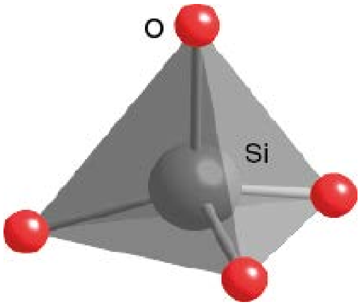
Aalborg University

Department of Chemistry and Biotechnology

Fly ash-based geopolymer cement as alternative to ordinary Portland cement in oil well cementing operations



A Thesis in

Oil and Gas Technology

by

Efstathios Kyrilis

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Professor Erik Søgaard

Professor Morten Simonsen

ABSTRACT

One of the challenges when drilling, especially in a HPHT(High Pressure High Temperature) environment [1], is the well integrity as far as the cement is concerned. It is well known that cement has a tendency to degrade in corrosive environment and high temperatures. Due to chemical attacks and formation movements and the consequent mechanical failure that was experienced in many cases many oil and gas companies decided to search for potential material for oil well cementing operations [2]–[5] . Alumino-silicates that are industrial waste and powdered residue from the combustion of coal having pozzolanic properties such as fly ash [6] and have geopolymerization potential have attracted scientific attention the last 10 years. In order to have a positive environmental impact combined with the use of a new material, it is important to seek materials that are in abundance locally. The current project aims at identifying any viable combinations of waste/residues that can result in a binder capable of withstanding chemical attacks and high temperatures while being strong enough to sustain formation stresses. In Denmark fly ash from power plants is an inexpensive source of aluminosilicates. There are two ways to produce cement/binder from aluminosilicate source. The oldest and most conventional (zeolitic method) is user-hostile while the user-friendly (geopolymerization) method yields less Uniaxial Compressive Strength (U.C.S.) [7]. The safety of the end-user is of utmost importance and the U.C.S. values do not give the actual point of failure of the placed cement [8]. Therefore, both methods were tested and a hybrid one too. For the geopolymerization method, an additional material is needed (electric arc furnace slag-EAFS was chosen over the frequently tested Ground Granulated Blast Furnace slag) that is not locally abundant (in Denmark) but is rather inexpensive and transportable through neighboring countries e.g. Germany. The main use of the new binder under test is oil well cementing applications. However, in order for a new product to be commercialized and achieve industrial acceptance must have characteristics that extend beyond the boundaries of oil industry. The Ordinary Portland Cement(OPC) with the addition of certain reagents can be applied in areas ranging from tunnel construction to oil well cementing operations. An OPC alternative must have the same versatility. One basic advantage that is widely recognized is the lower CO_2 footprint (compared to OPC) of the geopolymerized/alkalinated binder manufacture [9]–[16]. Ultimately, the new binder must achieve similar performance in popular OPC applications (if not better).

At *Chapter 1* a literature review is provided so the reader would get accustomed to the terminology regarding cementing operations, history, process and the potential of geopolymerization method (and the conventional method too). A brief introduction of the application of cement in oil wells in also provided.

Chapter 2 is dedicated to experimental procedures (materials, mix designs, preparation, test methods and test analysis).

The experimental results are the topic of the *Chapter 3* where the properties of the binder, Uniaxial Compressive Strength (U.C.S.) tests, pH and rheology measurements, penetrometer tests, durability tests, Differential Scanning Calorimetry measurements and X-Ray Diffractometry analysis are presented.

Next, at *Chapter 4* discussion of the results presented is done where the effects of some test parameters e.g. curing temperature is analysed.

Finally, *Chapter 5* concludes the current study with the reached conclusions and some topics for further/future investigation.

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ACKNOWLEDGEMENTS

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Chapter 1-Literature Review

1.1 Oil well cementing operations

Generally, cement when used in the oil industry has as primary purpose to hold the casing in place and to prevent fluid migration between subsurface formations creating a zonal isolation (figure 1).

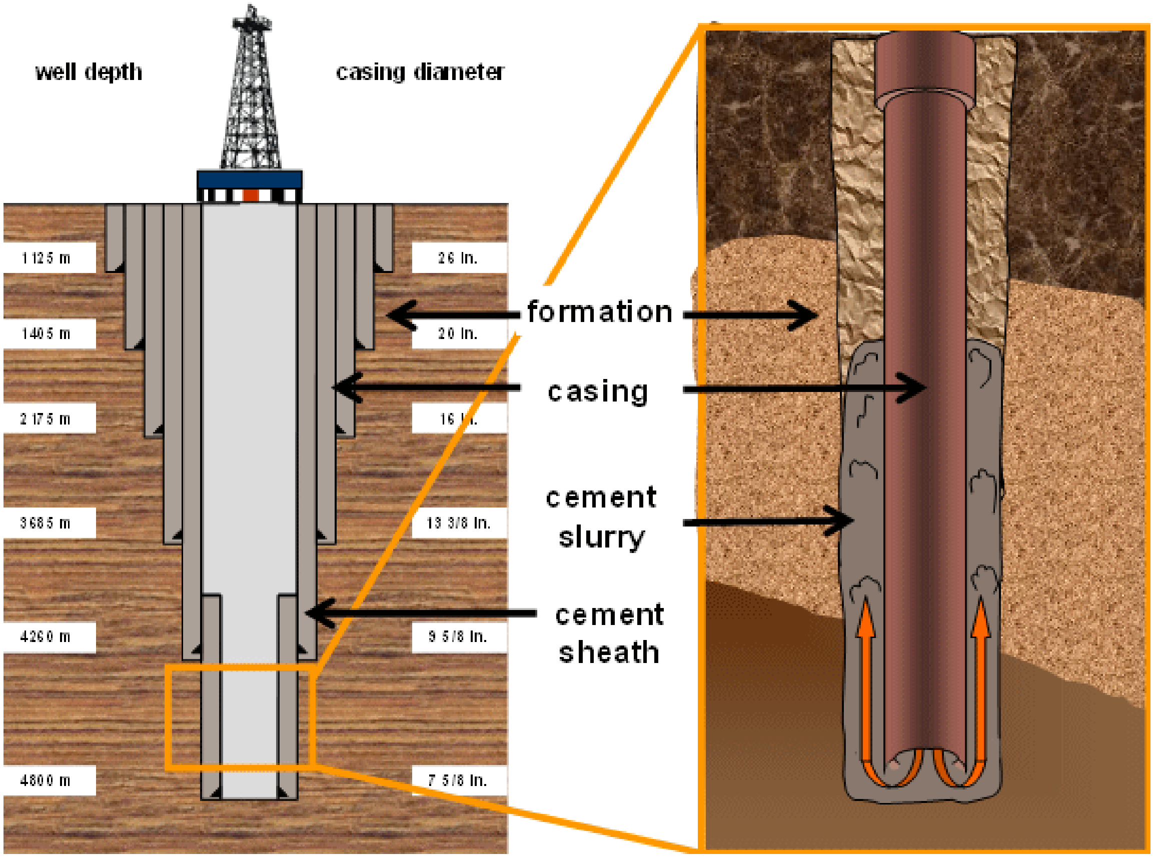


Figure 1- Schematic of a cased and cemented oil well; cement slurry placement method (www.bauchemie-tum.de)

Cementing operations are divided into two main categories: primary cementing and remedial cementing [17].

1.1.1 Primary cementing

The purpose of primary cementing is to provide zonal isolation. With the term “cementing” one is referring to the process of mixing a slurry of cement, potential additives and water and pumping it down through casing to critical points in the annulus around the casing or in the open hole below the casing string. There are two fundamental functions of the cementitious slurries (once they harden):

- To minimize the fluid movement between the formations
- Bonding and supporting the casing

Once this is achieved effectively, other requirements imposed during the life of the well will be met, such as:

- Economic
- Liability
- Safety
- Government regulations

1.1.2 Zonal isolation

Zonal isolation is indirectly related to production; however, this is a vital task that must be performed effectively to allow production or stimulation operations to be conducted. A quality well cementing operation depends on this primary operation. In addition to isolating oil-, gas-, and water-bearing zones, cement also aims at:

- Protecting the casing against corrosion
- Preventing blowout incidents by quickly forming a seal
- Protecting the casing from shock loads in deeper drilling
- Sealing off zones of lost circulation or thief zones

1.1.3 Remedial cementing

Remedial cementing is performed to correct problems linked with the primary cement job most of the times. An effective and economical approach to remedial cementing would be to avoid it by thoroughly planning, designing, and executing all drilling, primary cementing, and completion operations. The need for remedial cementing that aims at restoring a well's operation is indicative of primary operational planning and execution ineffectiveness, that results in costly repair operations with rarely satisfactory result [8]. Remedial cementing operations is divided into two basic categories:

- *Squeeze cementing*. It is basically a dehydration process. A cement slurry is prepared and pumped down a wellbore to the area of interest or the squeeze target (fracture or opening). The area is isolated, and pressure is applied from the surface to effectively force the slurry into all voids.

- *Plug cementing*. In oil well operations, a plug is used so as to prevent fluid flow in a wellbore, either between formations or between a formation and the surface. Thus, an efficient plug should provide a hydraulic and mechanical seal. Some of the most popular applications for plugging are: well abandonment, sidetracking/directional drilling, lost circulation control (plug across thief zone), well control (no safe margin between pore and fracture pressure), wellbore stability (unstable formations)

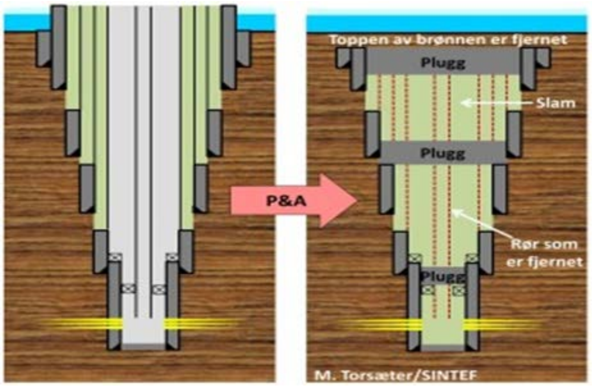


Figure 2- Illustration of permanent well plugging (www.sintef.no)

1.2 Cementing operation planning

As it is stated in the last paragraph an effective primary cementing plan that results in meeting the requirements for successful cementing operation can decrease the chance of a costly remedial operation in the future. A well-researched drilling program and the right setting of the objectives is crucial in the planning phase for minimizing problems and maximizing progress. As for the cement operations the drilling program (or the cementing program) should have as necessary data the following[8] :

- Necessary plugs for casings and liners
- Types of cements, slurry types, gradients, cement tops and special requirements
- Mixing methods for each slurry
- Anticipated bottomhole temperatures (static and circulating), slurry densities and yields
- Mud, spacers (viscosified fluid that may be densified with insoluble, solid weighting agents and are used to separate drilling fluids,[18] and cement slurries) and cement compatibilities
- Cement volumes estimation
- Advice as to how maximum mud displacement can be obtained. Required mud properties prior to cementing, spacers, flushes, scavenger slurries, any reciprocation or rotation during displacement as well as the displacement regime
- 24-hour compressive strength
- Minimum pumpable time (given by thickening time)

For the case of well abandonment/suspension:

- Anticipated well configuration on rig departure
- Required zonal isolations
- Whether casing will be cut and pulled
- Cement plug depths
- Whether suspension caps will be required
- Reference of governmental regulations or company policies regarding abandonment
- Equipment checklists (for all the cementing cases)

All these combined with information derived from LWD and MWD tools such as the encountered lithology, directional profile or formations requiring special treatment can have a positive impact on the cementing program.

1.3 Important slurry properties

1.3.1 Density

Cement (OPC) powder requires specific amounts of water to hydrate it completely. For OPC systems this means that insufficient amount of water will left some powder unreacted whereas excessive water will remain as “free water” on the of the slurry while slurry is settling. For OPC class G cement the required water to cement ratio (in w/w terms) is 0.44[19]. For casing cement operations two types of slurries are used:

A light (lead) slurry that is ahead and a denser (tail) slurry that is placed around the shoe

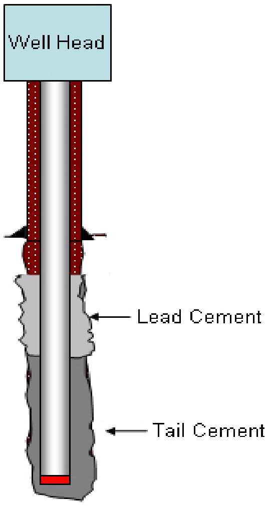


Figure 3- Lead and tail cement (www.drillingformulas.com)

This is a method to avoid increased circulating and hydrostatic pressures in the wellbore. This increase occurs due to the use of the dense slurry for the entire operation instead of an extended lead [8]. One of the cementing design objectives is to remove mud from the annulus with a spacer and then displace the spacer totally with the cement slurry without leaving channels or other flaws. It is obvious that the spacer mud have a higher density than the mud and lower density compared to cement [20]. Cement slurry density should be higher than the density of drilling fluid in the well but not to the point that formation fracture will occur while remaining at pumpable condition. For that, the density of cement slurry is generally 1.8-1.9 g/cm^3 and therefore much higher than usual drilling fluid's density [21]. However, in real oilfield applications a wider cement paste/binder density range is sought. As presented in a Schlumberger patent [22], the tested geopolymer cement/binder formulations propose a density range between 1.45 g/cm^3 up to 1.84 g/cm^3 either in reducing the water content, or in adding fillers. The most extreme density values reported are 0.9 g/cm^3 and 3.2g/cm^3 [23]. However, a cement slurry with density higher than 2.0 g/cm^3 may reduce the efficient rheological features of the slurry and consequently decrease the displacement efficiency [21]

1.3.2 Thickening time

With time the cement slurry thickens continuously until its workability (ability to flow) is lost. In order to ensure safety during the cementing operations and also achieve to pump the cement slurry to the desired location in annulus in the well, the cement slurry should be flowable during a certain time [21]. This time (thickening time) of the cement slurry can be measured (at downhole pressure and temperature) by either a consistometer (in Bearden units, Bc or a Vikat needle apparatus [18].

1.3.3 Rheology

A rheological state that enhances displacing drilling fluid by cement slurry is favorable for the workability of the slurry. Furthermore, the rheological state of the cement slurry is useful data for estimating the friction loss of circulation in the cementing process. That way, one is able to avoid borehole from leakage incidents[21]. Special treatment is required for thixotropic cement slurries. It is of utmost importance not to stop pumping unnecessarily during the operation due to the high risk of large downhole pressures when starting to pump. These kind of slurries are suitable for squeeze cementing e.g. curing lost circulation [8].

1.3.4 Compressive strength

The measurement is basically used for comparative study and is not an absolute measurement of the placed cement strength [8]. Additionally, in U.C.S. test the real environment of the cement is not simulated. The cement is the intermediate material between casing and formations and as such is not only stressed vertically by the overburden (in a vertical well) in a uniaxial manner but rather biaxially by the casing (see figure 4) and the formation.

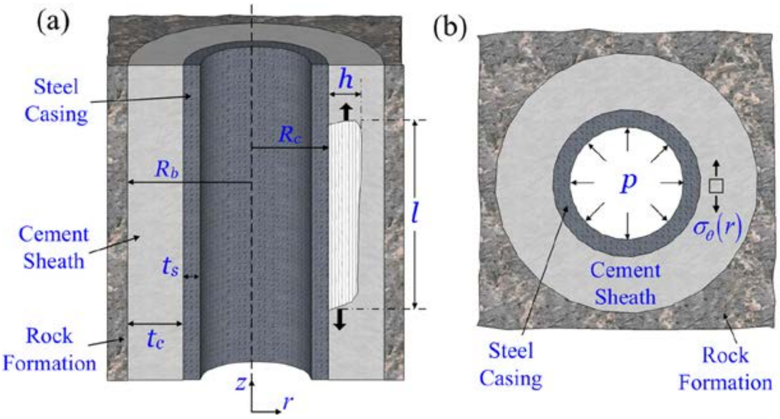


Figure 4- (a) A cross section along the length of a well. The sheath fills the gap between the casing and the formation. (b) A cross section normal to the well. The pressure inside the steel casing causes a stress field in the cement sheath [24].

The use of ultrasonic cement analyzer for measuring compressive strength is a non-destructive mean of monitoring the strength buildup while curing in bottomhole pressure and temperature regime. More importantly when developing a new mixing design, it saves a lot optimization time since the researcher has an idea of the quality of the material even before it is cured.

The minimum required casing support strength is 3.5 MPa, so as the start safely putting the well into production [8], [21]. For sections with perforating operations a minimum 14 MPa strength is mandatory [8].

1.3.5 Temperature rating

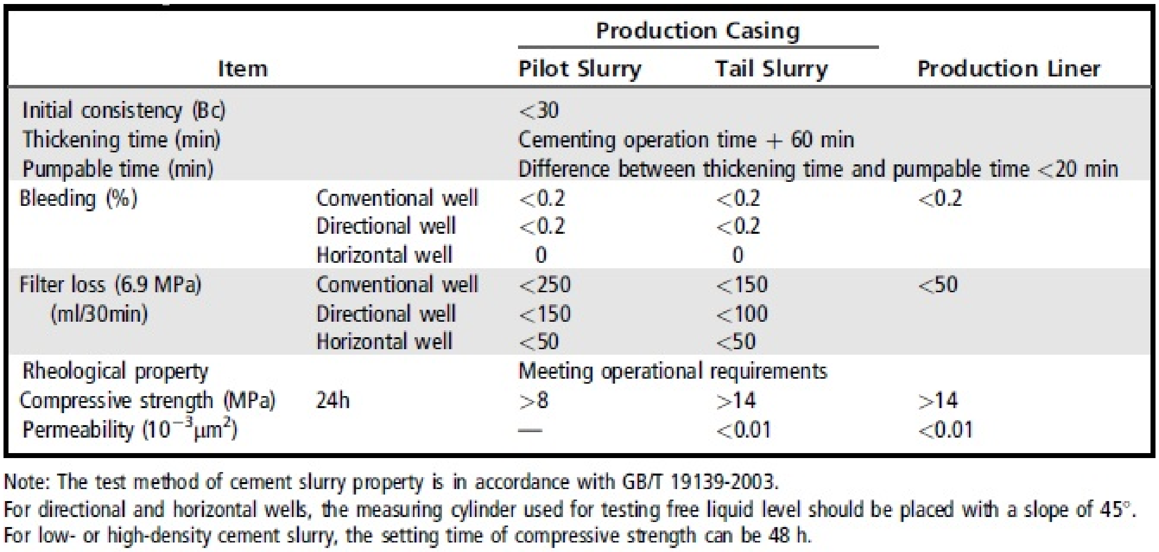
Compressive strength development and thickening time are functions of well temperature. To partially tackle cementing problems associated with well temperature accelerators or retarders can be used to adjust the pumpable time and likewise affect the strength development [8]. The knowledge of the actual temperature that cement slurry encounters in not as easy to obtain as it seems. The well under static conditions will have a temperature gradient. Upon pumping initiation and when circulating the slurry, the local temperature around the wellbore will decrease [8]. Consequently, there are two temperatures at every well depth, circulating(BHCT) and static(BHST). BHCT is used for pumpable time estimations while BHST is relevant to strength buildup. In practice, BHST at the depth of the top of cement must be less than BHCT (slurry design) but not significantly less. If this happens, the slurry can take too much time to be cured [8].

1.3.6 Summary of basic requirements for cement slurry

A design of lead (often called pilot also) and tail slurry is often mandatory for displacement efficiency enhancement. As far as displacement efficiency is concerned it is known that it increases with an increase in pumping rate of the slurry. As a drawback, there is a risk of formations being fractured at higher flow rates [25]. Thus, the slurry is advisable to be pumped at flow rates that will attain an equivalent circulating density safe enough to not fracture the formations [26].

Cement permeability should be low enough to succeed zonal isolation, cement slurry bleeding should not endanger the even density distribution and consistent strength of the slurry. Moreover, filter loss is preferable to be as low as possible to avoid slurry properties' quality decrease associated with the loss (e.g. not favorable rheology profile) [21].

The required basic cement slurry properties can be summarised in the following table:



Item		Production Casing		Production Liner
		Pilot Slurry	Tail Slurry	
Initial consistency (Bc)		<30		
Thickening time (min)		Cementing operation time + 60 min		
Pumpable time (min)		Difference between thickening time and pumpable time <20 min		
Bleeding (%)	Conventional well	<0.2	<0.2	<0.2
	Directional well	<0.2	<0.2	
	Horizontal well	0	0	
Filter loss (6.9 MPa) (ml/30min)	Conventional well	<250	<150	<50
	Directional well	<150	<100	
	Horizontal well	<50	<50	
Rheological property		Meeting operational requirements		
Compressive strength (MPa)	24h	>8	>14	>14
Permeability ($10^{-3}\mu m^2$)		—	<0.01	<0.01

Note: The test method of cement slurry property is in accordance with GB/T 19139-2003.
For directional and horizontal wells, the measuring cylinder used for testing free liquid level should be placed with a slope of 45°.
For low- or high-density cement slurry, the setting time of compressive strength can be 48 h.

Table 1-Basic requirement for cement slurry [21]

1.3.7 Cement displacement efficiency enhancement

The degree of displacement (η) by cement slurry is given by the equation:

$$\eta = \frac{cement\ slurry\ Volume}{annulus\ Volume}$$

When η is equal to 1 then 100% displacement has occurred. If the displacement is really low then some solutions are these [21]:

- *Centralizer* employment. Under high degrees of annulus eccentricity, the displacement can be extremely low. This is often the case in directional drilling wells. A centralizer ensures that eccentricity of casing in the borehole is reduced as much as possible an even circumferential flow velocity.

- *Favorable flow regime*. Displacement under turbulent flow is the most effective solution to advance (in the most uniform way) the displacement of drilling fluid (see figure below)

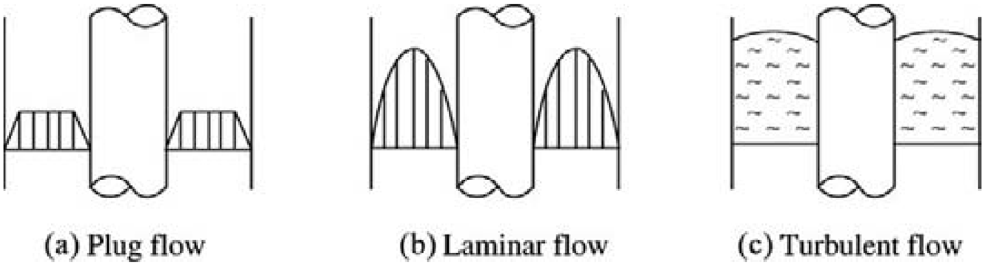


Figure 5-Flow velocity distributions for different flow regimes [21]

- *Casing rotation.* Rotating the casing results in even displacement of the drilling fluid in the whole annulus. In order not to impose excessive stresses on the casing a rotating speed in the range of 10-20 rpm is advisable.
- *Pad fluid.* Includes washing fluid (to wash the borehole wall) and spacer fluid.
- *Density difference* between displacement fluid and drilling fluid. This creates a buoyancy on drilling fluid resulting in enhanced displacement.

1.4 Usual integrity issues in HPHT and corrosive well cementing

HPHT wells present several cementing challenges [1] as the established cementing practices have proven inefficient in many cases of HPHT wells and new materials and technology are in demand so as to overcome these issues [27]. In HPHT wells the bottom pressure and temperature exceed 150^{o}C and 690 bar respectively [28]. It is notable that an area with high temperature is not necessarily accompanied by high pressure and vice versa [1]. These are harsh pressure and temperature conditions especially for the plain OPC due to strength retrogression (decreased compressive strength and increased permeability of cement) occurring over 110^{o}C [29],[20].

One of the issues that engineers face when cementing in a HPHT well is that the mud removal method using turbulent flow (1.3.7. section) is practically unachievable due to high densities of both drilling fluid (mud) and spacer. Under HPHT conditions in order to achieve turbulent flow one must reach a flow rate over 3.2 m^3/min, which is impossible, since only 0.48-0.79 3.2 m^3/min is practically reachable. If flowrate exceeds that level, then the dynamic pressure created will result in bottomhole pressure higher than enough to fracture pressure. To manage the highest practical flow rate in the annulus, modelling the hydraulic flow when operating in HPHT conditions is vital [20]. Slurry density of up to 2.1 g/cm^3 can be achieved by adjusting solids content in the OPC slurry. Slurry densities greater than this are frequently needed in HPHT wells, and can be achieved by adding reagents like hematite and manganese tetraoxide to the slurry design [20],[1].

HPHT well environment will favor gas migration (resulting in soil and aquifer contamination) due to higher pore pressures and reduced margins between pore pressure and slurry’s hydrostatic pressure. An efficient cement operation must minimize the risk of forming micro-annuli and thus, secure cement sheath’s integrity. The use of foamed cement is a resistant to gas migration choice, flexible and with considerable success [1].

Overall, cementing in HPHT regime is challenging and meticulous lab testing is required, modelling of hydraulics and thorough spacer requirements planning. Attention to details is mandatory and can make a difference since cementing integrity is an area with major issues historically and with a resulting significant impact [1].

Since many HPHT reservoirs globally have corrosive compounds like CO_2 and H_2S it an additional problem that needs to be tackled. The coexistence of high temperatures and corrosive compounds affects directly the casing design and moreover, impose safety, health and environmental issues that need to be taken care of. Added to that, some completion fluids and especially brines can be very corrosive (chloride stress corrosion) [1]. Corrosion is not a primary issue for the casing cement, but a corrosion resistant cement can withstand easier any incident due to a leakage incident or diffusion of these corrosive gases.

Finally, in the case of plug and abandonment of a HPHT well, a geomechanical simulation is the most effective way to plan a cementing operation that would isolate effectively the fluids along the well while reducing the contamination risks and the costly remedial cementing. This is vital since HPHT well that is about to be abandoned has the initial reservoir pressures lowered to almost hydrostatic range while remaining in high temperature. Geomechanical simulation will help in understanding more coherently the thermal changes and provide the larger changes in effective stress in the cap rock, where critical plugs are put in place for production intervals isolation. The aforementioned stress changes (thermally induced) can change the shape of the wellbore and endanger cement sheath integrity.

For all these challenges, apart from the placement techniques/meticulous plans/modelling etc. the role of cementing material’s chemistry is important.

1.5 OPC system

Modern cement (the use of cement in constructions ages back to Ancient Ages [7],[30]) was patented in 1824 Joseph Aspdin and was named Portland cement. OPC is obtained by thoroughly mixing argillaceous (clay/shale) and calcareous (limestone/chalk), or other silica-/alumina- and iron oxide-bearing materials, burning them at a clinkering temperature (around 1400^{o}C) and grinding the resulting clinker [31].

According to ASTM [32],[33], Portland cement (OPC) is a hydraulic cement (sets and hardens by chemical interaction with water and that is capable of doing so under water) produced by pulverizing portland-cement clinker, and usually containing calcium sulfate.

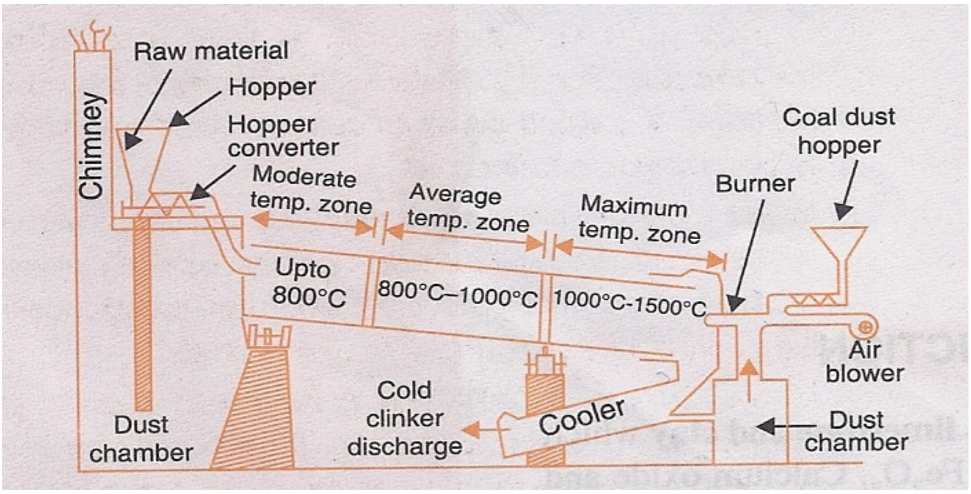
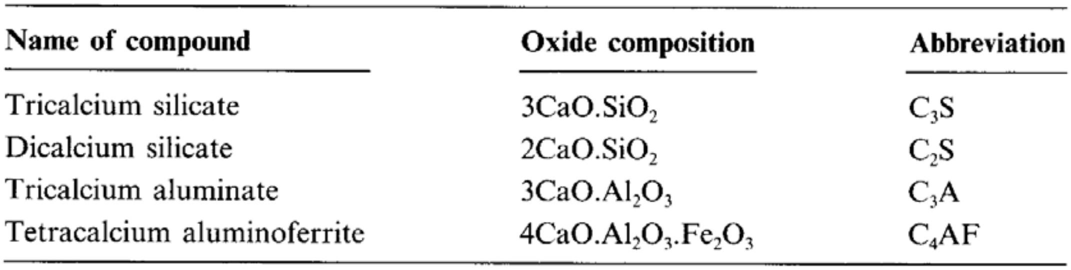


Figure 6- Rotary kiln for manufacture of OPC (www.chemistry-assignment.com)

No other material except gypsum, water and grinding aids may be added after burning.

The major OPC compounds are listed below (their abbreviations included)



Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

Table 2- Major constituents of OPC [31]

The abbreviations (used by cement scientists) denotes each oxide by a letter, e.g. CaO is C, SiO_2 is S, Al_2O_3 is A and Fe_2O_3 is F. In the same manner, water in hydrated cement is described by letter H.

C_3A in OPC at high percentages is a potential disruption factor since it forms ettringite (calcium sulphoaluminate) upon sulphate attack, while the strength contribution of this compound to OPC is low [31].

The addition of gypsum to clinker is extremely important and is dependent to C_3A content and OPC's alkali content.

The silicates C_3S and C_2S are the most crucial constituents of OPC regarding the strength buildup. In the presence of water, they form hydrated products (C_3S has higher hydration rate comparably), which in time produce a firm and hard mass. The hydrated product of C_3S is the microcrystalline $C_3S_2H_3$ and some amount of $Ca(OH)_2$ (also known as Portlandite). The hydration of cement constituents is exothermic (heat of hydration). The common symbol for calcium silicate hydrates is C-S-H. The hydration reactions can be described like this [30]:

$$\boxed{2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH}$$

Equation 1- Hydration of C_3S

$$\boxed{2C_2S + 4H \longrightarrow C_3S_2H_3 + CH}$$

Equation 2- Hydration of C_2S

$$\boxed{C_3A + 6H \longrightarrow C_3AH_6}$$

Equation 3- Hydration of C_3A

The reaction of pure C_3A is quicker than that of calcium silicates, is rather rapid reaction that can lead to flash set. To tackle this, amounts of gypsum are added to the cement clinker [31].

1.6 GPC system

1.6.1 Terminology

Geopolymers (GP) are macromolecules (chains or networks of mineral molecules to be more exact) having definite molecular weight and size, that are linked with covalent bonds. These two basic aspects (structure and size) are easily established in both solid state or in solution, using electron microscopy and light-scattering respectively. In comparison, gel (OPC gel) denotes an indefinite amorphous compound which is dimensionally unresolved [7]. Geopolymer cement (GPC) system is completely different compared to OPC system. In GPC the forming mechanism is not hydration and neither the product is a gel. In the C-S-H structure, the SiO4 tetrahedra from which is composed are of the (Q_0), (Q_1) and likely (Q_2) category (easily determined by Nuclear Magnetic Resonance Magic Angle Spectrum analysis for isotope ^{29}Si. These categories denote simpler structures (monomers, dimers etc.) while GP are structurally tri-dimensional aluminosilicates [7] composed mainly by (Q_4) that has a 3-D lattice structure, and that is the reason for them being stable to acidic attacks.

The basic characteristics of these inorganic polymers are [34]:

a) The hardened material is X-ray amorphous at ambient and medium temperatures, but X-ray crystalline at temperatures >500°C

b) There are two different ways to manufacture GP depending on the pH of the medium:

- alkaline medium (Na, K, Ca) hydroxides and alkali-silicates resulting in poly(silicates) – poly(siloxo) type or poly(silico-aluminates) – poly(sialate) type
- acidic medium (Phosphoric acid) yielding poly(phospho-siloxo) and poly(alumino-phospho) types

As an example [34][7], one of the geopolymeric precursors, MK-750 (metakaolin) with its alumoxyl group –Si-O-Al=O, reacts in both systems, alkaline and acidic. Same for siloxo-based and organo-siloxo-based geopolymeric species that also react in both alkaline and acidic medium. In the late 1970's, Joseph Davidovits, invented and developed the method of geopolymerization and coined the term "geopolymer" to classify the newly discovered geosynthesis that produces inorganic polymeric materials that are now used for a number of industrial applications [7][34] .

1.6.2 The geopolymerization mechanism

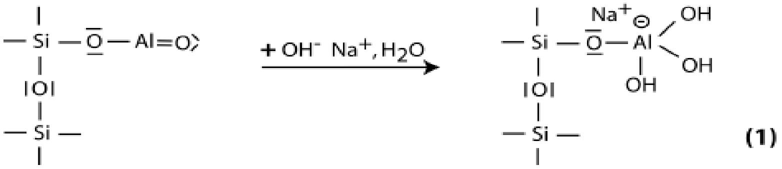
Apart from inventing the geopolymerization as a chemical process, J. Davidovits also set a logical scientific terminology based on different chemical units, essentially for silicate and aluminosilicate materials, classified according to the Si:Al atomic ratio:

Si:Al = 0, siloxo
Si:Al = 1, sialate (acronym for silicon-oxo-aluminate of Na, K, Ca, Li)
Si:Al = 2, sialate-siloxo
Si:Al = 3, sialate-disiloxo
Si:Al > 3, sialate link.

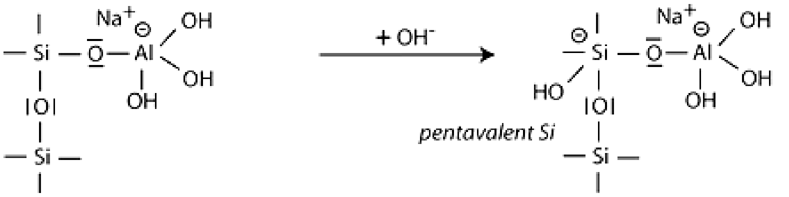
This terminology was presented to the scientific community at a IUPAC conference in 1976 [34]. The reaction of polymerization must not be comfused with simple alkalination (coined falsely “alkaline activation” [35], [36]-amorphous aluminosilicates are extremely reactive reagents, no need for “activation”). Alkalination is just the first step of the GP method [37]. Stopping the procedure at this point does not result in a stable structured material with good properties (except UCS) [38], [37].

In order to explain better the steps of geopolymerization mechanism, MK-750 (since is extremely reactive and was thoroughly tested for a long time [7]) is used as an example taken from the Geopolymer Institute website [39]:

Step 1: alkalination and formation of tetravalent Al in the side group sialate -Si-O-Al-$(OH)_3$-Na^+,



Step 2: alkaline dissolution starts with the attachment of the base OH- to the silicon atom, which is thus able to extend its valence sphere to the penta-covalent state,

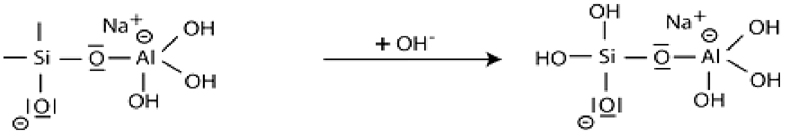


(2)

Step 3: the subsequent course of the reaction can be explained by the cleavage of the siloxane oxygen in Si-O-Si through transfer of the electron from Si to O, formation of intermediate silanol Si-OH on the one hand, and basic siloxo Si-O- on the other hand.

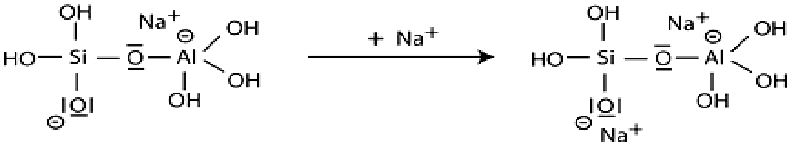
(3)

Step 4: further formation of silanol Si-OH groups and isolation of the ortho-sialate molecule, the primary unit in geopolymerization.



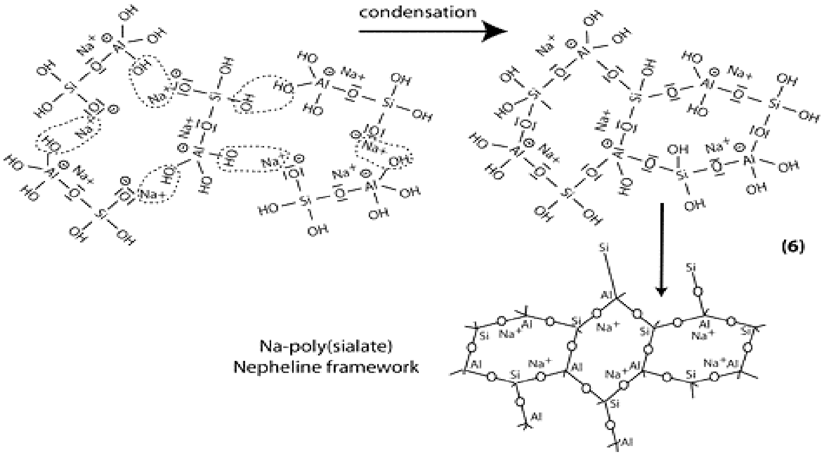
(4)

Step 5: reaction of the basic siloxo Si-O- with the sodium cation Na$^+$ and formation of Si-O-Na terminal bond.

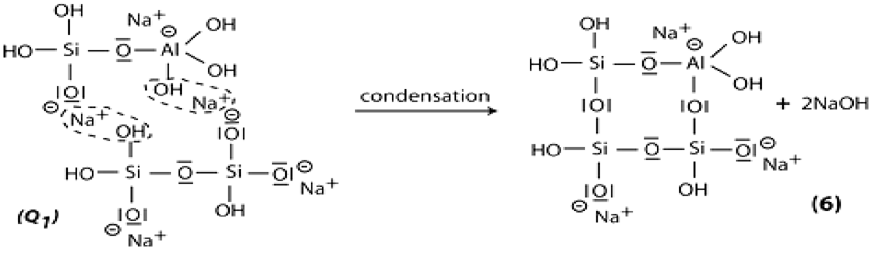


(5)

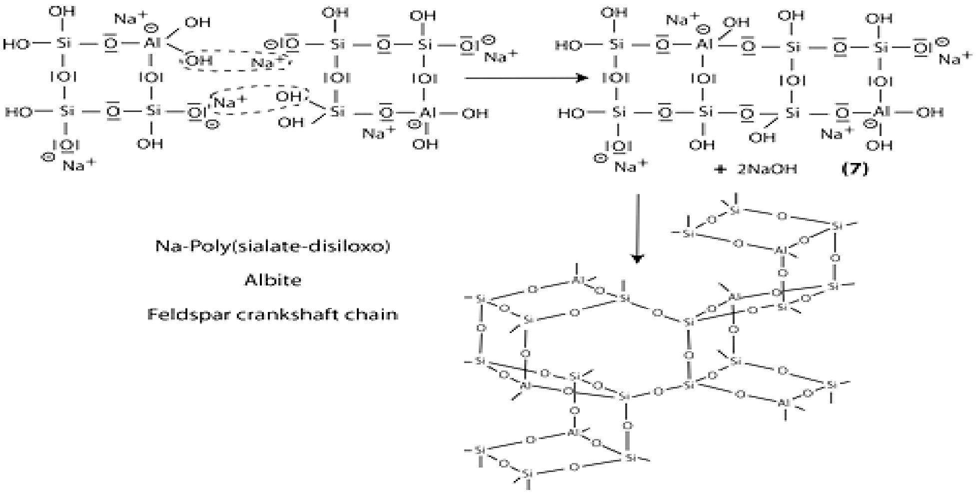
Step 6a: condensation between ortho-sialate molecules, reactive groups Si-ONa and aluminum hydroxyl OH-Al, with production of NaOH, creation of cyclo-tri-sialate structure, whereby the alkali NaOH is liberated and reacts again and further polycondensation into Na-poly(sialate) nepheline framework.



Step 6b: in the presence of waterglass (soluble Na- polysiloxonate) one gets condensation between di-siloxonate Q_1 and ortho-sialate molecules, reactive groups Si-ONa, Si-OH and aluminum hydroxyl OH-Al-, creation of ortho-sialate-disiloxo cyclic structure, whereby the alkali NaOH is liberated and reacts again.



Step 7: further polycondensation into Na-poly(sialate-disiloxo) albite framework with its typical feldspar crankshaft chain structure.



To make even clear the difference of the conventional method and the GP method another diagram is supported from the Geopolymer Institute for better visualization [37]:

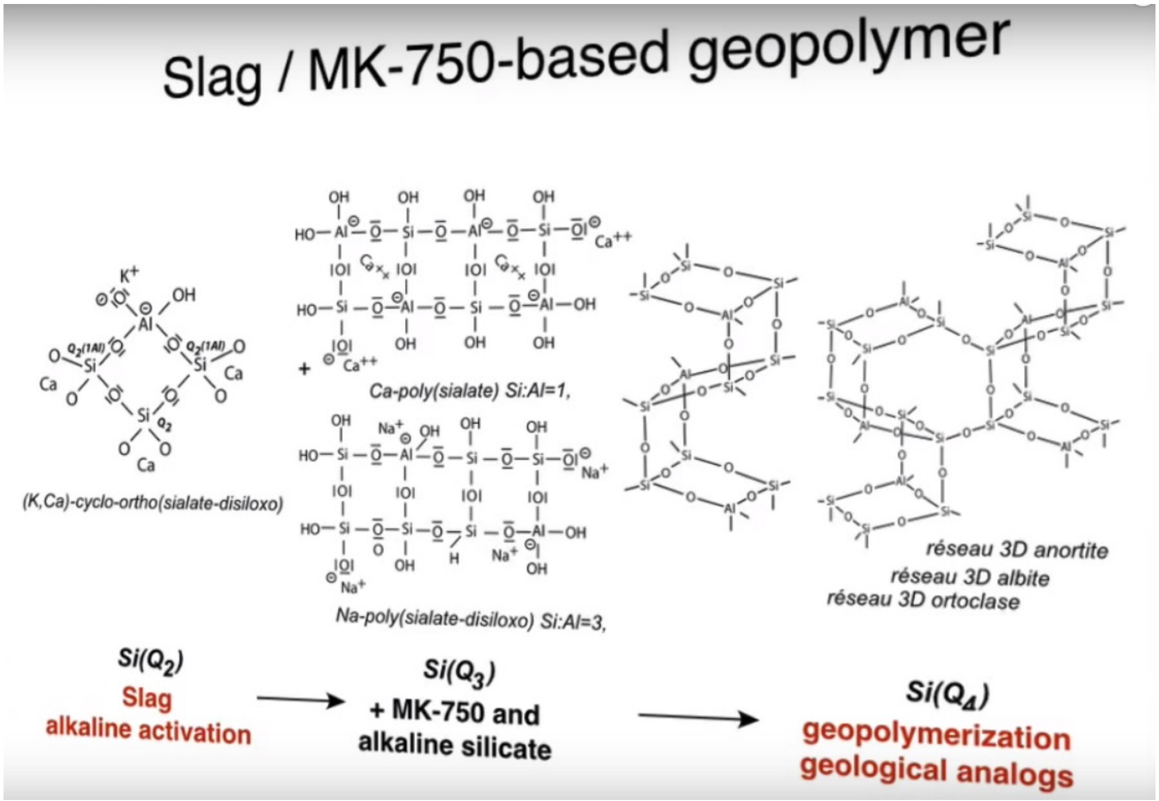


Figure 7-The difference between conventional method and geopolymerization

As it can be seen, if we stop the process at the early stages, not only we have the Si(Q_2) but we have the K^+ (or the Na^+) out of the structure, giving to the material bad physical properties as the free alkali can migrate fast in contact with water. That way the produced material will have lot of leachates [40]. But if we continue, and we add aluninosilicate (e.g. MK-750) to the slag together with soluble silicate we get Si(Q_3) and finally Si(Q_4) which gives better overall properties. The only reason to do only the alkalination part is if the focus in only the UCS and not so much in the stability of the product and resistance to corrosion and chemical attacks [7].

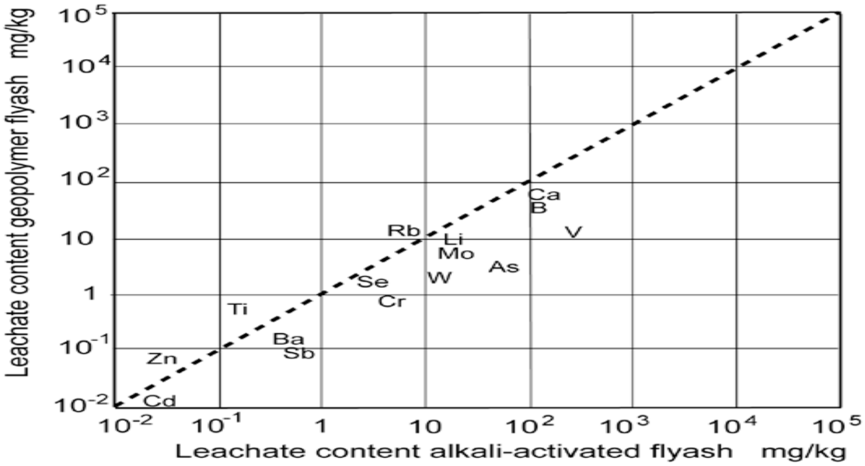
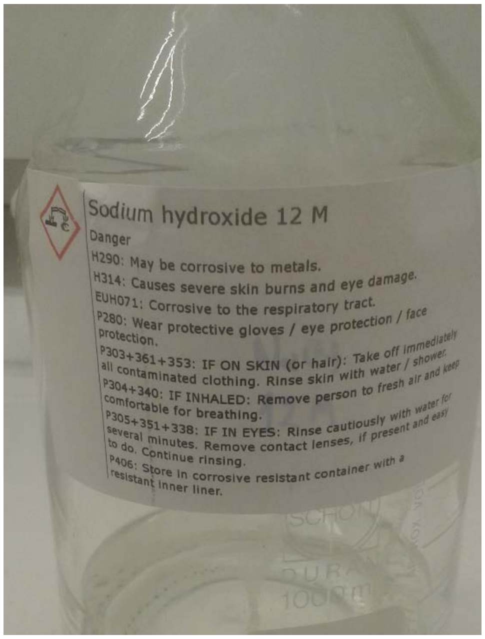


Figure 8- Leachable contents (EN12457-2 leaching test) of matrices obtained from geopolymeric process and conventional alkali-activated (zeolitic) procedure [40], [41]**.**

1.6.3 User-friendly systems

As mentioned before, GP method and its subdivision (zeolitic method called “alkaline-activation”) need alkaline (or acidic) medium to initiate the process, resulting in dealing with very corrosive environment.

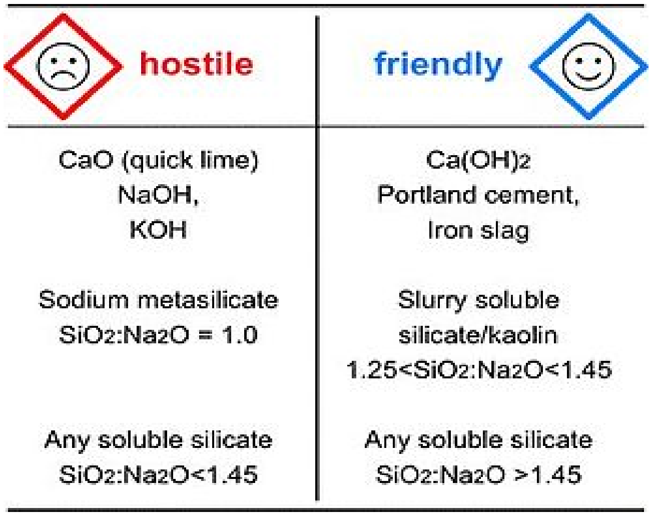


Picture 1- Standard solution of NaOH 12M prepared for the tests marked with the relevant label

In picture 1, one can see the “Corrosive” label marked on the bottle for 12M NaOH (same goes for the 4M, 6M KOH solutions in water). The GP process regardless the amount of alkaline hydroxide or the soluble silicate falls into two categories regarding the safety:

- Corrosive system
- Irritant system

Corrosive products must be handled with gloves, glasses and masks. It is not user-friendly a system that includes high amounts e.g. NaOH 12M.



hostile	friendly
CaO (quick lime) NaOH, KOH	$Ca(OH)_2$ Portland cement, Iron slag
Sodium metasilicate $SiO_2:Na_2O = 1.0$	Slurry soluble silicate/kaolin $1.25<SiO_2:Na_2O<1.45$
Any soluble silicate $SiO_2:Na_2O<1.45$	Any soluble silicate $SiO_2:Na_2O >1.45$

Figure 9-Classification of chemicals according to safety rules [34].

Is obvious by the figure that the conventional method is user-friendly while the GP method can be classified as such, depending on the soluble silicate composition (more about silicates follows at next chapter).

1.7 Project focus

The oil cement operations do not impose severe danger to the danger as the field of application is underground. However, having a product with inefficient chemical stability and the potential to create many leachates [40] is not ideal in the long term. The investigation was divided into different sections. The first was focused on the pumpability of the produced slurry while the other was mainly seeking high strength. The main objective however after a lot of research was, regardless if is the pumpability or the strength the crucial parameter for the process, to produce a material with as much user-friendly process as possible. The other important aspect of the research was the restriction to use low or zero amounts of raw materials that are either expensive or are not abundant.

Chapter 2-Experimental procedures

2.1 Materials

The materials used for this project were provided by various companies that showed interest for the project except the KOH/NaOH pellets and the first 2 batches of potassium silicate (MR=3,14) that Aalborg University had to purchase.

2.1.1 Fly-ash

Fly ash is a byproduct of the combustion of pulverized coal in electric power generating plants. Upon ignition in the furnace, most of the volatile matter and carbon in the coal are burned off. During the combustion procedure, the mineral impurities in the coal matrix (such as clay, feldspar, quartz, and shale) fuse in suspension and are carried away from the combustion chamber by the exhaust gases.

Picture 2- Fly ash class F (provided by emineral,Denmark)

In the process, the fused material cools and solidifies into spherical glassy particles called fly ash. The fly ash is then collected from the exhaust gases by electrostatic precipitators or bag filters. Fly ash is a finely divided powder resembling OPC. Most of the fly ash particles are solid spheres and some are hollow cenospheres. Also present are plerospheres (pheres containing smaller spheres). In contrast, ground materials (OPC), have solid angular particles. The particle sizes in fly ash vary from less than 1 µm (micrometer) to more than 100 µm with the typical particle size measuring under 20 µm. Only 10% to 30% of the particles by mass are larger than 45 µm. Fly ash is primarily silicate glass containing silica, alumina, iron, and calcium. Minor constituents are magnesium, sulfur, sodium, potassium, and carbon. Crystalline compounds are present in small amounts. The relative density (specific gravity) of fly ash generally ranges between 1.9 and 2.8 and the color is generally gray or tan [42]

For the needs of the project 3 batches of fly ash-ash (class F) were delivered form Emineral (Denmark) with the following compositions (data from AAU's XRF):

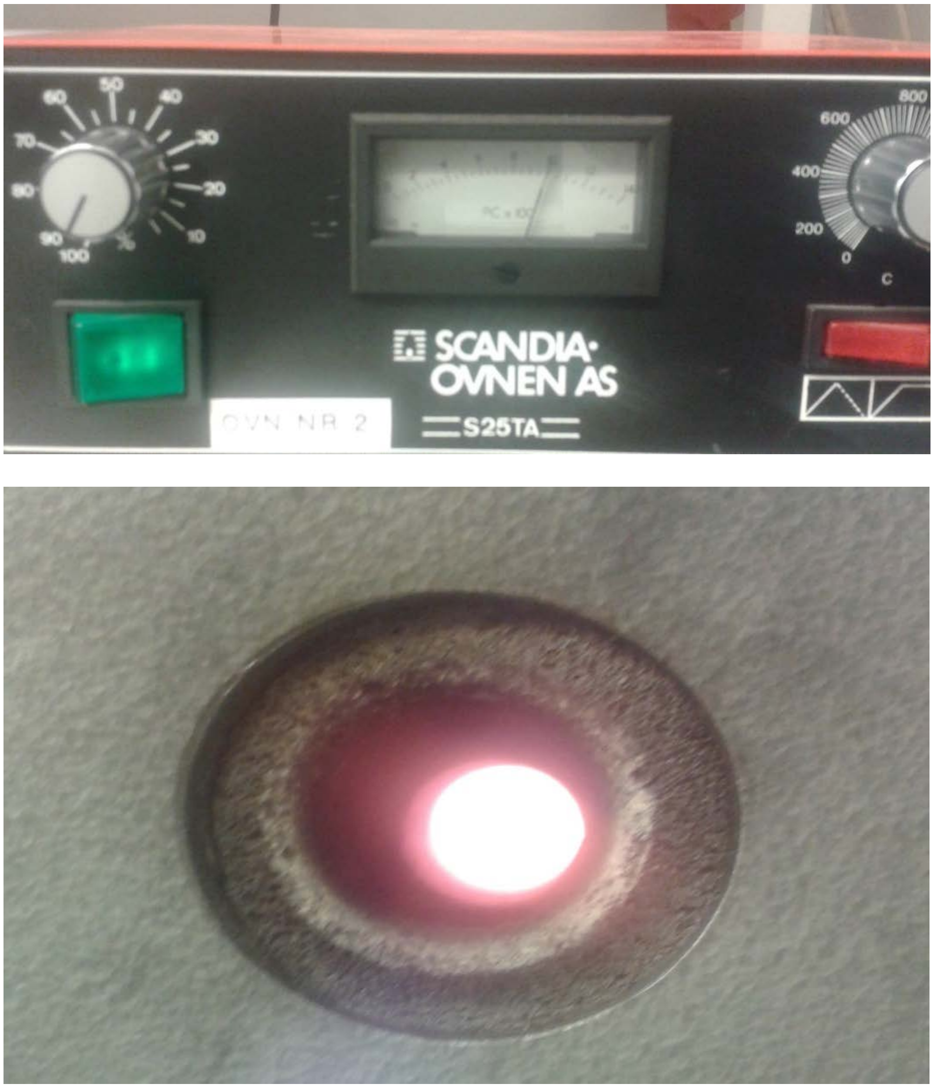
Chemical composition (% w/w)			
Oxides	FFA2	FFA3	FFA4
MgO	1,5	1,68	2,52
SO3	1,32	1,16	1,48
CaO	4,88	4,61	4,79
SiO2	55,2	56,5	51,9
Al2O3	25,9	25,3	28,6
Fe2O3	6,43	6,02	5,76
LOI	4,633972	1,1135302	0,787535792

Table 3- XRF analysis of available fly-ashes.

According to ASTM C 618 all of three batches can be classified as fly ash class F (FFA) as they have low amount of CaO (<10% w/w).

The weight loss of fly ashes burned at temperatures ≤1000°C implies carbonates' presence, combined water some clays, as well as free carbon combustion. Carbon is the most important component of loss on ignition (LOI). The water required for workability of hydraulic binders depends on the carbon content of fly ashes. A higher carbon content of a fly ash denotes that more water is needed to produce a slurry of normal consistency.

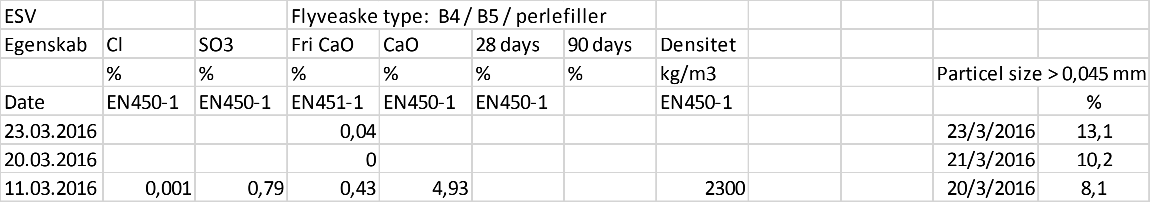
LOI measurements were carried out in a university's furnace according to ASTM [43],[44]. FFA has the most favorable [7] Si/Al ratio of the 3 fly-ashes (2,23) and was chosen for the mixing designs.



Picture 3-Furnace used for LOI measurements and high temperature curing

Picture 4-Samples of 2 different batches of FFA after exposure to 1050ºC for LOI tests.

The supplying company (Emineral) supplied the latest chemical analysis conducted according to EN450-1:



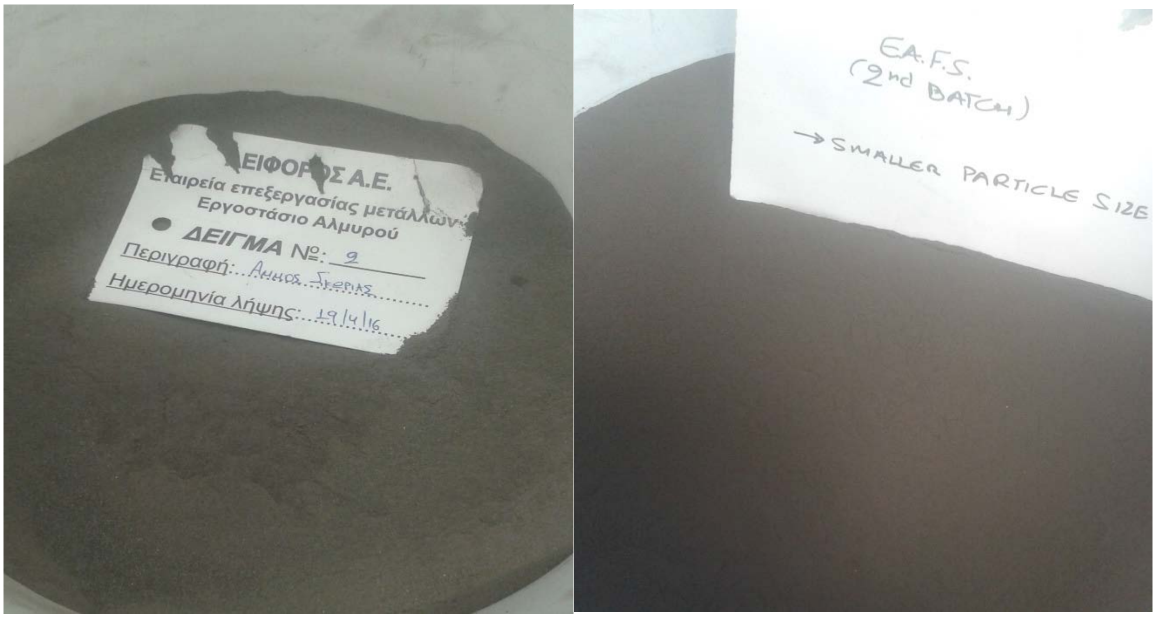
ESV			Flyveaske type: B4 / B5 / perlefiller								
Egenskab	Cl	SO3	Fri CaO	CaO	28 days	90 days	Densitet				
	%	%	%	%	%	%	kg/m3			Particel size > 0,045 mm	
Date	EN450-1	EN450-1	EN451-1	EN450-1	EN450-1		EN450-1				%
23.03.2016			0,04							23/3/2016	13,1
20.03.2016			0							21/3/2016	10,2
11.03.2016	0,001	0,79	0,43	4,93			2300			20/3/2016	8,1

Table 4-Particle size and free lime content of fly ashes (provided by Peter Lundquist, Emineral)

More data from Emineral regarding fly ashes is available in Appendix.

2.1.2 Electric Arc Furnace slag

Electric arc furnace slag (EAFS) is a waste product from steel industry that is amorphous (cooled rapidly) that is already an usual additive in the OPC blends, especially for the ones that must be “green” (less CO_2 emissions).



Picture 5-EAFS that was used in experiments (provided by aeiforos,Greece)

The common use of slags as cementitious additives is attributed to the fact that they enhance strength and increase setting time.

XRF analysis was performed for both batches with the following results:

Chemical composition (% w/w)	**EAFS**	**EAFS 2**
MgO	3,97	2,75
SO3	0,617	0,397
CaO	29,4	27,4
SiO2	15,7	17,4
Al2O3	15,1	14,2
Fe2O3	28,1	29,5
LOI	<3	<3

Two different batches were delivered (EAFS 2 has a small retention % at 63μm sieve).

2.1.3 Microsilica

Micro silica (MS), which is also known as silica fume, is a fine pozzolanic (high potential to cement) material [45]. It is a by-product of silicon manufacture procedure in an electric furnace. During the production, silica fume rises as an oxidized vapor from the furnaces and then after cooling it condenses and it can then be collected and stored. Before producing the final product, microsilica can be used, impurities are removed and the particle size is controlled. This reagent is available in solid and liquid form, but liquid form is also common. It contains high amounts of SiO2 (usually more than 85%).

Microsilica is used in many cementitous products (concrete, ceramic and polymers) [28]. Micro silica also increases the impermeability of the binder, due to its small particle size compared to the OPC particles.

The microsilica used during the tests by (Elkem, Norway) had a grade of 940 and was undensified and has 98,5% (w/w) is of under 45μm. The composition of the MS (using XRF) is presented in the following table.

Chemical composition (% w/w)	**MS940-U**
K_2O	1,13
SO3	0,28
CaO	0,32
SiO2	97,30
Al2O3	0,67
Fe2O3	0,24
LOI	1,71

Picture 6-1% water of water content was measured (was the highest) due to poor storage conditions

2.1.4 Other reagents

Metakaolin (MK) is an aluminosilicate that is highly reactive when is produced from calcination of kaolinite at 750°C. Unfortunately, the only MK available was MK Metastar 501 and not the MK-750. However, the reagent was tested but the further investigations were aborted due these reasons:

- MK 501 needs loads of water to maintain workable, in the expense of losing a lot of strength instead.

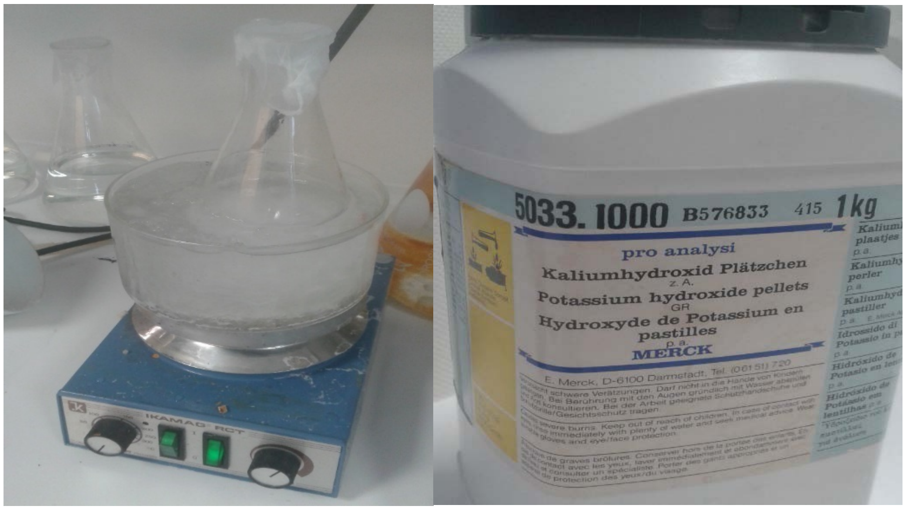
- Is energy consuming (is a product of calcination in high temperatures)
- The scope of the project is to exploit the abundance of waste products with pozzolanic potential locally. MK is not being in such abundance as fly ash.
- MK has been investigated a lot from many researchers, and even a patent for oil well cement was developed from Schlumberger company [22] using MK-750.

Aluminium dross is, like EAFS, a waste product of steel industry that was provided also by Aeiforos(Greece) so as to be tested. Although aluminium dross has over 90% wt. Al_2O_3 (combined with small amount of SiO_4) did not yield good results and that was partly due to way it is produced. After extensive discussion with Aeiforos production manager, I was informed that unlike EAFS this reagent is allowed to cool down gradually and is not subjected in rapid cooling. Therefore, it is allowed to form crystals and consequently minimize its reactivity.

2.1.5 Alkaline solutions

The solution largely tested in the current project was KOH. The reasons were many. At the beginning of the project it was rather intriguing that not so much research was conducted using KOH alkaline solution. This was explained, partially, due to the fact that is more expensive than the sodium one. Although K-silicate has 10 times smaller viscosity compared with Na-silicate at a given molar ratio MR, KOH is not an optimal alkaline medium for the conventional zeolitic method due to the fact that has a lower (compared to NaOH) degree of reactivity for this system [7]. However, zeolitic method uses almost no amount of soluble silicates while geopolymeric method relies solely on them. As a result, in conventional method one uses sodium alkaline medium and potassium in the geopolymeric method. In many studies [7], [46], [47] the Na is agreed that promotes more effectively the aluminoslicate dissolution than K. However, the geopolymerization is not governed by the rate of aluminosilicate dissolution and therefore K-containing systems show high UCS values.

The production of highly concentrated KOH/NaOH is extremely exothermic. One must be careful of the temperature and not put all the flakes in the distilled water at once. For the production of 6M KOH and 12M NaOH a method to cool the beaker was applied while the mixture is magnetically stirred (see picture)



Picture 7-- Standard solution of 12M NaOH prepared for the tests while cooling the beaker;potassium hydroxide pellets used in tests.

2.1.6 Soluble silicates

For the manufacture of sodium silicate, a mixture of quartz and sodium carbonate is fused at around 1400^{o}C (see the figure below). This happens according to the reaction:

$$\boxed{nSiO_2 + M_2CO_3 \rightarrow M_2O \cdot nSiO_2 + CO_2}$$

Equation 4-Alkali silicate glass production

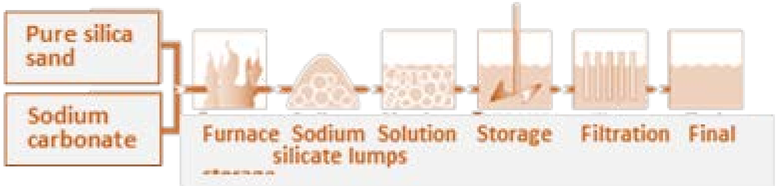
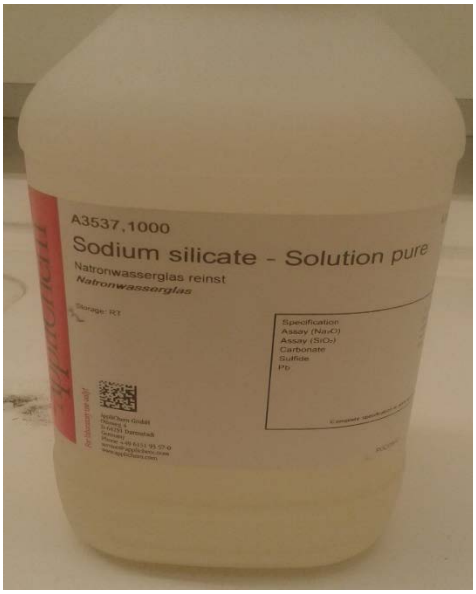


Figure 10- schematic of soluble silicates manufacture procedure (provided by Bollerup-Jensen)

The high temperatures (up to 1500°C for both potassium and sodium silicate glass) are needed so as to combine rapid and complete fusion while melt viscosity is low enough to produce a continuous stream of molten glass from the furnace. A furnace has the capacity to manufacture on average 50 t. soluble silicates per day.

The range of soluble silicates applications falls into three broad categories: chemical, detergent and adhesive. Dishwashing ingredients incorporate sodium silicate as a corrosion inhibitor and processing aid. They are offered as granular, powder or liquid products. Major manufacturers produce soluble silicates that contain only a minimum of impurities because these applications require extreme cleanliness. Sodium silicate is also consumed as a silica source for further chemical synthesis, in the production of zeolites, silica gels and geopolymers. As for the third group, soluble silicates act as adhesives in foundry industry.



Picture 8- Sodium silicate solution with MR=3.5 (Applichem, Germany)

Soluble silicates are combinations of water, SiO_2 and alkali metal oxide M_2O (where M=Li,K or Na). The chemical formula of soluble silicates is $xSiO_2:M_2O\cdot zH_2O$, x is the degree of polymerization while z denotes the water molecules. According to geopolymer terminology $(Na,K)\text{-}(Si\text{-}O\text{-}Si\text{-}O)_n$ is designated as (Na,K)-poly(siloxonate). The poly(siloxonates)-poly(silicates) are versatile reagents due to the fact that the degree of their polymerization can be easily modified and the presence or absence or absence (substituted by liquid,powder or granules) of water. Soluble silicates are mainly defined by the $SiO_2:M_2O$ ratio that industry standards impose to be the molar ratio and not the weight ratio (in some cases is also called “modulus”). Nevertheless, for sodium silicates there is a small difference between molar and weight ratio (molecular weights of Na2O and SiO2 are almost the same). Metal oxide M_2O and and silica SiO_2 cannot be combined in all proportions for practical reasons. Their solubility and the instability in ambient temperature define the range the MR which for commercial silicates falls into 0,4-4,0 (for sodium silicates).

Picture 9-Water glass from Bollerup-Jensen produced especially for the scope of the project (MR=1,3)

The focus on a user-friendly system but with sufficient alkaline environment made crucial for the that aspect of the research, the use of a K-silicate with MR ranging from 1,3-2,0. The commercially supplied potassium water glasses are on near 3.2 MR range making the use of KOH solutions mandatory. The use of K-silicate with that MR combined with water would rule out the use of any hydroxide rendering the process immediately user-friendly. Tests are programmed using different MR of K-slicate (diluting the new water glass with amounts of the water glass with 3,14 MR) but they will not be presented here due to report's delivery deadline.

2.2 Mix designs

Different mix designs were tested. The delivery of the slag and the addition of MS940 make it necessary to do numerous tests so as to have a representative idea of the effect of some procedure parameters.

2.2.1 Workability mix designs

The focus of this set of tests was to find a mixing design that has a UCS value of around 15 MPa (for 7 days of 90ºC curing) while being pumpable. To achieve this mix, we used a 1:1 (w/w) mixture of K-silicate (MR=3,14) based on recent research [5] conducted in the University of Stavanger, and and KOH solutions (4M and 6M was decided to be tested).

A decisive parameter for the pumpability of the slurries was having readings at 200 RPM at least was crucial (more about rheology on 3.2 chapter). The NaOH system was not tested thorougly as it is known to give more viscous overall results (the more the Na-silicate in the liquids stream the more viscous is expected to be [7]).

2.2.1.1 Fly-ash

For the set target as to workability a mix design with Liquid to Solid ratio (LSR) of almost 0,53 was achieved with 0,3 Water to Solids ratio (W/C). this procedure was time-consuming due to the absence of a necessary device for measuring either the consistency or the thickening time of the slurries. Added to that, fly-ashes from different batches were used since 350 mL of slurry were needed for the viscometer tests and the same raw materials were used by 3 people simultaneously. The different batches had same behavior except FFA 3 that possessed enhanced workability and was chosen for further testing.

0,53 was a bit much compared to recent studies with CFA (class C fly ash) [5]. The addition of microsilica was then decided.

2.2.1.2 Fly ash and microsilica

The addition of fly ash resulted in minimizing the the LSR to 0,45 and in the same time have an equally workable slurry. The substitution of FFA with MS940 in the fixed 0,45 ratio was found to be optimum at 20% w/w.

2.2.2 Optimum strength mix designs

The manufacture of a product that has limited application will hinder its commercialization and industrial acceptance. Therefore, a product that can sustain high stresses and or has high density (HPHT oil well cementing) with some additives or modification is desirable. Davidovits [7] has developed a system that provides good strength and is user friendly. Additionally, this system has better performance compared to OPC in high temperatures and in chemical attacks. For that system a blast furnace slag is used [7] as a vital reagent. Since the focus of the project was not to reproduce other researchers work it was decided to use the EAFS and investigate its performance. A recent study [48] with EAFS and OPC blended showed at 1:1 ratio in the solids stream resulted in the optimum results. Therefore, the same ratio was decided to be chosen for this research too.

Due to the absence of K-silicate with the desired MR range (1,3-2,0) tests were performed by either decreasing the KOH so as to have a maximum 20-30% (w/w) contribution in the liquid stream or with the same low amount water was used instead (pure GP method). A hybrid method similar to the one at 2.2.1.1 was tested too.

2.2.2.1 Conventional method

The conventional (known as zeolitic) method consists of attacking the fly ash structure with strong alkali solution so as to dissolve particles that will form the binder's matrix.

For this, only KOH or NaOH was used. For comparison, mixtures with pure FFA and pure EAFS at the solids stream were tested.

2.2.2.2 Geopolymerisation method

As mentioned in 2.2.2 for this method only 20-30% of KOH 6M (4M was excluded, since preliminary tests gave really low UCS values) was used, or water of the same amount, together with 80-70% K-silicate respectively.

2.2.2.3 Hybrid method

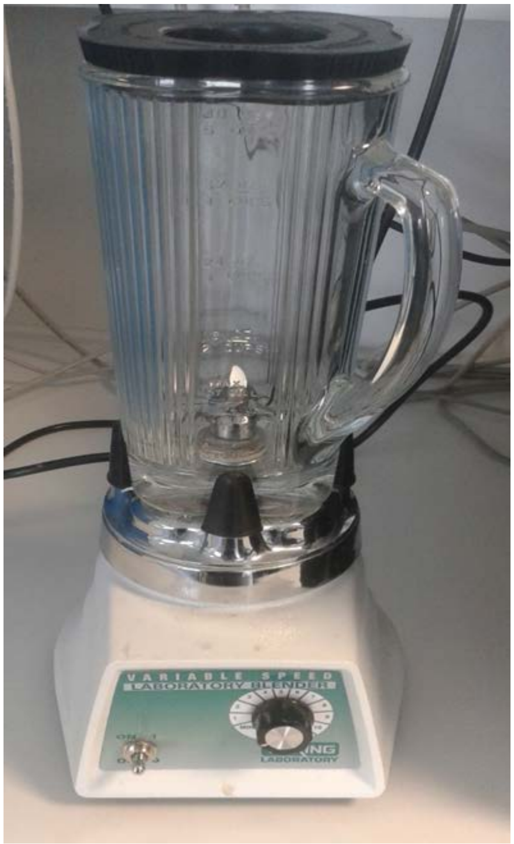
A hybrid method is a method to make ends meet. This is based on the amount of alkaline solution (KOH or NaOH) used that is chosen to be as moderste as possible (slurry remains workable with acceptable strength values) for a given soluble silicate (MR ratio is fixed). Similarly to 2.2.1.1 the solids (FFA, EAFS) were mixed with 1:1 (or nearly 1:1) soluble silicate/alkaline hydroxide ratio.

2.3 Preparation

2.4 Test method and analysis

The devices that were used for the tests:

- Mixers: 1 for primary mixing (see pic below) and 1 for homogenizing the slurry



Picture 10-Waring industries laboratory mixer

- Viscometer
- Ambient pressure oven
- Vicat needle apparatus
- Diamond cutter
- Universal test machine

- Differential Scanning Calorimeter

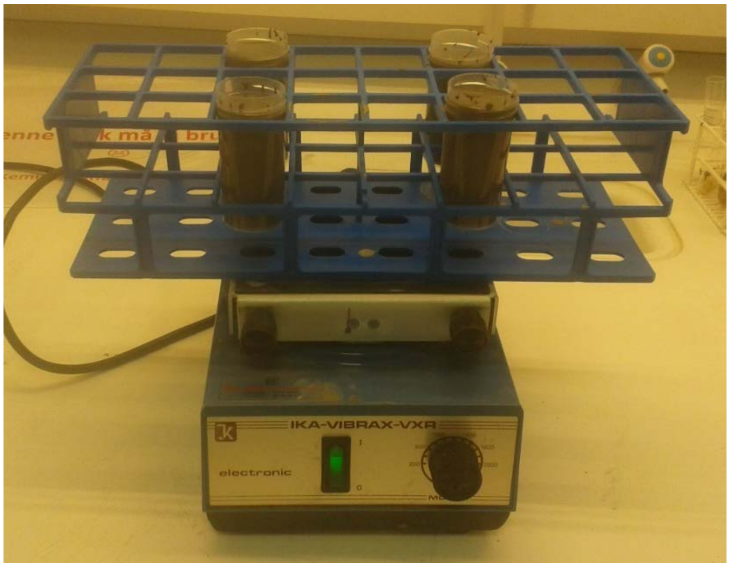
Picture 11-DSC that was used for the scope of the project

- X-Ray Diffractometer
- Furnace (for high temperatures)

As for the procedure it can be summarized at these steps:

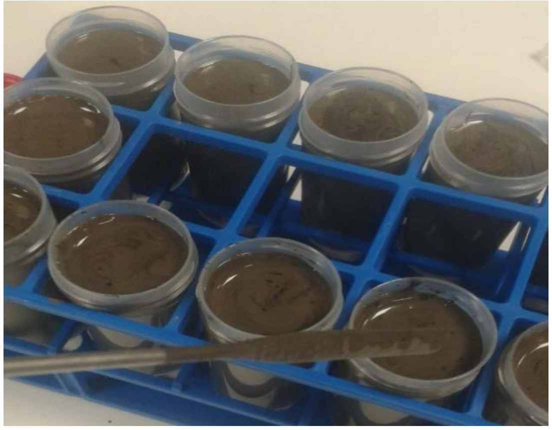
1. Preparation (if necessary) of KOH/NaOH solution in water (at least 2 days before the experiments). Alternatively, production of standard solutions for a large number of tests is more convenient.
2. Mixing the strong alkaline solution with the potassium/sodium silicate at least 1 day before the experiments).
3. Mix the different solids for 2-5 mins (depending on how fast the mixture is homogenized)
4. Put the required amount of hardener (soluble silicate and or strong alkali solution) to the mixer containing the solid.

5. Mix solid(s) with liquids at low speed (4000 rpm) for 15 seconds. Then for another 35 seconds at high speed (12000 rpm) according to standards [18]. Use of a spoon is mandatory to ensure full wettability of the solids (if necessary).
6. Slurry is put into a bigger mixer and mixed for 20 minutes in low speed (1500 rpm) so as the mixture is homogenized. Alternatively, if slurry is setting fast a vibrating table for 5 mins is used.



Picture 12-Vibrating table with GPC samples.

7. The slurry is put into the viscometer container and we start to measure. Or,
8. If no rheological property is needed to be defined, we cast the slurry to predefined number of molds. If slurry is too viscous then a rod assists in better placement in the mold. For the DSC tests a small amount is collected and put to the sample receiver immediately.



Picture 13-A rod is used to ensures better slurry compaction

9. Samples are cured at chosen temperature for X days' time (X=1 or 7).
10. After chosen curing time (no aging of samples), the samples are exposed to room temperature to cool down. It proved more effective to demold the samples immediately after getting them out of the oven (using a light plastic hammer to press the bottom or the cement sample out of the mild) instead of using the saw afterwards. The saw demolding solution proved detrimental for the samples integrity (especially at durability tests).

Picture 14-Demolding the samples with a saw (weak samples in danger of being damaged)

11. Samples are crushed 45 minutes after preparing them for the UCS test. Selected samples having the best strength (or with e.g. a unique feature like small or big pores) are stored in sealed containers until XRD or DSC is performed.

Chapter 3-Experimental results

3.1 Properties of binder

The density is a property that defines under which well conditions (mud density, fracture gradients etc.) as discussed in chapter 1. Fly-ash slurries gave values ranging from 1,8-1,95 SG for LSR between 0,45-0,53. The addition of the miscrosilica lowered the density to even 1,7 SG, while substitution of 50% by electric arc fly ash yielded even 2,3 SG (SLR ratio fixed to optimum 0,45) depending on potassium silicate amount and MR. Both situations were expected since microsilica is lighter than fly ash while slag is containing significant amounts of Fe_2O_3 (in the form of haematite Fe_2O_3 is a frequently used weighting agent in cementing industry [49]).

3.2 Rheological properties of slurry

At the initial stage of the project and due to absence of any device that could give us an idea about the setting time of the geopolymer cement intensive studies were performed to examine the rheological properties of different GPC mixing designs. The viscometer used was rotational type Fann 35A with R1-B1-F1 configuration [50] and apart from the stress versus strain behavior, the gel strength was measured for specific time increments .

Picture 15-Fann 35A. Dial reading is almost zero. Maximum reading value is 300.

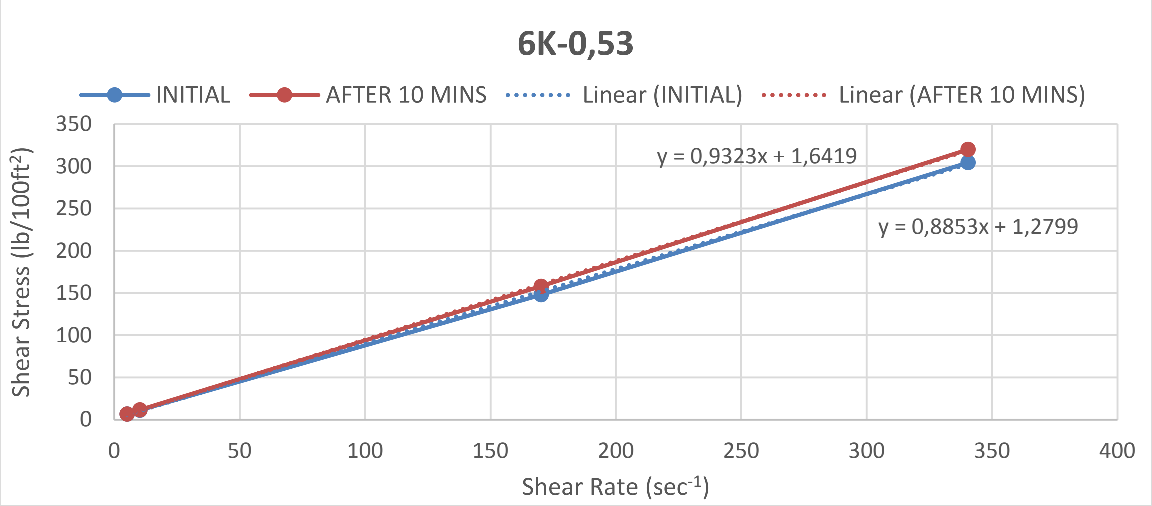


Figure 11-Rheological behavior of FFA (K-sil/KOH as hardener) with L/S=0,53

After numerous tries (only with FFA) the lowest L/S ratio (LSR) achieved was 0,53. As a hardener, the choice was a mixture of 1:1 (w/w) K-silicate (MR=3,14, Bollerup-Jensen Denmark) and KOH (pellets 98% purity, Merck, Germany) added in deionized water (mixture prepared at least 24h before so the mixture is settled and stabilized resulting in 6M solution)

θ								
RPM	INITIAL				10 mins			
	DOWN	UP	AVG	RATIO	DOWN	UP	AVG	RATIO
3	6,5	6,5	6,5	1	6,5	6,5	6,5	1
6	10,5	10,5	10,5	1	11	11	11	1
100	139,5	138	138,75	1,0109	149	147,5	148,25	1,010169
200	287	284	285,5	1,0106	300	300	300	1
300	n/a			Gel Strength (10 secs)				7
600				Gel Strength (10 mins)				9,5

Figure 12-Rheological data obtained by Fann 35A for FFA with LSR=0,52

The rheological data tables were made according to standards [18]. The LSR 0,45 gives a shear thinning slurry (see graph below). Apparent viscosity is shear stress to shear strain ratio for obtained for each shear strain increment.

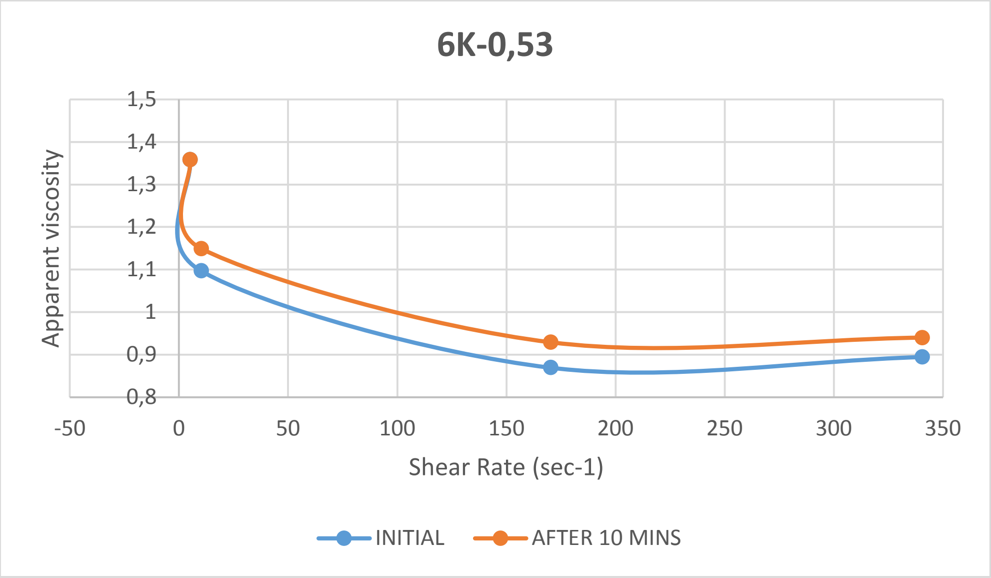


Figure 13-Shear thinning FFA slurry (decreasing apparent viscosity with increasing shear rate)

Shear thinning is a rather desirable property for drilling fluids. Viscosity will be relatively low at high shear rates prevailing in drill pipe and thereby reduce the pump pressure [51].

There are different rheological models for non-Newtonian fluids. For a Bingham plastic fluid model, the relationship between shear rate (γ) and shear stress (τ), is defined as a function of the two parameters YP (yield point) and PV (plastic viscosity) [52]:

$$\tau = YP + PV*\gamma$$

Equation 5

The clarification for all the slurries if they are fitting better to Bingham or Herschel-Bulkley rheological model

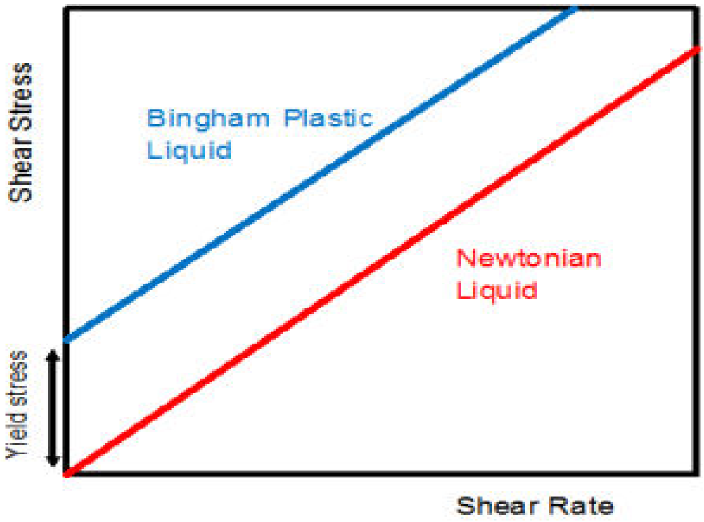


Figure 14- Newtonian and Bingham models typical rheographs

Adding the MS940 we were able to achieve a LSR 0,45. If it is not stated otherwise, this is the ratio that was fixed for all the mix designs as it gives good workability in most mix designs and more importantly is near (0,44) the OPC’s usual W/C ratio.

Table 5-Rheological data for FFA blend with 20% MS (0,45 LSR achieved)

RPM	INITIAL			
	DOWN	UP	RATIO	AVG
3	18	18	1	18
6	24	23	1,043478261	23,5
100	150	149	1,006711409	149,5
200	276	275	1,003636364	275,5
300	n/a	n/a	Gel Str. (10 secs)	15
600	n/a	n/a	Gel Str. (10 mins)	32

The rheogram of the new blend:

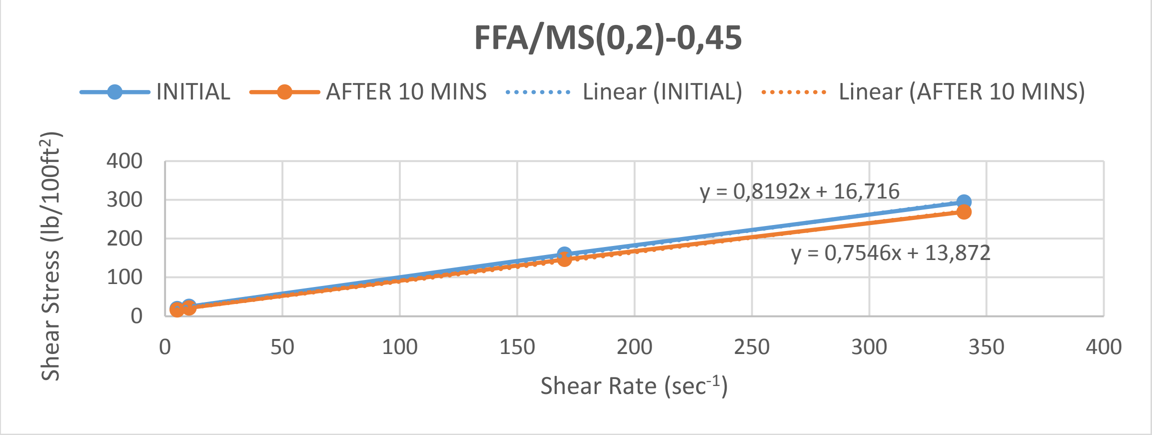


Figure 15-Rheogram indicates an increased deviation from Newtonian behavior (see the equations on graph)

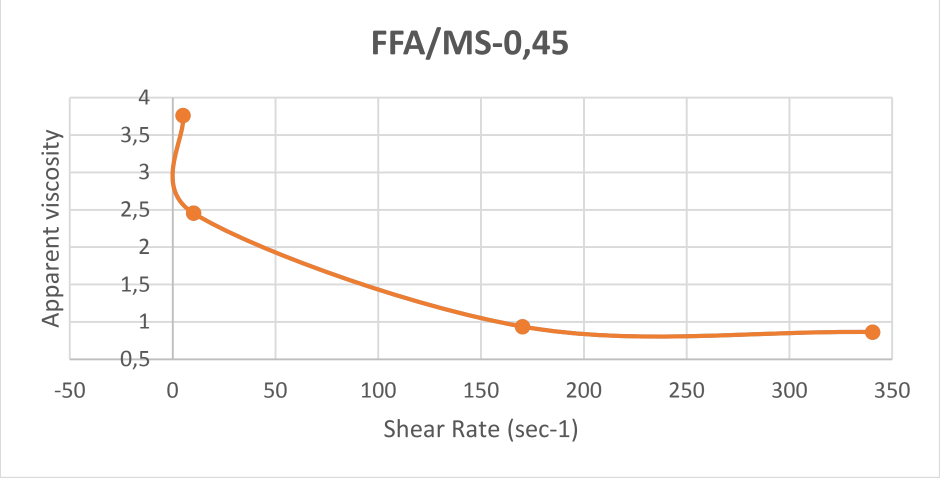
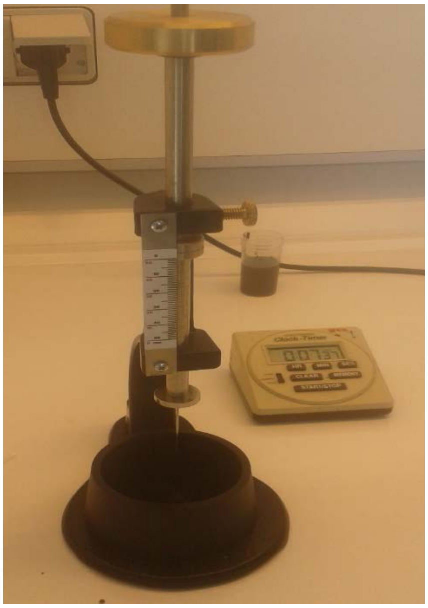


Figure 16-The new blend is still shear thinnin

3.3Vicat needle tests

In order to obtain valuable information as to how long is the produced slurry pumpable thickening time tests were performed in order to obtain the initial and final setting time of the GP slurry following the BS 196-3 standard. For hybrid method (only FFA and 51% NaOH solution with Na-silicate with MR around 3,4) and GPC method with K-sil (MR=1,3) 77,7% (remaining liquid is distilled water) slurries were prepared and tested.



Picture 16-Vicat needle apparatus with initial setting time needle on

The results of the tests can be seen in the table (it should be noted that for the test the EAFS 2 was used, smaller particle sized):

Mix design	*Initial setting time (mins)*	*Final setting time (mins)*
Hybrid	40	46
Geopolymeric	38	58

These are results obtained for slurries maintained at 90°C after casting them into the plastic molds and during the whole test time. The values obtained at ambient temperature (23°C) are totally different. The geopolymeric method-obtained cement has 214 minutes initial setting time and 330 minutes final setting time. This is the proof of geopolymers (when using actual GP method and not just alkalination) can set at room temperature without the need for any heat treatment so as to speed up the setting process.

3.4 Uniaxial Compressive Tests

All the containers used for samples were cylindrical (not perfect cylinder though) with 60 mm height and 30 mm diameter. The tests were conducted in the Material lab of Aalborg University in Esbjerg using the universal test machine LR50K (Lloyd instruments) using a loading speed of 10mm/min.

As a reference in all the tests (acting as controller), samples of OPC were prepared with the identical mixing procedure, curing conditions and exposed to exactly the same conditions as the GPC samples. In this manner, the comparison between OPC and GPC can be more reliable and tangible. In the next 3 graphs the behavior of OPC under different condition is depicted.

3.4.1 Conventional method

Batch	Stress at Maximum Load (MPa)
FFA-100%KOH-1d	5,175453713
FFA-100%KOH-7d	13,12187543

Table 6-UCS buildup of FFA without any use of soluble silicate present in the mix

3.4.2 GPC method

Batch	Stress at Maximum Load (MPa)
FFA-20%KOH-1d	13,28943927
FFA-20%KOH-7d	29,12828992
FFA-30%KOH-7d	29,50575576

Table 7- Strength development of mixture with the least impossible amount of KOH (going lower than 20% endangers workability and yields less UCS due to viscosity-induced bad compaction)

3.4.3 Hybrid method

Batch	Stress at Maximum Load (MPa)
00.45-7d	22,82622862

Using 1:1 KOH 6M with K-silicate only with FFA in the mixture gives after 7 days an intermediate result between the three methods (13 and 28,5 MPa were the values obtained form the other methods)

3.5 Durability tests

Due to minimum time available it was decided after researching popular practice from other researchers [48], [53]–[60] to do some accelerated chemical attack tests and also expose a batch of samples to be compared in 400ºC (is not to simulate a real well condition but rather to investigate the long term integrity). Therefore, the samples were cured at least 1 day in 90ºC then demolded and exposed to the selected attack on glass containers. As controller samples of OPC were also exposed to same conditions

3.5.1 Boiling water

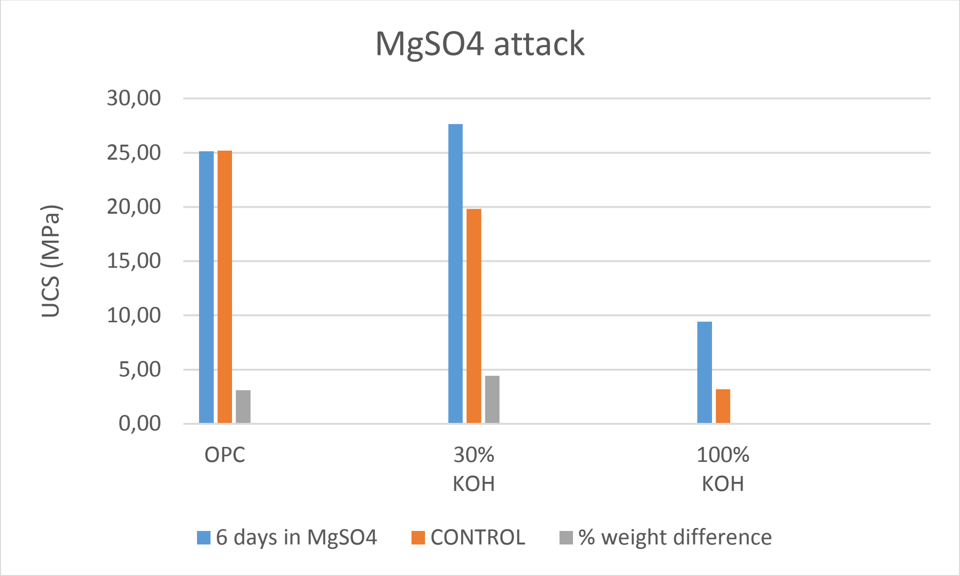
Non-fully condensed GP materials are sensitive to water and even show swelling behavior, or even they are destroyed. One of the tests to determine the quality of the GP produced is exposing it to boiling water for 20 minutes. The produced GP material during this process was intact for over an hour. Only blends with low or no hydroxide were tested.

Picture 17-Boiling GPC sample for 1 hour to test long-term durability

3.5.2 Sulfate attack

For this attack mixtures of 1:1 FFa and EAFS were tested and compared with OPC (mixtures had the conventional 100% KOH (always 6M) and 30% KOH (the remaining liquid is K-silicate). As it was expected OPC (that is High Sulfate Resistant Classified) was able to maintain most of its strength (comparison with control samples). The samples were attacked by MgSO4 as it is the most dangerous or all sulfates according to bibliography.

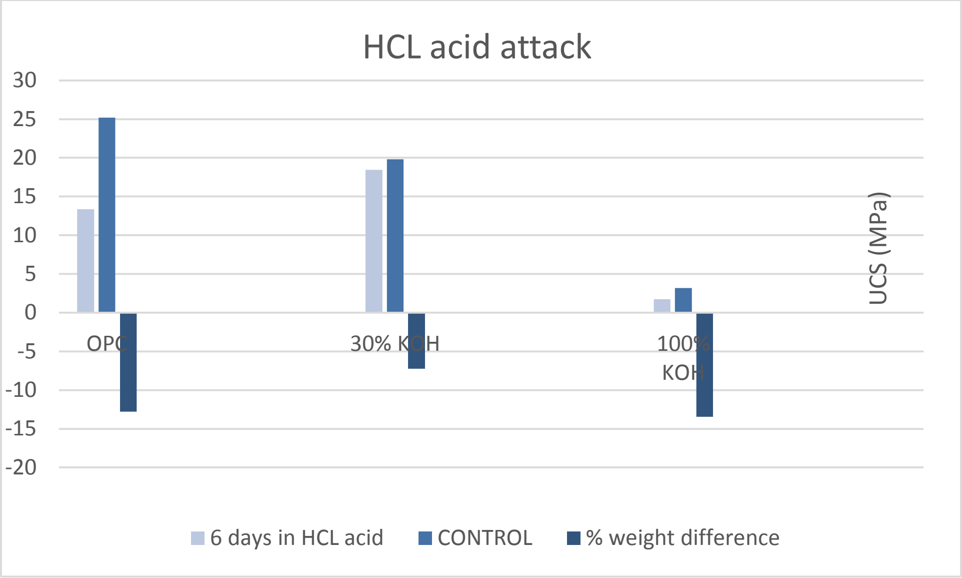
Picture 18-Surface deterioration of OPC after sulfate attack ($MgSO_4$).



Picture 19-Different cement samples after exposure to $MgSO_4$

3.5.3 HCL acid attack

Picture 20-Samples after HCL acid attack

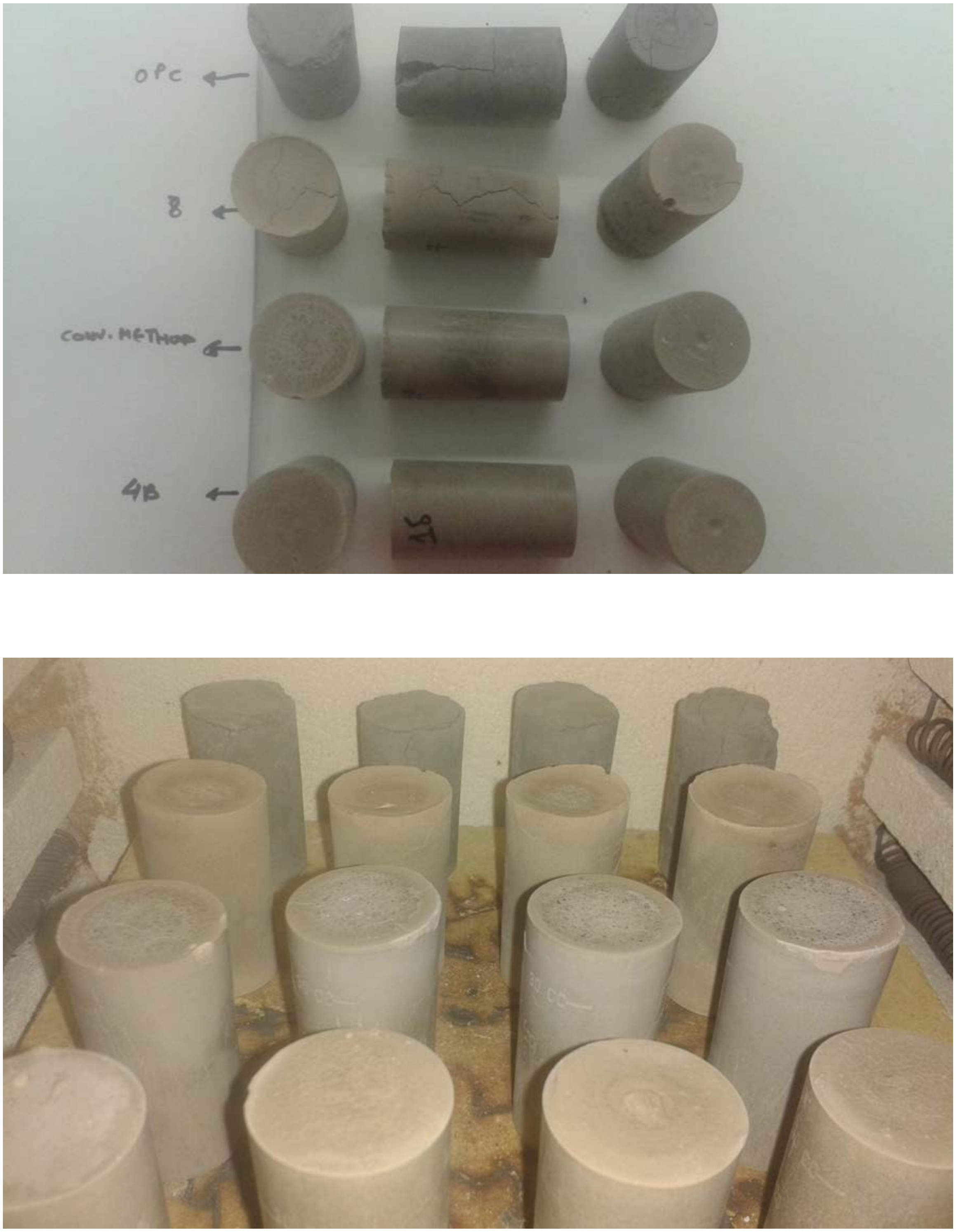


3.5.4 Sulfuric acid attack

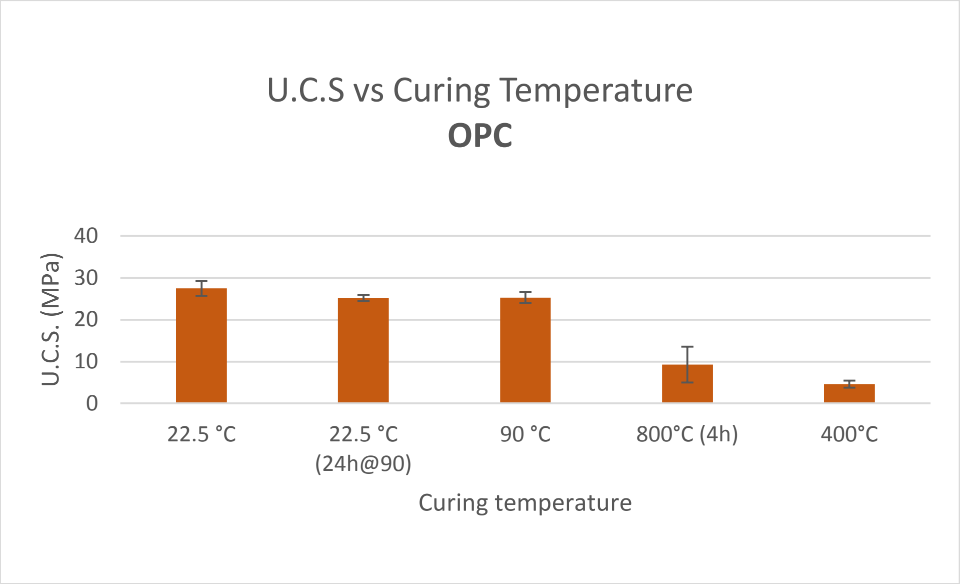
Due to improper mixing this batch of GPC was removed carelessly from molds and destroyed some of them. Therefore, the results were taken from not intact samples and therefore will not be presented.

Picture 21-Samples after attack with 40% sulfuric acid

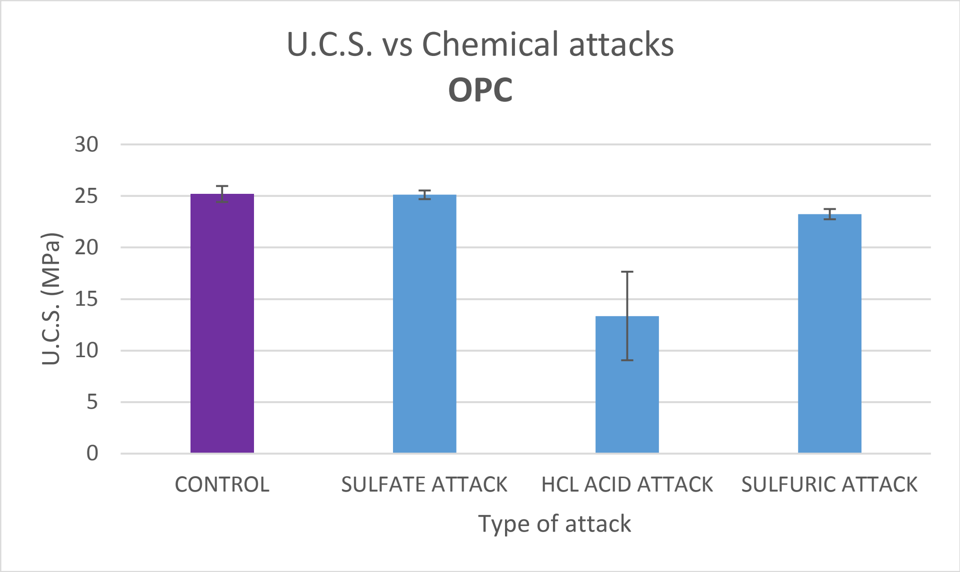
3.5.5 High Temperature exposure (400ºC)



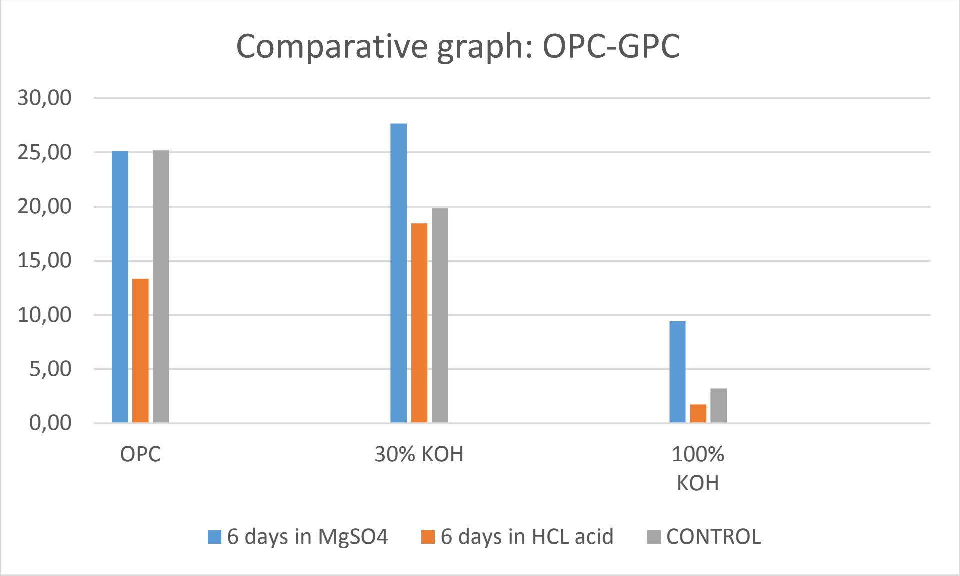
Picture 22-Samples after curing for 6 days at 400ºC (1 day before were cured at 90oC).



For OPC the effect of the Temperarure increase can be seen in the picture above. OPC overall performance



And comparison with the GP products :



After 90 degrees Celsius OPC deteriorates. In comparison GPC maintained (except the conventional method ones) the loss of UCS near 30%.

3.6 Differential Scanning Calorimetry analysis

It has been obeserved [7], that stabilization of GP towards heat treatment occurs after shrinkage and dehydration. Therefore, the GP products follow reversible heat expansion and, due to shrinkage, irreversible shrinkage. The following figure illustrates this feature that has is identical to ceramics behaviour. Also, it is proven [61] that the coefficient of thermal expansion for geopolymers with Si:Al ratio of 2 is matching the one of ceramics. This is very important for the comparison between the OPC and GPC system when they are exposed in high temperatures.

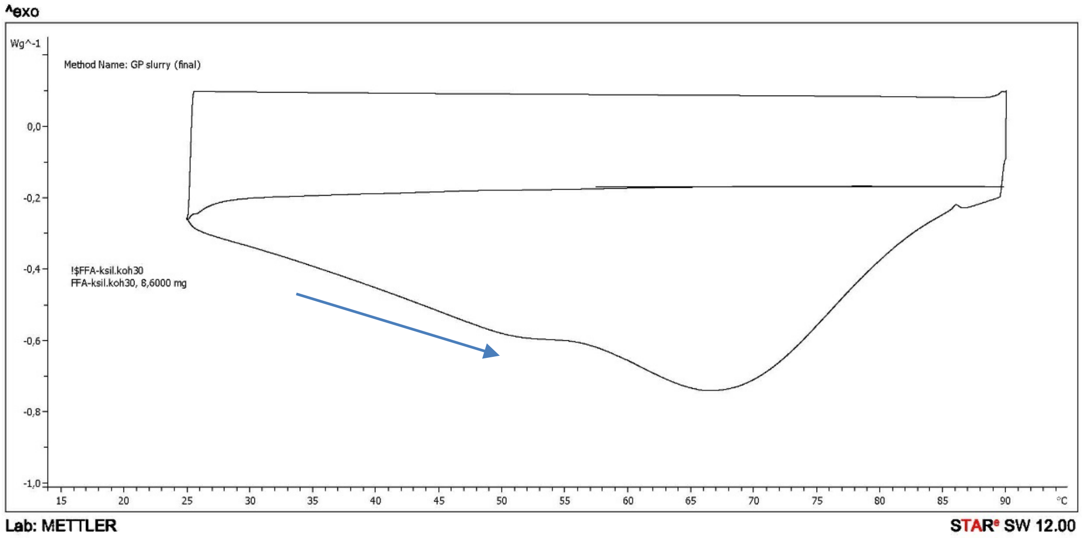


Figure 17-DSC with first and second heating on FFA-Ksil(70%)/KOH 6M (30%).

The broad endothermic pic is due to chemically bonded water evaporation. After reaching 90^{o}C the sample is cooled to 25 ^{o}C, and has no longer have an endothermic phase during second heating. Therefore, the curve becomes monotone and flat.

3.7 X-ray Diffraction analysis

The use of XRD is very important to determine the phases of fly-ash, microsilica and slag and observe if they are amorphous or not [62], [63]. Crystallinity is not a welcomed aspect of a aluminosilicate and for fly ashes under the conventional production regime (zeolitic method), the main crystalline phase (mullite) must be under 5% [36]. To obtain that kind of information is achievable using advanced techniques like quantitative XRD analysis [63]. The latter requires much analysis and is beyond the scope of this project. Nevertheless, if FFA cement is produced with the GP method then high UCS values can be obtained even with over 15% of mullite in the FFA according to European Research Project GEOASH [40].

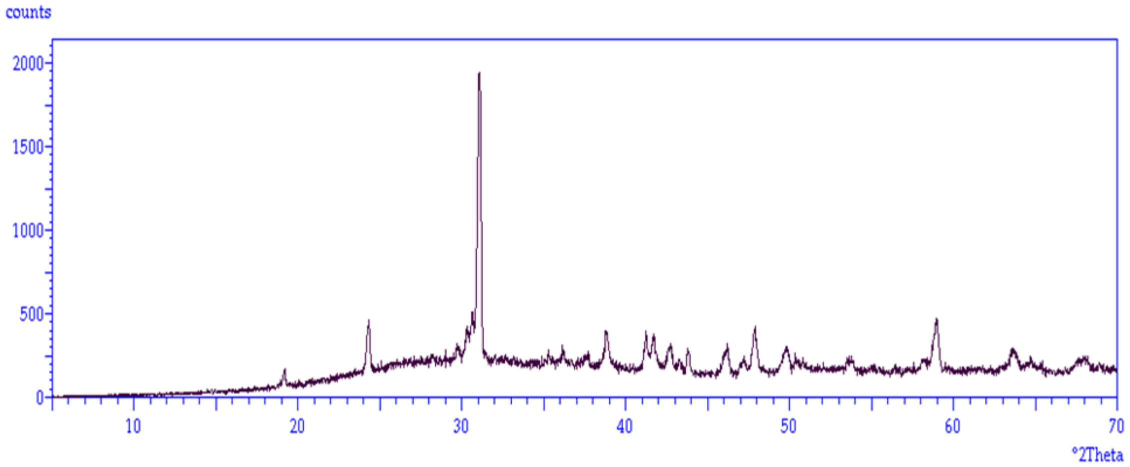


Figure 18-FFA 2 analysis.

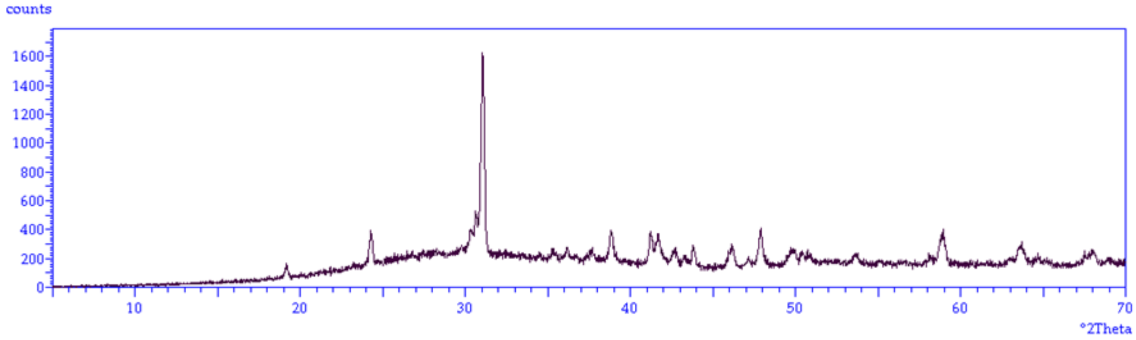


Figure 19-FFA 3 analysis (the peak is less intense then in FFA 2)

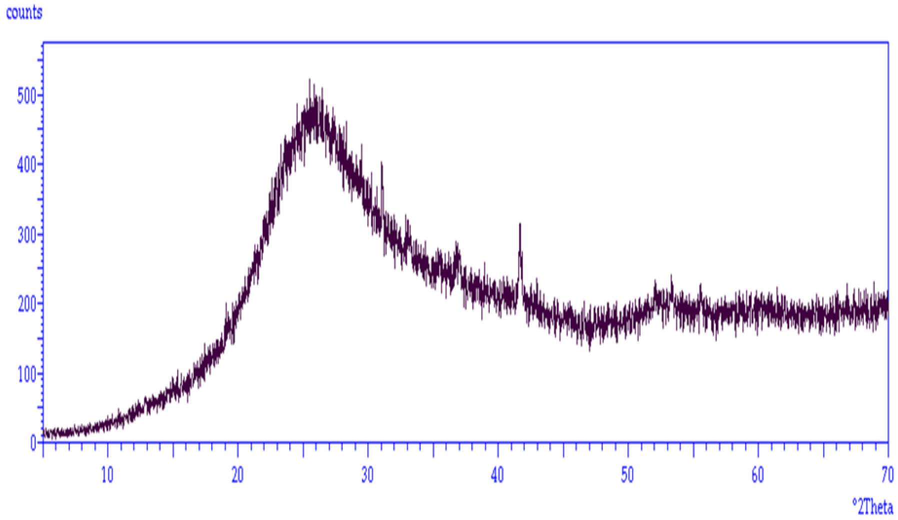


Figure 20-Microsilica graph with the typical round hump for MS around 35º

3.8 pH measurements

The pH of both the powders that were used and the cured samples was measured. For the cured cement samples, it was mandatory to be crushed and milled to have a uniformly to powder size. 5 g of each powder/cement was mixed with 50 mL deionized water [5], [61]and rigorously mixed so as to dissolve as much solid as possible.

Picture 23-phmeter that was used for the measurements

Additionally, and for comparison between the different alkaline setups during the experiments, the pH of hydroxides and soluble silicates was measured. PHM210 phmeter (picture above) was employed and the solutions were tested after 1,10 minutes and 1 hour after mixing with the water. The results can be visualized below.

Batch	pH (5 mins)
GP method (30% H2O)	11,17
Zeolitic method(Na)	12,04
OPC	12,48
FFA-Ksil/KOH(1:1)-0,53 LSR	11,37
FFA(2)-Ksil/KOH(1:1)	11,28
FFA(3)-Ksil/KOH(1:1)	11,5
Hybrid method (Na)-0,40 LSR	11,83
FFA-SLAG-Zeolitic (K)	11,86

For the powders and solutions, the results are:

Batch	pH		
	5 mins	10 mins	60 mins
FFA 2	10,99	10,87	10,87
FFA 3	11,19	11,13	11,11
FFA 4	11,29	11,25	11,17
EAFS	11,04	10,98	10,86
MK-501	5,26		5,56
MS-940	8,5	8,43	8,4
KOH (6M)	14,79		
NaOH (12M)	13,7		
K-silicate (MR=3,14)	12		
Na-silicate (MR=3,4)	11,21		
KOH (6M)/K-sil=1:1	14,14		

One observation was that from all the powders FFA 3 changed its pH the least (0,7%).

Chapter 4- Discussion

4.1 Amount of alkaline solution effect (NaOH/KOH)

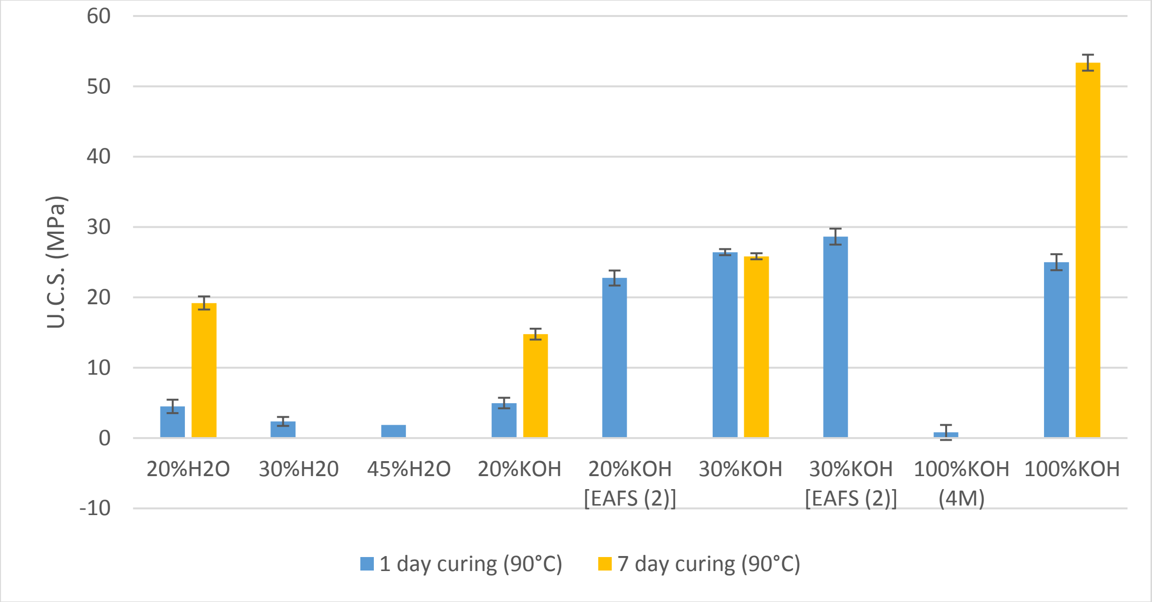


Figure 21-Effect of alkalinity in the EAFS/FFA=1:1 mixing design

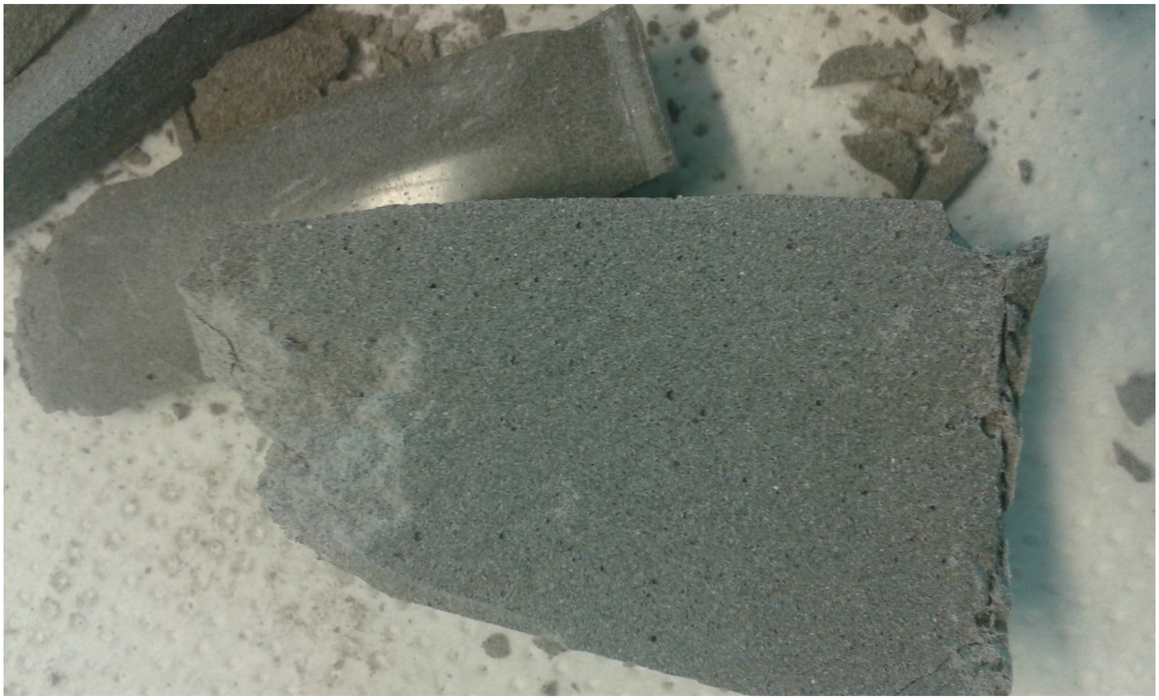
In figure 10, it is clear that substituting 20% of KOH solution (in the liquids mixture that contains 80% K-silicate) yields better 7-day strength. Adding more water (decreasing K-silicate contributions to 70%) gives a more workable mixture but less early strength. Therefore, it seems for a soluble silicate with fixed MR the optimum percentage of water addition is between 20 and 30%. Also, 4M KOH gives significantly less UCS. Increasing the amount of KOH from 20% to 30% gives even better strength results. It seems that strength is proportional to the amount of strong alkali present and that is in line with the findings for NaOH solutions[56],[64],[7]. Also striking is the fact that new EAFS (85%<63 μm), having thinner particles compared to the old (85%<300 μm) yields better strength even at the early stage of curing.

4.2 Effect of microsilica

Batch	Stress at Maximum Load (MPa)
6k-20.45-1d	6,798998626
6k-20.45-7d	14,38966

The addition of MS may have increased only a little the UCS but we were able to have a more workable mixture with 0,45 LSR

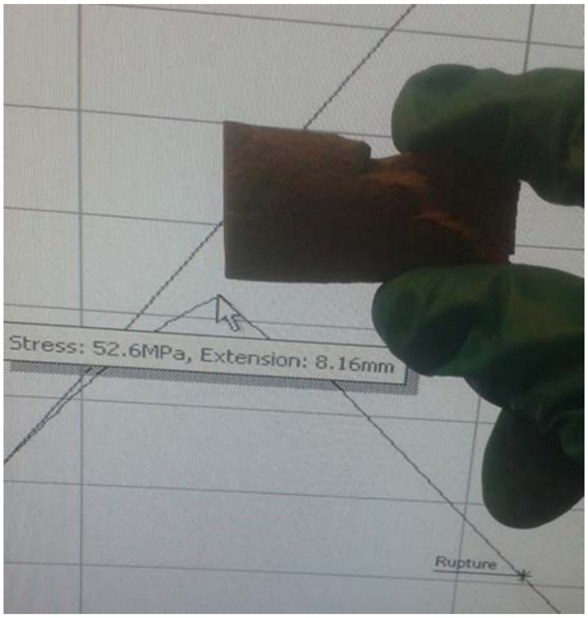
4.3 Effect of EAFS



Picture 24-Structure of a crushed sample with FFA, KOH 6M and K-sil.

A mixture of aluminosilicate oxide, slag and alkalis KOH,NaOH does not make the mixture to harden. NaOH and KOH are regulators of the setting but not the hardening of the binders [7].

This is proven from the results of the current project. What was also confirmed is that the unreacted silicates (not geopolymerized) or those that did not transform into weakly basic calcium silicate, will hydrate according to the C-S-H mechanism known by OPC system [7].



Picture 25- Samples from the mixing design that gave the highest UCS value;over 53 MPa was measured

These hydrates are known to be very sensitive to acid leaching.

Picture 26-Effect of smaller particle size of EAFS (no pores visible)

Picture 27- Pores are present despite the lowered amount of KOH (30% w/w)

Chapter 5-Conclusion and final remarks

Even after the results some conclusions were made regarding the fly ash-based binders.

After the completion of 80% of the tests (that is until the day of the report was concluded) is needed to summarise the following:

- Fly ash class F is not a filler material for OPC, not to mention that does not need activation. It is an inexpensive material with that can produce quality cement with better characteristics than OPC when it comes to HPHT environment and acid attacks.
- For the best results one needs to have done a thorough research about the chemistry and morphology of the GPC system. More research is required to identify the GPC forming

mechanisms when adding to the blends materials like EAFS that is not tested as much as MK-750 and Blast Furnace Slag.

- The dispersion of materials from different sources/processes renders the efforts for a standard GPC difficult, however the GPC formed by industrial waste is here stay (India and China are huge producers of fly-ash while being also the countries with high needs for cement material).
- The CO_2 emissions reduction percentage during the manufacture of GPC is debatable. Fly ash is produced in power units that actually produce CO_2.Also, EAFS is a by-product of high energy consumption process. Therefore, for the time being GPC is just the most efficient way to manage industrial waste and is not a pure “green” solution.
- GPC has the potential to be a real “green” solution if geological material is added in as raw material for the and also, if the research on volcanic tuffs manages to substitute alkaline solution that are currently used for the method [7].

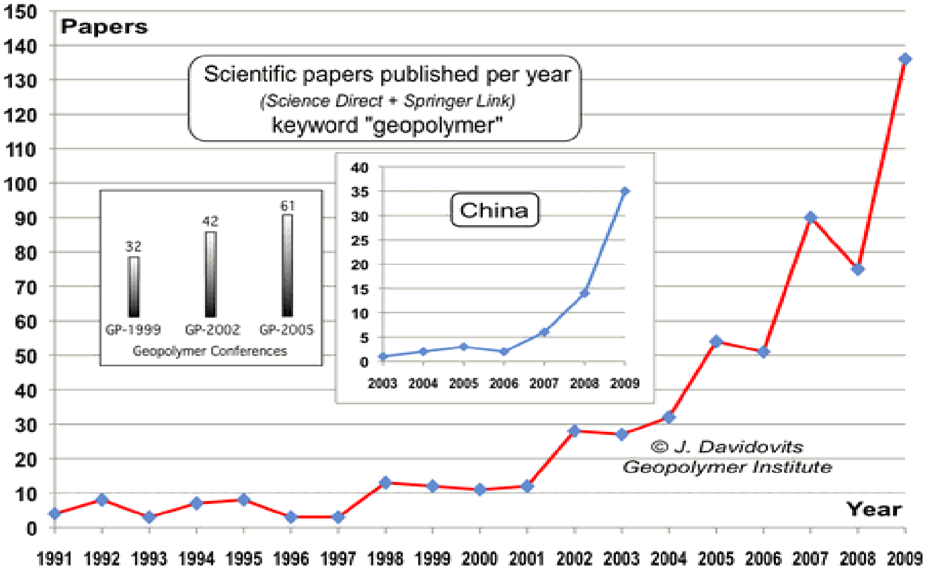


Figure 22- The research on GP materials is rapidly increasing

More specifically concerning the current project:

- Since durability tests are vital for the quality control of the product, a new set is being conducted with K-silicate (MR=1,3) to verify its superiority (or not) over system using hydroxide alkalination.
- FFA is a versatile material producing various densities of slurry ranging from 1,85 (adding MS940) to 2,2 (adding EAFS) while remaining in acceptable range of strength.
- The application of the conventional method to well cementing seems favorable. The method needs heat to increase the rate of dissolution which is given by the BHCT itself.
- However, it proved the method that produced the weakest products when it was tested for chemical attacks.

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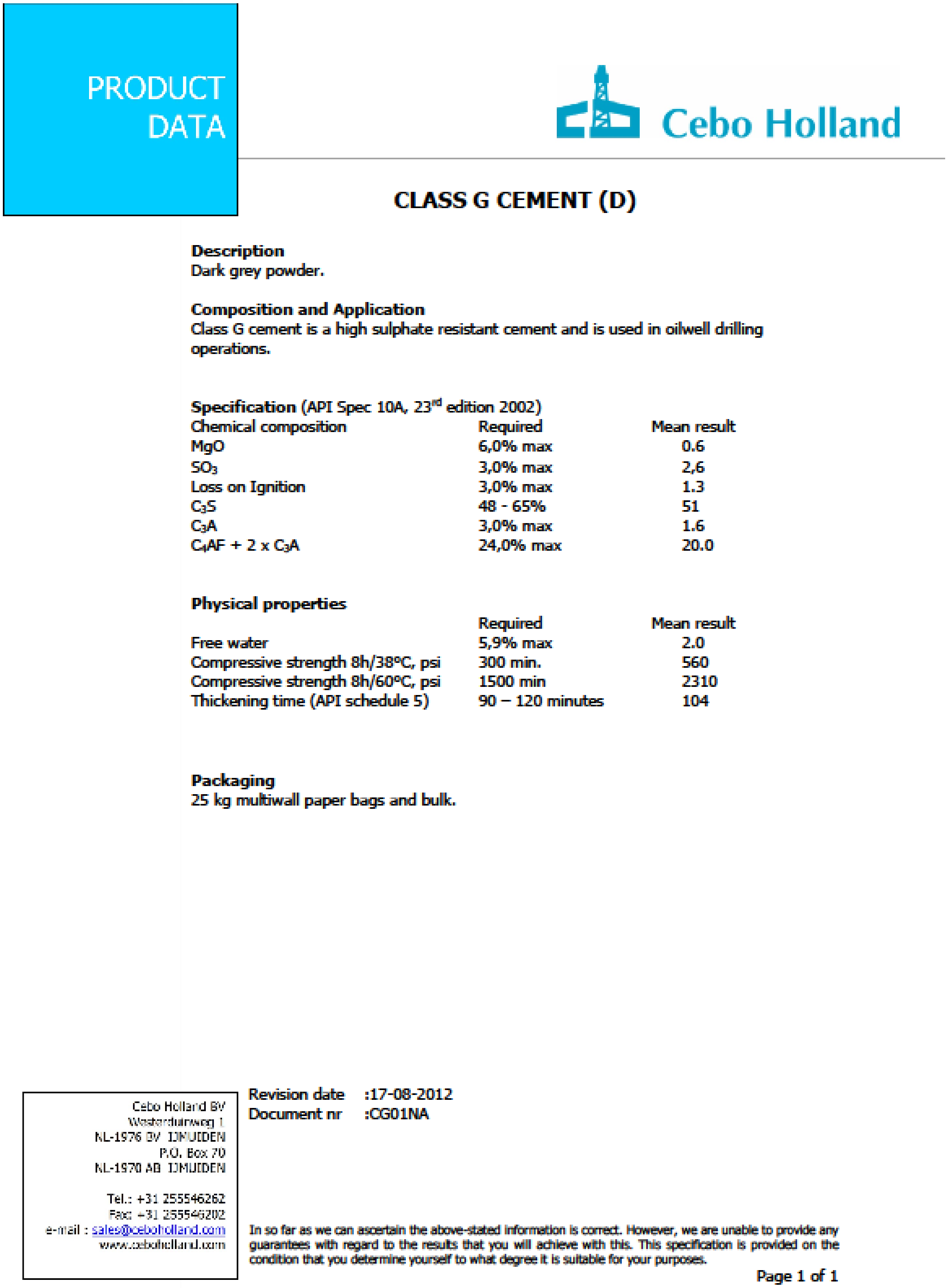
Appendix A

Chemical analysis



PRODUCT
DATA

Cebo Holland

CLASS G CEMENT (D)

Description
Dark grey powder.

Composition and Application
Class G cement is a high sulphate resistant cement and is used in oilwell drilling operations.

Specification (API Spec 10A, 23rd edition 2002)

Chemical composition	Required	Mean result
MgO	6,0% max	0.6
SO_3	3,0% max	2,6
Loss on Ignition	3,0% max	1.3
C_3S	48 - 65%	51
C_3A	3,0% max	1.6
$C_4AF + 2 \times C_3A$	24,0% max	20.0

Physical properties

	Required	Mean result
Free water	5,9% max	2.0
Compressive strength 8h/38ºC, psi	300 min.	560
Compressive strength 8h/60ºC, psi	1500 min	2310
Thickening time (API schedule 5)	90 – 120 minutes	104

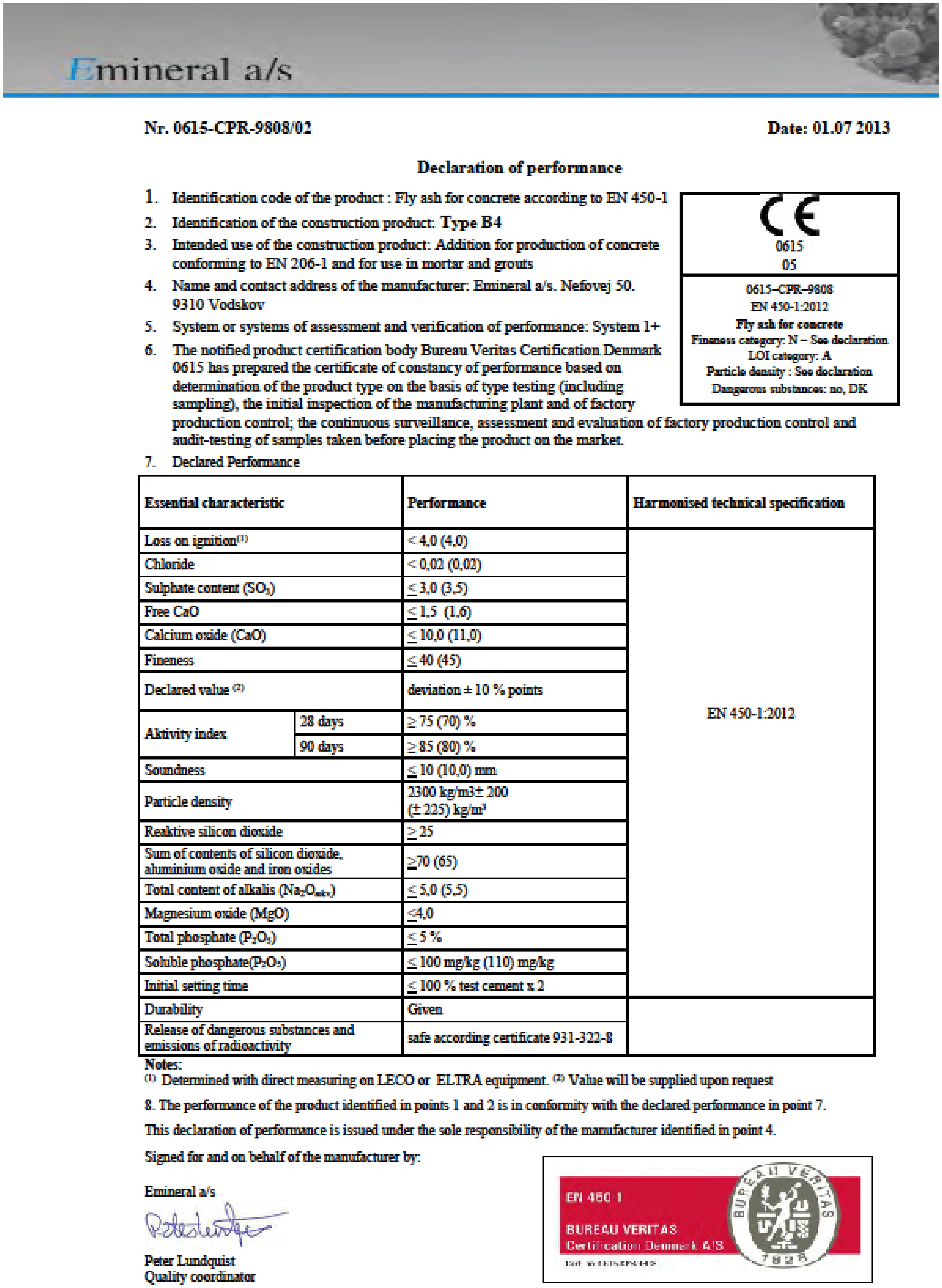
Packaging
25 kg multiwall paper bags and bulk.

Cebo Holland BV
Westerduinweg 1
NL-1976 BV IJMUIDEN
P.O. Box 70
NL-1970 AB IJMUIDEN

Tel.: +31 255546262
Fax: +31 255546202
e-mail : sales@cebohollland.com
www.cebohollland.com

Revision date :17-08-2012
Document nr :CG01NA

In so far as we can ascertain the above-stated information is correct. However, we are unable to provide any guarantees with regard to the results that you will achieve with this. This specification is provided on the condition that you determine yourself to what degree it is suitable for your purposes.



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)	EN 450-1:2012
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) %	
	90 days	≥ 85 (80) %	
Soundness		≤ 10 (10,0) mm	
Particle density		2300 kg/m3± 200 (± 225) kg/m^3	
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

APPEndix B-Miscellaneous graphs,pics

Picture 24-Failure pattern of mix design for GPC with NaOH 30% (cured at 7 days@90oC)

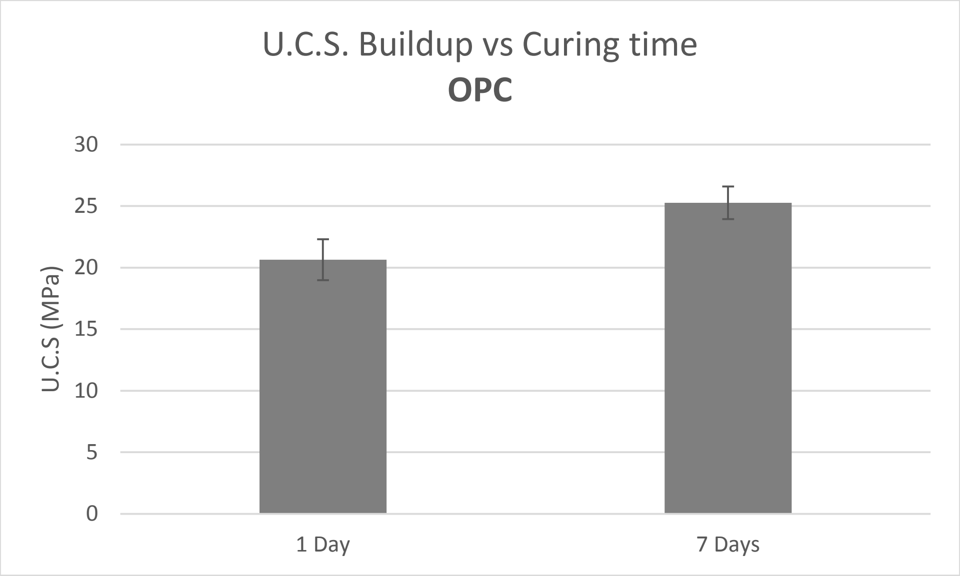


Figure 23-OPC strength buildup

Elastic behavior of sample