leq$ 0,5 %.(3)
Partcle density	EN 1097-7	Dekl.værdi $\pm$ 100 kg/m³	2280 kg/m³
Release of dangerous substances and emissions of radioactivity		Safe according certificate 931-322-8	

Notes
((1) Emineral determined with direct measuring on ELTRA or LECO equipment.
(2) Declared range characteristic may change, values will be supplied upon request.
(3) Reduced test volume according to DS/EN 13043:2002 pkt. B.5.3. note 4.

8. The performance of the product identified in points 1 and 2 is in conformity with the declared performance in point 7
This declaration of performance is issued under the sole responsibility of the manufacturer identified in point 4.

Signed for and on behalf of the manufacturer by:

Peter Lundquist
Quality Coordinator

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AALBORG UNIVERSITY
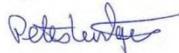
1. Identification of the Product and Supplier

Product name:	**Elkem Microsilica ®**
Product application:	Cementitious systems.
Address/Phone No.:	**Elkem AS,** **Silicon Materials** P.O. Box 334 Skøyen N-0213 Oslo, Norway Telephone: + 47 22 45 01 00 Telefax: + 47 22 45 01 11 http://www.materials.elkem.com
Contact person:	Bernd Friede, e-mail: bernd.friede@elkem.no
REACH registration number:	01-2119486866-17-0000
REACH and CLP helpdesk:	REACH Website: http://echa.europa.eu/help/nationalhelp_contact_en.asp CLP Website: http://echa.europa.eu/clp/clp_help_en.asp
Emergency Phone No.:	http://echa.europa.eu/help/nationalhelp_contact_en.asp

2. Hazards Identification

Classification of the substance	The product does not meet the criteria for hazard classification in accordance with Directive 67/548/EEC (DSD) and Regulation (EC) No1272/2008 (CLP).
Hazard symbol/Hazard pictogram:	N/A (not applicable)
Symbol letter/Indication of danger:	N/A (not applicable)
Signal word:	N/A (not applicable)
R-/H-phrases:	N/A (not applicable)
S-/P-phrases:	N/A (not applicable)

Microsilica may contain small amounts of crystalline quartz (< 0.5 %). The amount of respirable crystalline silica in the product is below 0.1 % and does not trigger a hazard-classification.

3. Composition/Information on Ingredients

Synonyms:	Silica fume, Amorphous silica (SiO_2), Silicon dioxide powder
IUPAC-name:	Silicon dioxide
CAS No.:	69012-64-2
EINECS No.:	273-761-1

4. First Aid Measures

Inhalation:	Remove exposed person from dusty area. Fresh air.
Skin contact:	Wash contaminated skin with water and/or a mild detergent.
Eye contact:	Rinse eyes with water/saline solution. If discomfort persists, obtain medical attention.
Ingestion:	Not applicable.

5. Fire Fighting Measures

The product is not combustible and there is no inherent risk of explosion.

Extinguishing media:	Not applicable Depending on surrounding fire.

6. Accidental Release Measures

Avoid exposure to dust of the product. Released material should be collected in suitable containers.

7. Handling and Storage

Handling:	Avoid dust generation. See section 8.
Storage:	Keep away from hydrofluoric acid (HF). Not to be stored at temperatures near to or below 0 °C.

8. Exposure Controls/Personal Protection

A) Occupational exposure controls:

Avoid inhalation of dust. Ensure good dust ventilation during use. Wear a particulate respirator according to EN 149 FFP 2S/3S during dust generating operations. Use protective gloves and eye protection. Facilities for eye flushing should be available.

Occupational Exposure Limits (ACGIH [1], 2014):

Substance	[CAS No.]	8hr TWA ppm	8hr TWA mg/m³	ACGIH TLV 15 minute STEL ppm	ACGIH TLV 15 minute STEL mg/m³	Notations
PNOS[2]	-	-	$10^{(I)}/3^{(R)}$	-	-	-
Silica, crystalline (SiO_2) Quarz*	[14808-60-7]	-	$0.025^{(R)}$	-	-	A2
Cristobalite*	[14464-46-1]	-	$0.025^{(R)}$	-	-	A2

[1] American Conference of Governmental Industrial Hygienists
[2] Particulates (Insoluble or Poorly Soluble) Not Otherwise Specified. Amorphous silica fume is considered to be PNOS. Specific TLVs for the individual substances have not been established or have been withdrawn, respectively.
(I) Inhalable fraction
(R) Respirable fraction

Specific limit values have been established for amorphous silica fume in the following countries:

	Limit value - 8 hrs mg/m³	Limit value - Short term mg/m³
Belgium	2	
Canada - Québec	2	
Denmark	2	4
Germany (AGS)	0.3 respirable aerosol	
Singapore	2	

Downstream users in other countries must comply with the respective national occupational exposure limit value (OEL) for dust in workplace atmosphere.

B) Environmental exposure controls

Target value and limit value for PM_{10} and $PM_{2.5}$ (Directive 2008/50/EC):

	Averaging period	Limit value	By date
PM_{10}	One day	50 µg/m³ ★	1 January 2005
PM_{10}	Calendar year	40 µg/m³	1 January 2005
		Target value	
$PM_{2.5}$	Calendar year	25 µg/m³	1 January 2010
		Limit value	
$PM_{2.5}$	Calendar year	25 µg/m³	1 January 2015

★ Not to be exceeded more than 35 times a calendar year.

9. Physical and Chemical Properties

Form:	Ultrafine amorphous powder (respirable dust). Dust forms agglomerates.
Colour:	Grey, off-white
Odour:	Odourless
Melting Point (°C):	1550-1570
Solubility (Water):	Insoluble/Slightly soluble
Solubility (Organic solvents):	Insoluble/Slightly soluble
Specific Gravity (water =1):	2.2-2.3
Bulk density (kg/m³) approx.:	150-700
Specific surface (m²/g):	15-30
Particle size, mean (µm):	≈ 0.15 (less than 0.1 % of primary particles > 45 µm)

10. Stability and reactivity

Conditions to avoid: See below

Materials to avoid: Hydrofluoric acid (HF).

Hazardous Decomposition Product(s):

The product reacts with hydrofluoric acid (HF) forming toxic gas (SiF_4).

Heating the product above 1000 °C can result in the formation of crystalline SiO_2-modifications as cristobalite / tridymite which may cause pulmonary fibrosis (silicosis).

11. Toxicological Information

The product does not meet the criteria for hazard classification according to Directive 67/548/EEC (DSD) and Regulation (EC) No1272/2008 (CLP).

Acute effects:

INGESTION:	Finely divided dust may cause mechanical irritation and dehydration of mucous membranes.
INHALATION:	Finely divided dust may cause mechanical irritation and dehydration of mucous membranes.
SKIN CONTACT:	Finely divided dust may cause mechanical irritation and dehydration.
EYE CONTACT:	Finely divided dust may cause mechanical irritation and dehydration.

Chronic effects:

Inhalation of microsilica dust is considered to entail minimal risk of pulmonary fibrosis (silicosis). However, chronic obstructive lung disease is suspected following long term exposure (years) for concentrations above recommended occupational exposure limits.

12. Ecological Information

Elkem Microsilica ® is not characterised as dangerous for the environment.

MOBILITY:	The product is not mobile under normal environmental conditions.
PERSISTENCE:	Not relevant for inorganic substances.
BIOACCUMULATION:	Not relevant.
ECOTOXICITY:	The product does not meet the classification criteria for ecotoxicological endpoints in accordance with Directive 67/548/EEC (DSD) and Regulation (EC) 1272/2008 (CLP).

13. Disposal Considerations

The material should be recovered for recycling if possible.
This material is not classified as hazardous waste according to Commission Decisions 2000/532/EC and 2001/118/EC. Prior to disposal of large quantities of this material advice should be sought from the Environment Agency Office.

14. Transport Information

UN	-
IMDG/IMO	Not subject to classification
ADR/RID	Not subject to classification
ICAO/IATA	Not subject to classification

15. Regulatory Information

A chemical safety assessment (CSA) has been carried out for the substance in accordance with Regulation (EC) 1907/2006 (REACH).

The text of this Product Safety Information is prepared in compliance with:

- Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

- Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP).

16. Other Information

According to Chapter 1.5.2 of the UN Globally Harmonized System of Classification and Labelling of Chemicals (GHS), Article 58 (2)(a), and Article 59(2)(b) of (EC) No 1272/2008 (CLP), which amends REACH article 31(1), safety data sheets (SDS) are only required for substances and mixtures that meet the harmonised criteria for physical, health or environmental hazards. Since this product does not meet these criteria, a SDS according to 453/2010/EC is not issued. In order to communicate relevant HSE-(health, safety and environmental-) information, this product safety information (PSI) is provided instead.

In accordance with REACH article 31(5), safety data sheets shall be supplied in an official language of the Member State(s) where the substance or mixture is placed on the market. This obligation, however, only applies for hazard-classified products which require a formal SDS. Since this product is not hazard-classified, the product safety information (PSI) is, in accordance with current regulation, provided in English language only.

REACH article 31(7) requires relevant exposure scenarios from the Chemical Safety Report (CSR) to be annexed to the SDS. However, according to REACH Annex I, section 0. (Introduction), subsection 0.6. no 4 and 5, exposure scenarios are only required for hazard-classified substances or mixtures. Since this product is not hazard-classified according to CLP, there is no requirement for exposure scenarios.

Legal Disclaimer:
The information given in this sheet is to the best of Elkem's knowledge and believed accurate and reliable as of the date indicated. However, no representation, warranty or guarantee is made to its accuracy, reliability or completeness. It is the user's responsibility to satisfy himself as to the suitability and completeness of such information for his own particular use.

Literature references are available upon request.

Elkem Microsilica ® is a trademark of Elkem AS.

Changes from revision 00 to 01: New corporate address. Paragraph 2 in section 16. Updated ACGIH values.