FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

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Experimental studies: Formulation of a New Geopolymer and Investigation of Effect of Nanoparticles

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Sodium hydroxide	Rheology	

Abstract

Well integrity survey from the Norwegian Continental Shelf (NCS) indicated that out of the 75 production and injection wells, cement recorded about 11% integrity issue. According to the NORSOK D-10 requirement for cement properties, the conventional Portland cement does not fulfil all the criteria. Integrity issues associated with cement is also documented in other parts of the word. In recent years, there has been a high focus on searching a cost-effective and reliable alternative material to the Portland cement as a well barrier. The application of geopolymers is one of the best candidates that is attracting the oil and gas industry. However, the work is still under research and development phases.

In this thesis work, during the first phase of the project, with the considered screening and qualifying criteria, three new geopolymer mixtures were formulated and characterized. During the second phase of the research, the effect of titanium oxide (TiO_2) and –COOH functionalized multi-walled-carbon-nanotube (MWCNT-COOH) on the neat geopolymers were investigated. Furthermore, the neat -and nanoparticle treated geopolymer were compared with Portland class G cement. The alkaline activator for the geopolymer consisted of 10M NaOH along with a home-made synthesized sodium metasilicate liquid made with different concentrations of (45.1%, milky color), (30%, clear color) and (45.1%, clear color). Moreover, a commercial sodium silicate solution was tested.

The application of the neat geopolymer to be utilized for **construction** and **oil well cementing** is based on the pumpability of the slurry and strength development. All the plugs cured at 62^{o}C and room pressure. The slurries were mixed by hand, which comprised of a lot of air. Despite these worst-case conditions of the geopolymers formulated in this thesis work, the results obtained are interesting and satisfactory. However, by reducing the uncertainties associated with the geopolymer slurry mixing, the author feels that even more improved results can be achieved. Moreover, the effect of TiO_2 and MWCNT-COOH nanoparticles solutions showed both positive and negative impacts on the mechanical and elastic properties of the neat geopolymers. The optimum and positive synergy of the nanoparticles with geopolymer were determined from the considered experimental condition.

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Thank you to Samdar Kakay for allowing me to use the UCS machines in the construction lab and showing me how to use them.

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A = cross sectional area (m^2)

E = Young’s modulus (GPa)

F_{max} = peak force load (kN)

G = shear modulus (GPa)

L= length (m)

K = bulk modulus (GPa)

M= modulus of elasticity (GPa)

M = mass (kg)

M_t = mass at time t (kg)

M_{t+1} = mass at time t+1 (kg)

RPM = rotations per minute

P = pressure (MPa)

OD = outer diameter (mm)

t = travel time (s)

T = temperature (°C)

v_p = P-wave velocity (m/s)

V = volume (m^3)

σ = stress (N/m^2)

ε = strain

ρ = density (kg/m^3)

ΔL = change in length (m)

ΔM =mass change (kg)

wt% = weight percentage

°C = degrees Celsius

θ_{300} = 300RPM dial reading

List of Abbreviations

API	American Petroleum Institute
CCS	Carbon capture storage
FA	Fly ash
HPHT	High temperature/high pressure
MWCNT-COOH	Multi-walled-carbon-nanotube with COOH-group
NaOH	Sodium hydroxide
Na_2SiO_3	Homemade sodium metasilicate liquid
NCS	Norwegian Continental Shelf
NORSOK	Norsk Sokkels Konkurranseposisjon
P&A	Plug and Abandonment
SF	Silica fume
SCP	Sustaining Casing Pressure
std.	Standard deviation
TiO_2	Titanium dioxide
UCS	Uniaxial compressive strength
WCR	Water cement ratio

1 Introduction

This thesis presents a new geopolymer formulation and characterization. The experimental works were categorized into two main parts. The first phase deals with the formulation of a novel geopolymer mixture based on homemade sodium metasilicate liquid. The second phase presents the effect of TiO_2 and MWCNT-COOH nanoparticle solutions on the three neat geopolymer systems formulated in phase one. The specimens were cured for 3 -and 10 days at 62^{o}C temperature.

The process of the geopolymer formulation, characterization and screening as pass/fail criteria were defined through several parameters:

- The design hypothesis, formulation of mixtures, and molding of plugs.
- Viscometer: the workability of the slurry to pass/fail the formulation.
- Visual inspection: geopolymer slurry and the physical makeup of the plugs after curing.
- Sonic: the travel time to quantify the elastic and physical parameters.
- Water absorption: the internal pore structure intensity and interconnections.
- Mechanical tests: to obtain uniaxial compressive strength and Young's modulus

1.1 Background

Oil well cementing and integrity

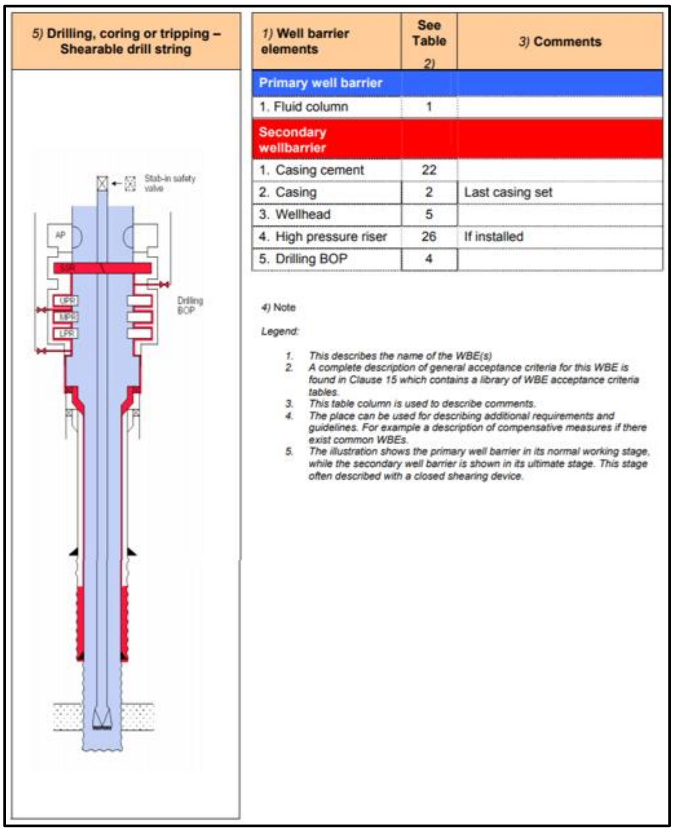
Cementing the wellbore is a necessary part of achieving integrity of a drilled petroleum well. The fundamental purpose of the cement is to create an impermeable seal and to zone isolate the rock formation from the wellbore, and prevent any fluid migration during the whole life of the well [1]. The cement is pumped downhole through the casing before it flows up the annuli. The cement slurry then hardens and binds to the casing and formation. The cement column acts as a safety well barrier by providing hydrostatic pressure to cope with pore pressure, acting as an impermeable seal, and by giving a corrosive barrier for the casing. There are two major wellbore cementing operations; primary and remedial cementing. Primary cementing is part of cementing the casing in place after each section is drilled. Remedial cementing can be performed with squeeze cementing with the action of trying to fix the primary cement, if e.g., microcracks have occurred in the cement so that gas can migrate up the annulus. Remedial cement can also be used to plug and abandon (P&A) wells that no longer have economical production, plug a pilot hole before side-tracking in terms of directional drilling, for lost circulation control, or formation testing.

NORSOK D-010 Standard

All petroleum wells in the North Sea must have at least two independent safety barrier envelopes, according to NORSOK D-010 (2013) and Oil & Gas UK (2015) safety regulations [2], [3], [4]. Depending on the well operation, the cement can act both as a secondary and/or primary well barrier. For example, during conventional drilling operations (Figure 1.1), the hydrostatic mud column acts as primary well barrier, and the casing cement column as one of several secondary barriers. For permanent P&A operation of a perforated well (Figure 1.2), both the liner cement and cement plug provide the primary well barrier, while the casing cement and casing plug give the secondary barrier.

For all petroleum well cementing operations, the cement slurry and the cement job quality are the two main factors for long-term integrity of the wellbore. Well integrity is defined by NORSOK D-010 as "*application of technical, operational and organizational solutions to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well*" [2, p. 4]. For this, NORSOK D-010 Standard also set a criteria for cement to have properties such as [2, p. 63]:

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



5) Drilling, coring or tripping – Shearable drill string

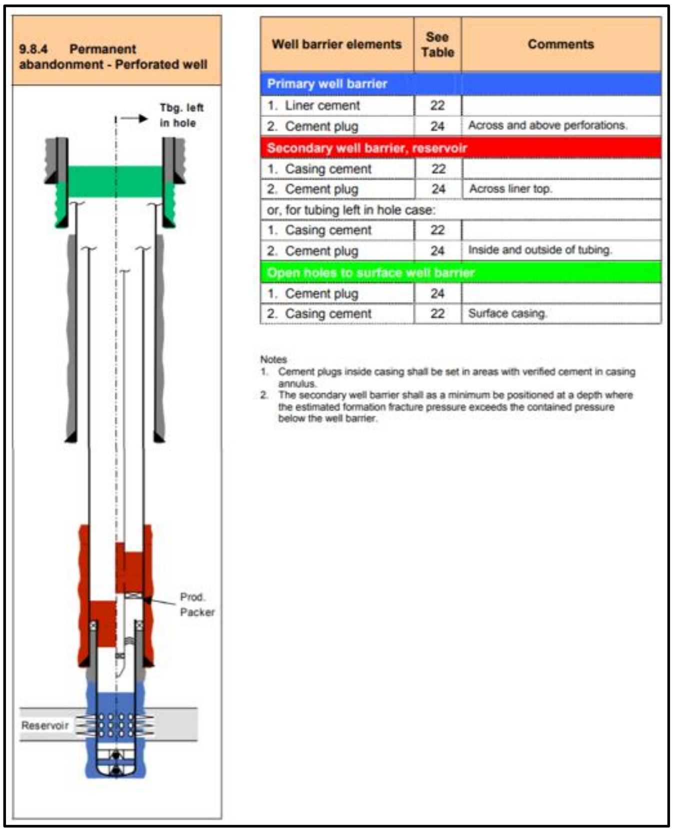
1) Well barrier elements	See Table 2)	3) Comments
Primary well barrier		
1. Fluid column	1	
Secondary wellbarrier		
1. Casing cement	22	
2. Casing	2	Last casing set
3. Wellhead	5	
4. High pressure riser	26	If installed
5. Drilling BOP	4	

4) Note

Legend:

1. *This describes the name of the WBE(s)*
2. *A complete description of general acceptance criteria for this WBE is found in Clause 15 which contains a library of WBE acceptance criteria tables.*
3. *This table column is used to describe comments.*
4. *The place can be used for describing additional requirements and guidelines. For example a description of compensative measures if there exist common WBEs.*
5. *The illustration shows the primary well barrier in its normal working stage, while the secondary well barrier is shown in its ultimate stage. This stage often described with a closed shearing device.*

Figure 1.1: Schematic of NORSOK D-010 Standard well barriers for conventional drilling, coring or tripping [2, p. 14].



9.8.4 Permanent abandonment - Perforated well

Well barrier elements	See Table	Comments
Primary well barrier		
1. Liner cement	22	
2. Cement plug	24	Across and above perforations.
Secondary well barrier, reservoir		
1. Casing cement	22	
2. Cement plug	24	Across liner top.
or, for tubing left in hole case:		
1. Casing cement	22	
2. Cement plug	24	Inside and outside of tubing.
Open holes to surface well barrier		
1. Cement plug	24	
2. Casing cement	22	Surface casing.

Notes
1. Cement plugs inside casing shall be set in areas with verified cement in casing annulus.
2. The secondary well barrier shall as a minimum be positioned at a depth where the estimated formation fracture pressure exceeds the contained pressure below the well barrier.

Figure 1.2: Schematic of NORSOK D-010 Standard well barriers for P&A wells (permanent P&A – perforated) [2, p. 71].

Examples of cement well integrity issues

Cement has been recorded as a well integrity issue in many petroleum wells all over the world. For instance, it was investigated by Birgit & Aadnøy (2010) through a well integrity survey with data from 7 operators on the Norwegian Continental Shelf (NCS) that 11% of 75 wells with reported well integrity issues (representative production and injection wells with various ages and development) failed due to cement integrity problems [5], as seen in Figure 1.3. Birgit and Aadnøy's (2010) well integrity survey results indicated that the common cement failures were; due to poor cement pumping job with no cement behind the casing and above the production packer, leaks along cement bonds or leaks through cement microannulus [5].

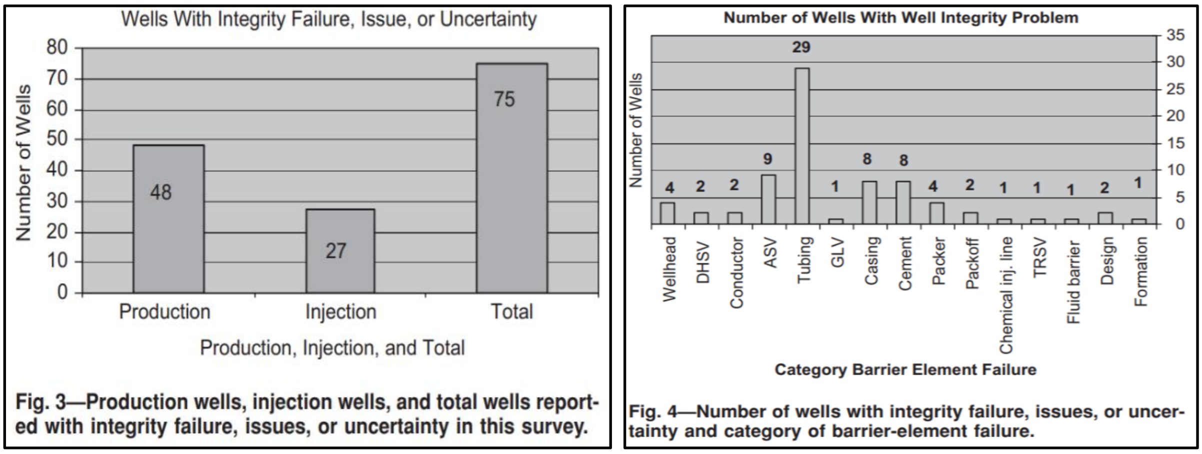


Fig. 3—Production wells, injection wells, and total wells reported with integrity failure, issues, or uncertainty in this survey.

Fig. 4—Number of wells with integrity failure, issues, or uncertainty and category of barrier-element failure.

Figure 1.3: Well integrity survey on NCS [5].

Cement related problems are also documented in different parts of the world. Bachu & Watson (2009) analyzed potential leakage pathways for more than 315,000 wells in the Alberta region, with data provided by the petroleum regulatory board in Alberta, Canada. Since 1995, 4.6% of those wells have been reported to have leakage to surface as surface-venting-casing flow through wellbore annuli and gas migration [6], [7, p. 3]. Bachu & Watson (2009) concluded that the majorities of leakages occurred due cementing during wellbore drilling, construction, or abandonment.

Besides, Nelson & Guillot (2006) illustrates in their *Well Cementing* book that based on data from 22,000 wells in the Gulf of Mexico, 8,000 to 11,000 of those wells have sustained casing pressure (SCP). The sustained casing pressure can be problematic in terms of cement as well barrier because it causes an improper balance of the pressures. This can give rise to gas/fluid flow into the cement-filled annulus during primary cement jobs and movement in the cement during production [8, p. 13].

Another example of cement well integrity issue is from a study conducted by Ingraffea et al. (2014). They statistically gather reasons for gas migration from more than 41,000 conventional and unconventional oil & gas wells drilled in Pennsylvania from year 2000 to 2012 [9]. Ultimately, their study emphasizes that 0.7-9.1% of the wells have casing and/or cement barrier failures – depending on conventional/unconventional well, region and time periods.

Primary cement jobs that fail can give the oil and gas industry high expenses. Westport Technology revealed in their 1995 study that 15% of primary cement jobs fail [10]. These cement problems are expensive to fix. It has been estimated that oil & gas producing companies spend about USD 470 million annually on remedial cementing operations [10], [8, p. 13]. About 1/3 of those cement failures were due to gas or fluid migration through the cement [11].

With much of the more easily available petroleum resources drilled and produced the last decades, and with increasing global energy demand, petroleum operators seek to drill in wells in more harsh areas and well conditions [12, p. 1]. For example, ultra-deepwater wells and high temperature/high pressure (HPHT) wells need an extra focus on well integrity because of extreme well conditions. Since the Deepwater Horizon incident in 2010 in the Gulf of Mexico, there has been an increased focus on well integrity. Although there were a series of failures that lead to the Deepwater Horizon blowout, cement was one of them [13].

Moreover, there is an upcoming demand for having stable cement solutions to give well integrity for the increase in need of plug and abandoning mature oil wells in the North Sea and Gulf of Mexico [4].

Causes of wellbore cement failure and potential leak pathways

Potential leak pathways for gas migration in a well are illustrated in Figure 1.4. Gas can migrate upwards through gaps along the casing-cement and formation-cement interface. This microannuli can be caused by cement shrinkage, de-bonding between casing/cement and formation/cement, poor cement job, insufficient mud removal, inadequate cement response to temperature/pressure variations, movement of casing due to rock subsidence, and with acid stimulations techniques [8, p. 14], [14]. Another possible leak pathway is through the cement pore space due to cement degradation [14]. Degraded casing as a result of corrosion is yet another leak pathway.

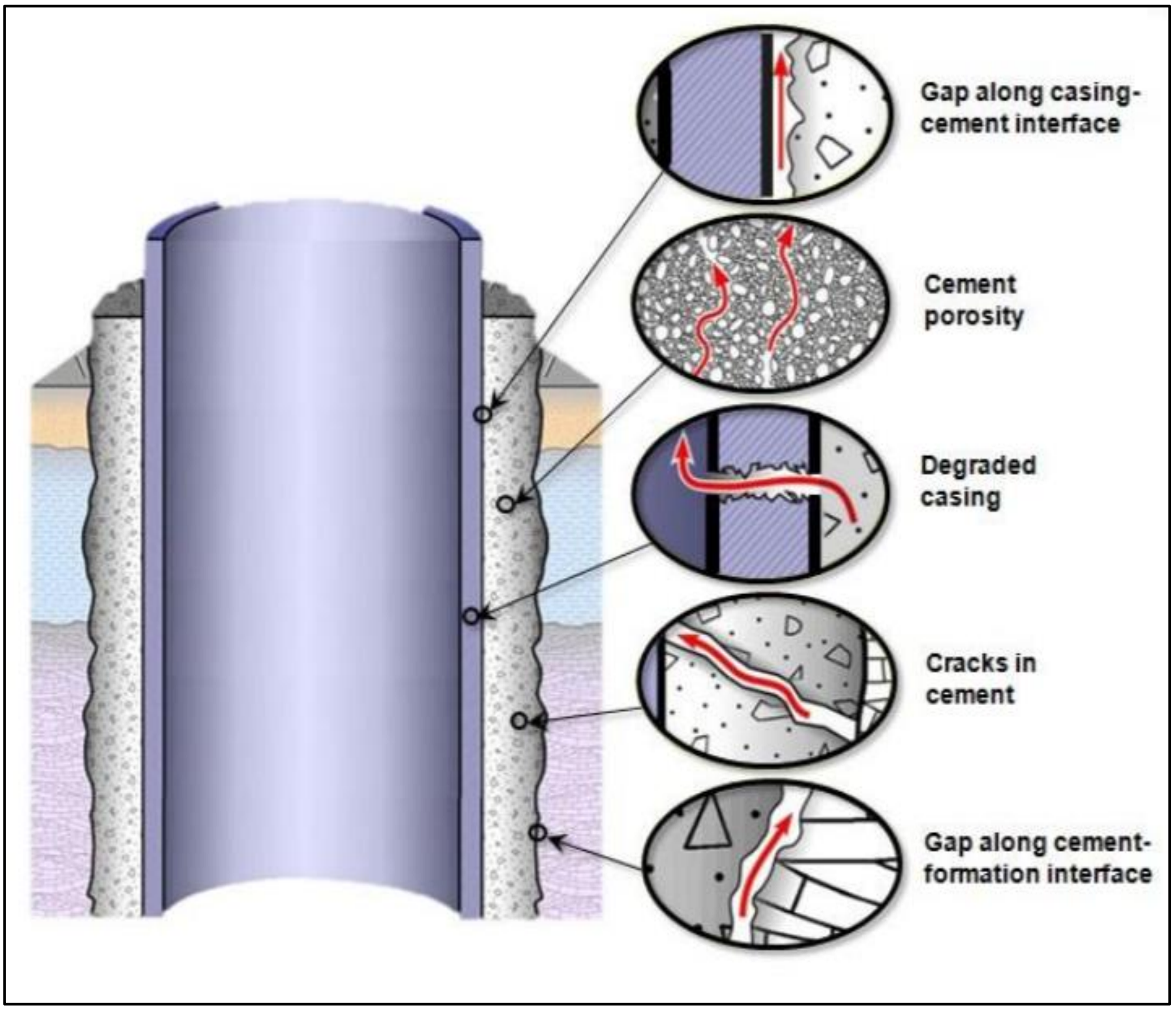


Figure 1.4: Illustration of potential leak paths related to the cement in a well [12, p. 4]

Moreover, cracks in the cement typically occur during production when the cement is subjected to various temperature and pressure fluctuations [8, p. 14]. Depending on the magnitude of these events, the casing and cement can expand and contract in multiple ways, and this imposes stress gradients that can gradually crack the cement sheath [8, p. 14].

Common plugging materials for P&A

Portland cement is by far the most common material for P&A and well construction. Nevertheless, other alternative materials exist. Vrålstad et al. (2019) presented an overview and description of some of them, shown in Table 1.1.

Table 1.1: Overview of current and alternative/emerging plugging materials for P&A [4].

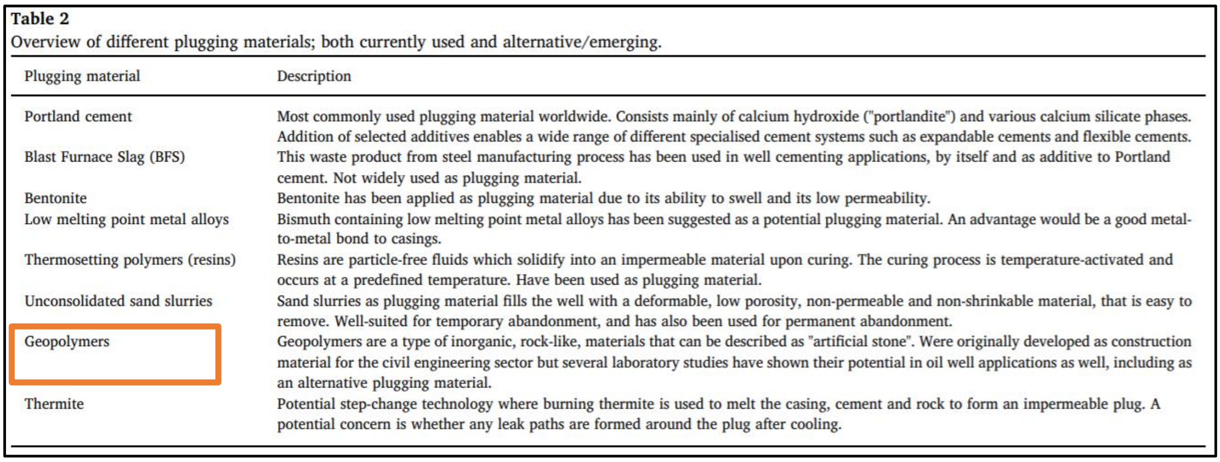


Table 2

Overview of different plugging materials; both currently used and alternative/emerging.

Plugging material	Description
Portland cement	Most commonly used plugging material worldwide. Consists mainly of calcium hydroxide ("portlandite") and various calcium silicate phases. Addition of selected additives enables a wide range of different specialised cement systems such as expandable cements and flexible cements.
Blast Furnace Slag (BFS)	This waste product from steel manufacturing process has been used in well cementing applications, by itself and as additive to Portland cement. Not widely used as plugging material.
Bentonite	Bentonite has been applied as plugging material due to its ability to swell and its low permeability.
Low melting point metal alloys	Bismuth containing low melting point metal alloys has been suggested as a potential plugging material. An advantage would be a good metal-to-metal bond to casings.
Thermosetting polymers (resins)	Resins are particle-free fluids which solidify into an impermeable material upon curing. The curing process is temperature-activated and occurs at a predefined temperature. Have been used as plugging material.
Unconsolidated sand slurries	Sand slurries as plugging material fills the well with a deformable, low porosity, non-permeable and non-shrinkable material, that is easy to remove. Well-suited for temporary abandonment, and has also been used for permanent abandonment.
Geopolymers	Geopolymers are a type of inorganic, rock-like, materials that can be described as "artificial stone". Were originally developed as construction material for the civil engineering sector but several laboratory studies have shown their potential in oil well applications as well, including as an alternative plugging material.
Thermite	Potential step-change technology where burning thermite is used to melt the casing, cement and rock to form an impermeable plug. A potential concern is whether any leak paths are formed around the plug after cooling.

Environmental issues with Portland cement

Portland cement is a key constituent in a variety of construction materials, like concrete and mort. Concrete is a ubiquitous construction material that is part of every city's infrastructure. Moreover, Portland cement is used extensively for wellbore cementing due to the low cost and availability of its constituent materials of clay, shale, limestone and water [15].

However, the industrial manufacturing of Portland cement gives off a massive carbon dioxide footprint by counting for up to 5% of the world's total anthropogenic CO_2 emissions [16, p. 20]. The carbon dioxide is mainly emitted as part of the chemical process of making clinker and burning fossil fuel.

Geopolymer as an alternative for Portland cement

Recently, there has been a high focus on finding a cost-effective and reliable alternative material to Portland cement as a well barrier. For oil & gas well cementing, adding fly ash to the cement is still in the research phase. This is because the cement downhole needs to withstand high pressures and high temperatures, as well as possible tectonic stresses. Therefore, it must be tested comprehensively before use for rig safety purposes.

Davidovits presented in his *State of the Geopolymer 2010* conference at the University of Picardie, France, 2010, that in the last ten years, there has been noticed a substantial increase in research on geopolymers [17]. Fly-ash based geopolymers are by many researchers seen as a potential alternative to conventional Portland cement to reduce the carbon footprint. This is due to the lower CO_2 emissions and fuel energy consumption in the preparation process. The fly ash is the main component in fly-ash based geopolymer and is a recycled material from coal combustion plants. Moreover, geopolymers wake interest due to their unique characteristics, like withstanding high temperatures and acidic environments [18], [19].

The re-use of fly ash from coal fire plants is said to be economical and green because coal fire plants will still be used for many years in some countries [20]. However, to be said, Davidovits (2020) argued for opposing sides of the use of fly-ash based geopolymers with the way the fly ash in this cement alternative supports the burning of coal [21].

To sum up: shortcomings of the conventional Portland cement as a safety well barrier and the high focus on global warming have prompted the need to improve the properties of Portland cement and finding alternative materials as well. Geopolymer is a new material which in this MSc thesis will be investigated for the purpose of being an alternative to Portland cement in oil well cementing operations.

In this master thesis research study, some of those possible cement failures that have been discussed above were used to make decisions when formulating the geopolymer mixtures in the screening process (for example cracking, shrinkage/expansion, compressive strength).

1.2 Problem formulation

For this MSc work, a new geopolymer was formulated based on using own home-made sodium metasilicate liquid combined with sodium hydroxide as alkaline activator. The following issues have been addressed:

- the homemade sodium metasilicate and the commercial sodium silicate alkaline performance with respect to concentration
- the alkaline activator solution ratio (silicate / sodium hydroxide)
- the solids ratio (fly ash / silica fume)
- the amount of extra water volume and its effect on workability, free water and UCS
- the impact dispersant has on workability, free water and UCS
- the effect of nanoparticle type and concentration (TiO_2 and MWCNT-COOH)
- comparison of novel formulated geopolymer with conventional Portland class G cement

1.3 Objective

The primary objective of this thesis work is to answer and describe the issues addressed in section 1.2. As part of the aim, the newly formulated geopolymer was designed for the application of petroleum well (well construction and plug & abandonment) and for civil construction work in cases where the workability is poor. For this, several experimental tests were designed. The homemade metasilicate and commercial silicate based geopolymers were formulated, and the best-qualified geopolymers that passed the screening tests were used to investigate the impact of nanoparticles.

1.4 Research design and background

Figure 1.5 outlines the summary of the research activities, which consists of a literature study and experimental works. The research method in experimental works comprises of two main phases. The first phase deals with formulating a reference geopolymer. Phase 2 is to study the effect of nanoparticles on reference/neat geopolymers from phase 1. The details in Figure 1.5 illustrates that three reference geopolymers were successfully formulated in phase 1 and are marked with blue arrows. They were each based on different concentrations of anhydrous sodium metasilicate solid powder in the homemade sodium metasilicate liquid.

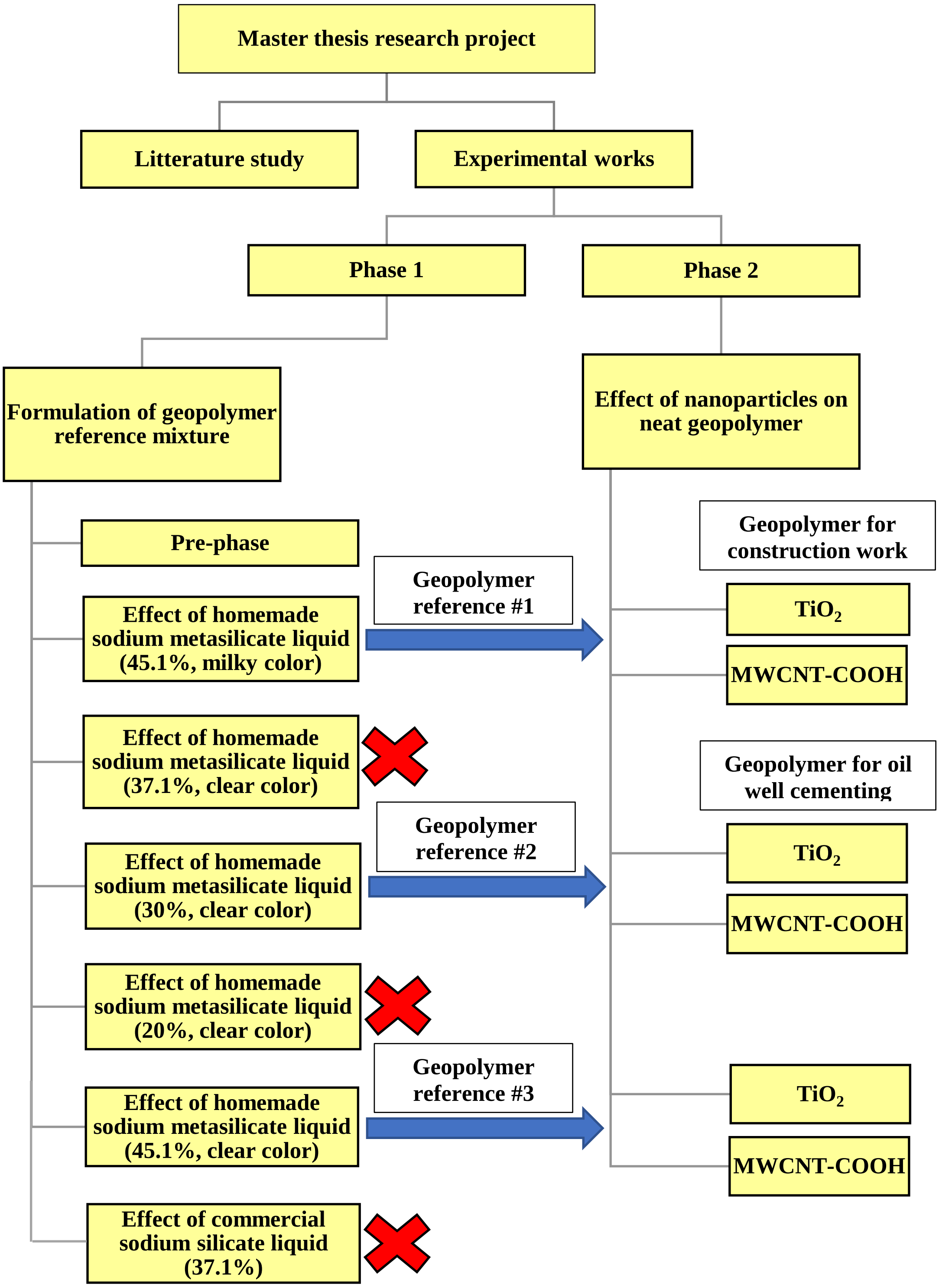


Figure 1.5: Diagram illustrating the phase 1 and 2 of this thesis.

1.4.1 Phase 1: Formulation of geopolymer reference mixture

The first geopolymer mixtures made in research phase 1 were primarily inspired by Ridha et al. (2015) [19]. In that paper, they used a geopolymer system of 70/30 (fly ash / silica fume) and an alkaline activator ratio of 2.5 (sodium silicate / sodium hydroxide) to evaluate the effect of nanoparticles on the acid resistance with respect to the mechanical and internal structure. For this MSc project, a new homemade sodium metasilicate (Na_2SiO_3) with different concentrations of sodium metasilicate combined with fixed 10M NaOH was used as alkaline activator. The first step was to select the desired fly ash to silica fume combination experimentally. The selection pass/fail criteria were set in terms of visual inspection of the plug and slurry (viscosity, air bubble formation, expansion, homogeneity, fractures, and porosity), workability (viscometer response) and destructive testing to obtain uniaxial compressive strength and Young's modulus. Moreover, the performance of commercial silicate geopolymer mixtures from literature was used for the selected 2.5 Na_2SiO_3 / NaOH ratio [22] and 10M NaOH (average between optimum NaOH concentration of 8M from one paper [23] and 12M from another paper [24]). Alkaline activator to solid binder ratio of 0.52 was selected based on optimum compressive strength values in a study conducted by Adam et al. (2019) [25].

In terms of curing temperature, Sindhunata et al. (2006) reported an increased reaction rate in forming geopolymer gel from 30°C to 75°C [26]. Also, 60°C and 65°C were successfully used to study compressive strength and flexibility of geopolymer in studies [23], [27], [28]. Hence, in this thesis, 62^{o}C was determined as the curing temperature for all the plugs. Ambient atmospheric pressure was selected as a worst-case scenario and time-saving simplicity to perform the experiments. Please note that elevating the curing pressure and temperature may result in higher compressive strength. However, this thesis work, the objective was to obtain a qualified reference system on which the effect of nanoparticles will be evaluated by reporting the relative change from the considered nanoparticle-free geopolymer.

The chosen chemicals and ratios explained above made up the new geopolymer formulated in this MSc project. However, many adjustments through various test matrixes were made to improve and optimize the geopolymer. Many challenges were faced because the performance of the geopolymer with chemicals and ratios taken from previous studies in papers did not go as expected with the chemical combinations used in this work. Therefore, this project has been a great learning process in understanding how this novel geopolymer formulation performs.

1.4.2 Phase 2: Effect of nanoparticles on neat geopolymer

In phase 2, the effect of selected nanoparticles was investigated systematically on the three geopolymer mixtures found in phase 1. The geopolymer plugs were characterized through destructive (i.e., uniaxial compressive strength) and non-destructive (i.e., rheology and workability, visual inspection, and ultrasonic compressional wave) measurements. The internal structure of the plugs was planned to be analysed through SEM and element analysis, but due to COVID-19, there was no time.

2 Literature survey

This chapter presents literature studies on conventional Portland cement and alternative geopolymer. The previous research found on geopolymers in the literature study helped to select the chemicals, ratios, concentrations, and curing time and temperature to formulate the novel geopolymer mixture. They were chosen with the goal of formulating a new geopolymer mixture that both gives as high compressive strength as possible and has pumpable workability for efficient oil well cementing operations. Criteria for oil well cement, i.e., impermeable for zone isolation, was content of the experimental tests with water absorption. Casing steel-geopolymer bonding and formation-geopolymer bonding performance was not directly tested but is written as part of a suggestion for further work.

Moreover, the research documented application of nanoparticle on previous geopolymer mixtures from literature will also be summarized.

2.1 Conventional Portland cement

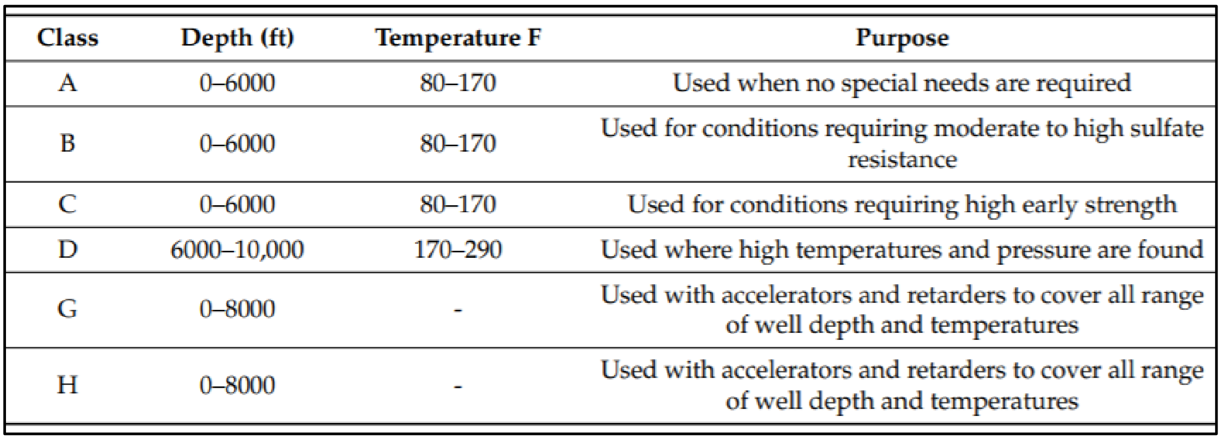
Portland cement is the most common plugging material for petroleum wells. It has been used as zone isolation and plugging material for well construction and P&A since the beginning of drilling petroleum wells. Back then, it was easily available from the construction industry, and because of its known strength, it was accepted quickly [4].

The slurry of Portland cement is used for oil & gas wells because it can be pumped easily and hardens readily [29]. The basic Portland cement can be modified with additives to meet demands for a specific well environment and operation. Some examples of additives are: early strength (accelerator), late strength (retarder), higher hydrostatic pressure of cement column (weighting agents), less dense or increase yield of cement slurry (extender), disperse particles or fluids (dispersants), fluid-loss agents, and loss-circulation agents.

Portland cement as binder material is made by mixing cement powder with water. The cement then cures through a chemical process called hydration, where the cement powder reacts with water. A complex sequence of reactions follows, where the tricalcium and dicalcium silicate hydrate to form the gelatinous “calcium silicate hydrate (CSH) phase“ [30]. The calcium silicate hydrate is formed during the early hydration and is an excellent binding material at temperatures below 110°C. For higher temperatures, a phenomenon called “strength retrogression” might occur, and it can reduce the compressive strength of Portland cement within one month.

The API (American Petroleum Institute) classes of Portland cement are shown in Table 2.1. Most frequently used are class G and H, which are often designed with additives to cover a wide range of well depths and temperatures.

Table 2.1: Portland cement classes for oil well cementing [1].



Class	Depth (ft)	Temperature F	Purpose
A	0–6000	80–170	Used when no special needs are required
B	0–6000	80–170	Used for conditions requiring moderate to high sulfate resistance
C	0–6000	80–170	Used for conditions requiring high early strength
D	6000–10,000	170–290	Used where high temperatures and pressure are found
G	0–8000	-	Used with accelerators and retarders to cover all range of well depth and temperatures
H	0–8000	-	Used with accelerators and retarders to cover all range of well depth and temperatures

As an example, the class G cement should be mixed with 0.44 water/solids weight ratio, according to API standard. After 8 hours of curing at 60°C, it is required to have a compressive strength greater than 10.3 MPa [31].

2.2 Geopolymer

Geopolymer binding material was described by Davidovits in 1997 as inorganic materials with a network of Si-O-Al polymeric bonds that can be synthetically formed by the reaction of an alkaline activator liquid with the silicon (Si) and aluminium (Al) from source material of geological origin or by-product materials [32], [33].

The physical properties of geopolymer make it attractive for oil well cementing. In research studies, they are shown to:

- Withstand high temperatures.
- Withstand corrosive environments.
- Have long-term durability.

Examples of these geopolymer properties will now be presented.

The oil well cement needs to **withstand high temperatures**. Nasvi et al. (2015) compared experimentally the mechanical behavior of fly-ash based geopolymer and Original Portland Cement (OPC) at different curing temperatures (25, 40, 50, 60, 70, 80 °C) after 48h curing [34]. The geopolymer possessed the highest strength at elevated temperatures while the OPC at lower, ambient temperatures, shown in Figure 2.1. This was because the geopolymer showed low geo-polymerisation reaction at ambient temperatures. Besides, the optimum curing temperature for high-strength geopolymer was ~60°C for geopolymer and ~50°C for OPC. Based on their research results, Nasvi et al. (2015) stated that their geopolymer could be suitable for oil well constructions in the deeper part of the wells.

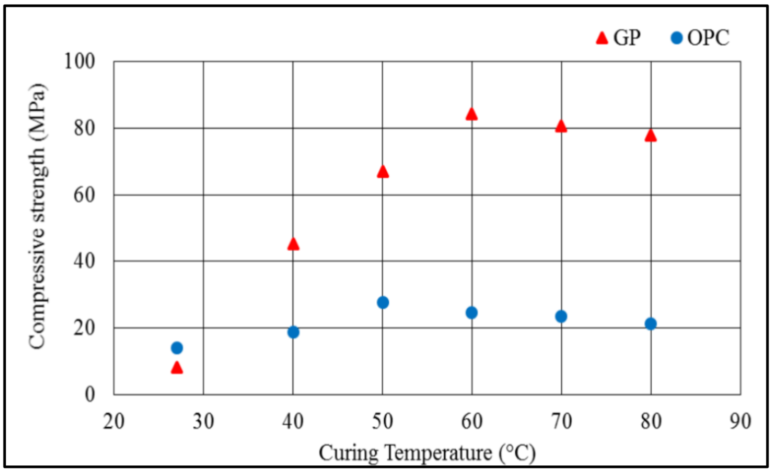


Figure 2.1: Variation of compressive strength with curing temperature [34].

Igbojekwe et al. (2015) developed a geopolymer mixture that showed an increase in the compressive strength with elevating curing temperatures, whereas the Portland cement lost strength [35]. For example, as seen in Figure 2.2, the Portland cement had higher UCS than geopolymer A cured at 150°F (66°C) for 24 hours. At 250°F (121°C), the compressive strength of the fly-ash based geopolymer had increased to about 4100psi while Portland cement decreased to 1400psi. They observed cracks on the surface of the Portland cement, while the geopolymer surface was stable, and this could have caused the early failure. Also, the geopolymer showed lower Youngs modulus (less stiffness) at 150°C, which is ideal for oil and gas cementing as the development and rate of propagation of cracks will be slower. Based on these results, they concluded that geopolymer formulation A appears to have the potential of being an alternative to Portland as a long-term durable well barrier.

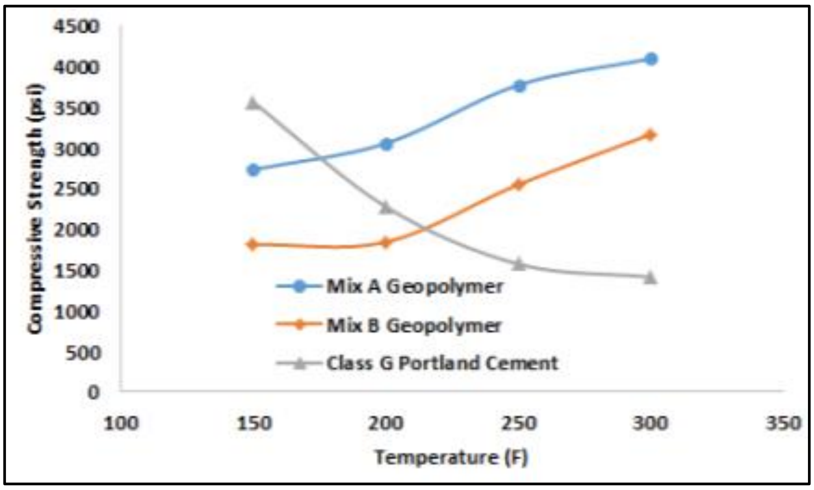


Figure 2.2: Compressive strength at various curing temperature conditions [35].

Another example from elevated temperature exposures is the great fire resistance of concrete geopolymers for construction works [36]. Lahoti et al. (2019) reviewed the properties of geopolymers subjected to elevated temperatures. They concluded that with careful mix design and control of factors like solids, aggregates, total alkali content, and water content, the geopolymer was seen to maintain more microstructural stability and did not break down as easily as the Portland cement concrete at elevated temperatures.

Related to **corrosive environments**, acidizing is a standard well stimulation technique to enhance petroleum production. When the pumped acid is downhole, this fluid can contact the Portland cement and subsequently dissolve and degrade the intergranular structure of the cement. Many researchers have compared the acidic resistance of geopolymers with Portland cement for various acids. Arrifin et al. (2013) showed that their blended fly ash geopolymer concrete had superior acid resistance properties compared to Portland cement after being exposed to 2% sulphuric acid (H_2SO_4) for 1.5 years [37]. Similarly, Thokchom et al. (2009) exposed a geopolymer to 10% sulphuric acid and 10% nitric acid [38]. The high residual compressive strength could confirm good acid resistance even though the samples were fully dealkalized. Moreover, Vafaei et al. (2019) studied the durability fly-ash based geopolymer exposed 24 months to sulphuric and hydrochloric acid (pH = 3) relative to Portland cement [39]. The geopolymer mortar showed significantly better performance both visually and in terms of compressive strength.

Another example of a geopolymer with superior properties in maintaining compressive strength under acidic environment compared to Portland class G cement is a study conducted by Rhidha et al. (2015) [19]. Their result was that after 24 hours in hydrochloric (HCl) and hydrofluoric (HF) acidic environment, the Portland cement had lost about 28% of its original strength, whereas the geopolymer had lost only 1.7%. Their explanation for this phenomenon was that the HCl and HF reacted with the calcium hydroxide (CaOH), which the Portland cement required to form the cement-binding product C-S-H. The geopolymer, on the other hand, does not use CaOH to create binding-material because it uses Si-O-Al bonding to form the gel.

The long-term durability of geopolymer cement is highly reflected by the ability to withstand high temperatures and corrosive environments.

Based on the brief introduction to geopolymer above, the literature study will now proceed to look at its different chemical material constituents.

2.2.1 Solids

The geopolymer binding gel forms through a complex reaction of an alkaline activator liquid and a solid that contains aluminum and silicon (aluminosilicate source) [40]. The most common solid source-material is **fly ash** because it is readily available as it is a by-product from coal fire plants. The chemical composition of the fly ash can vary depending on the coal fire plant and type of burned coal. Generally, there are two fly ash types, F (low calcium content) and C (high calcium), controlled by the age of the combusted coal. The fly ash particles usually have spherical shape and size in range from 0.3µm to 250µm [41].

Another aluminosilicate source is **silica fume**. It is a by-product of the melting process in the silicon industry. Silica fume is known to have a higher particle surface area and is more reactive than fly ash [40].

Many researchers have improved the mechanical properties of fly-ash based geopolymers using silica fume. Sugamaran (2015) investigated the effect of various silica fume concentrations (0, 5, 10, 15, 20wt%) on fly-ash based geopolymer [42]. The samples were cured for 8h and 24h at 200°F and 3000psi. The plot in Figure 2.3 concluded that 15% addition provided the highest compressive strength reading. Moreover, they stated that the 20% silica fume content resulted in lower strength than the optimum because the geopolymer experienced a crack as it was taken out of the oven. As they said, this observation could be due to the high specific surface area of the silica fume, causing agglomerates to form that inhibits the geopolymerisation to develop completely.

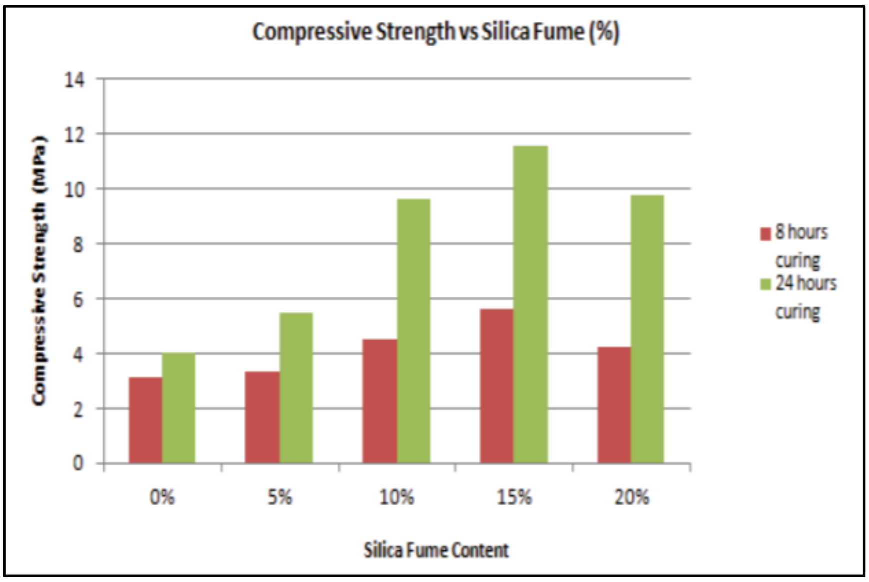


Figure 2.3: Compressive strength results for varying silica fume concentrations [42].

As represented by Figure 2.4, Okoye et al. (2016) investigated the effect of different silica fume concentrations (5-40%) in a fly ash geopolymer mixture with 2.5-ratio of sodium silicate to 14M sodium hydroxide [43]. They could report the result of increasing compressive strength with higher silica fume concentrations. A possible explanation they gave was that the silica fume consists of fine spherical particles of amorphous silicon dioxide that enters the pores of the concrete, making it more compact.

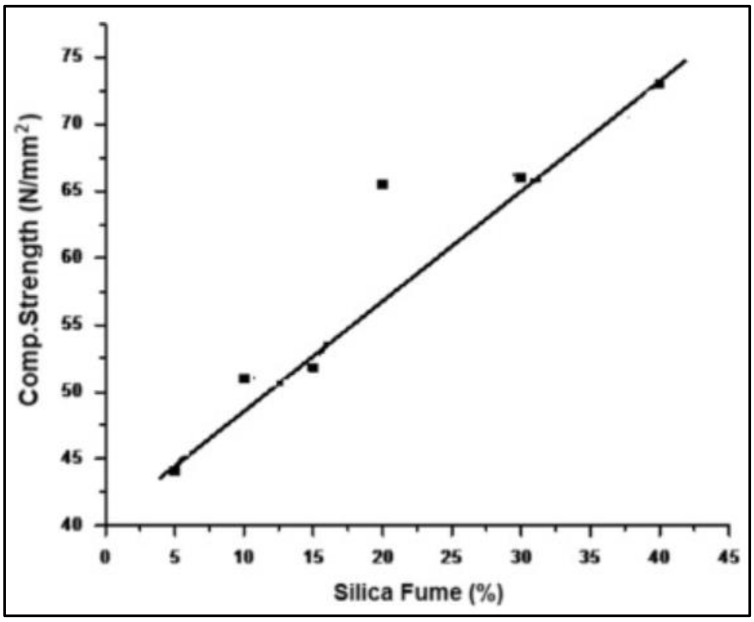


Figure 2.4: Effect of silica fume content on compressive strength [43].

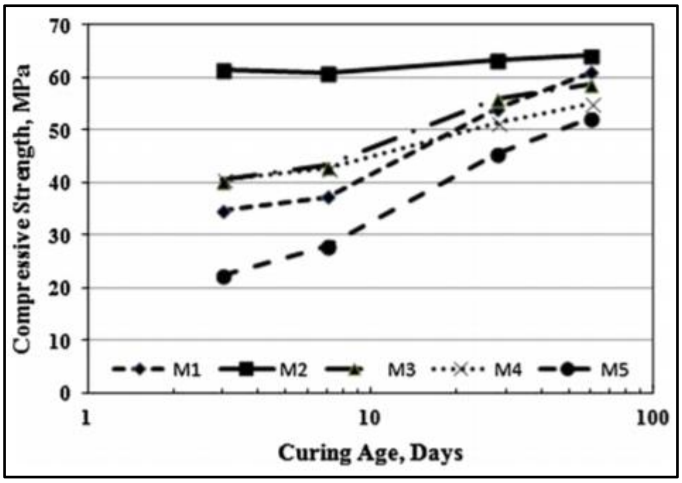
2.2.2 Alkaline activator

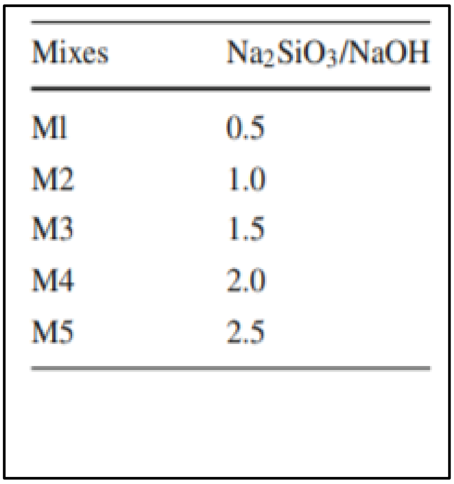
Many research studies have been performed with a mixture of sodium silicate and sodium hydroxide as alkaline activator. Geopolymer mixtures have been reported to perform differently depending on their ratio, type of silicate (i.e., SiO_2/Na_2O-ratio), molarity of NaOH, solids type and curing temperature.

2.2.2.1 Sodium silicate to sodium hydroxide ratio

Rattanasak et al. (2009) studied different NaOH molarities and Na_2SiO_3 / NaOH ratios (sodium silicate / sodium hydroxide ratios) for a fly-ash based geopolymer cured at 65°C for 48h [44]. Two distinct mixing procedures were tested. In the first mixing procedure, the NaOH was added to the solids 10 min before sodium silicate (separate mixing), and in the second, they were added simultaneously. The highest strength geopolymer was obtained up to 70MPa for mixture of 10M NaOH, sodium silicate to NaOH ratio of 1.0 and with separate mixing procedure.

A similar result was reported by Morsy et al. (2013) [45]. They also investigated the effect of different sodium silicate / sodium hydroxide ratios (0.5, 1.0, 1.5, 2.0, 2.5) on a fly-ash based geopolymer with 10M NaOH. As observed in Figure 2.5, ratio of 1.0 achieved the most significant strength for all reported 3, 7, 28 and 60 days curing at 80°C. They observed with SEM micrograph that the 1.0 ratio-geopolymer gel was the most homogenous and had the least porous microstructure.





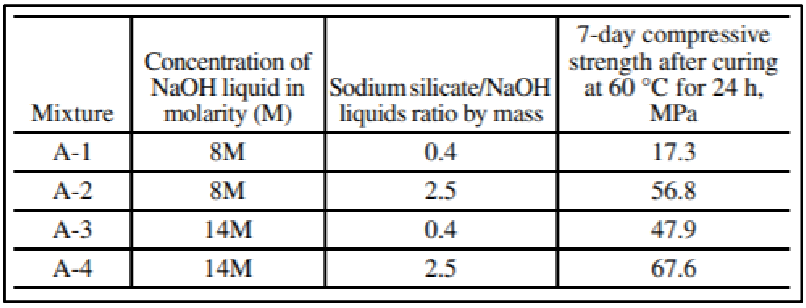
Mixes	$Na_2SiO_3/NaOH$
M1	0.5
M2	1.0
M3	1.5
M4	2.0
M5	2.5

Figure 2.5: Effect of sodium silicate / NaOH ratio on fly ash geopolymer cured at 80°C [45].

Hardjito et al. (2004) presented the highest compressive strength of a fly-ash based geopolymer with 2.5 sodium silicate / sodium hydroxide ratio, compared to 0.4, as shown in Table 2.2 [22]. With constant 8M NaOH, the 2.5 ratio-geopolymer developed a 7-day compressive strength of

56.8 MPa after curing at 60°C, and the 0.4 ratio system showed strength of 17.3 MPa. Similar relative strength development can be observed for 14M NaOH.

Table 2.2: Effect of sodium silicate / NaOH liquids ratio and NaOH molarity on compressive strength [22].



Mixture	Concentration of NaOH liquid in molarity (M)	Sodium silicate/NaOH liquids ratio by mass	7-day compressive strength after curing at 60 °C for 24 h, MPa
A-1	8M	0.4	17.3
A-2	8M	2.5	56.8
A-3	14M	0.4	47.9
A-4	14M	2.5	67.6

2.2.2.2 Sodium hydroxide molarity

Ng et al. (2018) performed a comparative study on fly-ash based geopolymer with different molarities of sodium hydroxide (6-14M) [23]. They used fixed sodium silicate / sodium hydroxide ratio of 2.5. The geopolymer made with 8M resulted in the highest strength of 35 MPa, and the strength results were consistent with values for water absorption, porosity and density measurements.

Bakri et al. (2011) prepared geopolymers with a sodium silicate / NaOH ratio of 2.5 to find optimum NaOH molarity [24]. They used sodium hydroxide with six molarities in range 6-16M. The samples were cured at 70°C. After 1 day of curing, the 10M NaOH-based geopolymer barely showed highest compressive strength with 61.4 MPa competing with the 12M. However, after the 2nd, 3rd and 7th day, the 12M NaOH geopolymer samples produced the highest strength. After 7 days, it was 94.6 MPa. Hamidi et al. (2016) stated that the rise in strength with increasing NaOH molarity could be because the higher molarity fastens the dissociation of the minerals in the solid raw material, yielding formation of even more geopolymer gel [27]. However, too high content of NaOH might disrupt the geopolymerisation with excess OH^-.

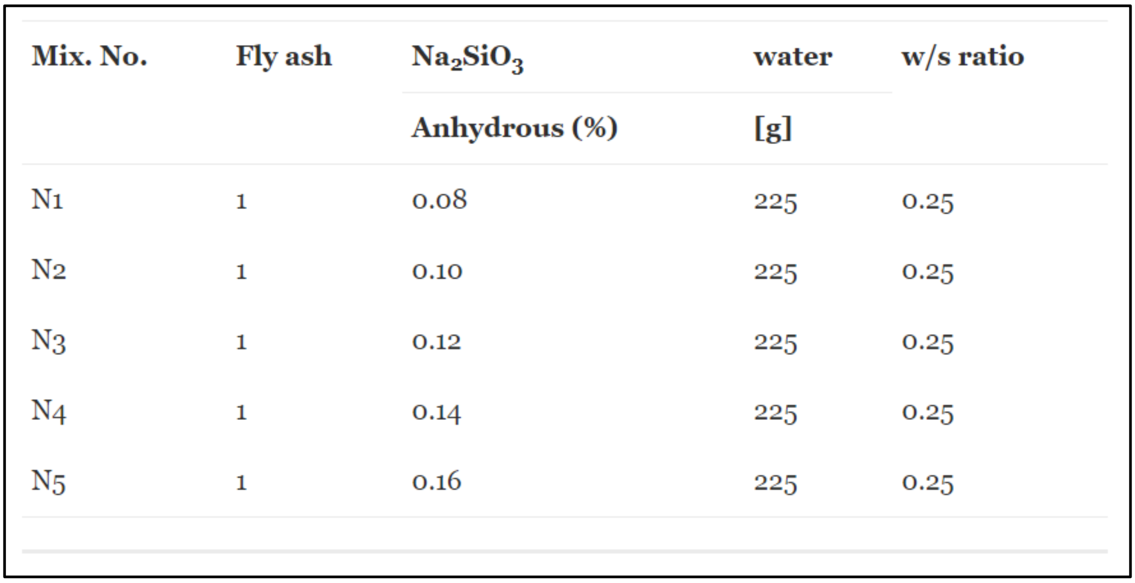
2.2.2.3 Sodium metasilicate

As described above with previous research works, liquid sodium silicate is one of the most common alkaline activators used to form geo-polymer gel. A literature search revealed that researchers previously also have formulated geopolymers with sodium metasilicate powder as alkaline activator, mixed dry with the solids. However, compared to liquid sodium silicate, the numbers of papers are more limited.

Bong et al. (March 2020) studied geopolymers made with sodium metasilicate pentahydrates and compared them against two control mixes [46]. The control mixes were made based on the common liquid mixture between commercial silicate and 12M NaOH as alkaline activator. Their overall result was that the sodium metasilicate pentahydrate-based geopolymer gave higher compressive strength than the control mixtures. This result was seen to be attributed to the amount of water that bound to the undissolved metasilicate particles.

Mohammed et al. (2019) used granular anhydrous sodium metasilicate powder as alkaline activator mixed with fly ash to form binding geopolymer gel [47]. They made mixtures with five concentrations of the sodium metasilicate (Na_2SiO_3), which are shown in Table 2.3. Experimental findings were that 12wt% of fly-ash concentration of the sodium metasilicate powder resulted in highest compressive strength of nearly 50 MPa. Another finding was that the flowability of the geopolymer slurry decreased with increasing content of sodium metasilicate. 12wt% Na_2SiO_3 exhibited a 6.7 percent reduction in flowability.

Table 2.3: Geopolymer mixtures with different anhydrous sodium metasilicate powder content (%) as alkaline activator [47].



Mix. No.	**Fly ash**	**Na_2SiO_3**	**water**	**w/s ratio**
		Anhydrous (%)	**[g]**	
N1	1	0.08	225	0.25
N2	1	0.10	225	0.25
N3	1	0.12	225	0.25
N4	1	0.14	225	0.25
N5	1	0.16	225	0.25

2.2.3 Alkaline activator to solids ratio

Adam et al. (2019) studied the effect of alkaline activator to solid binder ratio on compressive strength of low calcium fly ash-based geopolymer [25]. They reported optimum range value of alkaline activator to solid binder ratio of 0.50 to 0.55, as observed in Figure 2.6. The systems were blended with sodium silicate to 10M NaOH ratio of 1.22 and cured at ambient conditions.

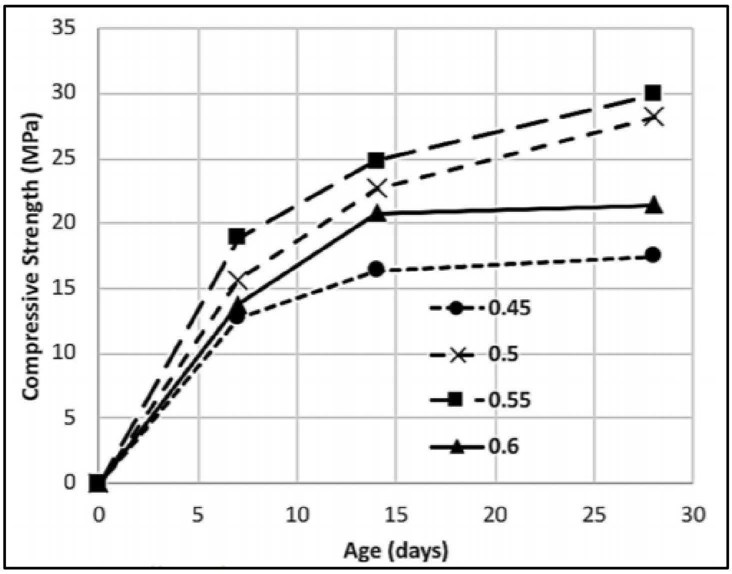


Figure 2.6: Effect of alkaline activator to solid ratio on compressive strength development [25].

Al Safi et al. (2019) presented similar results [48]. They studied the effect of various liquid activator to solid ratios on a blast furnace slag-based geopolymer mortar. Optimum strength was achieved with a 0.52 ratio. They used a different system with some Portland cement blended-in additional to sodium silicate to 12M NaOH ratio of 2.0. Moreover, the mixtures were cured at 80°C for one day before six days of ambient ageing.

2.2.4 Lignosulfonate dispersant additive

Lignosulfonates have been used for decades in concrete as an admixture plasticizer and retarder to increase setting time and the reduce amount of additional water needed [49, p. 146].

Kamsuwan & Srikhirin (2010) investigated the effect of lignosulfonate as an additive on a geopolymer paste with focus on mechanical properties, viscosity and setting time [32]. They tested with lignosulfonate dosages of 0.1-1.5wt% of fly ash. There was a trend of decreasing viscosity with increasing concentration of lignosulfonate, which indicates improved workability. For 1.5wt% lignosulfonate, the viscosity had dropped 21% from the reference (0wt% dispersant). Another positive result was the higher compressive strength of the geopolymer plugs with increasing lignosulfonate concentration. The systems cured for 28 days.

Luukkonen et al. (2019) tested the suitability of different commercial superplasticizers on an alkali-activated blast-furnace slag geopolymer mortar [50]. 0.5wt% of lignosulfonate was the most promising and best-performing superplasticizer by improving workability significantly (minus 27% viscosity) and increasing setting time (plus 70%) as well as compressive strength (plus 19%). Additionally, they could conclude that an optimized combination of superplasticizer and water doubled the compressive strength from 19 to 40 MPa at 28 days of aging.

2.3 Nanoparticle effect on geopolymer

Nano-materials like CNT, nano-silica and graphene can change the properties of geopolymer considerably [51]. Sing et al. (2018) reviewed different nanoparticles, presenting how they differently modify the geopolymer [51]. They concluded that nanoparticles incorporated in geopolymers have massive potential for future civil engineering applications with their improved compressive and flexural strength.

Geopolymers are shown to have high strength in range 40-80^{o}C [51]. Properly designed mixture can even give compressive strength higher than conventional Portland class G cement at these elevated temperature conditions [34]. However, a drawdown with geopolymer is generally low strength development at ambient curing temperature [51]. Researchers have tried to improve this in various ways, with, i.e., additives like slag, lime and ultra-fine fly ash [51]. Nanoparticles have also been tried, with 1% of nano-SiO_2 successfully improving the compressive strength of metakolin-based geopolymer [51].

Vast amounts of nanoparticles exist, and they affect geopolymer and other cement binder materials in different ways. The following presents some previous research studies on the two nanoparticles TiO_2 and MWCNT-COOH, and how they modify properties of geopolymer.

2.3.1 TiO_2

Duan et al. (2016) revealed that addition of nano-TiO_2 into fly ash geopolymer mixture enhanced both early and late compressive strength [52]. The improvement in strength increased with both TiO_2 concentration (tested up to 5%) and curing time (tested for 90 days), as shown in Figure 2.7. They performed a microstructure analysis that uncovered that the incorporation of TiO_2 accelerated the formation of geopolymer gel and resulted in more compact plugs with fewer cracks. They used a combination of sodium silicate and 10M NaOH as alkaline activator.

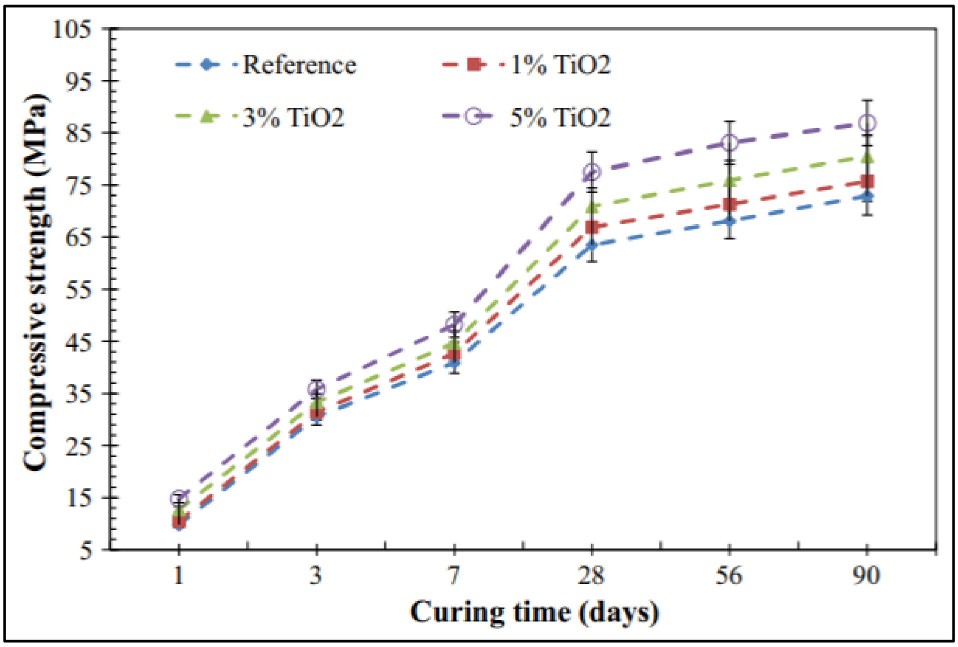


Figure 2.7: Effect of nano-TiO_2 on compressive strength of fly ash geopolymer [52].

Syamsidar et al. (2016) investigated the effect of TiO_2 on fly ash type C geopolymer with concentrations 0, 5, 10 and 15% [53]. Interestingly, 10% TiO_2 incorporated in geopolymer slurry gave highest compressive strength, meaning the trend showed increase from 0 to 10% titanium dioxide added before decline with higher concentrations. The compressive strength of the various titanium dioxide concentrations is shown in Table 2.4.

Table 2.4: Compressive strength of geopolymer with TiO_2 [53].

Sample ID	Compressive Strength (MPa)
HDS 0% TiO_2	25.79
HDS 5% TiO_2	28.98
HDS 10% TiO_2	39.65
HDS 15% TiO_2	37.56

2.3.2 MWCNT-COOH

Multi-walled carbon nanotubes are a unique form of nanotubes consisting of multiple layers of single-walled nanotubes [54], illustrated in Figure 2.8. One single-walled nanotube is a graphene sheet of hexagonally arranged carbon atoms rolled into a cylinder. The carbon nanotubes can be functionalized with different chemical groups, for example hydrophilic carboxyl (-COOH) or hydroxyl (OH) group to improve properties. Carbon nanotubes have a diameter in range 3 to 30nm [55].

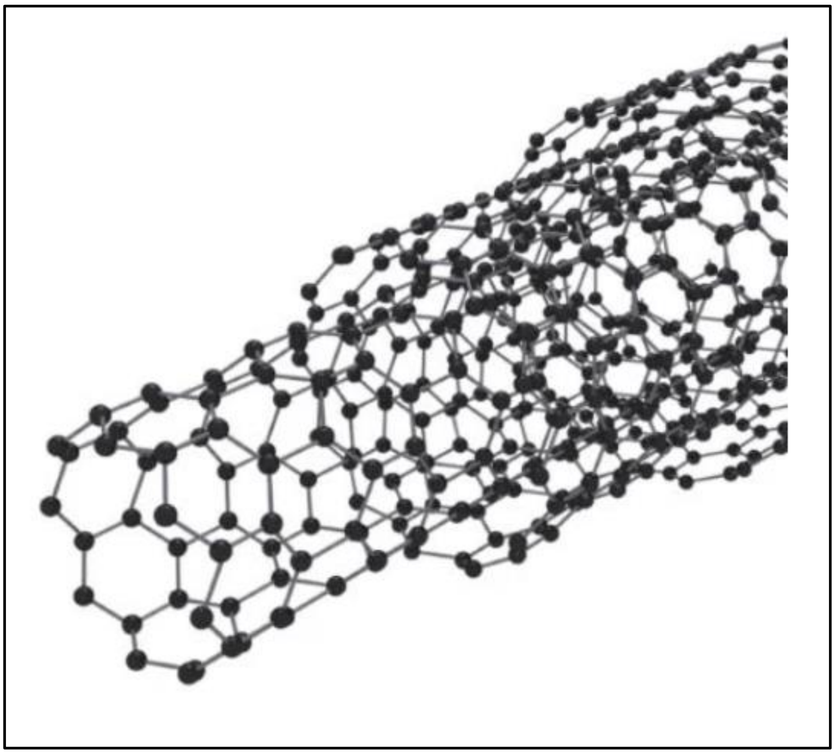


Figure 2.8: Illustration of multiwall carbon-nanotube [54].

The CNTs have shown to be great reinforcement material for geopolymer [51]. Rovnavi et al. (2016) added 0.05-0.2wt% of solids of MWCNT to geopolymer mortar to study fracture properties [56]. Results showed that the MWCNT increased both the elastic modulus and compressive strength. The optimum UCS was for 0.15% MWCNT (**Error! Reference source not found.**). However, the fracture properties were reduced, making the fly-ash based less resistant to fractures with added MWCNT.

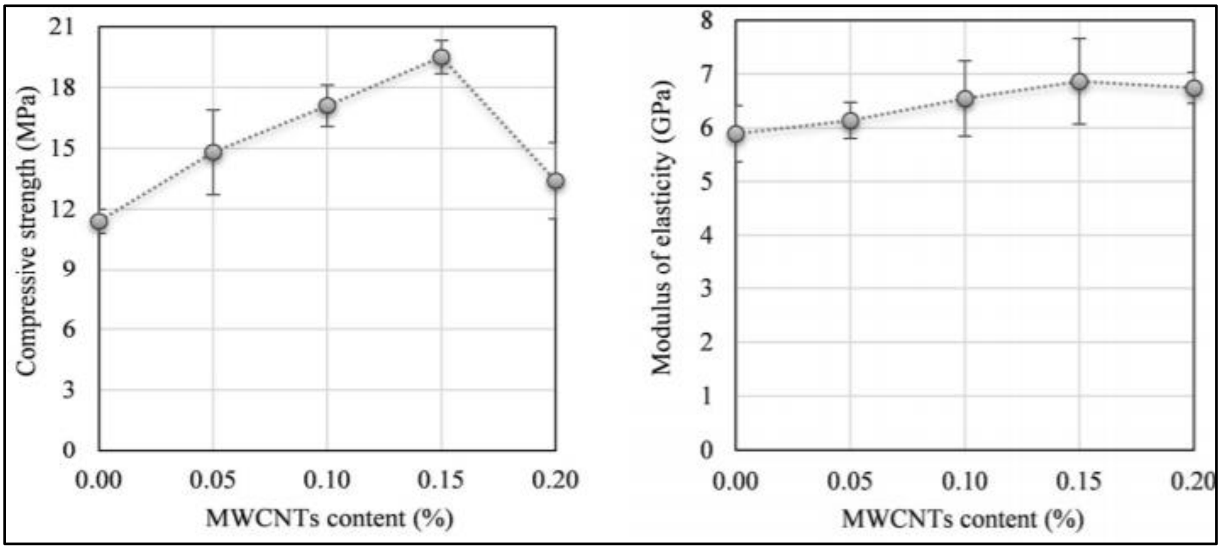


Figure 2.9: Compressive strength and modulus of elasticity vs. MWCNT concentrations [56].

Saafi et al. (2013) got a different result in terms of enhancing the fracture energy [57]. Still, the trend for compressive strength and Young's modulus was the same: increasing to an optimum MWCNT-concentration. The geopolymer system reached optimum compressive strength at 0.5wt% multiwall nanotube. They could observe uniform distribution of the incorporated MWNCT up to 0.5wt%, while at 1.0wt%, the matrix showed poorly distributed and agglomerated multiwall nanotubes. The improved UCS with mixed-in MWCNT is reported by several authors to be due to increased compactness, bridging between microcracks, and offering extra nucleation for geopolymer formation [51].

Moreover, Krater et al. (2016) found in their study that 0.1% MWCNT resulted in the highest compressive strength repeatedly after all four days tested; 7, 14, 28 and 90 days [58], as seen in Figure 2.10. The systems were cured at 40°C.

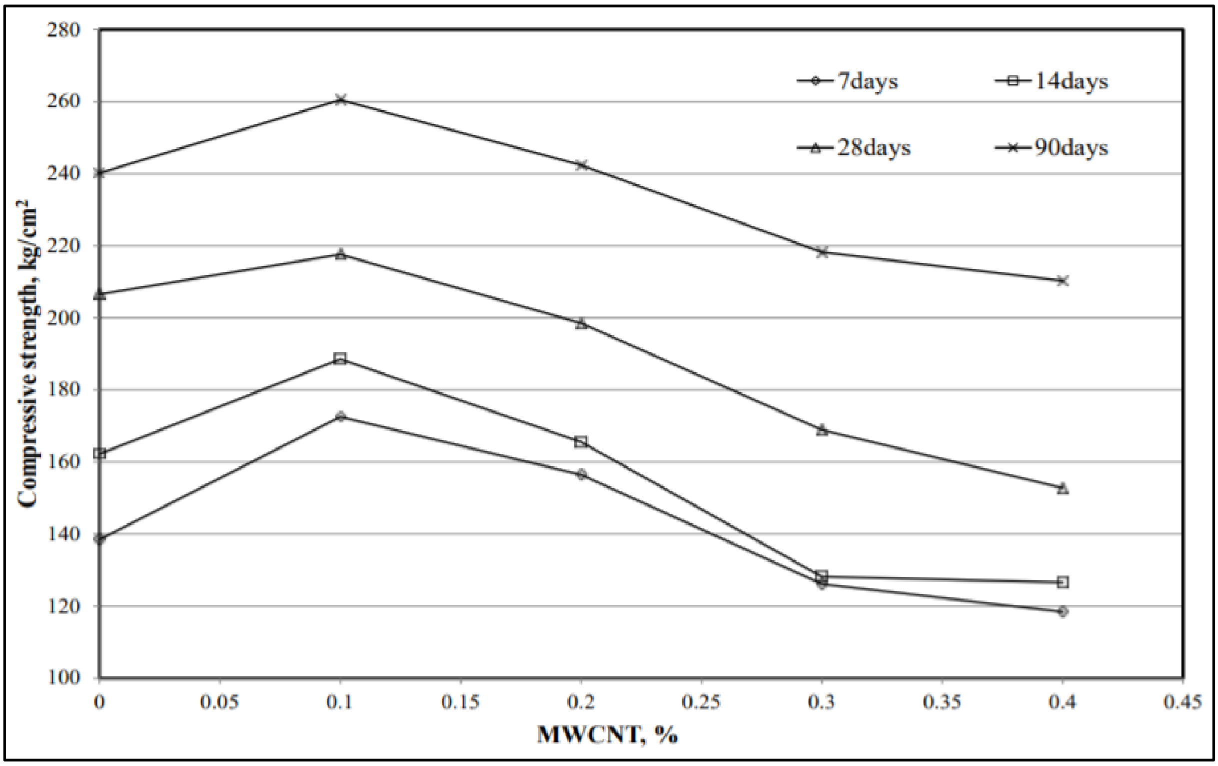


Figure 2.10: Compressive strength vs. MWCNT percentage for geopolymer mixture [58].

3 Theory

The following chapter presents the equipment and theory behind the experimental tests.

3.1 Destructive test

Three destructive uniaxial compressive machines were used. The Zwick/Roell Z020 machine, Figure 3.1 a), was used first. Subsequently, some of the geopolymer plugs could withstand a compressive force load of 20kN. Therefore, it was necessary to switch to the Zwick/Roell Z050 machine, shown in Figure 3.1 b). Both mentioned machines are automatic, meaning that when pressing the start button in the computer software, the plugs are crushed automatically.

After the lab at university opened, subsequently to the COVID-19 lockdown, it was found convenient to use a UCS machine in the mixing lab. This is a manual hand-pumped hydraulic compressing apparatus. Referring to Figure 3.1 c), the black handle on the right side had to be manually compressed by hand for each stroke. It gives the same output as the a) and b) machines, but the manual hand pumping might affect the slope of Force load vs. %Deformation since it is compressed with larger strokes.

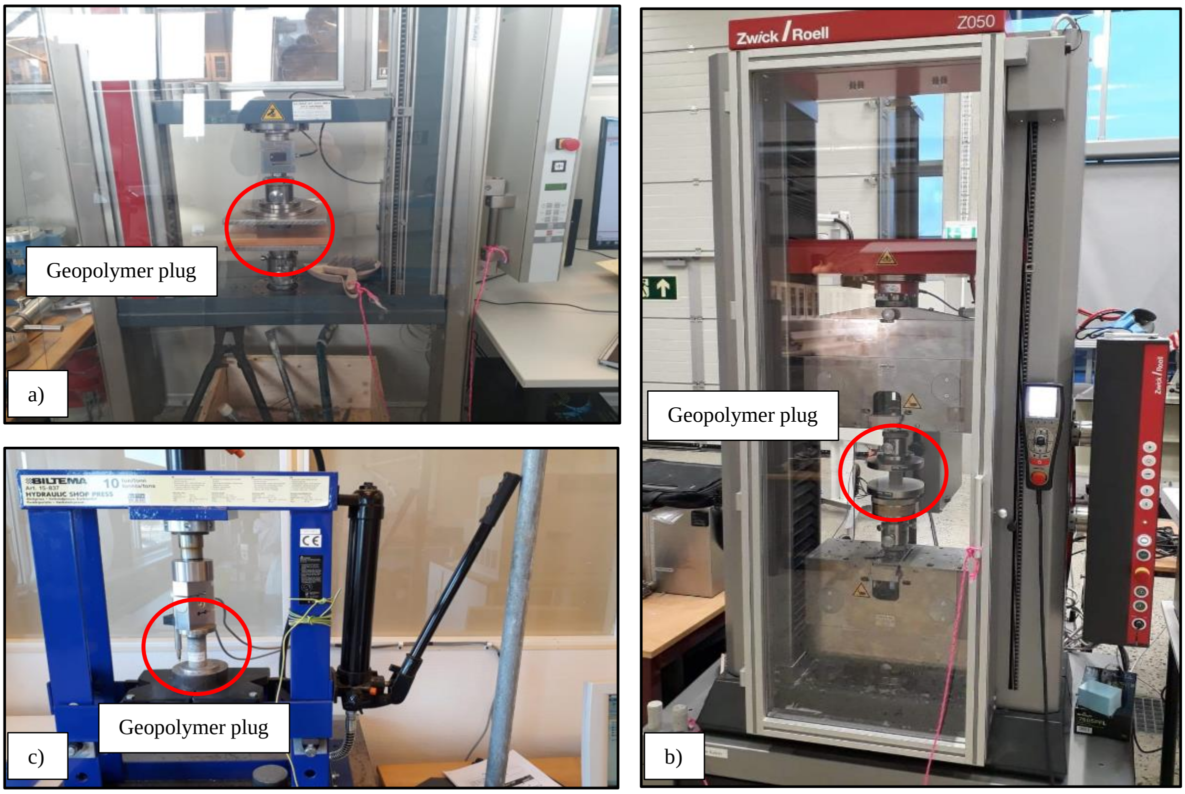


Figure 3.1: a) Zwick/Roell Z020 machine. b) Zwick/Roell Z050 machine. c) Manually hydraulic operated.

The general characterizations of all the three compressive hydraulic machines are specified below:

Zwick/Roell Z020

- Can take maximum load force of 20kN.
- Hydraulic crushing machine that automatically loads the plugs with force and crush them in user-defined force/sec steps when press “start” in computer software.
- Was set at 50N/s compressive force load

Zwick/Roell Z050

- Can take maximum load force of 50kN.
- Hydraulic crushing machine that automatically loads the plugs with force and crush them in user-defined force/sec steps when press “start” in computer software.
- Was set at 50N/s compressive force load

Hand-pumped machine

- Can take maximum load force of about 30kN.
- Hydraulic crushing machine where force load is applied to the plugs by manual hand-pumping by the operator.

The output from all the three destructive UCS machines is Standard Force vs. %Deformation plots. Figure 3.2 displays an example. Converting the force-deformation to stress-strain, one can determine the material properties like uniaxial compressive strength (UCS) and Young’s modulus (E).

Using the peak force load (F_{max}), and dividing by cross-sectional area (A), the uniaxial compressive strength (σ) can be calculated as:

$$\sigma = \frac{F}{A} \tag{3.1}$$

Uniaxial compressive strength (UCS) is the maximum compressive stress applied to a sample of material before cracking/failing. It is also known as unconfined compressive strength because there is no confining stress on the sample during the test.

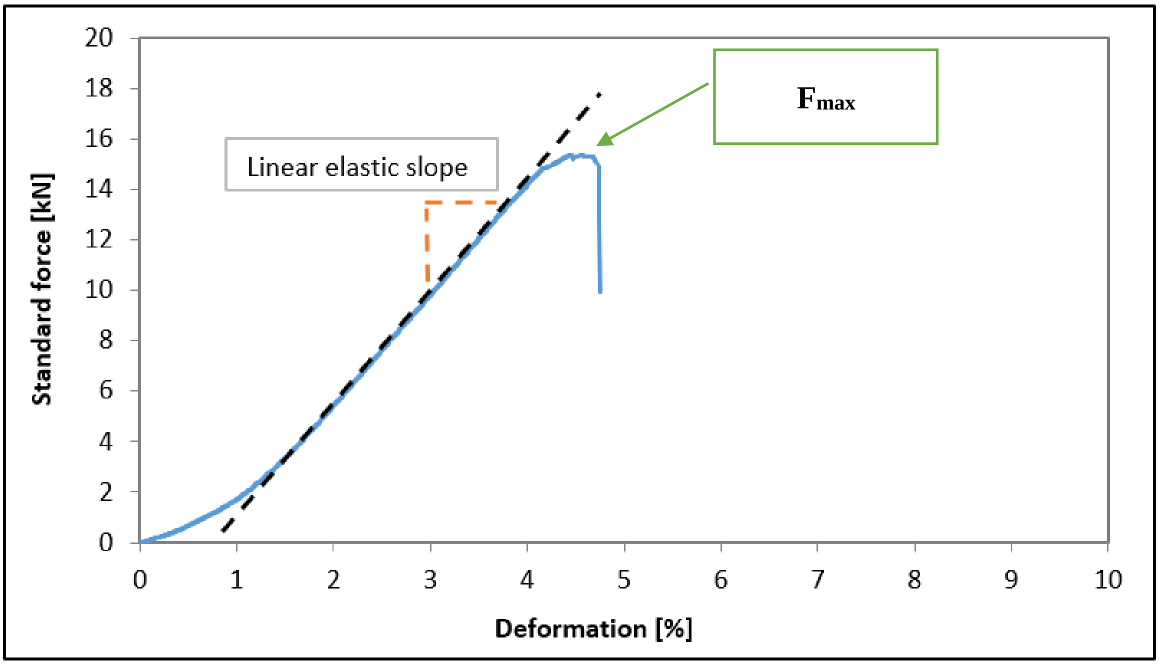


Figure 3.2: Example of Standard Force vs. %Deformation curve from UCS machine.

The Young's modulus (E) is also a mechanical property of interest, which is the measure of the stiffness of the geopolymer plugs. It is determined from the slope of the linear elasticity region of the stress (σ) – strain (ε) curve as:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} \tag{3.2}$$

Strain (ε) is the intensity of the deformation and is given by the change in axial length (Δl) of plug divided by initial length (l):

$$\varepsilon = \frac{\Delta l}{l} \tag{3.3}$$

Generally, it is desirable to design cement having a property with high tensile strength to low Young's modulus, implying higher resilience (i.e., cement absorb more energy before failing). The high E indicates brittle material that fails by fracturing with short deformation, while the low value indicates more ductile material and fails by plastic yielding with longer deformation.

3.2 Non-destructive tests

The non-destructive tests were performed before the destructive test of the geopolymer and cement plugs.

3.2.1 Rheology

Fann Viscometer Model 35 was used to measure the rheological properties of geopolymer and cement slurries. A picture of this apparatus is shown in Figure 3.3.

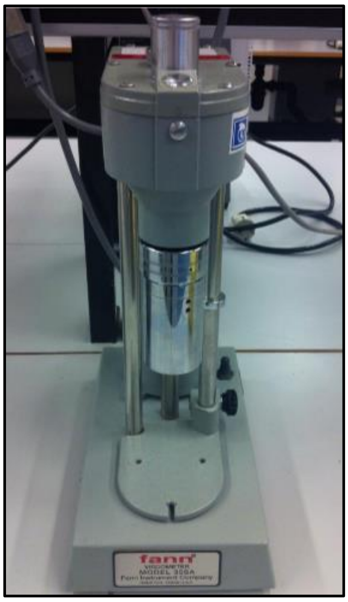


Figure 3.3: Illustration of Fann Viscometer Model 35 used to measure rheology of geopolymer cement slurry [59].

Typically, the rheology of cement uses the viscometer dial readings for the RPM's up to 300 (not 600). Therefore, the rheology criteria for good enough workability for oil well cementing operations were set to 300 RPM reading below 300. Figure 3.4 shows an example of the rheology measurements of this thesis work.

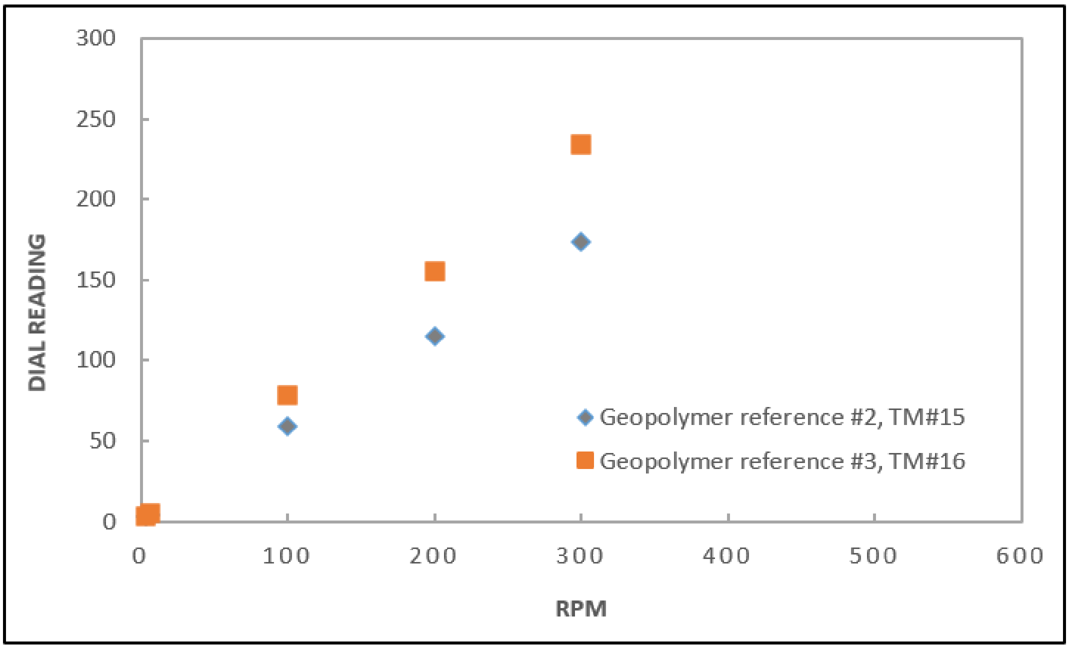


Figure 3.4: Example of rheology measurement of geopolymers in test matrix TM#15 and 16.

3.2.2 Sonic

Figure 3.5 shows a picture of the Pundit 7 sonic device used to measure the transit time of P-waves through the geopolymer plugs. The samples plug was placed in tightly in between two sensors where one transmits the compressional sound wave and the other receives it. Before each set of measurements, the machine was calibrated with a silicon plug with known travel time of 25μs.

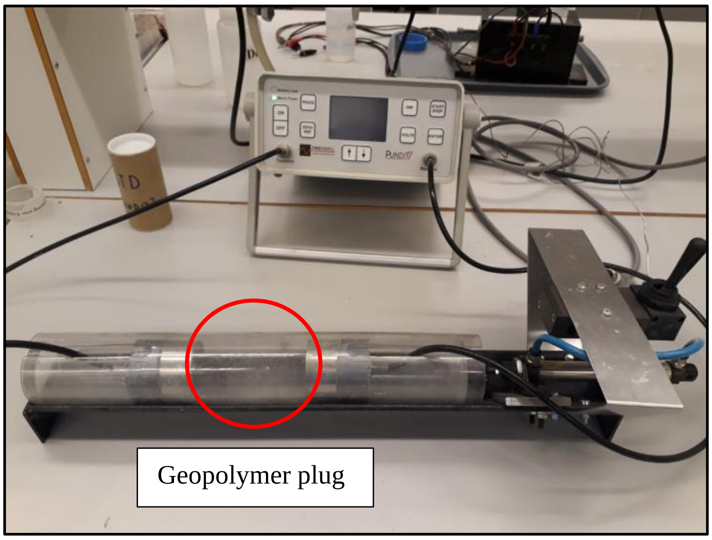


Figure 3.5: Pundit 7 sonic travel time measuring device.

From the measured travel time through the length of the plugs, the compressional sonic wave velocity (or P-wave velocity) can be calculated as:

$$v_p = \frac{l}{t} \tag{3.4}$$

Where, v_p is the P-wave velocity (m/s), l is the length of the specimen (m), t is the P-wave's traveling time (sec).

The compressional wave velocity can also be related with the elastic and physical properties of the core plug by the equation [60, pp. 175-180]:

$$v_p = \sqrt{\frac{K+\frac{4}{3}G}{\rho}} \tag{3.4}$$

Where, K is the bulk modulus (GPa), G is the shear modulus (GPa) and ρ is the density (kg/m^3).

The bulk modulus (K) describes the material's resistance to volumetric change with hydrostatic load, while the shear modulus (G) is the resistance for the angular deformation for the applied shear loading.

The modulus of elasticity (M), which is the modulus we are interested in and the objective from the sonic measurement, describes the total resistance the geopolymer cement plug has against external load. It combines both the bulk modulus and the shear modulus with the equation:

$$M = K + \frac{4}{3}G \tag{3.6}$$

Where, M is the modulus of elasticity (GPa).

From the P-wave velocity and the density, the modulus of elasticity can be calculated with the following equation:

$$M = K + \frac{4}{3}G = v_p^2\, \rho * 10^{-9} \tag{3.7}$$

The density of cement plug is given by:

$$\rho = \frac{m}{V} \tag{3.8}$$

Where, m is the mass (kg), V is the volume (m^3).

3.2.3 Water absorption

One of the main criteria for the cement property requirement according to NORSOK D-010 is that cement shall be impermeable. Permeability is the property of rock that allows fluid flow through it. The degree of the fluid flow depends on the internal pore structure, i.e., how the pores are connected. The permeability of a core plug is quantified from lab flooding experiments as well as using Darcy law. However, due to lack of equipment, in this thesis work, the degree of mass fluid absorbing under room temperature and pressure was used to compare the degree of internal pore structure.

The mass change between the consecutive days is calculated as:

$$\Delta M = \frac{M_{t+1} - M_t}{M_t} * 100 \tag{3.9}$$

Where, ΔM is the change in mass (%), M_t is the mass at time t, and M_{t+1} is the mass at time $t + 1$

4 Experimental materials and methods

This chapter first presents the materials used to make geopolymer and Portland cement (chapter 4.1). Then, the methods of sample preparation and mixing are explained (chapter 4.2).

4.1 Materials

4.1.1 Conventional oil well class G cement

The geopolymers were compared with class G oil well cement as part of the screening process. The formulated reference geopolymer mixtures were also compared with the conventional class G cement.

The Portland G-class cement was obtained from NORCEM AS (Stavanger, Norway) [61]. Table 4.1 and Table 4.2 provide the physical properties and chemical composition of the cement. This cement type is highly sulfate resistance and tested in accordance with API SPEC 10A/NS-EN ISO 10426-1.

Table 4.1: Physical properties of Portland cement [61].

Density (lb/gal)	**Surface Area (m^2/kg)**	**Max. Consistency (Bc)**	**Thickening time (Min)**
16	317	13	108

Table 4.2: Chemical composition of Portland cement (*I.R = insoluble residue) [61].

Cr(VI)	**SO_3**	**C_3A**	**C_2S**	**C_4AF+ $2C_3A$**	**Na_3O**	**MgO**	**I.R***	**Loss on Ignition**
0.00	1.73%	1.7%	55.6%	15.2%	0.48%	1.43	0.1%	0.79%

Cement was made by mixing the Portland cement class G powder with water in 0.44 water/solid ratio, by API standard. Figure 4.1 shows a picture of the Portland cement powder.

Figure 4.1: Portland class G cement powder.

4.1.2 Geopolymer chemicals

The geopolymer gel is formed by reaction between alkaline activator and solid binder.

4.1.2.1 Fly ash

In this project, low-calcium (CaO, lime) fly ash class F was used, shown in Figure 4.2. Fly ash typically has the composition in Table 4.3. The chemical was provided by NORCEM AS [61].

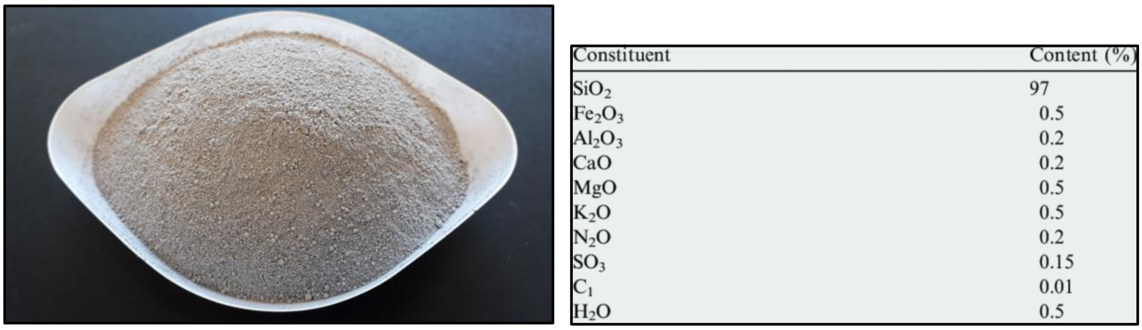
Figure 4.2: Fly ash class F.

Table 4.3: Typical fly ash composition [62].

SiO	**Al_2O_3**	**Fe_2O_2**	**CaO**	**MgO**	**SO_3**	**Na_sO & K_2O**
54.90	25.80	6.90	8.70	1.80	0.60	0.60

4.1.2.2 Silica fume

Densified (without air) silica fume was used in this project combined with fly ash to make up the solids for the geopolymers. Figure 4.3 presents a picture of the silicate fume powder and its typical chemical composition. Silica fume was obtained from NORCEM AS [61].



Constituent	Content (%)
SiO_2	97
Fe_2O_3	0.5
Al_2O_3	0.2
CaO	0.2
MgO	0.5
K_2O	0.5
N_2O	0.2
SO_3	0.15
C_l	0.01
H_2O	0.5

Figure 4.3: Silica fume photo and its chemical composition [63].

4.1.2.3 Alkaline activator liquid

Alkali activator is necessary for the geo-polymerisation process to form the binding gel. A combination of Na_2SiO_3 and 10M NaOH with 2.5 ratio were chosen as alkaline activator based on literature study in Chapter 2.2.2. The alkaline liquid was used with 0.52-ratio to the solids (from Chapter 2.2.2).

The source of Na_2SiO_3 in this work was a homemade sodium metasilicate liquid. Different concentrations were tried out with the goal of formulating a geopolymer with high UCS strength and good workability. A commercial sodium silicate liquid was also tested for comparison. Some of their properties are compared in Table 4.4.

Table 4.4. Homemade sodium metasilicate vs. commercial sodium silicate.

Homemade sodium metasilicate liquid	**Commercial sodium silicate liquid**
Homemade (made in the lab in small batches same day as geopolymer)	Commercial made and ready-to-use
Type of silicate: **metasilicate**	Type of silicate: **silicate**
Linear formula for the sodium metasilicate powder: Na_2SiO_3	Linear formula for the sodium silicate liquid: $Na_2O\ (SiO_2)x \cdot xH_2O$

4.1.2.3.1 Homemade sodium metasilicate liquid

Sodium metasilicate anhydrous 18 mesh granular powder was ordered from Sigma-Aldrich [64]. A sample is shown in Figure 4.4, and the known composition is presented in Table 4.5.

Figure 4.4: Sodium metasilicate powder.

Table 4.5: Chemical composition of the sodium metasilicate powder.

SiO_2	Molecular weight
~50-53%	122.06 g/mol

4.1.2.3.2 Commercial sodium silicate liquid

37.1% sodium silicate liquid, reagent grade, was ordered from Sigma-Aldrich [65]. The known chemical composition is shown in Table 4.6.

Table 4.6: Chemical composition of the commercial silicate liquid.

Na_2O	SiO_2	Density
~10.6%	~26.5%	1.39g/mL at 25°C

4.1.2.3.3 NaOH

Figure 4.5 shows NaOH pellets of 97% purity and 10M NaOH solution. NaOH pellets was purchased from Sigma-Aldrich [66].

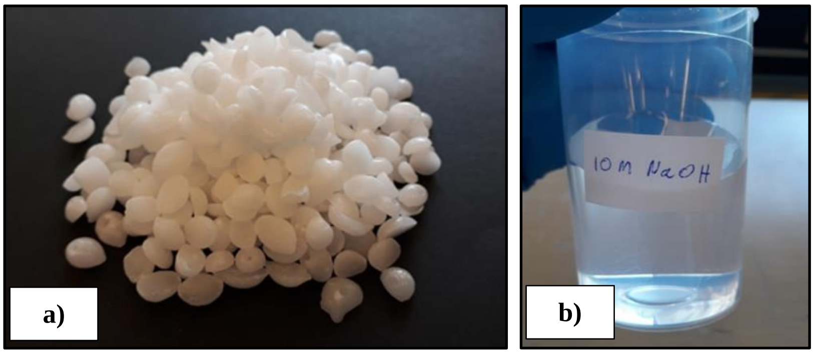


Figure 4.5: a) NaOH in pellets state. b) 10M NaOH solution.

4.1.2.4 Lignosulfonate

Lignosulfonate dispersant was used as an admixture to improve the workability of the geopolymer slurry. Figure 4.6 shows the lignosulfonate in powder state and being mixed with water. The chemical was obtained from M-I Swaco.

Figure 4.6: a) Lignosulfonate in powder state. b) 0.75g lignosulfonate dispersed in 23g water.

4.1.3 Nanoparticles

Two types of nanoparticles were used to investigate their effect on the chosen formulated geopolymer references, namely TiO_2 and MWCNT-COOH. The nanoparticle solutions dispersed in water are shown in Figure 4.7 and Figure 4.8, respectively. Nano-TiO_2 and MWCNT-COOH were purchased from US Research Materials [67] and [68], respectively.

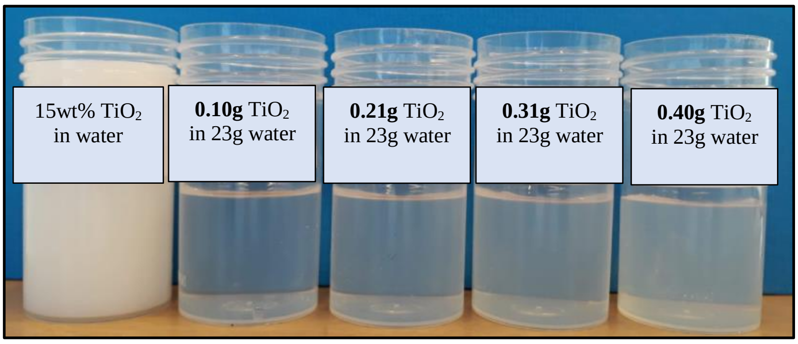


Figure 4.7: The leftmost cup contains 15% TiO_2 in water. The other cups have increasing amount of TiO_2 dispersed in 23g water.

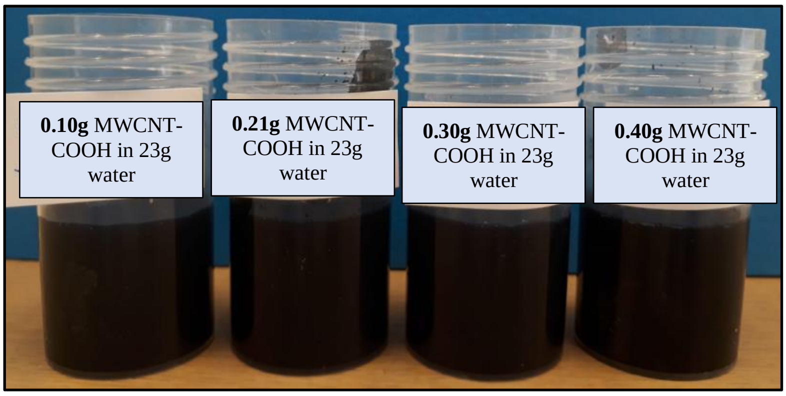


Figure 4.8. Cups with increasing amount of nanoparticle MWCNT-COOH dispersed in 23g water.

4.2 Sample preparation and mixing

This chapter describes the methods used to prepare and mix chemicals to make the geopolymer sample plugs.

4.2.1 Alkaline solution

As described in Chapter 4.1.2.3, the alkaline activator consisted of two components:

- 10M NaOH liquid
- Homemade sodium metasilicate liquid OR commercial sodium silicate liquid

4.2.1.1 10M NaOH solution

The preparation of 10M NaOH was straight forward. The NaOH pellets were mixed water with magnetic stirring for 2h.

4.2.1.2 Homemade sodium metasilicate liquid

Preparing the homemade sodium metasilicate liquid was much more complex and time-consuming. Table 4.7 presents the different homemade sodium metasilicate liquid concentrations made throughout this MSc project and their measured pH. The measured pH of 10M NaOH and commercial sodium silicate is also presented in this table. The pH was measured with the Mettler Toledo pH-meter shown in Figure 4.9. The maximum pH that could be measured with the pH-meter was 14. With pH values of 14+, the homemade sodium metasilicate liquids and 10M NaOH are extremely alkaline. The commercial silicate solution is also highly alkaline, with 13.09 in pH.

Table 4.7: Measured pH of the different homemade sodium metasilicate liquids made in this MSc thesis, as well as 10M NaOH and commercial sodium silicate liquid.

	pH
Homemade sodium metasilicate liquid (45.1%, milky color)	14+
Homemade sodium metasilicate liquid (45.1%, clear color)	14+
Homemade sodium metasilicate liquid (37.1%, clear color)	14+
Homemade sodium metasilicate liquid (30%, clear color)	14+
Homemade sodium metasilicate liquid (20%, clear color)	14+
Commercial sodium silicate liquid (37.1%)	13.09
10M NaOH	14+

Figure 4.9: Mettler Toledo pH-meter.

Five homemade sodium metasilicate concentrations were made throughout this project, as presented in Table 4.7.

4.2.1.2.1 Homemade sodium metasilicate liquid (45.1%, milky color)

The high-concentrated sodium metasilicate fluid was the first liquid made in this MSc project. It was used for test matrix (TM) **TM#4** and **TM#17-18**. A picture of it is shown in Figure 4.10. As can be seen, all the particles are not completely dissolved and hence the “milky” color of the solution.

Figure 4.10: Homemade sodium metasilicate liquid (45.1%, milky color) at 40°C.

We started the project from scratch without having a pre-knowledge about the synthesis of metasilicate solution. Most of the literature documented alkaline binder solutions are commercially based and use sodium silicate (not sodium metasilicate). However, in this thesis, the project plan was to prepare the alkaline solution with different concentrations of sodium metasilicate in order to figure out how the geopolymer behavior varies with concentration.

The liquid preparation started by weighting up the solid anhydrous sodium metasilicate powder and liquid water. Then, little by little, the powder was poured into the water while stirring with a stirring rod. A heat bath was applied by first boiling some water in a water boiler before pouring it into the pink bucket. The heat bath process is illustrated in Figure 4.11. However, at the beginning of this project, it was not clearly understood how much heat to apply to the system, so the heat bath process was somewhat inconsistent. In general, the heat bath temperature was kept at 95-40°C for 2 hours. The wide range of heat bath temperatures made the solid sodium metasilicate particles just partly dissolve in water, and thereby the "milky color" seen in Figure 4.10.

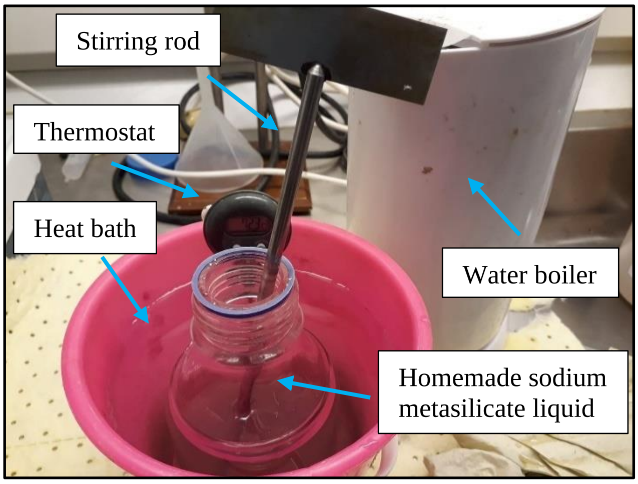


Figure 4.11: Heat bath process of making homemade sodium metasilicate solution.

4.2.1.2.2 Homemade sodium metasilicate liquid (45.1%, clear), (37.1%, clear), (30%, clear), (20%, clear)

They are all characterized by a clear, transparent, water glass color. Their visual appearance is compared in Figure 4.12 - Figure 4.14. It can be observed from Figure 4.12 that increasing concentration of anhydrous sodium metasilicate in water results in darker color. In addition, the (20%, clear)-homemade metasilicate has similar color to water. Moreover, they were made and used for test matrixes <u>**TM#5-7, 9-16, 20-23**</u>.

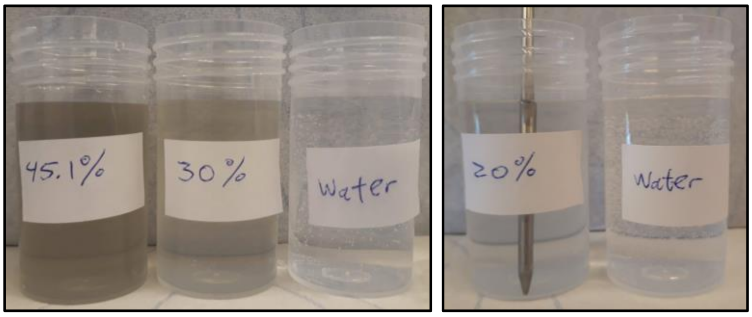


Figure 4.12: Comparing the color of homemade sodium metasilicate liquid of concentrations (45.1%, clear), (30%, clear), (20%, clear) with water at 35°C.

Figure 4.13 shows the clear color for the homemade sodium metasilicate liquid with concentrations (45.1%, clear) and (30%, clear). They are the same liquids as in Figure 4.12, but the only difference is that there is a stirring rod in the (45.1%, clear) showing the clarity and transparency.

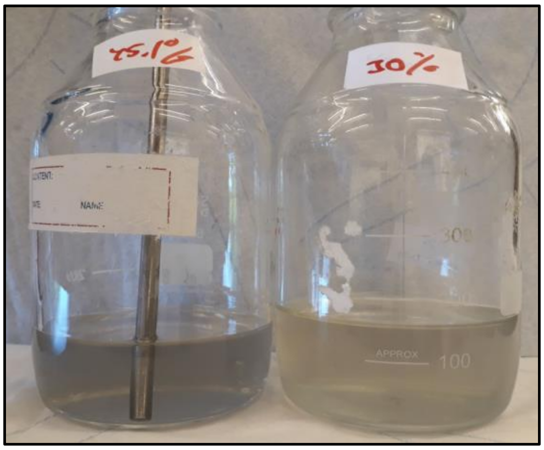


Figure 4.13: Left batch: (45.1% clear). Right: (30%, clear). 35°C temperature.

Figure 4.14 shows the homemade sodium metasilicate liquid (37.1%, clear) that has been made 30 minutes ago and has now cooled down to 51.3°C.

Figure 4.14: The homemade sodium metasilicate liquid (37.1%, clear) cooled down to 51.3°C.

The clear, transparent color seen in Figure 4.12 - Figure 4.14 was achieved by changing heat bath water more often, and maintaining the heat bath with temperature 95-75^{o}C for 2 hours.

4.2.1.3 Commercial sodium silicate liquid (37.1%)

The commercial silicate liquid was bought in a liquid state and was ready to use upon arrival at the lab. It had a clear color, similarly to water (Figure 4.15). Geopolymer mixtures were made with this chemical in **TM#13**.

Figure 4.15: Comparing the color of the commercial sodium silicate liquid (37.1%) with water at ambient temperature.

4.2.2 Slurry and geopolymerisation

Mixing procedure

With all the chemicals weighted up, the first step was to mix the homemade sodium metasilicate (or commercial sodium silicate) with the 10M NaOH. They were stirred by hand for 10 seconds before added to the solids. The alkaline liquid and solids were then hand-stirred with a spoon for 2-4 minutes, first rapidly to make a homogenous slurry and then slowly to remove air bubbles. Extra ex-situ water (and/or lignosulfonate dispersant) was then added to improve the workability. Moreover, the slurry was poured into plastic molding cups while vibrating the cups to remove air bubbles. The slurries in the plastic cups were then rested for about 20min before put in the oven to avoid spilling when carrying them. After that, the slurries were put in the oven, cured at 62°C and ambient pressure for 3 days (TM#19-23 were also 10 days cured).

For each batch of geopolymer and Portland cement slurry made, **two** plugs were made representing the exact same mixture. The molding plastic cup was of outer dimensions 34.5x69.0mm (diameter x length).

After 3 (or 10) days curing in the oven, the plugs were cut with a knife out of the plastic cups and then exposed in air for 18-24h before the free water part of the plug was cut. The plugs were then polished with sandpaper. Then, they were measured for sonic travel time, mass, diameter and length. The plugs in TM#4 were also tested for water absorption. Finally, they were tested for uniaxial compressive strength.

Important notes:

1. The homemade sodium metasilicate liquids (all concentrations) were made in the lab 1-2 hours before being mixed with the 10M NaOH and added to solids.
2. The homemade sodium metasilicate liquids (30%, clear) and (20%, clear) were kept at 30°C before added to the 10M NaOH.
3. The homemade sodium metasilicate liquids (45.1%, milky), (45.1%, clear), (37.1%, clear) were kept at 40°C before mixed with the 10M NaOH.

Regarding the first point, it was tried to let the blended homemade sodium metasilicate liquid stand for 24h, but it crystallized and hardened. The second and third point was done because of the instability of the partly dissolved sodium metasilicate in water at low temperature.

4.2.3 Cutting and polishing after curing

Cutting

Struers Discotom-5 was used to remove the free water part of geopolymer plugs. Two pictures were taken and are shown in Figure 4.16. The free water part is located at the top, and it contains less solids and more fractures and pores as well.

Figure 4.16: Struers Discotom-5 machine used to cut free water of the geopolymer plugs.

Polishing

All the geopolymer and Portland cement plugs were polished with sandpaper after cutting until their top surface was approximately horizontal. If the surface is not uniform during compressive testing, the inclined part can generate huge stress in the plugs, and the result will not be representative. To reduce the uncertainty of point load effects, a tiny water leveler was used for verifying horizontal top surface combined with a test performed by turning the plug upside down and checking its stability, see Figure 4.17. Bosch sandpaper with 120 grain size was bought at Clas Ohlson.

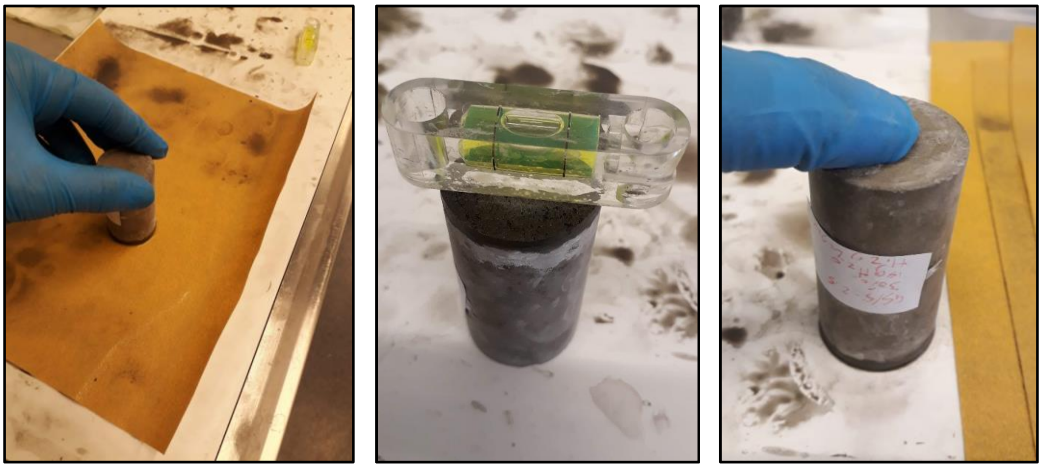


Figure 4.17: Process of making top surface of the plugs horizontal after cutting. Left picture: polishing by hand with sandpaper. Middle: water leveler on top surface. Right: plug upside down to check if evenly flat.

5 Experiment designs and results

The literature study in Chapter 2 aimed at searching for chemicals, ratios and concentrations to have a starting point for formulating the novel geopolymer. This chapter presents the experiment designs and results from this research project. The experimental work was divided into two parts, phase 1 and phase 2, as illustrated in Figure 1.5.

As mentioned, the goal with phase 1 was to formulate a new geopolymer mixture with the idea of producing an alternative for Portland cement in oil well cementing operations. Then, the goal with phase 2 was to investigate the effect of nanoparticles on the newly formulated geopolymer mixture obtained in phase 1.

The results obtained from phase 1 and phase 2 will be presented in Chapter 5.1 and Chapter 5.2, respectively. Moreover, the test matrix design/background/reason for each test matrix will be well-defined and explained. After a test matrix is defined, the results will be presented. This was thought to be the easiest and most organized way because the next test matrix was designed based on the results from the previous test matrix.

5.1 Phase 1: Formulation of geopolymer reference mixture

The test matrixes (number and objective) in phase 1 are shown in Table 5.1. They are presented and categorized based on:

- The chronological time order they were conducted.
- The concentration of sodium metasilicate powder in the home-made sodium metasilicate solution. The concentration was reduced from 45.1% to 37.1% to 30% to 20% from test matrix 4 to 12. Diluting (adding in-situ water) the homemade sodium metasilicate liquid was a strategy to improve the workability of the geopolymer slurry.

The test matrixes presented in Table 5.1 are conducted as part of the different periods marked in yellow. Phase 1 was a screening process in order to formulate and optimize a novel geopolymer mixture that passed all the screening criteria, so it could be considered as an alternative to Portland cement, and be used as a reference to study the effect of nanoparticles in phase 2.

Table 5.1: Test matrixes in phase 1 summarized with number and objective. “Air time”, the time the geopolymer/cement plugs were exposed to ambient conditions after curing in oven and before UCS test is shown as well.

Test matrixes in phase 1		
Test matrix number	**Objective with test matrix**	**Air time (days)**
Pre-phase (geopolymer without homemade sodium metasilicate liquid)		
Test matrix 1	Different fly ash and silica fume ratios	No UCS test
Test matrix 2	Adding in-situ extra water to study expansion in TM#1	No UCS test
Test matrix 3	Replacing extra added water with 10M NaOH to study expansion in TM#1	No UCS test
Effect of homemade sodium metasilicate liquid (45.1%, milky color)		
Test matrix 4	Different fly ash and silica fume ratios, and investigating 2.5 vs. 2.0 Na_2SiO_3/NaOH ratio	1
Effect of homemade sodium metasilicate liquid (37.1%, clear color)		
Test matrix 5	Effect of diluting homemade sodium metasilicate liquid to 37.1%, and improving workability with lignosulfonate	1
Test matrix 6	Improving workability with lignosulfonate	1
University of Stavanger closed on March 12 (COVID-19 global pandemic)		
Test matrix 7	Effect of 0.55 vs 0.52 alkaline liquid / solid ratio	57
Portland cement for comparison with TM#7-13		
Test matrix 8	Comparing geopolymers in TM#7-13 with Portland cement	56
Effect of homemade sodium metasilicate liquid (30%, clear color)		
Test matrix 9	Effect of diluting sodium metasilicate liquid to 30%	56
Test matrix 10	Improving workability with extra ex-situ water and lignosulfonate	53
Test matrix 11	Continuing on TM#10 with different extra added water and lignosulfonate concentrations	50
Effect of homemade sodium metasilicate liquid (20%, clear color)		
Test matrix 12	Improving workability by diluting to 20%	52/48
Effect of commercial sodium silicate liquid (37.1%)		
Test matrix 13	Replacing the homemade sodium metasilicate liquid with commercial sodium silicate liquid	48
University of Stavanger partly re-opened on April 27 (COVID-19 global pandemic)		
Selection of the geopolymer references		
Test matrix 14	Formulation of **geopolymer reference #1**	1
Test matrix 15	Formulation of **geopolymer reference #2**	1
Test matrix 16	Formulation of **geopolymer reference #3**	1

Curing time

All the plugs in phase 1 were cured for 3 days in oven at 62°C. The “Air time (days)” column in Table 5.1 refers to the time the plugs were exposed to ambient temperature after curing in oven and before UCS test. **TM#1-3** was part of the pre-phase so the geopolymer systems were not tested for UCS. The geopolymer plugs in **TM#4-6** were exposed to ambient temperature of 1 day, while **TM#7-13** were affected by the COVID-19 pandemic. **TM#7-13** had different “air time” depending on when the plugs were made.

COVID-19 pandemic (the University of Stavanger was closed for 1.5 months)

The COVID-19 highly affected the works in TM#7-13 since the University of Stavanger was closed for 1.5 months (March 12 to April 27). Consequently, the plugs in these test matrixes had to be exposed to ambient temperature many days beyond the planned 1 day. Additionally, 1-2 weeks before the COVID-19 lockdown, the availability of the UCS machines were restricted. After 1.5 months, the lab at the University of Stavanger re-opened, and the plugs were mechanically crushed.

The long aging time at ambient conditions probably resulted in higher UCS. However, the important thing is that all the plugs in TM#7-13 can be compared because the situation was nearly equal to them all. As seen in Table 5.1, the geopolymer/cement plugs in TM#7-13 had a time being exposed to ambient air varying between 48 and 57 days. The nine days difference was thought to be neglectable.

Also, the rest of the experimental works (TM#14-23) in this MSc project were affected by the coronavirus pandemic because 1.5 months of laboratory work was lost. Consequently, things had to be rushed when the school opened again in order to complete the study program on time.

5.1.1 Screening process

The formulated geopolymer slurries and plugs were checked through various pre-defined screening tests to find the proper geopolymer mixture. The pass/fail screening tests for phase 1 are illustrated in Figure 5.1.

This diagram was applied for **TM#9-16**. In these test matrixes, the geopolymers were formulated for use in oil well cementing. For the test matrixes **TM#1-7**, the rheology was not measured with viscometer because the slurries were too viscous.

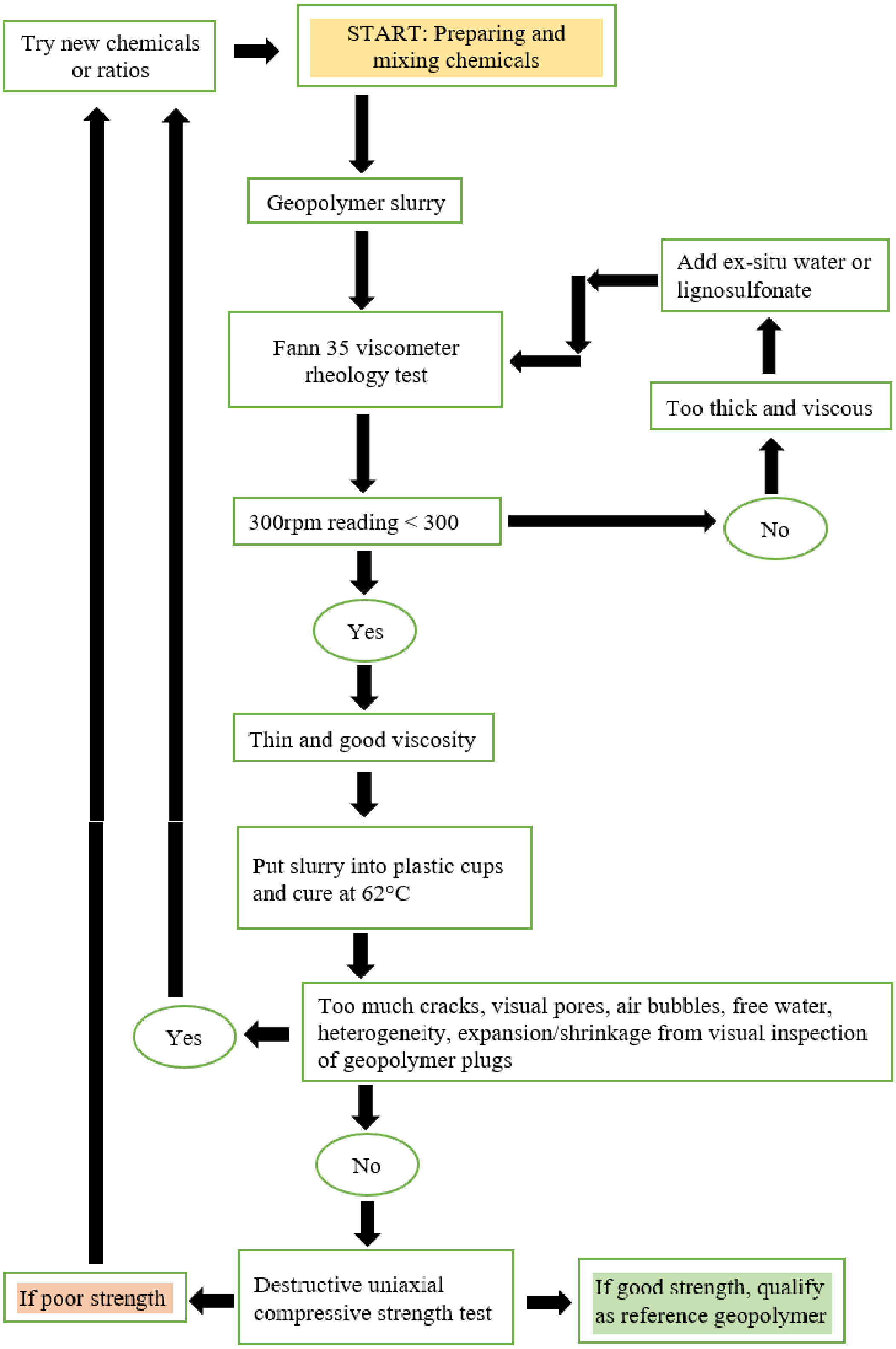


Figure 5.1: Flow chart of screening tests for formulation of geopolymer reference mixture in phase 1.

The experimental tests for all test matrixes (TM) in phase 1 are shown in Figure 5.2.

- Destructive tests
  - Uniaxial compressive test **(TM#4-16)**
    - Uniaxial compressive strength, UCS **(TM#4-16)**
    - Young's modulus, E **(TM#4-6, 14-16)**
- Non-destructive test
  - Rheology measurement **(TM#8-16)**
  - Visual inspection: **(TM#1-16)**
    - Visual cracks, pores and air bubbles of plug after curing
    - Free water (homogeneity) of plug
    - Expansion or shrinkage after curing
  - Sonic, mass, diameter and length measurement **(TM#4-16)**
    - Modulus of elasticity, M **(TM#4, 14-16)**
  - Water absorption **(TM#4)**

Figure 5.2: Summary of the destructive and non-destructive tests performed for phase 1 (test matrix 1-16).

5.1.2 Pre-phase

The main objective with the pre-phase was to learn how to make geopolymer and experiment with different chemicals and ratios. The goal was to create a geopolymer with high UCS strength, so the workability and rheology were not considered for the time being. However, extra ex-situ water was added when required for the slurry to be poured easily from the mixing bucket to plastic cups for curing.

In the pre-phase of this MSc research project, the first geopolymer was synthesized without really knowing how it would look like or its characteristics (i.e., rheology of slurry, visuality or strength of plug).

Sodium metasilicate powder was ordered from Sigma-Aldrich, and it took 1.5 weeks upon arrival. Because of the delay, the first geopolymer was formulated with solid (fly ash / silicate fume) and alkaline binder consisting of only 10M NaOH (as NaOH pellets were already available in the lab).

The geopolymer plugs in TM#1-3 were not mechanically crushed, so the uniaxial compressive strength (UCS) of the plugs is not reported.

5.1.2.1 Test matrix 1

Design idea: The objective was to investigate the best combination of fly ash and silicate fume with fixed 10 M NaOH as alkaline activator. The geopolymer plugs were evaluated with visual inspection such as expansion, free water, cracks, pores and structural deformation.

Geopolymer mixtures: The four geopolymer mixtures formulated in test matrix 1 (TM#1) can be seen in Table 5.2. The names, e.g., "70/30-0 (ex-situ water)" refers to the content of chemicals in the geopolymer mixture:

- 70: 70wt% of solids consist of fly ash.
- 30: 30wt% of solids consist of silica fume.
- 0: sodium metasilicate liquid / 10M NaOH ratio that equals 0 since only 10M NaOH is used as alkaline activator.
- Extra added water
    - (ex-situ water): extra water added ex-situ into geopolymer slurry (TM#1).
    - (in-situ water): extra water added in-situ by diluting homemade sodium metasilicate liquid (TM#2).
    - (NaOH instead of extra water): extra water replaced by 10M NaOH (TM#3).

The total solids were 191g (fly ash + silica fume), and the total alkaline activator was 100g (10M NaOH).

Table 5.2: Composition of the four geopolymer mixtures in TM#1 as well as chemical ratios and 300rpm viscosity reading.

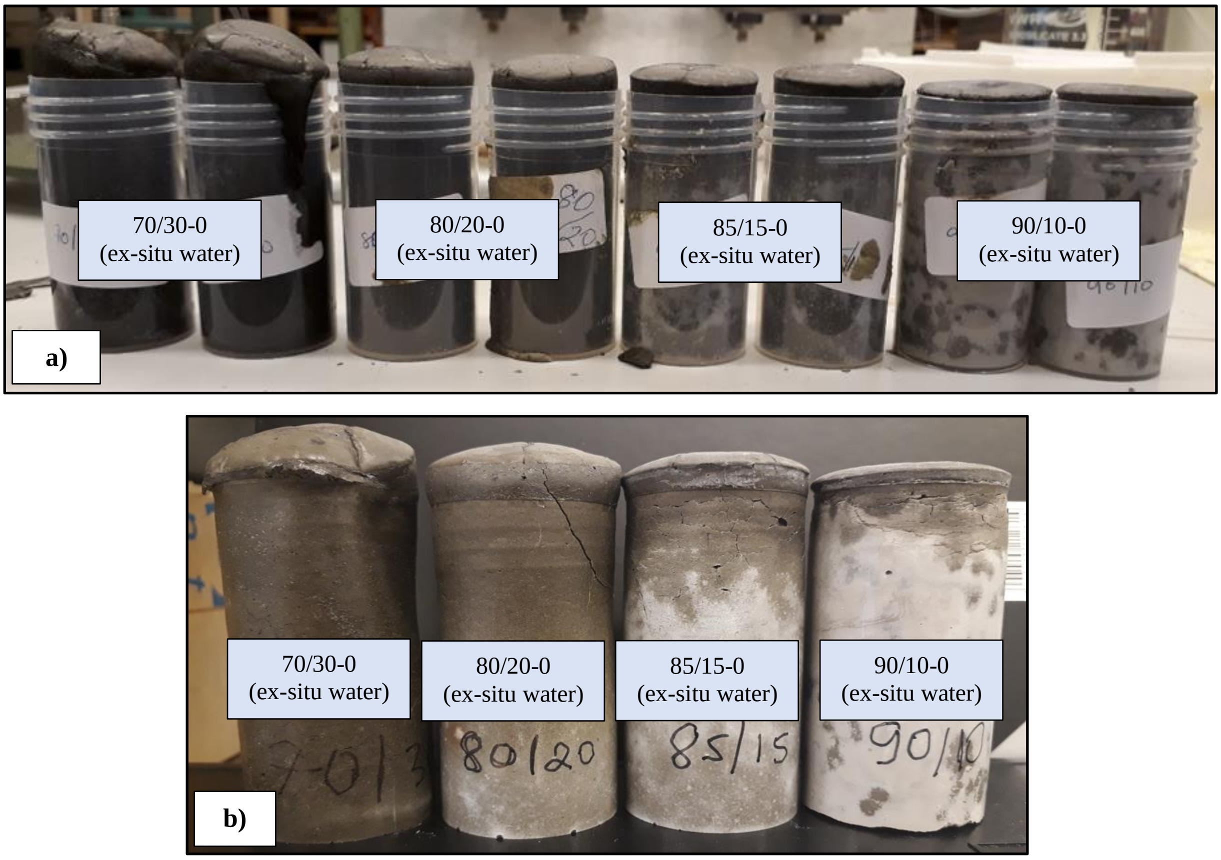
	70/30-0 (ex-situ water)	80/20-0 (ex-situ water)	85/15-0 (ex-situ water)	90/10-0 (ex-situ water)
Silica fume (g)	57	38	29	19
Fly ash (g)	134	153	162	172
10M NaOH (g)	100	100	100	100
Extra ex-situ water (g)	15	3	1	0
Fly ash (wt% of solids)	70	80	85	90
Silica fume (wt% of solids)	30	20	15	10
Na_2SiO_3 / NaOH ratio	0	0	0	0
Alkaline liquid / solids ratio	0.52	0.52	0.52	0.52
Total liquid / solids ratio	0.60	0.54	0.53	0.52
Viscosity	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$

Plug preparation: Extra ex-situ water was added to all the four geopolymer slurries until they had approximately the same viscosity.

Rheology: The rheology was not measured with viscometer because the slurry was too thick. It was decided not to add more water because it was expected to cause too much free water.

Visual inspection: The visual inspection of the plugs after being cured at 62°C for 3 days showed an expansion as the silica fume content and extra water increased. For instance, the 70/30, in Figure 5.3a), recorded longer than the others. The expansion of the 70/30 geopolymer was measured to be 15.5mm from top of plastic cup to top of plug. Additionally, the 70/30 had deformed structurally, seen in Figure 5.3b). Among the considered concentrations, the 90/10 were found out to be best in terms of expansion and structural integrity.

In order to evaluate the internal pore structure, the top of the samples were polished with sandpaper down to 68mm (top surface of plastic cup), with the results shown in Figure 5.3 c). At this length, they all had large pores and cracks as a result of the free water. The pore-structures may also be due to entrapped air.



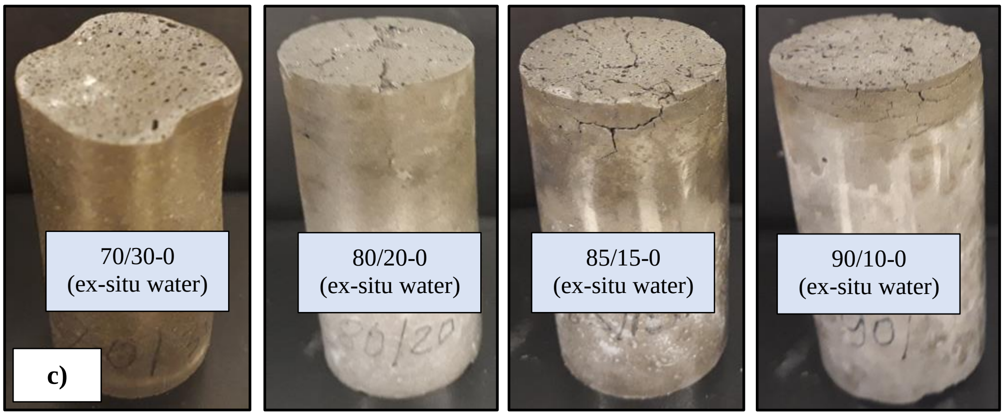


Figure 5.3: TM#1. a) plugs taken out of oven after 3 days of curing. b) plugs taken out of plastic cup. c) top surface polished.

5.1.2.2 Test matrix 2

Design idea: In order to answer the reason for the observation in test matrix 1 (i.e., plug length expansion with both increasing silica fume content and added water), a geopolymer based on 70/30 (FA/SF) was designed with in-situ added water mixed with 100g 10M NaOH solution instead of ex-situ water. The "70/30-0" mixture was chosen to study the effect of ex-situ vs in-situ added water on expansion because it showed the most expansion in test matrix 1.

Geopolymer mixture: One geopolymer mixture was made (two plugs). The chemical composition is displayed in Table 5.3.

Table 5.3: Composition and 300rpm viscosity reading of the geopolymer mixture in TM#2.

	70/30-0 (in-situ water)
Silica fume (g)	57
Fly ash (g)	134
10M NaOH (g)	100
Extra in-situ water (g)	15
Viscosity	Not measured but $\theta_{300} > 300$

Plug preparation: The water and the 10M NaOH were mixed for about 10-15min. The fluid mixture was then blended with the 70/30-mixture.

Visual inspection: The "70/30-0 (in-situ water)" plug expansion length was measured to be 15.4mm for both samples, which is more or less the same as in TM#1. Therefore, it cannot be concluded if the ex-situ water, in-situ water, or silica fume caused the expansion.

5.1.2.3 Test matrix 3

Design idea: It was decided to replace the extra-added water by NaOH (then in total 115g 10M NaOH was used) to answer the reason for the expansion.

Geopolymer mixtures: In similar way as TM#2, one geopolymer system was synthesized (two plugs). The chemical composition is shown in Table 5.4.

Table 5.4 Composition and 300rpm viscosity reading of the geopolymer mixture in TM#3.

	70/30-0 (NaOH instead of extra water)
Silica fume (g)	57
Fly ash (g)	134
10M NaOH (g)	115
Extra in or ex-situ water (g)	0
Viscosity	Not measured but $\theta_{300} > 300$

Visual inspection: The condition of the two “70/30-0 (NaOH instead of extra water)” plugs was 15.4mm, which was approximately the same expansion as in TM#1-2. Hence, the hypothesis is that it might be the silica fume that caused the axial growth.

5.1.3 Effect of homemade sodium metasilicate liquid (45.1%, milky color)

After using about two weeks on experimenting in the pre-phase (TM#1-3), the sodium metasilicate powder (ordered from Sigma-Aldrich) arrived at the University of Stavanger. For all the remaining test matrixes (TM#4-23), a combination of homemade sodium metasilicate and NaOH was used as alkaline activator for making the geopolymer. Exceptions are TM#13 that used commercial sodium silicate mixed with NaOH, and TM#8,19 where Portland cement plugs were produced.

The geopolymers in TM#4 was made with **milky colored** homemade sodium metasilicate (45.1%, milky). The white, milky color in Figure 4.10 reveals that it contains several undissolved powders.

TM#4 aimed to synthesize a geopolymer based on the homemade sodium metasilicate liquid (45.1%, milky) that resulted in strong UCS. The slurries were very viscous and cannot be used for oil well cementing. However, the mixtures might be good enough for civil construction purposes. This test matrix was a first try to make a strong, durable geopolymer, and it illustrates that this MSc project has been a learning process. With later test matrixes, the rheology was improved.

5.1.3.1 Test matrix 4

Design idea: For constant alkaline Na_2SiO_3/NaOH-ratio of 2.5 and constant alkaline activator/solid-ratio of 0.52, geopolymers with different ratios of FA/SF were tested. The FA/SF used were: 70/30, 90/10, 95/5, and 100/0.

Besides, for constant 95/5 fly ash to silica fume ratio, 2.0-ratio was compared with 2.5. The 95/5-ratio was chosen since the low content of silica fume exhibited the least expansion from the result comparison in TM#1-3.

Geopolymer mixtures: Four geopolymer mixtures were made in TM#4, giving eight plugs in total. Their composition is shown in Table 5.5. The names of the mixtures are based on the same principle as explained in TM#1. For example:

- 70/30 = fly ash / silica fume wt% ratio.
- 2.5 or 2.0 = homemade sodium metasilicate liquid (45.1%, milky) / 10M NaOH ratio.
- +25g water is extra added ex-situ water for workability.

Table 5.5: Geopolymer mixtures made in TM#4. Homemade sodium metasilicate (45.1%, milky) = Na_2SiO_3.

	70/30-2.5 (45.1%, milky) +25g water	95/5-2.5 (45.1%, milky) +9g water	100/0-2.5 (45.1%, milky) +6g water	95/5-2.0 (45.1%, milky) +6g water
Silica fume (g)	61	10	0	10
Fly ash (g)	141	192	202	192
Na_2SiO_3 (g)	75	75	75	75
10M NaOH (g)	30	30	30	30
Extra ex-situ water (g)	25	9	6	6
Viscosity	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$

Sample preparation: The oven did not work, so the plugs stood 19h at room temperature to the next day before they were put in the oven. The curing time was 3 days in the oven at 62°C.

Rheology: The geopolymers in TM#4 required more extra ex-situ added water than in TM#1-3 to achieve the same workability. The fast geopolymerisation is reflected in Figure 5.4 a), where the mix of solids and alkaline activator reached a powdery state immediately for the 70/30-2.5 mixture in Table 5.5. In b), 25g water is added, which made the mixture to a fluid slurry.

The rheology was not measured because even with the amount of extra water, it was seen to have viscometer 300RPM reading of $\theta_{300} >> 300$.

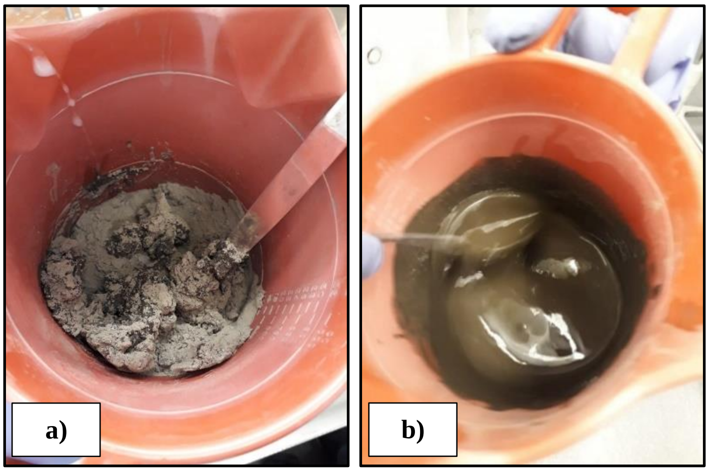


Figure 5.4: a) mixing of solids and alkaline activator **before** adding extra ex-situ water. b) mixing of solids and alkaline activator **after** adding extra ex-situ water.

Visual inspection: After a visual inspection, the “70/30-2.5 (45.1%, milky) +25g water” geopolymer mixture did not qualify for further investigation. The screening test hence categorized the formulation as fail. Both its slurry, Figure 5.5 a), and plug state, Figure 5.5 d), showed high amount of air bubbles.

According to the screening tests/criteria, the other three geopolymer mixtures, the “100/0-2.5 (45.1%) +6g water”, “95/5-2.5 (45.1%) +9g water” and “95/5-2.0 (45.1%) +6g water” passed the visual inspection. From Figure 5.5 a-d), they had all little air bubble generation in the slurry, small expansion during curing, few visible pores and little free water. The 100/0 plug appeared to have the lowest amount of visual pores and air bubbles on the top surface after being polished to 68mm, as seen in Figure 5.5 c)-d).

Figure 5.5: TM#4. a) geopolymer slurries. b) plugs after curing. c) plugs polished, side view. c) plugs polished, top view.

Water absorption and sonic measurement: After curing in oven for three days at 62°C, the geopolymers were removed from the plastic cups and exposed to open air for 24h. Their top surface was polished with sandpaper before they were measured for the geometries (mass, diameter and length) and the sonic travel time. Then, the plugs were immersed in water for 24h. The process was repeated, and the compressional wave velocity and the density of the plugs were measured for consecutive days. The plug's hydration process was going on until the mass change from water absorption became nearly negligible, presented in Figure 5.6. Based on these four measurements, the modulus of elasticity (M) was calculated for each plug, as shown in Figure 5.7.

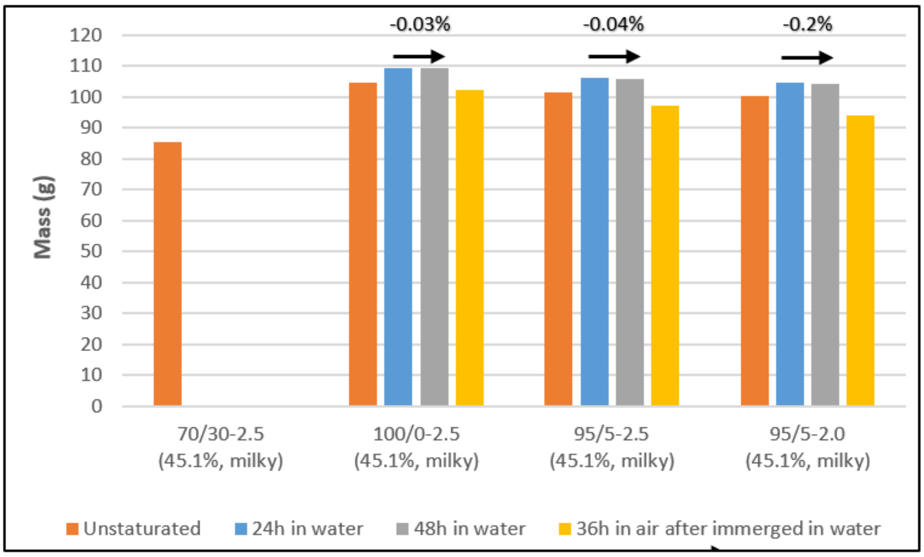


Figure 5.6: Measured mass of geopolymers in TM#4, from water absorption test.

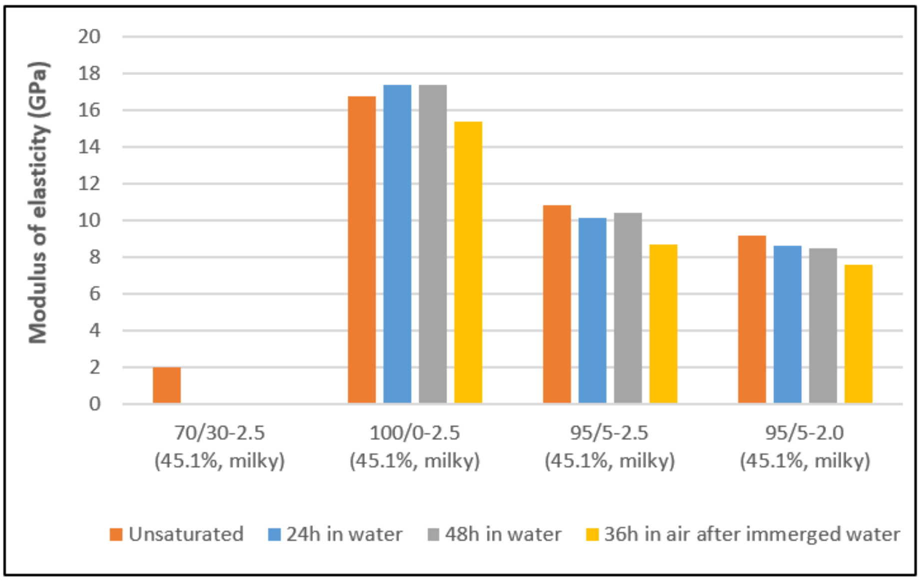


Figure 5.7: Calculated modulus of elasticity of the geopolymer plugs in TM#4.

By the visual inspection, the two “70/30-2.5 (45.1%, milky)” geopolymer plugs did not pass the water absorption test. After immersion in water for 24h, parts of the plugs crumbled and pieces fell off, documented with Figure 5.8. Therefore, the measurements on the 70/30 geopolymer were only conducted in unsaturated state.

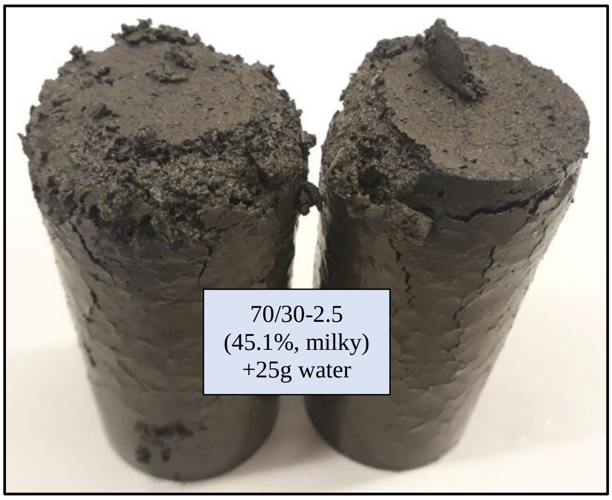


Figure 5.8: 70/30 geopolymer failed water absorption test.

The 100/0-2.5, 95/5-2.5 and 95/5-2.0 plugs passed the water absorption test. The difference in water absorbed between 24h and 48h was very small, presented in Figure 5.6. So, the water absorption test was stopped after 48h. As seen in Figure 5.6, the maximum decrease in mass (absorbed mass of water) between 24h and 48h was 0.2%, for the “95/5-2.0 (45.1%)” geopolymer, which is an insignificant decrease. This means the geopolymer plugs did not allow more water inflow in the pore spaces anymore. The modulus of elasticity was also almost constant between 24h and 48h immersion, as shown in Figure 5.7.

Interestingly, all the geopolymers in test matrix 4, except the “70/30-2.5 (45.1%)”, had a very reflective plastic-like (or glass) surface that likely comes from the high alkalinity of the homemade sodium metasilicate liquid (45.1%). This characteristic of the surface of the geopolymers can be the reason for the good performance with low water absorption in the water absorption test. The 70/30 did not have this type of surface likely because it was poorly geopolymerised, as seen in Figure 5.8.

Figure 5.7 shows the final result from the sonic measurements, the modulus of elasticity. Furthermore, as the plugs had been exposed in air for 36 hrs, they had lost most of the fluids absorbed during 72 hrs. Hence, the measured velocity and density reduced in dry state, and the modulus of elasticity were lower than those saturated with water. Results showed that the modulus of elasticity of the silica fume-free geopolymer exhibited higher than silica fume-based system. In the presence of 5% silica fume, the 2.5 alkaline activator ratio showed a relatively higher modulus of elasticity than the 2.0 activator's ratio.

UCS test: Since the "70/30-2.5 (45.1%, milky) +25g water" geopolymer mixture failed both the visual inspection and the water absorption test, it was screened out and was not considered for mechanical tests. The three other geopolymer mixture plugs were mechanically crushed after being immersed in water for 72 hours and exposed to ambient air for 36 hours.

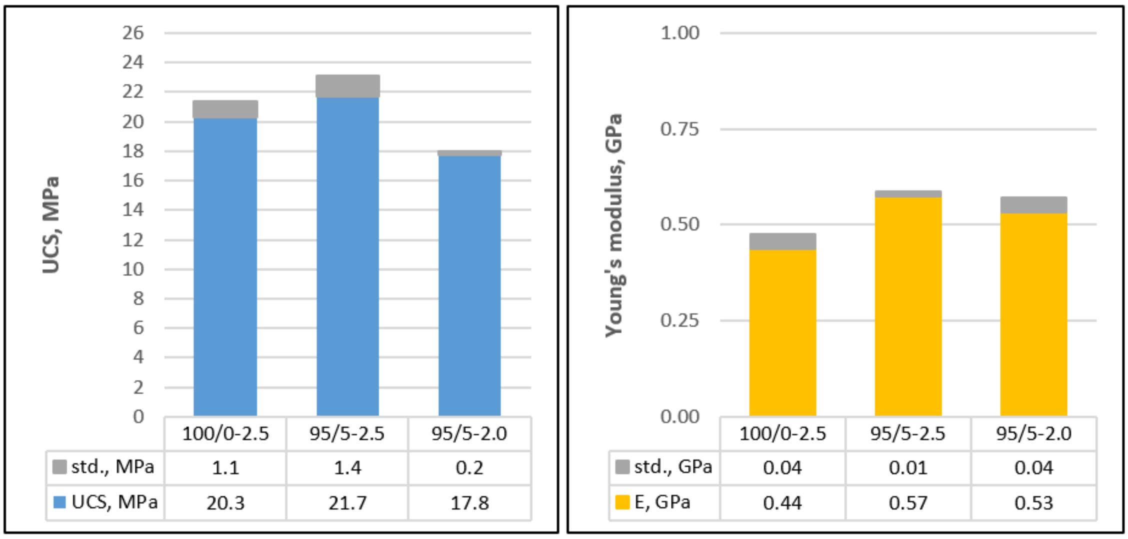
Figure 5.9 shows the UCS results. The "95/5-2.5" geopolymer had a strength of 21.7 MPa, which is 7% higher than the "100/0-2.5" and 22% higher than the "95/5-2.0". Therefore, the "95/5-2.5" based geopolymer formulation was chosen to proceed with. Young's modulus is also shown in Figure 5.9. The "95/5-2.5" exhibited the highest stiffness, which is not beneficial. However, it was considered more important to have strong UCS value.

To supplement the decision of choosing "95/5-2.5" as best system, it was observed from the Standard Force Load vs. %Deformation plots in Figure 5.10 that both the geopolymer mixtures with FA/SF ratio of 95/5 had smoother curves than 100/0. The 100/0, with the least smoothness of the curve, seemed to have more crack development during compression.

Ultimately, all the following geopolymer mixtures in this MSc work were based on the three ratios:

- Fly ash / silica fume ratio of 95/5.
- Homemade sodium metasilicate liquid / 10M NaOH ratio of 2.5.

The Force vs. %Deformation plots for the geopolymer mixtures in TM#4, as well as for the other test matrixes in this work, are given in Appendix B.



	100/0-2.5	95/5-2.5	95/5-2.0
▨ std., MPa	1.1	1.4	0.2
🟦 UCS, MPa	20.3	21.7	17.8

	100/0-2.5	95/5-2.5	95/5-2.0
▨ std., GPa	0.04	0.01	0.04
🟨 E, GPa	0.44	0.57	0.53

Figure 5.9: UCS and Young's modulus from destructive test, TM#4.

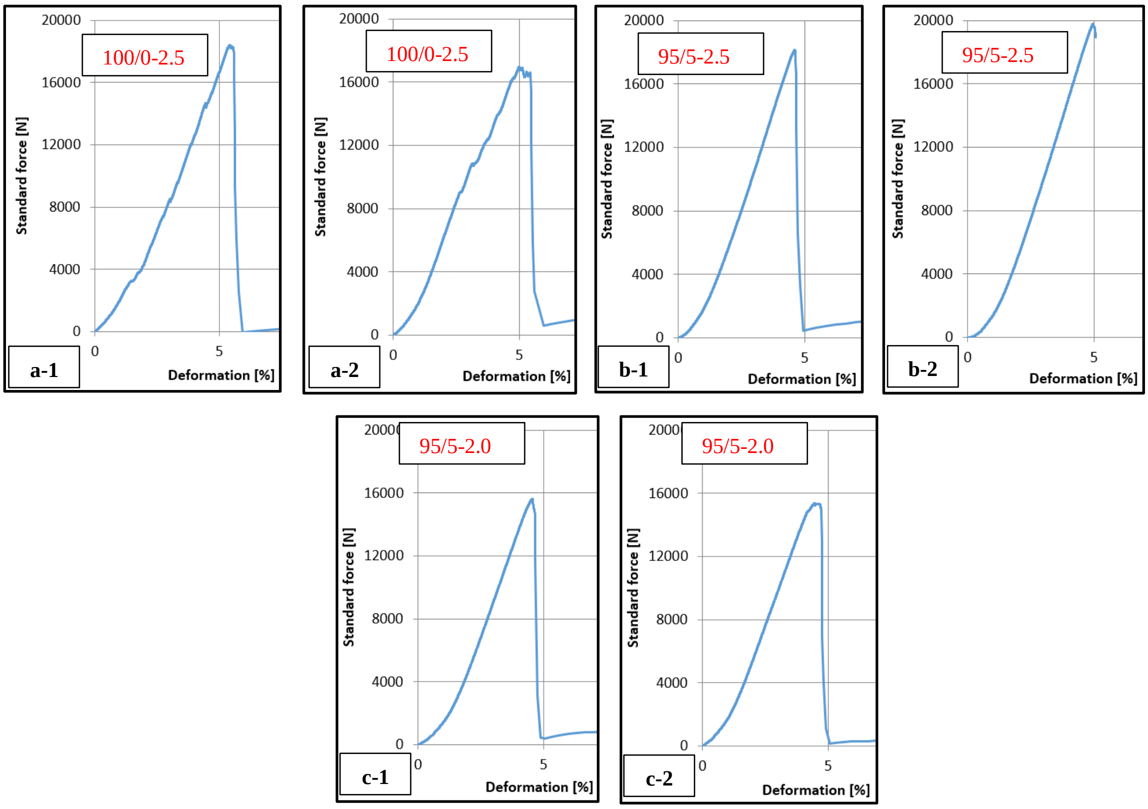


Figure 5.10: Standard Force vs. %Deformation for the three geopolymer mixtures in TM#4 (2 x plugs for each mixture).

Screening fail/pass: Based on the high visual viscosity, the system will definitely have an issue of pumpability when try to pump downhole in an oil well. Therefore, due to this reason, the system was categorized as **fail** for being used in oil well cementing operations. However, instead, the author feels that the "95/5-2.5 (45.1%, milky color) +9g water" could be used for construction works due to high UCS and thick slurry with the amount of water added. Thus, this geopolymer formulation was used as reference for construction works to study effect of nanoparticles in TM#17-18. For that use, it was modified to have slightly thinner slurry with 30g ex-situ water, and it was named **geopolymer reference #1** (referring to Figure 1.5). Geopolymer reference #1 is defined in **TM#14**.

5.1.4 Effect of homemade sodium metasilicate liquid (37.1%, clear color)

The goal was to formulate a geopolymer suitable for oil well cementing operations. But, the geopolymers in TM#4 were too thick for that purpose with 300RPM reading on viscometer far beyond 300. So, to improve the workability and at the same time reducing free water, two strategies were implemented:

- Diluting the homemade sodium metasilicate liquid from 45.1% to 37.1%.
- Adding lignosulfonate dispersant.

Homemade sodium metasilicate liquid (37.1%, clear color) was made so that it could be compared with the commercial sodium silicate (37.1%). It had a clear, transparent color, as shown in Figure 4.14.

5.1.4.1 Test matrix 5

Design idea: Test matrix 5 was designed to see the effect of lignosulfonate dispersant on the geopolymer, and also to see the effect of reducing the concentration of homemade sodium metasilicate liquid to 37.1%. Only two concentrations of lignosulfonate were tested because at this time, the lignosulfonate was just tested to see if it worked (i.e., provide improved results on workability, reduce free water and increase/decrease in UCS).

Geopolymer mixtures: Three geopolymer mixtures were formulated, presented in Table 5.6. The “95/5-2.5 (37.1%, clear color) +2.3g water” was used as the reference in the study of the effect of lignosulfonate (or “ligno”). For the two other blends, 1.1 and 1.7g ligno were added. Initially, the selected concentrations of ligno were not based on a published article, but just an attempt to see how the additive is strong enough to thin the system for the considered 2.3 g water.

Table 5.6: Geopolymer mixtures made in TM#5. Homemade sodium metasilicate (37.1%, clear) = Na_2SiO_3.

	95/5-2.5 (37.1%, clear) +2.3g water	+1.1g ligno	+1.7g ligno
Silica fume (g)	10	10	10
Fly ash (g)	192	192	192
Na_2SiO_3 (g)	75	75	75
10M NaOH (g)	30	30	30
Extra ex-situ water (g)	2.3	2.3	2.3
Lignosulfonate(g)	0	1.1	1.7
Viscosity	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$

Sample preparation: The lignosulfonate was dispersed in the 2.3g water before mixed with slurry.

The hypothesis of adding lignosulfonate dispersant:

- Improve workability and give thinner geopolymer slurry (from paper [32], [50], and theory of dispersants).
- Reduce free water (from paper [32], [50] and theory of dispersants).
- Increase UCS strength (from paper [32], [50]).

Rheology: Even with extra ex-situ added water, the slurry was too thick to be measured with viscometer. The extra ex-situ water was added until satisfied workability with hand-stirring.

Diluting the homemade sodium metasilicate liquid to 37.1% improved workability. Less water was required compared to the same 95/5-2.5 geopolymer mixture in test matrix 4 in order to achieve the same workability. This was probably because a homemade sodium metasilicate liquid of concentration 37.1% was used instead of 45.1%. In addition, the 37.1% liquid had a clear color, while the 45.1% fluid was milky colored. The added lignosulfonate also made the slurry thinner, but it was still too thick for viscometer measurement.

Similar to test matrix 4, more water could have been added to improve workability. But, more water was at this point in time thought to give a lot of free water and resulting low UCS value.

Visual inspection: Figure 5.11 a) shows that there was a small expansion but slightly reducing with increasing lignosulfonate content. From Figure 5.11 b)-c), it can be seen that the free water reduced significantly with higher concentration of lignosulfonate dispersant.

As illustrated with Figure 5.11 b), it was decided to polished the geopolymer plugs to the level of the free water interface for the plug with the **least** free water, which was the formulation with +1.7g ligno. The highly porous and brittle free water structure of the ligno-free geopolymers can be observed after the plugs were polished to 68mm, shown in Figure 5.11 c).

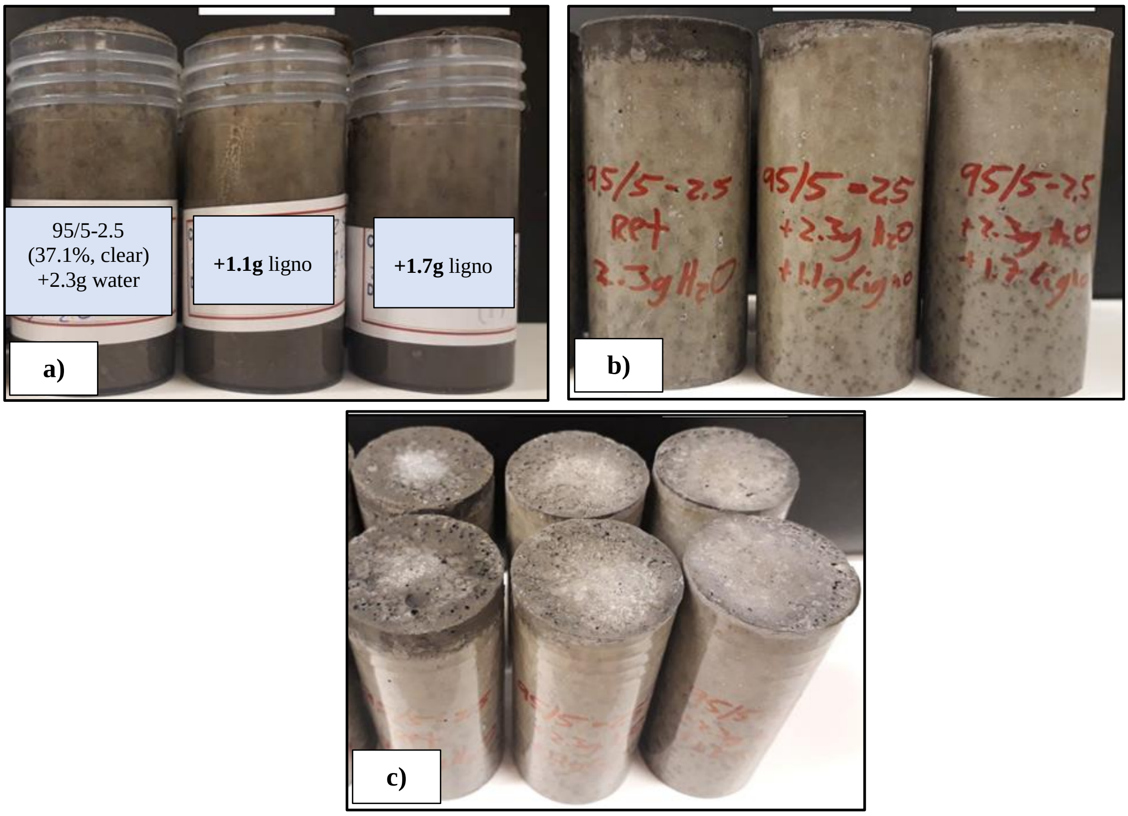


Figure 5.11: TM#5. a) plugs out of oven. b) plugs polished, side view c) plugs polished, top view.

UCS test: Incorporating 1.1g and 1.7g into the geopolymer slurry significantly improved the workability and reduced free water. Additionally, the UCS appeared to be approximately the same as the reference without ligno, as seen in Figure 5.12. This is an exciting result because the reference had much more free water with cracks and visual pores than the two ligno-modified geopolymers, as seen in Figure 5.11 c).

While the workability was improved by diluting the homemade sodium metasilicate liquid to 37.1%, the UCS seemed to have been reduced significantly compared to the “95/5-2.5 (45.1%, milky) +9g water” geopolymer in TM#4. The “95/5-2.5 (37.1%) +2.3g water” geopolymer showed a strength of 13.6 MPa, shown in Figure 5.12. The (45.1%) geopolymer in TM#4 had 21.7 MPa, from Figure 5.9. The plugs in both test matrixes had 68mm before UCS test.

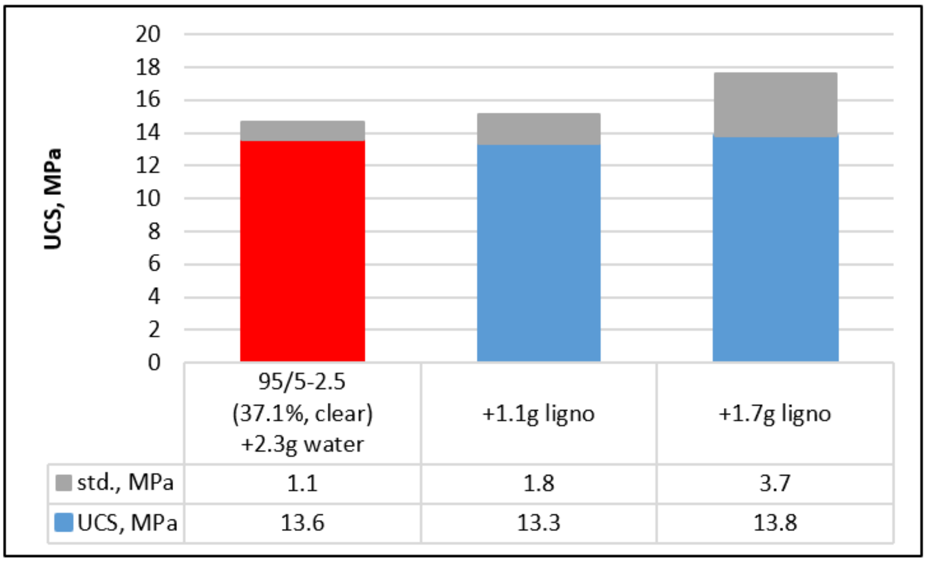


Figure 5.12: UCS for geopolymers in TM#5.

Figure 5.13 shows that the 1.1g and 1.7g ligno-modified geopolymer systems had 13% and 10% lower Young's modulus than the ligno-free system.

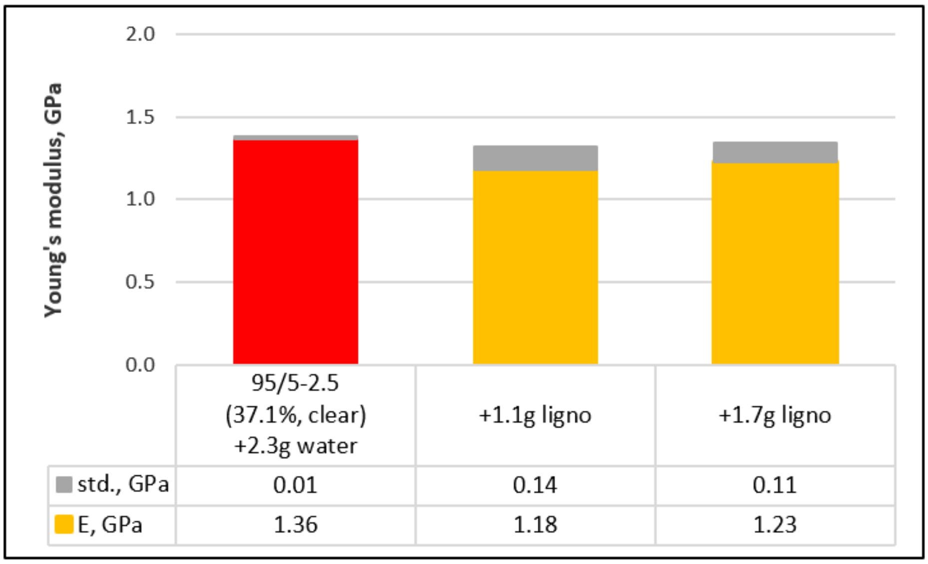


Figure 5.13: Young's modulus for geopolymers in TM#5.

Screening fail/pass: The mixtures are categorized as **fail** for oil well cementing operation because they are too thick for pumping in the well. It would rather be good enough for construction works in cases where compressive strength in range 13.3 to 13.8 MPa is sufficient.

5.1.4.2 Test matrix 6

Design idea: The blending of 1.1g (0.54% by weight of solids) and 1.7g ligno (0.83wt%) in test matrix 5 showed promising results with lower free water. Therefore, it was decided in test matrix 6 to investigate the effect of ligno more comprehensively.

Geopolymer mixtures: Five geopolymer systems were made, as seen in Table 5.7. The control mixture had 15g ex-situ water and no lignosulfonate incorporated. The four other systems had an increasing amount of ligno added to the control mixture. Unfortunately, a mistake was made when weighing the NaOH alkaline activator. By mistake, 10g of 10 M NaOH was used instead of 30g, giving a total of alkaline liquid only 85g and making the Na_2SiO_2/NaOH-ratio to 7.5 instead of the desired 2.5. However, the plugs were still cured and tested as intended, with the hope that they could give an indication of the effect of lignosulfonate.

Table 5.7: Geopolymer mixtures made in TM#6. Homemade sodium metasilicate (37.1%, clear) = Na_2SiO_3.

	95/5-7.5 (37.1%, clear) +15g water	+0.25wt% ligno	+0.50wt% ligno	+1.00wt% ligno	+1.50wt% ligno
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	85	85	85	85	85
Extra ex-situ water (g)	15	15	15	15	15
Lignosulfonate(g)	0	0.51	1.01	2.02	3.03
Viscosity	Not measured $\theta_{300} > 300$	Not measured $\theta_{300} > 300$	Not measured $\theta_{300} > 300$	Not measured $\theta_{300} > 300$	Not measured $\theta_{300} > 300$

Sample preparation: 15g extra water was added to the control mixture after mixing the activator with solids. For the four other geopolymer systems, the lignosulfonate was dispersed in 15g with water before mixed with the slurry.

Rheology: It was observed that the slurry was too viscous to be measured by a viscometer. One can observe that more extra ex-situ water was required to achieve same the workability for the ligno-free geopolymer in TM#6 (15g water, giving 0.50 liquid/solid ratio) compared to TM#5 (2.3g water, giving 0.53 liquid/solid ratio).

Visual inspection: The first visual observation is that the Na_2SiO_3/NaOH=7.5 ratio based geopolymer in TM#6 from Figure 5.14 a) appeared to have higher expansion than 2.5-ratio in TM#5 from Figure 5.11 a). However, there seemed to be less free water, as seen in Figure 5.14 b). Similar to TM#5, the trend in TM#6 was reducing free water with increasing lignosulfonate concentration, as shown in Figure 5.14 b)-c). The plugs were polished to 68mm.

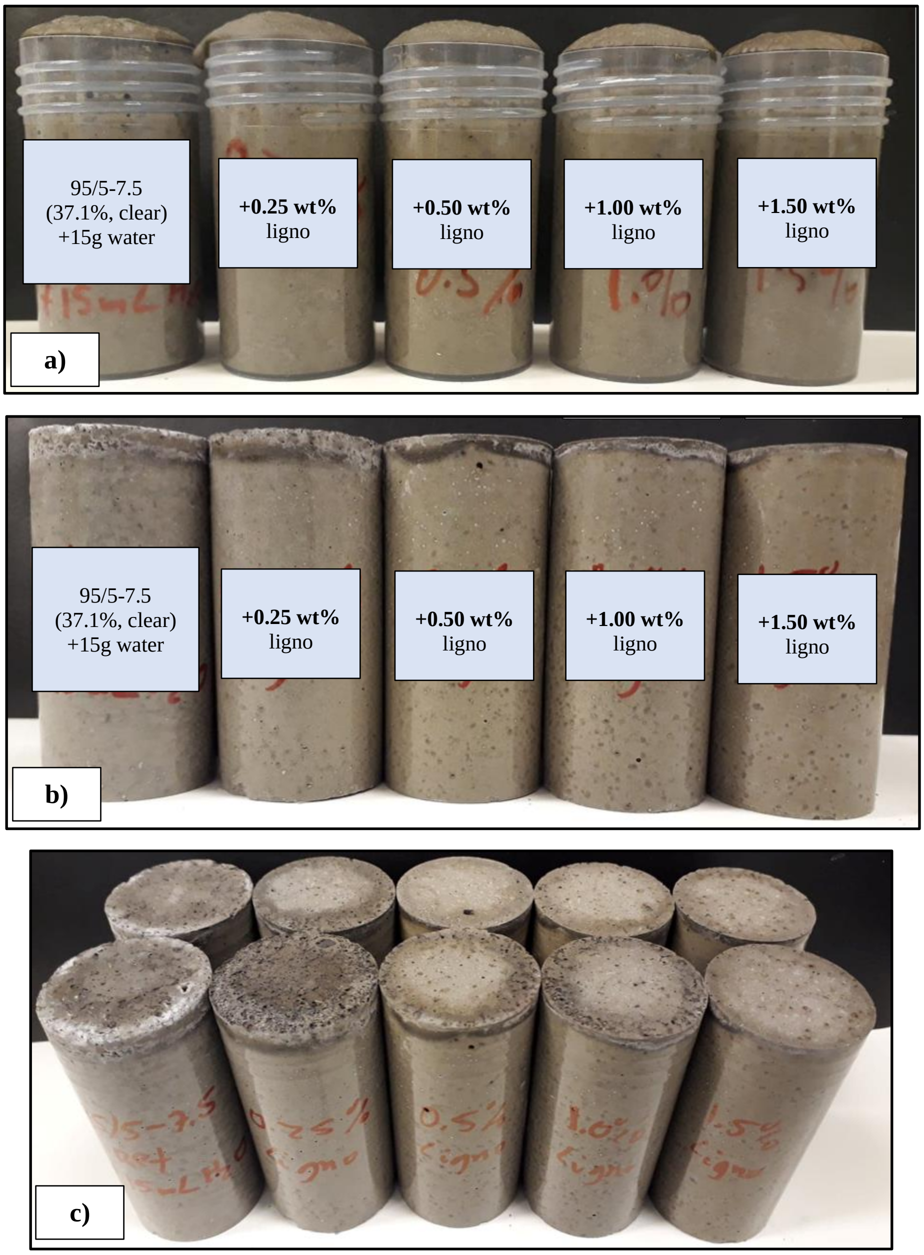
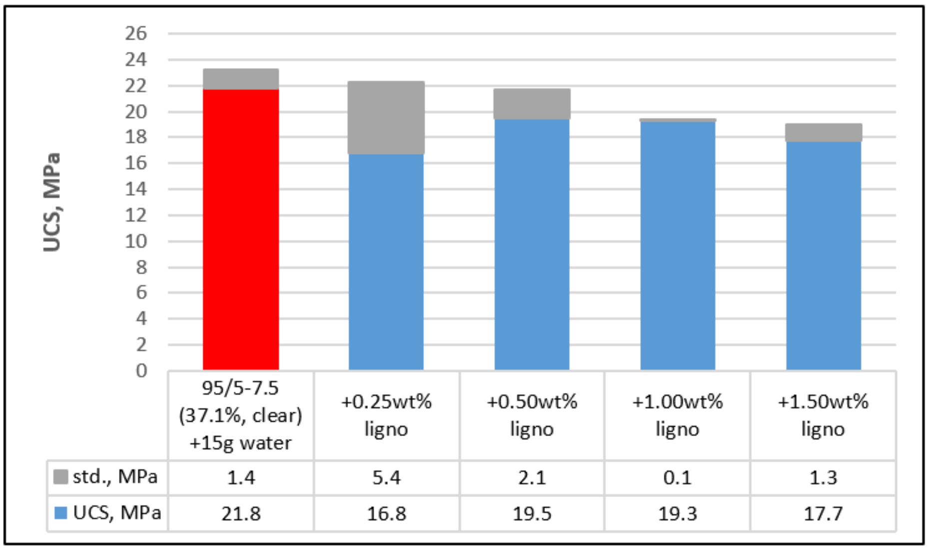


Figure 5.14: TM#6. a) plugs out of oven. b) plugs polished, side view. c) plugs polished, top view.

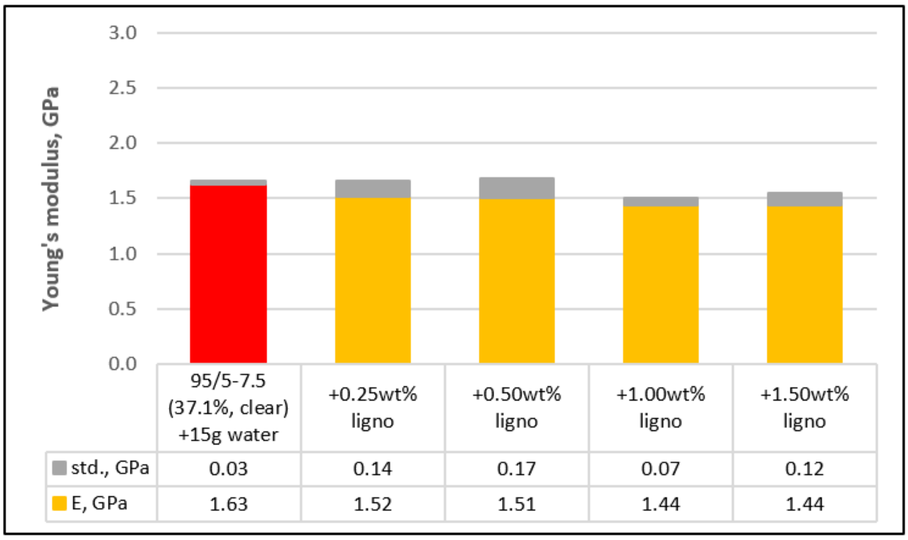
UCS test: As displayed in Figure 5.15, the lignosulfonate-free reference neat geopolymer showed higher UCS than the ligno-blended geopolymer. But, there is no clear trend with increasing ligno concentration. However, there seems to be a trend if the UCS-drop for 0.25wt%-ligno is excluded, and it might be reasonable to exclude based on the high standard deviation compared to the other samples. The high standard deviation reflects a large spread between the two 0.25wt%-ligno plugs. Comparing the UCS result with Figure 5.14, c) it makes sense that one of the 0.25wt%-ligno plugs had much lower UCS based on the relative high free water content and large pores on the top. So, if excluding the one 0.25wt%-plug (13.0 MPa) with much free water, then left is the other plug that had 20.6 MPa, and the resulting trend for UCS is much clearer – decreasing UCS with increasing ligno content.



	95/5-7.5 (37.1%, clear) +15g water	+0.25wt% ligno	+0.50wt% ligno	+1.00wt% ligno	+1.50wt% ligno
■ std., MPa	1.4	5.4	2.1	0.1	1.3
■ UCS, MPa	21.8	16.8	19.5	19.3	17.7

Figure 5.15: UCS for geopolymers in TM#6.

Similar to the trend in TM#5, the Young's modulus decreased with increasing wt% of lignosulfonate also in TM#6 (Figure 5.16). This means that the geopolymer with a high 1.50wt% concentration of ligno formed more elastically for a given force compared to the control mixture. The largest decrease was for 1.00wt% and 1.50wt% ligno, with 12% reduction relative to control mixture.



	95/5-7.5 (37.1%, clear) +15g water	+0.25wt% ligno	+0.50wt% ligno	+1.00wt% ligno	+1.50wt% ligno
■ std., GPa	0.03	0.14	0.17	0.07	0.12
■ E, GPa	1.63	1.52	1.51	1.44	1.44

Figure 5.16: Young's modulus for geopolymers in TM#6.

Screening fail/pass: Since the systems are too viscous, the pumpability of the slurry to be used in an oil well is difficult. Hence the formulation is considered as **fail** for oil well application. However, since the formulation provided strong UCS, the author feels that it might be good enough for construction purposes.

5.1.4.3 Test matrix 7

Design idea: The aim was to investigate the effect of 0.55 alkaline liquid / solid ratio. To improve the workability of the geopolymer slurry, TM#7 was designed to formulate a geopolymer with 0.55 alkaline liquid to solid ratio by still using the homemade sodium metasilicate liquid with 37.1% concentration. The results were compared with the 0.52-ratio.

Geopolymer mixture: The composition of the 0.55 -and 0.52-ratio systems are shown in Table 5.8. One plug was made for each of the two geopolymer mixtures because the slurries were so viscous that it was only enough to fill one 34.5x69.0mm plastic cup.

Table 5.8: Geopolymer mixtures made in TM#7. Homemade sodium metasilicate (37.1%, clear) = Na_2SiO_3.

	95/5-2.5 (37.1%, clear) Solids reduced 6% 0.55-ratio	95/5-2.5 (37.1%, clear) 0.52-ratio
Silica fume (g)	9.4	10
Fly ash (g)	180.5	192
Total alkaline activator (g)	105	105
Extra ex-situ water (g)	0	0
Viscosity	Not measured but $\theta_{300} > 300$	Not measured but $\theta_{300} > 300$

Sample preparation: Here, the sample preparation is exactly the same as the reference prepared in TM#5, except that no extra water was added for the plugs in TM#6, and the solids content was reduced by 6% for the 0.55-system.

Rheology: The viscosity was not measured because the mixtures were thick and had a swift setting time.

Visual inspection: The plugs were polished with sandpaper to 64mm. This is the same length as the shrunk Portland cement in TM#8, which will be explained in TM#8. At this length, the geopolymer made with alkaline liquid / solids ratio of 0.52 appeared to have more free water, seen in Figure 5.17. Interestingly, the 0.55-ratio had more cracks on the top surface, but the 0.52 had more visual pores.

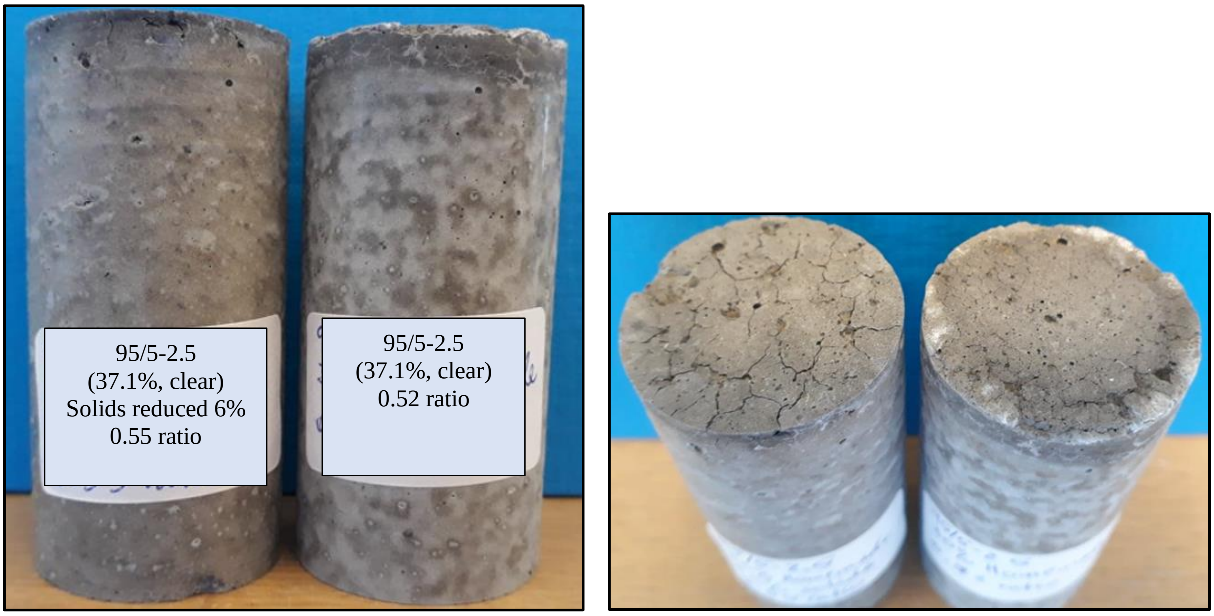


Figure 5.17: Geopolymer plugs in TM#7 after 3 days of curing in oven. Side view and top view.

UCS test: Similar to the situation with TM#8-13, the geopolymers in TM#7 could not be mechanically tested according to the planned date. Unfortunately, the laboratory was suddenly closed due to the coronavirus lockdown of Norway, and therefore, the plugs in TM#7 had to rest at room temperature for 57 days. This might explain the high UCS in Figure 5.18. The 0.52-based geopolymer showed 5% lower UCS compared to the Portland cement, while the 0.55 geopolymer was 11% higher.

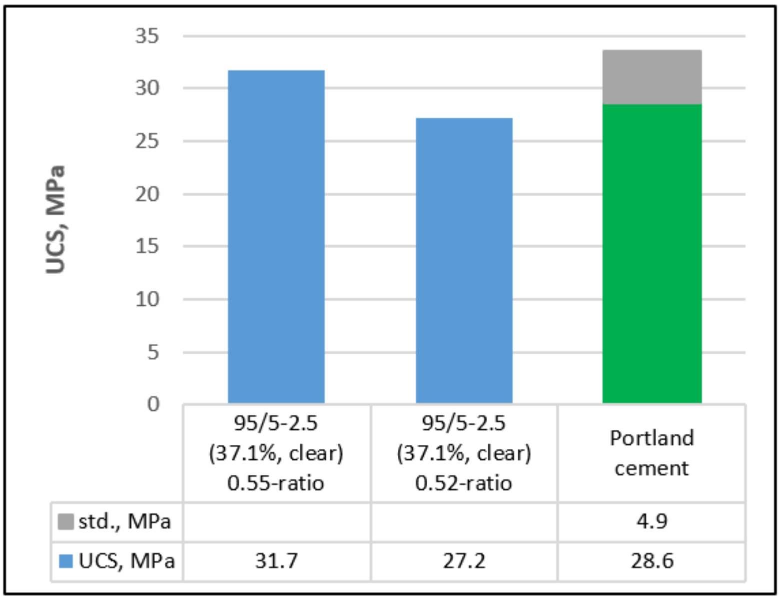


Figure 5.18: UCS of geopolymer plugs in TM#7, compared with Portland cement.

Due to the COVID-19 pandemic, there was no time to look more at the 0.55-ratio geopolymer and the possibility of using it as a reference in the study of nanoparticles. For example, more extra water could have been added until rheology measurement 300 reading < 300.

Screening fail/pass: Both geopolymer systems showed high UCS and were comparable with the Portland cement strength. Notice that both the Portland cement plugs and geopolymer plugs were exposed to air at room temperature for 56 and 57 days additionally to the 3-day curing at 62°C. Moreover, the slurry was very thick. Subsequently, the two mixtures **fail** the criteria for oil well cementing.

5.1.5 Portland cement for comparison with TM#7-13

5.1.5.1 Test matrix 8

Design idea: The design reason here was to compare geopolymers in TM#7-13 with 0.44 water/ cement ratio (WCR) Portland cement in order to assess the relative strength of the geopolymer with respect to the conventional Portland class G cement. Ultimately, the goal was to decide on which formulated neat geopolymer mixture to go ahead for further investigation of the effect of nanoparticles.

Portland cement mixtures: Two slurries of 0.44 WCR Portland class G cement were synthesized, and as usual, two plugs per slurry. Table 5.9 shows the composition and the measured 300RPM viscometer reading.

Table 5.9: Composition of Portland cement system made in TM#8.

	Portland cement Class G 0.44 water/solid ratio
Portland cement powder (g)	250
Water (g)	110
Viscosity	$\theta_{300} = 235$

Sample preparation: Similar to the geopolymer systems, the mixture was hand-stirred for 2-4 min until a uniform, homogenous slurry was achieved.

Rheology: Table 5.10 shows the measured rheological properties of the two cement slurries, which showed the criteria of **pass** because of the $\theta_{300} < 300$.

Table 5.10: Rheology measurement of the cement class G slurries in TM#8.

	1st slurry: Portland class G cement	**2nd slurry: Portland class G cement**
RPM	**Reading θ**	**Reading θ**
600	235	235
300	146	146
200	120	120
100	86	86
6	28	28
3	18	19
Pass/fail	Pass	Pass

Visual inspection: As shown in Figure 5.19 a)-b), after 3 days of curing at 62°C, the Portland class G cement had shrunk. This is due to the cement particle settling and resulting in free water on the top that evaporated due to heating. The shrinkage observation is the opposite of the behavior of the geopolymer, which showed expansion. However, the Portland cement also showed two phases, where on the top, the amount of free water is higher, and there are less particles, as seen in Figure 5.19 c). This behavior could maybe have been reduced if the slurry had been conditioned with a mixing machine for some minutes to remove the air from the systems.

The length of the cement plugs after shrinkage was ~64mm. The top surface was polished with sandpaper until smooth and horizontal. The geopolymer plugs in TM#7-13 were cut to this 64mm length for comparison of UCS. The reason for choosing the shrinkage-length of Portland is that if the free water level for the geopolymer plugs is below the shrinkage level of Portland cement, the geopolymers then have a weak-point below the shrinkage level of Portland cement. The weak-point comes from the porous and highly brittle characteristic of the free water, as well as many air bubbles and cracks. Additionally, the free water layer of the geopolymers is not fully geopolymerised due to its high water content.

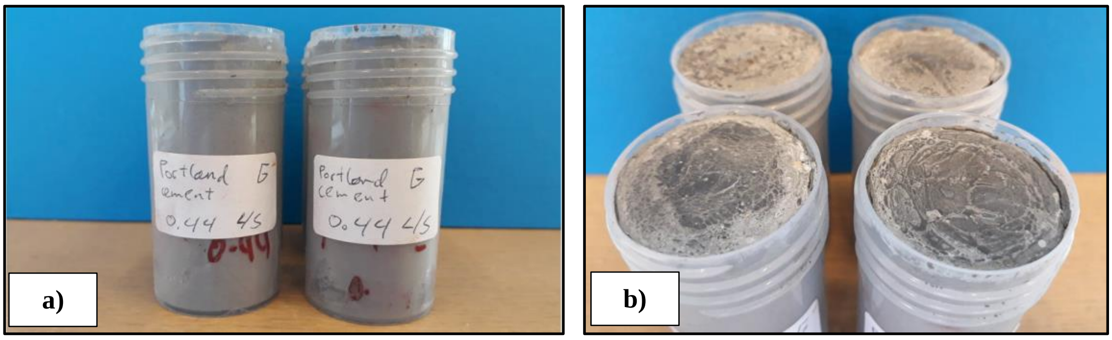


Figure 5.19: TM#8. a) plugs out of oven, side view. b) plugs out of oven, top view. c) plugs polished.

UCS test: Figure 5.20 shows the measured UCS values of the four plugs. As we can see, values are ranging from 23.1 to 35.0 MPa. This wide range could be due to the differences in surface irregularities or defects inside the plugs while filling slurry in the molding cup. For better representation, the average UCS value of the four plugs was calculated as (28.5±4.9) MPa.

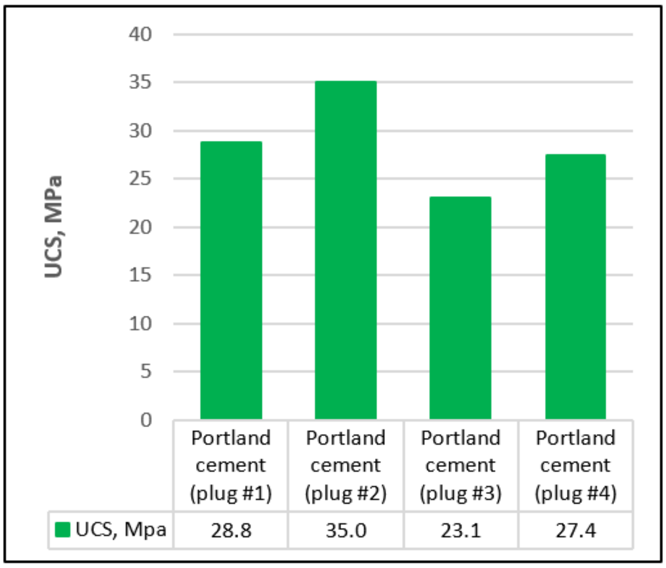


Figure 5.20: UCS of Portland class G cement after 3 days curing at 62°C and resting 56 days at room temperature. TM#8.

5.1.6 Effect of homemade sodium metasilicate liquid (30%, clear color)

The test results obtained from TM#5 indicated that the effect of lignosulfonate on the reference neat geopolymer formulated with 37.1% sodium metasilicate activator did not show any significant impact on the UCS value. Another promising result with adding lignosulfonate to the slurries was that the top layer (free water dominated) was significantly reduced as compared to the reference plug. Even though the workability was improved with the dispersant admixture, a shortcoming was too thick slurries to be measured with viscometer. Therefore, it was decided to try to improve the workability of the geopolymer slurry by reducing the concentration of the homemade sodium metasilicate liquid to 30%.

Higher lignosulfonate than the concentrations added in TM#6 was not considered since it was thought to decrease UCS as the trend in TM#6 indicated. It was also expected that adding more extra water would increase the free water, resulting in plugs containing more extended top weak layer, which will consist of more cracks and pores as well.

30% concentration of homemade sodium metasilicate liquid was synthesized to be used in TM#9-11. Unlike the (45.1%, milky color) concentration, all sodium metasilicate particles in the 30% concentration were dissolved, and the resulting solution was clear, transparent color, like water glass, as seen with pictures in Figure 4.12-Figure 4.13. By visual inspection, one can observe that the 30% concentration is less viscous than the 45.1% (Figure 4.10), and much easier to dissolve in water.

5.1.6.1 Test matrix 9

Design idea: All the geopolymer mixtures in TM#5-7, formulated with 37.1% concentration homemade sodium metasilicate liquid, resulted in too thick slurry and poor workability. Therefore, it was decided to improve the workability by diluting the homemade sodium metasilicate liquid to 30% and try to add lignosulfonate dispersant as powder.

Geopolymer mixtures: Here, the investigation was to study how an extra 23g water with 0.75g lignosulfonate could improve or have an impact on the rheological parameters. The results were compared with no water and ligno-free blended neat geopolymer, as formulated in Table 5.11.

Table 5.11: Geopolymer mixtures made in TM#9. Homemade sodium metasilicate (30%, clear) = Na_2SiO_3.

	95/5-2.5 (30%, clear)	95/5-2.5 (30%, clear) +23g water +0.75g ligno powder
Silica fume (g)	10	10
Fly ash (g)	192	192
Total alkaline activator (g)	105	105
Extra ex-situ water (g)	0	23
Lignosulfonate (g)	0	0.75
Viscosity	Measured $\theta_{300} > 300$	Measured $\theta_{300} > 300$

Sample preparation: The 0.75g lignosulfonate was added as powder to the geopolymer slurry.

Rheology: As shown in Table 5.12, the slurries formulated above were thick, and both recorded the viscometer response was beyond the maximum limit for RPM 300 and 600. Besides, 200RPM reading of the neat water/ligno free system was higher than the limit, whereas the water/ligno blended system recoded below the limit as 269. According to the defined criteria, the 300RPM reading is required to be less than the limit (300).

Table 5.12: The two geopolymer mixtures formulated in TM#9 that failed the rheology test.

	95/5-2.5 (30%, clear) +0g water	**95/5-2.5 (30%, clear) +23g water +0.75g ligno powder**
RPM	**Reading θ**	**Reading θ**
600	>300	>300
300	>300	>300
200	>300	269
100	281	135
6	19	9
3	11	5
Pass/fail	Fail	Fail

Visual inspection: The pictures in Figure 5.21 are taken after the plugs were cured for 3 days at 62°C, exposed to air for 56 days (due to COVID-19 lockdown), cut to 64mm length, and polished with sandpaper. The free water and amount of porous air bubbles appeared to be slightly higher for the system without extra water and ligno, looking at Figure 5.21 a)-b).

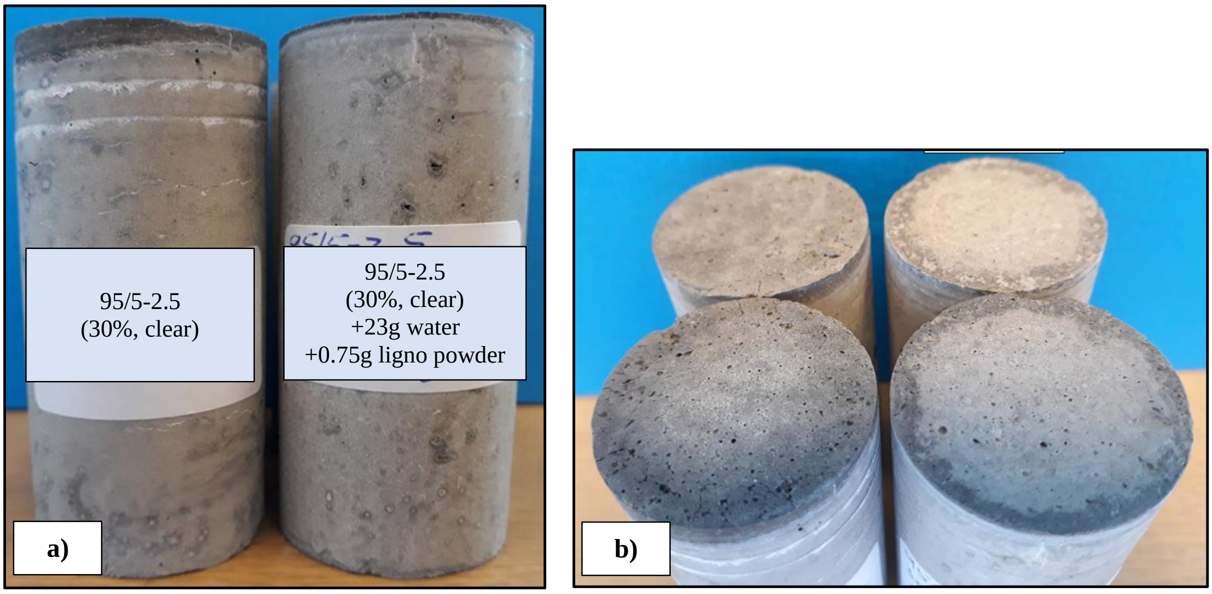


Figure 5.21: TM#9. a) plugs polished, sideview. b) plugs polished, top view.

UCS test: Figure 5.22 compares the measured UCS of the geopolymers with the Portland cement. In terms of measurement, the geopolymer systems indicated a quite lower standard deviation. The “95/5-2.5 (30%, clear)” plugs showed high strength of 24.2 MPa on average, 15% lower than the Portland cement. Besides, it appears that the combination of adding 23g water + 0.75g ligno (as powder) decreased the UCS quite significantly.

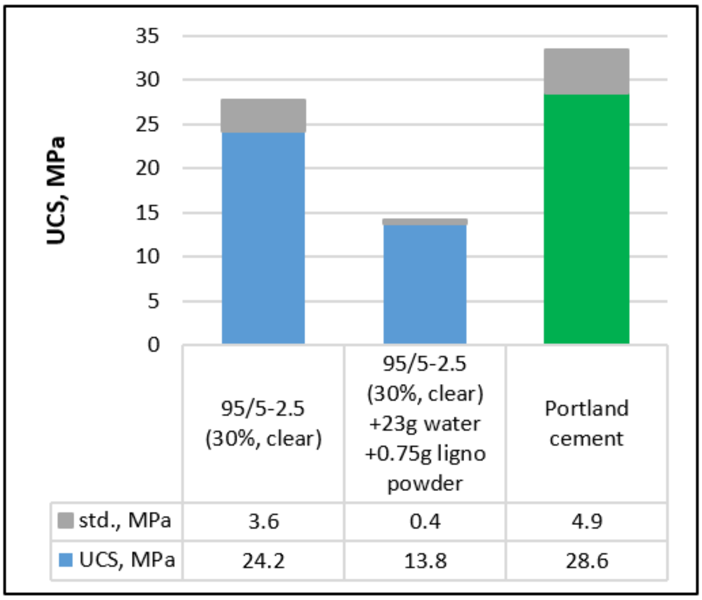


Figure 5.22: UCS of geopolymer plugs in TM#9, compared with Portland cement.

Screening fail/pass: The rheology was significantly improved by diluting the homemade sodium metasilicate liquid to 30%. However, according to the screening criteria, the formulation is considered as **fail** for oil well cementing due to high viscosity ($\theta_{300} > 300$). In terms of strength, the formulation without lignosulfonate is reasonable as compared with the Portland cement. Therefore, **geopolymer reference #2**, which was used as a reference for the study of effect of nanoparticles in TM#20-21 in phase 2, is very similar and based on those two geopolymer formulations (see **TM#15** in phase 1).

5.1.6.2 Test matrix 10

Design idea: During test matrix 9, the blending of 0.75g lignosulfonate as powder showed a thinning effect to improve the slurry’s workability. But still, the 300RPM dial reading was greater than 300. This suggests the need to further reduce the viscosity by trial error by the addition of more water and lignosulfonate concentrations until the desired viscosity measurement is achieved (i.e., θ_{300} reading < 300 limit). The idea here was, therefore, to improve the workability of geopolymer in TM#9 while trying to maintain good UCS strength and low free water.

Geopolymer formulation: A total of three geopolymer mixtures were formulated, presented in Table 5.13. The first attempt started with 3.1g ligno (1.5wt% of solids) mixed with 23g ex-situ water. This thinner solution (water + lignosulfonate) resulted in a very low viscous slurry, which recoded the viscometer reading at 300RPM as $\theta_{300} = 171$. In order to reduce the amount of superplasticizer, the second slurry was prepared by mixing 1.2g ligno in 23g water. The slurry was still thin, and the viscometer reading at the 300RPM resulted in within the pre-defined range, i.e., $\theta_{300} = 175$. This suggested for further reduction of the amount of water to 18g, mixed with 1.2g ligno.

Table 5.13: Geopolymer mixtures made in TM#10. Homemade sodium metasilicate (30%, clear) = Na_2SiO_3.

	95/5-2.5 (30%, clear) +23g water +3.1g ligno	95/5-2.5 (30%, clear) +23g water +1.2g ligno	95/5-2.5 (30%, clear) +18g water +1.2g ligno
Silica fume (g)	10	10	10
Fly ash (g)	192	192	192
Total alkaline activator (g)	105	105	105
Extra ex-situ water (g)	23	23	18
Lignosulfonate(g)	3.1	1.2	1.2
Viscosity	$\theta_{300} = 171$	$\theta_{300} = 175$	$\theta_{300} = 255$

Sample preparation: The thinner additive was prepared by mixing lignosulfonate with water to have good dispersion.

Rheology: Table 5.14 shows the measured viscometer responses for two attempts to fulfil the viscometer criteria. The first attempt was prepared by mixing 15g water with 1.2g ligno. The measured viscometer result showed that $\theta_{300} > 300$ and considered to be fail. In order to obtain less viscous, 3g water more water was added, and the measured 300RPM value is lower than the maximum limit, and hence, it was considered as pass. The three geopolymer mixtures that passed the viscometer test are shown in Table 5.15.

Table 5.14: Pass/fail screening of rheology criteria by adding more and more ex-situ water. TM#10.

	1st try: 95/5-2.5 (30%, clear) +15g water +1.2g ligno →	**2nd try: +3g water** →	**95/5-2.5 (30%, clear) +18g water +1.2g ligno**
RPM	**Reading θ**	**Reading θ**	
600	>300	>300	
300	>300	255	
200	201	174	
100	101	90	
6	7	6	
3	4	4	
Pass/fail	Fail	Pass	

Table 5.15: The three geopolymer mixtures formulated in TM#10 that passed the rheology test.

	95/5-2.5 (30%, clear) +23g water +3.1g ligno	**95/5-2.5 (30%, clear) +23g water +1.2g ligno**	**95/5-2.5 (30%, clear) +18g water +1.2g ligno**
RPM	**Reading θ**	**Reading θ**	**Reading θ**
600	>300	>300	>300
300	171	175	255
200	113	117	174
100	58	60	90
6	4	4	6
3	2	3	4
Pass/fail	Pass	Pass	Pass

Visual inspection: The slurries in plastic cups in Figure 5.23 a) illustrates how thin they were. The slurry with admixtures 23g water and 3.1g ligno had sunk in the middle of the cup because it was so low-viscous. The aged and cut plugs in Figure 5.23 c) had free water amount indicating that thinner slurry yielded more free water. They appeared to have the same expansion, as observed in Figure 5.23 b).

The top part of the plugs contained much free water and was more porous. The top surfaces were removed by polishing with sandpaper down to 64mm length, shown in Figure 5.23 d). The two plugs with 3.1g and 1.2g ligno dispersed in 23g water still had much free water after polishing, and that part was thought to be too porous and brittle to be mechanically destructed in UCS test. The plugs were therefore screened out.

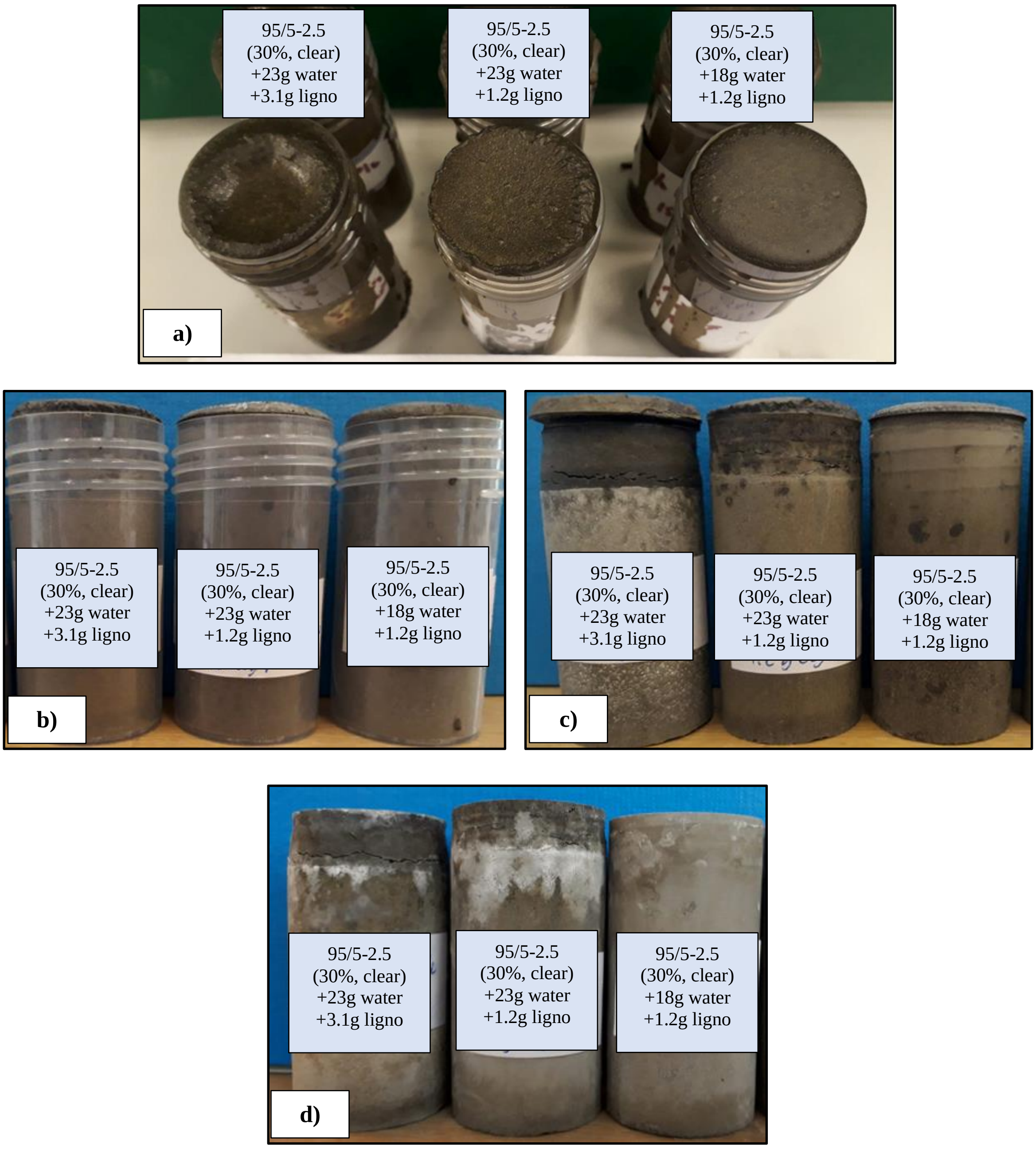


Figure 5.23: TM#10. a) slurry. b) plugs out of oven. c) plugs out of plastic cup. d) plugs cut.

UCS test: The UCS testing proceeded with the one plug-mixture that looked fine. Figure 5.24 shows the test results. The geopolymer plugs exhibited considerable 62% lower strength than the Portland cement plugs.

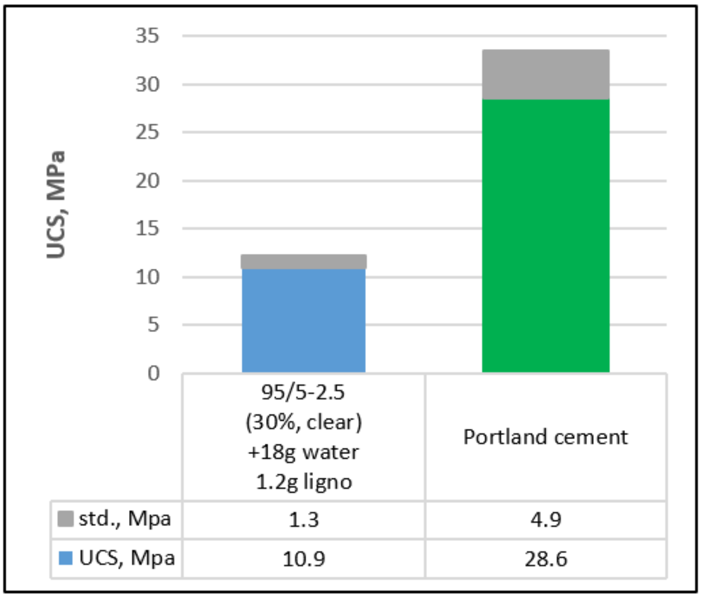


Figure 5.24: UCS of geopolymer plugs in TM#10, compared with Portland cement.

Screening fail/pass: The formulation, according to the pre-defined criteria, had good rheology but low strength compared to the cement. Thus, it did **not pass** for use in oil well cementing.

5.1.6.3 Test matrix 11

Design idea: Results from TM#10 showed that the geopolymers with 3.1g and 1.2g lignosulfonate dispersed in 23g water were very weak with much free water as compared with the Portland cement. Therefore, during TM#11, it was decided to increase the amount of water to 23g water and reduce the amount of ligno to still have good workability, and at the same time, reduce free water and have good UCS. Notice that due to COVID-19, the plugs in TM#7-13 were destructed on the same day, so the weak UCS of the plugs in TM#10 was not known at the time TM#11 was designed.

Geopolymer mixtures: Table 5.16 shows the geopolymer mixtures. The first formulation was with 75g ligno and the second with 1.0g.

Table 5.16: Geopolymer mixtures made in TM#11. Homemade sodium metasilicate (30%, clear) = Na_2SiO_3.

	95/5-2.5 (30%, clear) +23g water +0.75g ligno	95/5-2.5 (30%, clear) +23g water +1.0g ligno
Silica fume (g)	10	10
Fly ash (g)	192	192
Total alkaline activator (g)	105	105
Extra ex-situ water (g)	23	23
Lignosulfonate(g)	0.75	1.0
Viscosity	$\theta_{300} = 181$	$\theta_{300} = 181$

Sample preparation: Like before, the lignosulfonate powder was dispersed in 23g water and mixed ex-situ with solids.

Rheology: Table 5.17 shows the rheological properties of the slurries. As shown, both were qualified as good enough workability. The difference in lignosulfonate concentration did not show any impact on the dial readings.

Table 5.17: The two geopolymer mixtures formulated in TM# 11 that passed the rheology test.

	95/5-2.5 (30%, clear) +23g water +0.75g ligno	**95/5-2.5 (30%, clear) +23g water +1.0g ligno**
RPM	**Reading θ**	**Reading θ**
600	>300	>300
300	181	181
200	120	120
100	62	62
6	5	4
3	3	3
Pass/fail	Pass	Pass

Visual inspection: The 1.0g ligno-blended geopolymer showed more free water than with 0.75g ligno, illustrated in Figure 5.25 a). While polishing with sandpaper by hand, the top piece of both the 1.0g ligno-added samples was very brittle and porous. They were therefore screened out for further testing. The difference in color between the picture in Figure 5.25 a) and b) comes from the exposure time at room temperature. Picture a) was taken the same day the plugs were taken out of oven, while b) was taken after the 50 days of ambient temperature exposure.

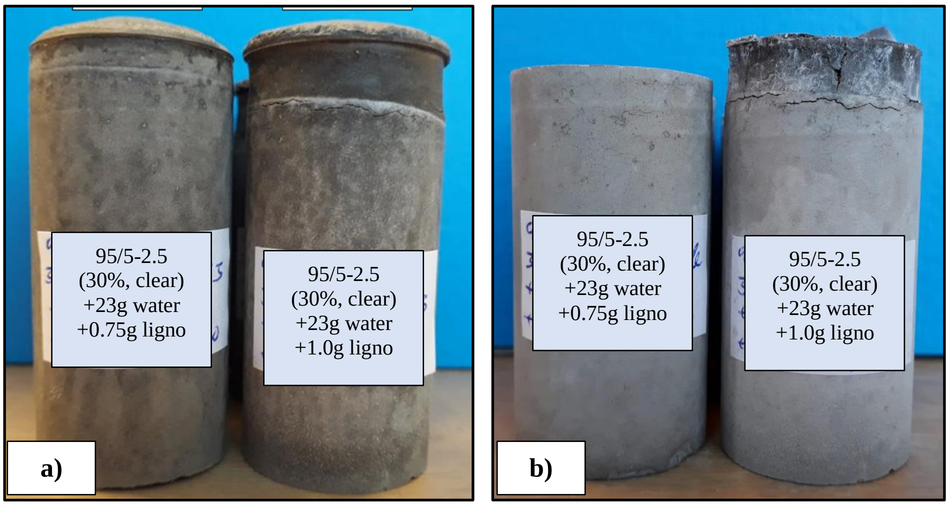


Figure 5.25: TM#11. a) plugs after 3 days of curing in oven at 62°C. b) after 50 days exposed to air and polished.

UCS test: Figure 5.26 shows the UCS of the geopolymer treated with 0.75g ligno. The strength was 74% lower than the Portland cement. Compared to the mixture incorporated with 1.2g ligno dispersed in 18g water in TM#10, the plugs in TM#11 had 31% lower UCS. So, it did not help to reduce ligno-amount to 0.75g and increase water to 23g.

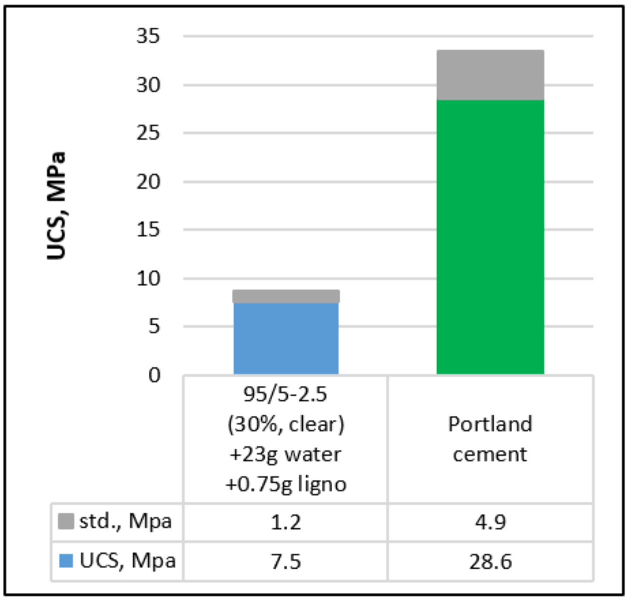


Figure 5.26: UCS of geopolymer plugs in TM#11, compared with Portland cement.

Screening fail/pass: The two mixtures **failed** the criteria for oil well cementing. They both achieved the rheology criteria, but admixture of 1.0g ligno dispersed in water resulted in high amount of brittle free water and was subsequently screened out. The 0.75g ligno-geopolymer failed due to the low strength.

5.1.7 Effect of homemade sodium metasilicate liquid (20%, clear color)

In order to reduce free water and improve workability with less extra water and ligno, the homemade sodium metasilicate liquid was diluted to reduce the concentration down to 20%.

5.1.7.1 Test matrix 12

Design idea: If not for the COVID-19 pandemic, the geopolymers in TM#7-10 would have been mechanically tested at an earlier time. Then, the 20% based geopolymers would most likely not have been made. However, it was synthesized because some of the 30%-geopolymer looked promising from visual inspection. Therefore, it was decided to dilute the homemade sodium metasilicate liquid to 20% in order to blend in less lignosulfonate and ex-situ water.

Geopolymer mixtures: Two geopolymer mixtures were formulated. Table 5.18 shows the formulation ingredients.

Table 5.18: Geopolymer mixtures made in TM#12. Homemade sodium metasilicate (20%, clear) = Na_2SiO_3.

	95/5-2.5 (20%, clear) +4g water	95/5-2.5 (20%, clear) +4g water +0.25g ligno
Silica fume (g)	10	10
Fly ash (g)	192	192
Total alkaline activator (g)	105	105
Extra ex-situ water (g)	4	4
Lignosulfonate(g)	0	0.25
Viscosity	$\theta_{300} = 299$	$\theta_{300} = 264$

Rheology: Table 5.19 shows the viscometer-response of the geopolymers formulated in Table 5.18. The result shows that the system without extra water and ligno was viscous and considered as fail since the 300RPM reading > 300. On the other hand, the 0.25g ligno dispersed in 4g water passed the criteria (θ_{300} < 300). Besides, the system with 4g water also fulfilled the viscometer criteria, illustrated with Table 5.20.

Table 5.19: Pass/fail screening of rheology criteria by adding more and more ex-situ water and lignosulfonate. TM#12

	1st try: 95/5-2.5 (20%, clear) +0g water → +0g ligno	**2nd try: +4g water +0.25g ligno**	**95/5-2.5 (20%, clear) +4g water → +0.25g ligno**
RPM	**Reading θ**	**Reading θ**	
600	>300	>300	
300	>300	264	
200	260	170	
100	127	88	
6	10	7	
3	5	4	
Pass/fail	Fail	Pass	

Table 5.20: The two formulated geopolymer slurries in TM#12 that passed rheology criteria.

	95/5-2.5 (20%, clear) +4g water	**95/5-2.5 (20%, clear) +4g water +0.25g ligno**
RPM	**Reading θ**	**Reading θ**
600	>300	>300
300	299	264
200	189	170
100	96	88
6	8	7
3	5	4
Pass/fail	Pass	Pass

Visual inspection: One plug from each mixture was taken out of the oven after 3 days. They immediately appeared weak because it was possible to scrape a mark with a nail on the surface. This is in contrast to the 45.1% plugs with plastic (glass)-like surface, possibly explained by high alkalinity and metasilicate content. The other half of the plugs were therefore cured for 7 days. Figure 5.27 shows a picture of the 7-days cured plugs. Even after 7 days of curing, the plugs still had traces of poor geopolymerisation reaction. The reference plug with no ligno admixture seemed to have a more solid and robust free water top with less cracks.

Figure 5.27: Geopolymer plugs cured 7 days in oven and exposed to ambient air in 48 days, TM#12.

UCS tests: Even though little amount of extra was required to achieve good workability, the geopolymer plugs based on homemade sodium metasilicate liquid (20%, clear) showed very low compressive strength. They were partly squeezed when compressed, and the highest achieved strength was for the 4g water-based geopolymer cured for 7 days with 5.9 MPa. This was a 31% increase from 3 days. On the contrary, the Portland cement reached 28.6 MPa before the maximum force load. In addition, the cement plugs exploded at peak load, indicating high build-up of internal stresses.

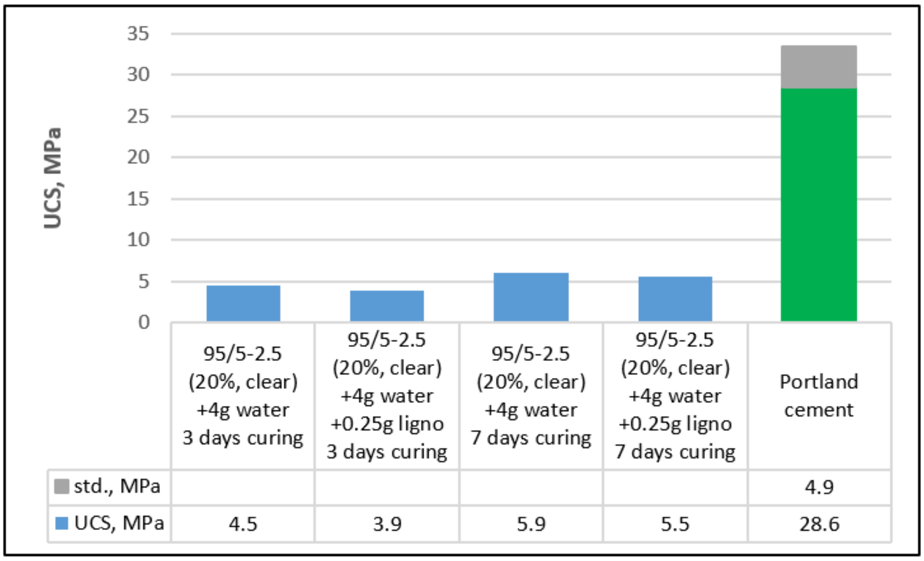


Figure 5.28: UCS for geopolymer plugs in TM#12, compared with Portland cement.

Screening pass/fail: It is observed that the 20% concentration of sodium metasilicate dissolved in water was not a strong enough alkaline activator, which produced poor compressive strength geopolymer. Therefore, the 20%-based geopolymer mixture was screened out and considered as a **fail**.

5.1.8 Effect of commercial sodium silicate liquid (37.1%)

The commercial sodium silicate was ordered from Sigma-Aldrich and was ready to use upon arrival.

5.1.8.1 Test matrix 13

Design idea: The aim was to investigate the effect of commercial sodium silicate liquid (37.1%) and compare with the homemade sodium metasilicate liquid-based geopolymer mixtures.

Geopolymer mixtures: Two types of mixtures were formulated, and the compositions are provided in Table 5.21. As shown, the 20g extra water was blended with 0.6g ligno. Also, a ligno-free water reference mixture was made.

Table 5.21: Geopolymer mixtures made in TM#13. Commercial sodium silicate (37.1%) = Na_2SiO_3.

	95/5-2.5 (37.1%, commercial) +20g water +0.6g ligno	95/5-2.5 (37.1%, commercial) +20g water
Silica fume (g)	10	10
Fly ash (g)	192	192
Total alkaline activator (g)	105	105
Extra ex-situ water (g)	20	20
Lignosulfonate(g)	0.6	0
Viscosity	$\theta_{300} = 280$	$\theta_{300} = 291$

Rheology: Table 5.22 shows the sequence of modifying the commercial silicate-based geopolymer to pass 300RPM reading. The first try started with 0.2g ligno dispersed in 4g water. Subsequently, on the fourth try, the dial reading was lower than 300. The two mixtures that passed viscometer criteria are shown in Table 5.23. The mixture with 20g water and 0.6g ligno was made again and measured for rheology, and the 20g water-geopolymer also passed the criteria.

Table 5.22: Rheology improvement for commercial-silicate based geopolymer, TM#13.

	1st try: 95/5-2.5 (37.1%, commercial) +4g water +0.2g ligno →	**2nd try: +8g water** →	**3rd try: +4g water +0.2g ligno** →	**4th try: +4g water +0.2 ligno** →	**95/5-2.5 (37.1%, commercial) +20g water +0.6 ligno**
RPM	**Reading θ**	**Reading θ**	**Reading θ**	**Reading θ**	
600	>300	>300	>300	>300	
300	>300	>300	>300	280	
200	>300	>300	269	184	
100	>300	70	134	92	
6	50	12	9	6	
3	30	6	5	3	
Pass/fail	Fail	Fail	Fail	Pass	

Table 5.23: Geopolymer mixtures that passed rheology test, TM#13.

	95/5-2.5 (37.1%, commercial) +20g water +0.6 ligno	**95/5-2.5 (37.1%, commercial) +20g water**
RPM	**Reading θ**	**Reading θ**
600	>300	>300
300	280	291
200	184	193
100	92	97
6	6	6
3	3	3
Pass/fail	Pass	Pass

Visual inspection: Figure 5.29 shows that the commercial-based geopolymer formed a high amount of porous free water top with some cracks. The plugs were cut to 64mm, as shown in the pictures. Interestingly, all the plugs had approximately the same free water length, even though lignosulfonate was incorporated in two of the mixtures.

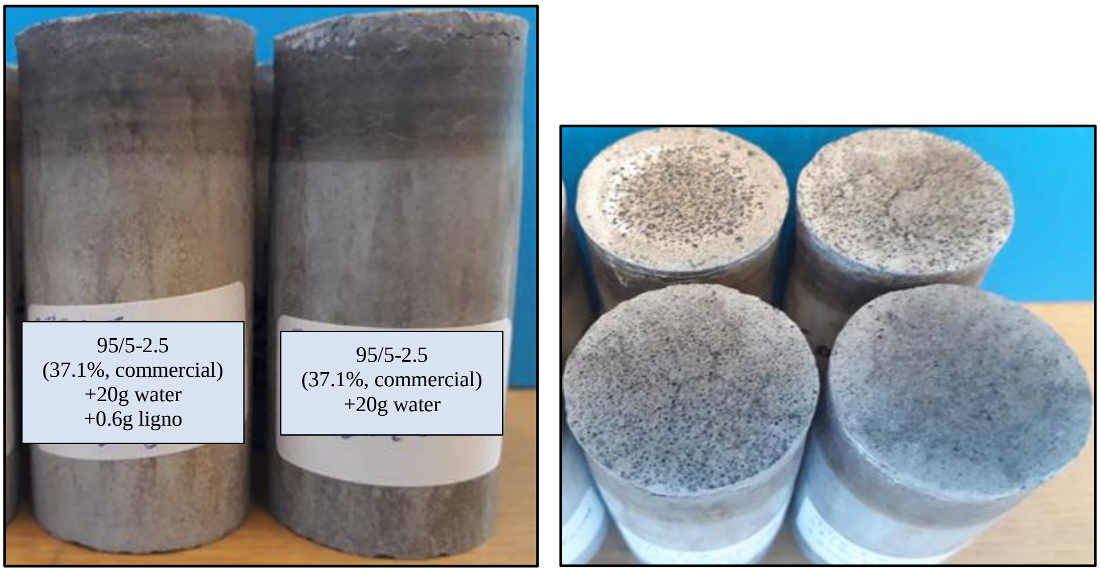
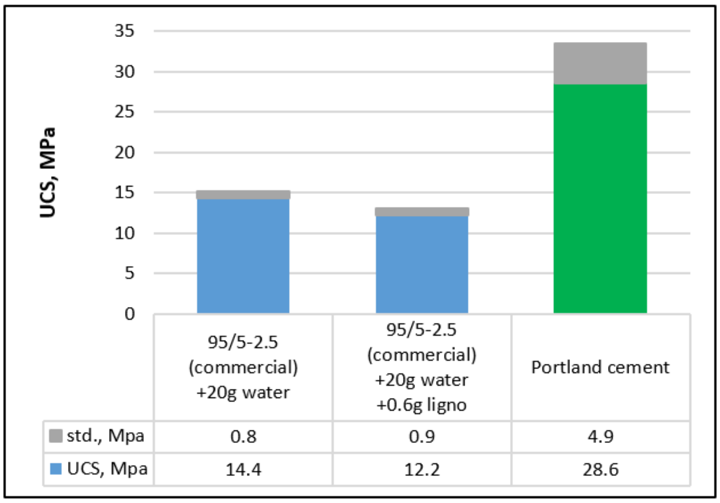


Figure 5.29: Commercial silicate-based geopolymer plugs after cut to 64mm.

UCS test: As displayed in Figure 5.30, the compressive strength of the commercial-silicate based geopolymer was 50% lower than that of Portland cement. But still, the geopolymer exhibited a high compressive strength considering the long free water length.



	95/5-2.5 (commercial) +20g water	95/5-2.5 (commercial) +20g water +0.6g ligno	Portland cement
▨ std., Mpa	0.8	0.9	4.9
■ UCS, Mpa	14.4	12.2	28.6

Figure 5.30: UCS results for geopolymer mixtures in TM#13, compared with Portland cement.

Screening fail/pass: The commercial silicate showed compressive strength not competitive with the Portland cement, likely due to the high free water content. It would have been interesting to cut this commercial-based geopolymer below the free water interface before performing the destructive UCS test. However, due to the coronavirus 1.5-month lockdown, there was no time to do that. Therefore, this geopolymer was screened out, and the reference geopolymers were formulated with the homemade sodium metasilicate liquid.

5.1.9 Selection of the geopolymer references

Based on the results from test matrix 1-13, three geopolymer references were formulated in TM#14-16. The three geopolymer reference mixtures are characterized by different concentrations of the home-made sodium metasilicate liquid. They are presented with Figure 5.31 as well as in Figure 1.5.

Construction works

- Geopolymer reference #1
    - Based on homemade sodium metasilicate liquid (**45.1%, milky**)

Oil well cementing

- Geopolymer reference #2
    - Based on homemade sodium metasilicate liquid (**30%, clear**)

- Geopolymer reference #3
    - Based on homemade sodium metasilicate liquid (**45.1%, clear**)

Figure 5.31: The three formulated geopolymer reference mixtures.

After the geopolymer and Portland cement plugs in **TM#7-13** were destructed to obtain uniaxial compressive strength, it was a short time until the MSc thesis was to be handed in. Hence, a geopolymer reference had to be chosen fast.

The UCS results from **TM#7-13** was not as expected or desired. Most of the geopolymer mixtures had good rheology for oil well cementing (300rpm reading < 300). Unfortunately, they showed low UCS compared to the Portland cement after 3 days of curing in oven at 62°C and 48-57 days of ambient air-exposure. Looking at compressive strength, the most promising of all the mixtures was the 30% sodium metasilicate-based geopolymer in **TM#9** without ligno and no extra water with its high compressive strength of 24.2 MPa. In **TM#15**, this geopolymer was modified with extra ex-situ water to become **geopolymer reference #2**.

The "95/5-2.5 (45.1%, milky) +9g water" geopolymer from **TM#4** was also considered to be used as a reference. It withstood a high compressive load of 21.7 MPa after 3-days curing at 62°C and resting 1 day at room temperature, despite 68mm length. The low free water content is also desirable. A shortcoming, however, was fast geopolymerisation process and thick slurry. Both geopolymer reference #1 and #3 were based on that geopolymer mixture. **Geopolymer**

reference #1 was designed with **TM#14**, and **geopolymer reference #3** was designed with **TM#16**.

5.1.9.1 Test matrix 14

Design idea: The design basis was to modify the geopolymer system in **TM#4** with slightly more extra water to get **geopolymer reference #1**.

Geopolymer mixture: The "95/5-2.5 (45.1%, milky) +9g water" geopolymer mixture was optimized to have 30g extra ex-situ water, as shown in Table 5.24.

Table 5.24: Composition of geopolymer reference #1, TM#14. Homemade sodium metasilicate (45.1%, milky) = Na_2SiO_3.

	95/5-2.5 (45.1%, milky) +30g water
Silica fume (g)	10
Fly ash (g)	192
Total alkaline activator (g)	105
Extra ex-situ water (g)	30
Viscosity	Not measured but $\theta_{300} > 300$

Screening fail/pass: This "95/5-2.5 (45.1%, milky) +30g water" mixture was first made in TM#17-18 to investigate the effect of nanoparticles. Therefore, the UCS test results are shown in **TM#17-18**. The system is now referred to as **Geopolymer Reference #1**. To be said, TM#14 and TM#17-18 were conducted after TM#4 and before TM#5 as a first try to study effect of nanoparticles.

5.1.9.2 Test matrix 15

Design idea: The aim was to modify the geopolymer system in **TM#9** that had no extra water to obtain **geopolymer reference #2**.

Geopolymer mixture: Table 5.25 shows the mixture blended. It was made with homemade sodium metasilicate (30%, clear).

Table 5.25: Composition of geopolymer reference #2, TM#15. Homemade sodium metasilicate (30%, clear) = Na_2SiO_3.

	95/5-2.5 (30%, clear) +23g water
Silica fume (g)	10
Fly ash (g)	192
Total alkaline activator (g)	105
Extra ex-situ water (g)	23
Viscosity	$\theta_{300} = 174$

Rheology: As Table 5.26 illustrates, 8g water was added to the "95/5-2.5 (30%, clear color)" mixture from TM#9, and the rheology was measured. But, it failed the 300RPM criteria. Therefore, another blending was made, and 23g water was worked in. With 23g amount of extra ex-situ water, the 300RPM reading was 174 (which is <300) and **passed** the rheology test.

Table 5.26: Rheology measurement of geopolymer reference #2, TM#15.

	95/5-2.5 (30%, clear color) +8g water	**95/5-2.5 (30%, clear color) +23g water**
RPM	**Reading θ**	**Reading θ**
600	>300	>300
300	>300	174
200	>300	115
100	172	59
6	11	4
3	7	3
Pass/fail	Fail	Pass

Screening fail/pass: When the lab re-opened April 27 after the COVID-19 lockdown, the days per week and hours per day for student access to the lab were very time-limited. Therefore, to save time, batches of nanoparticles TiO_2 and MWCNT-COOH (cured for both 3 and 10 days) were made the same day as the mixture in Table 5.25 was formulated. Thus, at that time, the compressive strength of the mixture in TM#15 was not known. Its results are shown in **TM#20-21**. The "95/5-2.5 (30%, clear) +23g water" system in TM#15 is from now referred to as **Geopolymer Reference #2**.

5.1.9.3 Test matrix 16

Design idea: The goal was to formulate **geopolymer reference #3** by optimizing the "95/5-2.5 (45.1%, milky) +9g water" geopolymer in TM#4 to qualify the workability for application in oil well cementing.

This was achieved in two ways.:

1. Synthesis of homemade sodium metasilicate liquid (45.1%, **clear color**) instead of (45.1%, **milky color**). Making this high-concentrated sodium metasilicate liquid with clear water glass color was now achieved by keeping the heat bath water at 95-75°C, as explained in chapter 4.2.1.
2. Add extra ex-situ water (+40g in total).

Geopolymer mixture: A batch of two plugs were made, with the composition shown in Table 5.27. Similar to the situation with TM#15, making the geopolymer in TM#16 was rushed. Nevertheless, it was found time cure and perform UCS test plugs to check if they passed the screening criteria. The first plug was tested for UCS after 1.5 days in oven and the second post to 3 days aging.

Table 5.27: Composition of geopolymer reference #3, TM#16. Homemade sodium metasilicate (45.1%, clear) = Na_2SiO_3

	95/5-2.5 (45.1%, clear) +40g water
Silica fume (g)	10
Fly ash (g)	192
Total alkaline activator (g)	105
Extra ex-situ water (g)	40
Viscosity	$\theta_{300} = 234$

Rheology: With 40g extra water, the viscometer reading of the (45.1%, clear color) metasilicate based geopolymer passed the rheology criteria, as shown in Table 5.28.

Table 5.28: Rheology measurement of geopolymer reference #3, TM#16.

	95/5-2.5 (45.1%, clear color) +40g water
RPM	**Reading θ**
600	>300
300	234
200	155
100	78
6	5
3	3
Pass/fail	Pass

Visual inspection: The two plugs made in TM#16 are shown in Figure 5.32. Their plastic (glass) shiny surface was similar as well as the amount of free water.

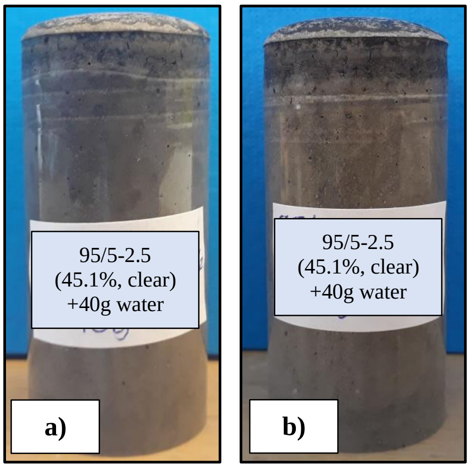


Figure 5.32: TM#16. a) geopolymer plug after 1.5 days curing. c) plug after 3 days curing.

UCS test: Figure 5.33 shows the development of compressive strength of 15.3 MPa from 1.5 days of curing in oven at 62°C to 20.4 MPa after 3 days of curing. The plugs were cut to 60mm and exposed to ambient air 1 day before UCS test.

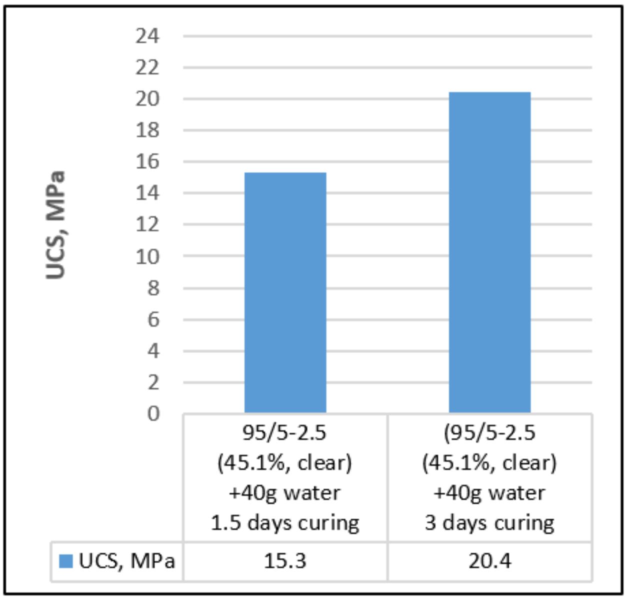


Figure 5.33: UCS results of geopolymer reference #3, TM#16.

Screening fail/pass: This geopolymer gel mixture **passed** all the screening criteria. It showed good workability ($\theta_{300} < 300$) and promising high strength. From now, it will be called **Geopolymer Reference #3**.

5.2 Phase 2: Effect of nanoparticles on neat geopolymer

In phase 2, the effect of nanoparticles was investigated on the three formulated geopolymer mixtures from phase 1. Nano-TiO_2 and MWCNT-COOH were selected for that purpose.

Phase 2 was divided into two periods: geopolymers for use in **construction works** and geopolymers for use in **oil well cementin**g operations. This is based on the rheology of the reference mixtures. Geopolymer reference #1 had thick, fast setting slurry. Therefore, it is not suitable for oil well cementing. It is suggested for construction work due to its high compressive strength. Both geopolymer reference #1 and #2 are designed to have a 300RPM reading below 300 when measured with viscometer. Ultimately, they are proposed for oil well cementing.

Table 5.29 lists the six test matrixes conducted in phase 2 as well as TM#19, where Portland cement samples were made for comparison.

Table 5.29: Test matrixes in phase 2 summarized with number and objective.

Test matrixes in phase 2	
Test matrix number	**Objective with test matrix**
Geopolymer for construction work	
Geopolymer reference #1	
Test matrix 17	Effect of nanoparticle MWCNT-COOH
Test matrix 18	Effect of nanoparticle TiO_2
Portand cement for comparison with TM#20-23	
Test matrix 19	Comparing geopolymers in TM#20-23 with Portland cement
Geopolymer for oil well cementing	
Geopolymer reference #2	
Test matrix 20	Effect of nanoparticle TiO_2
Test matrix 21	Effect of nanoparticle MWCNT-COOH
Geopolymer reference #3	
Test matrix 22	Effect of nanoparticle TiO_2
Test matrix 23	Effect of nanoparticle MWCNT-COOH

Curing time

The geopolymer mixtures in **TM#17-18** were cured for 3 days in oven at 62°C. In **TM#19-23**, one batch of mixtures was cured in oven at 62°C for 3 days and the other batch for 10 days. All the plugs were exposed to ambient temperature for 1 day after curing in oven and before the UCS test.

The experimental tests for all test matrixes in phase 2 are shown in Figure 5.34.

- Destructive tests
    - Uniaxial compressive test **(TM#17-23)**
        - Uniaxial compressive strength, UCS
        - Young's modulus, E
- Non-destructive test
    - Rheology measurement **(TM#19-23)**
    - Visual inspection: **(TM#17-23)**
        - Visual cracks, pores and air bubbles of plug after curing
        - Free water (homogeneity) of plug
        - Expansion or shrinkage after curing
    - Sonic, mass, diameter and length measurement **(TM#17-23)**
        - Modulus of elasticity, M

Figure 5.34: Summary of the destructive and non-destructive tests performed for phase 2 (test matrix 17-23).

5.2.1 Geopolymer reference #1

The effect of nanoparticles MWCTN-COOH (TM#17) and TiO_2 (TM#18) was investigated on geopolymer reference #1. Geopolymer reference #1 can also be notated as "95/5-2.5 (45.1%, milky) +30g water", based on the previous naming of the geopolymer mixtures. It is composed of 95/5-ratio of fly ash / silicate fume, Na_2SiO_3/NaOH ratio of 2.5, a high-concentrated homemade sodium metasilicate liquid (45.1%, milky) and 30g water ex-situ. The "milky" comes from the white, milky color of the fluid due to partly dissolved anhydrous sodium metasilicate in water, explained in chapter 4.2.2.

5.2.1.1 Test matrix 17

Design idea: The objective was to study the effect of nanoparticle MWCNT-COOH on geopolymer reference #1.

Geopolymer mixtures: Table 5.30 shows the five geopolymer mixtures in TM#17 (2x5=10 plugs). Geopolymer reference #1 was made for each mixture, then the corresponding amounts of MWCNT-COOH were dispersed in the 30g ex-situ water before blended in.

Table 5.30: Geopolymer reference #1 with various concentrations of MWCNT-COOH. **3 days** cured. TM#17.

	Geopolymer Reference #1	+0.050g MWCNT-COOH	+0.10g MWCNT-COOH	+0.22g MWCNT-COOH	+0.33g MWCNT-COOH
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	30	30	30	30	30
MWCNT-COOH (g)	0	0.050	0.10	0.22	0.33
Viscosity	Not measured but $\theta_{300} > 0$				

Visual inspection: There was no effect of multiwall carbon nanotube on the expansion during curing, as observed in Figure 5.35 a). The nano-modified geopolymer with 0.05g MWCNT-COOH in Figure 5.35 b) appeared to have slightly more free water than the reference. The 0.1g and 0.2g-nanotube plugs seemed to have less free water.

The plugs were cut to 53mm, which was below the free water interface, illustrated with Figure 5.35 c). The top surface was smooth and with basically no visual pores, which looked promising. Additionally, small white (gray) grain clusters could be seen within the geopolymer-matrix, looking from the top. This could perhaps be the silica fume.

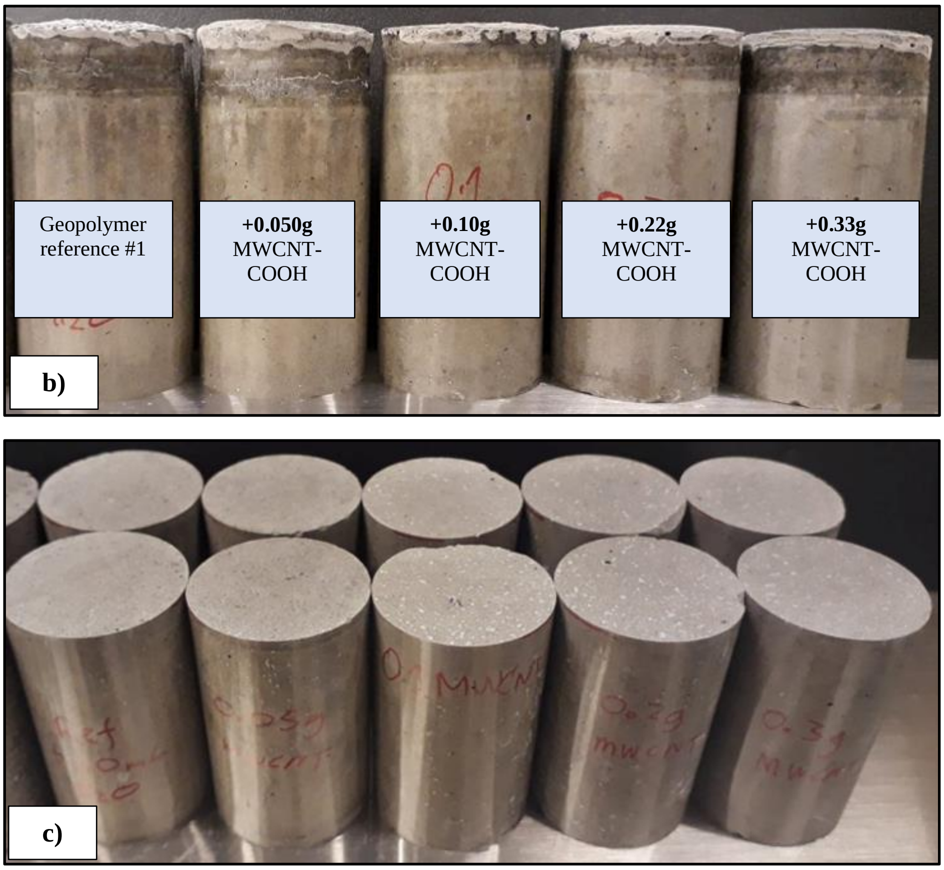
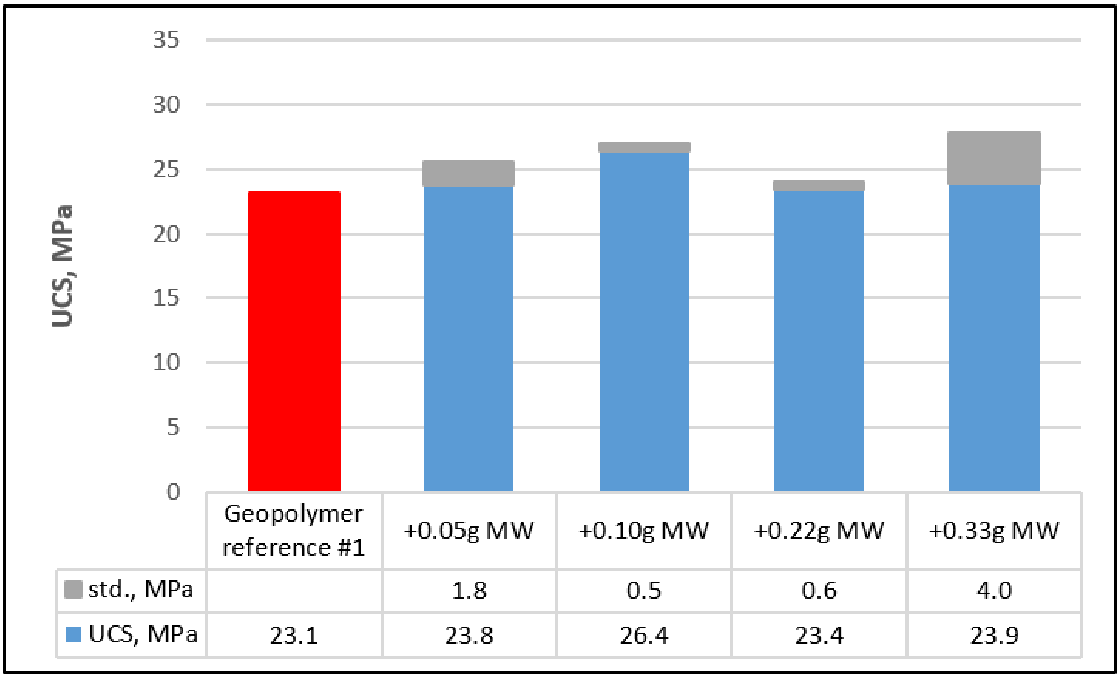


Figure 5.35: TM#17. a) plugs out of oven b) showing free water. c) plugs cut to ~53mm, below free water interface

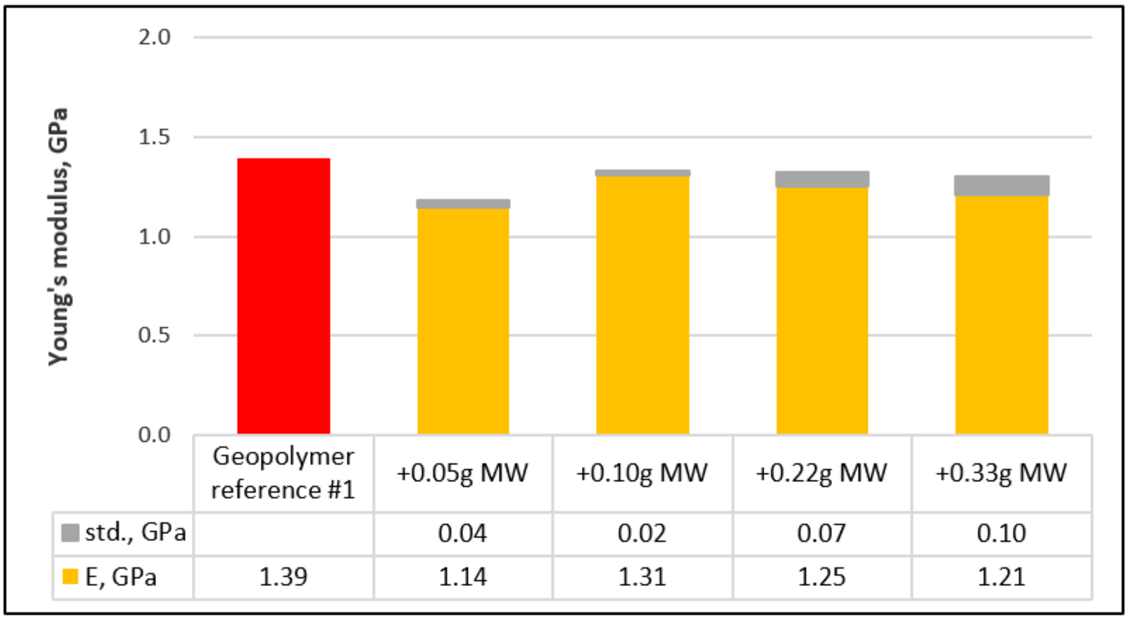
UCS test: Figure 5.36 shows a trend of rising compressive strength with increasing concentration of MWCNT-COOH up to an optimum. The optimum appears to be the mixture blended with 0.10g carbon-nanotube with 26.4 MPa. That is 14% higher than the nano-free reference. Unfortunately, only one of the two reference plugs were recorded for UCS, thereby no standard deviation.



	Geopolymer reference #1	+0.05g MW	+0.10g MW	+0.22g MW	+0.33g MW
▨ std., MPa		1.8	0.5	0.6	4.0
🟦 UCS, MPa	23.1	23.8	26.4	23.4	23.9

Figure 5.36: UCS results for effect of MWCNT-COOH on geopolymer reference #1, **3 days** cured, TM#17. "MW" is abbreviation for MWCNT-COOH.

Looking at the data for Young's modulus in Figure 5.37, the value is lower for all concentrations of MWCNT-COOH. The most considerable difference was for 0.05g, with 18% lower Young's modulus. Interestingly, 0.10g added MWCNT-COOH gave both highest UCS and highest Young's modulus among the nano-concentrations in TM#17.



	Geopolymer reference #1	+0.05g MW	+0.10g MW	+0.22g MW	+0.33g MW
▨ std., GPa		0.04	0.02	0.07	0.10
🟨 E, GPa	1.39	1.14	1.31	1.25	1.21

Figure 5.37: Young's modulus for effect of MWCNT-COOH on geopolymer reference #1, **3 days** cured, TM#17. "MW" is abbreviation for MWCNT-COOH.

5.2.1.2 Test matrix 18

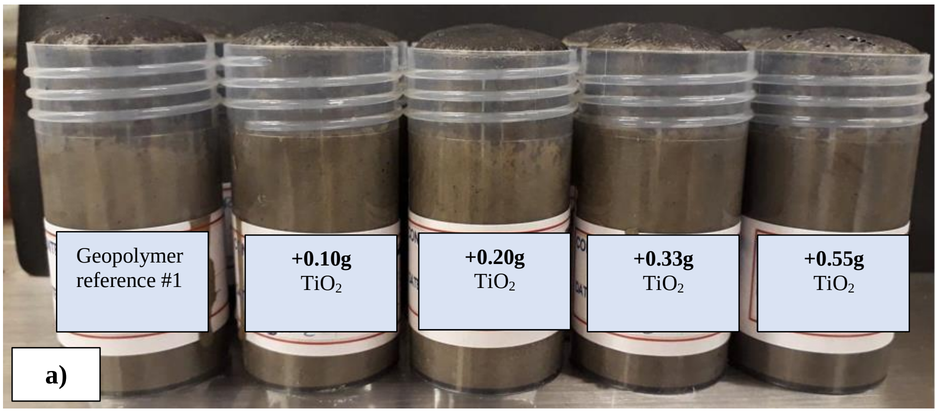
Design idea: The aim was to investigate the effect of nanoparticle TiO_2 on geopolymer reference #1.

Geopolymer mixtures: Five geopolymer mixtures were also made in TM#18, presented with Table 5.31. For curiosity, the 0.55g amount of TiO_2 was used instead of the 0.050g in the MWCNT-COOH study.

Table 5.31: Geopolymer reference #1 with various concentrations of TiO_2. **3 days** cured. TM#18

	Geopolymer reference #1	+0.10g TiO_2	+0.20g TiO_2	+0.33g TiO_2	+0.55g TiO_2
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	30	30	30	30	30
TiO_2 (g)	0	0.10	0.20	0.33	0.55
Viscosity	Not measured but $\theta < 300$				

Visual inspection: There was no difference in the expansion, looking at Figure 5.38 a). Even though the 0.55g TiO_2-blended geopolymer had the lowest amount of free water, seen in Figure 5.38 b), it appeared to be the weakest during cutting because a big piece fell off on both samples, observed in Figure 5.38 c). 1mm/s speed was used on the cutting machine. Maybe that was too fast, difficult to say, but there was no visible damage to the other plugs in TM#18.



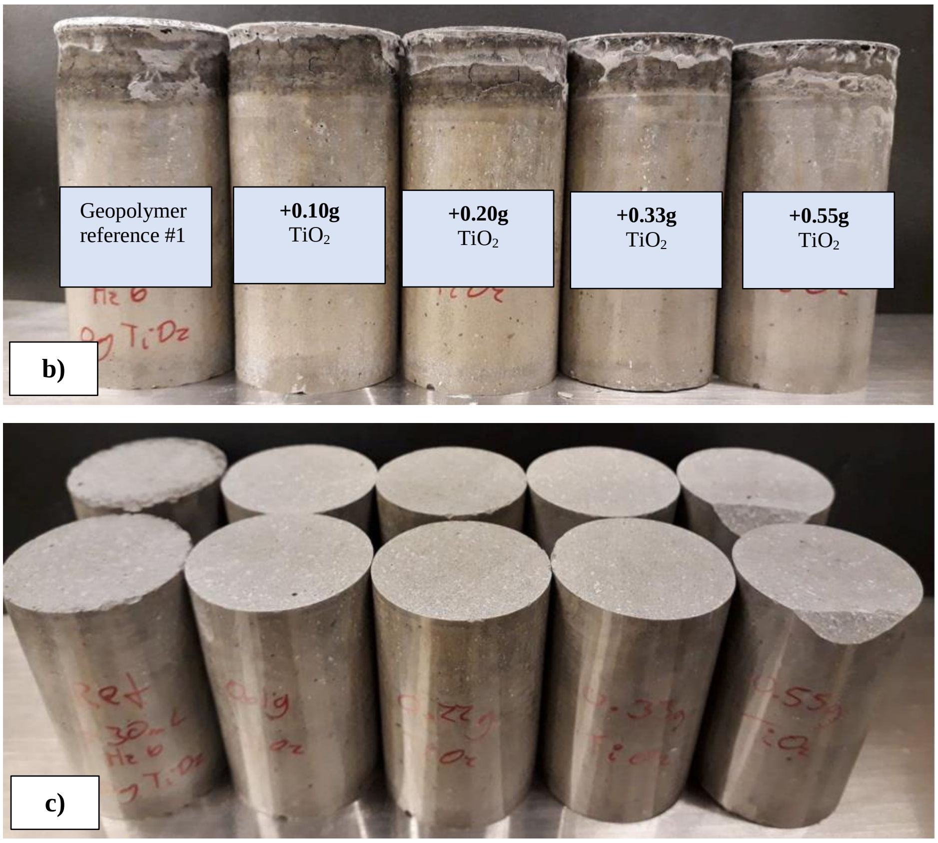
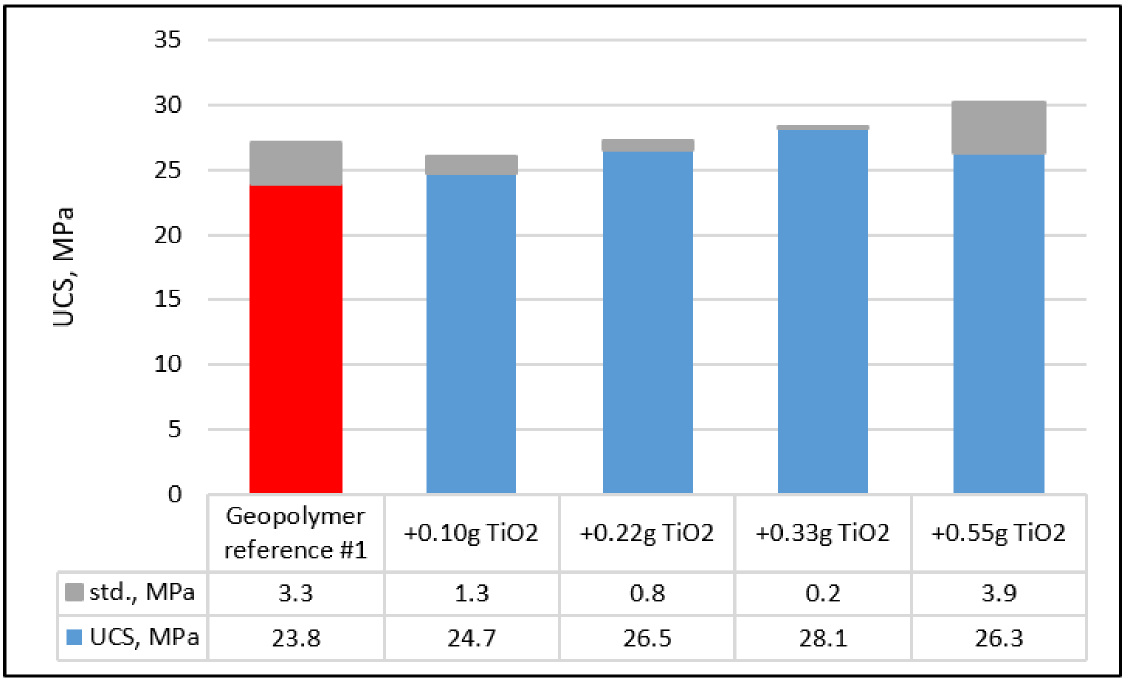


Figure 5.38: TM#18. a) plugs out of oven, b) showing free water. c) plugs cut to ~53mm, below free water interface

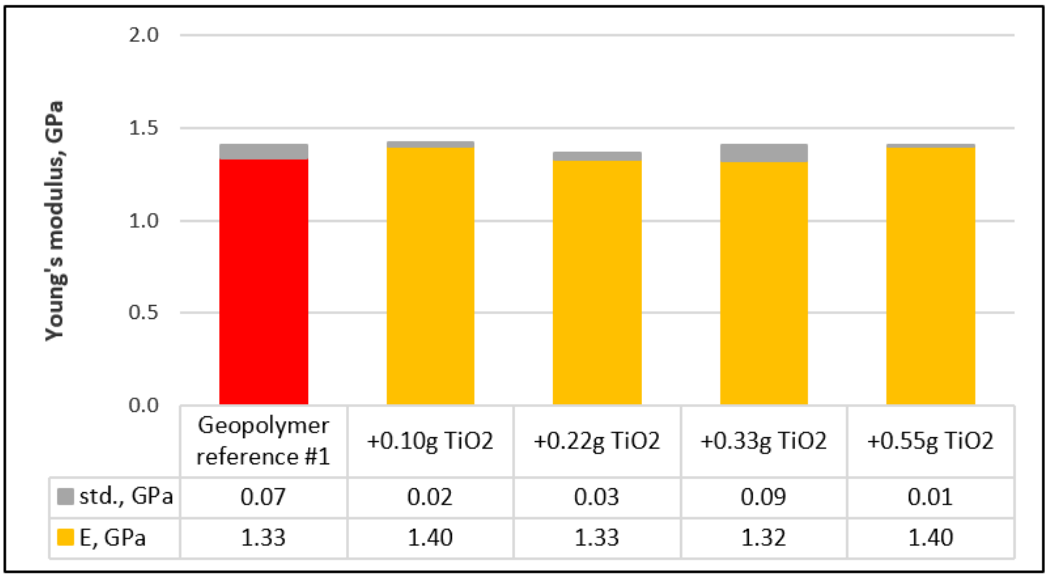
UCS test: Fascinatingly, there is a similar bell-shaped curve for the nano-TiO_2 geopolymer (Figure 5.39), as seen in Figure 5.36 for MWCNT-COOH. Optimum strength was achieved for 0.33g TiO_2, which increased the strength of the neat reference geopolymer by 18% to 28.1 MPa.



	Geopolymer reference #1	+0.10g TiO2	+0.22g TiO2	+0.33g TiO2	+0.55g TiO2
▨ std., MPa	3.3	1.3	0.8	0.2	3.9
■ UCS, MPa	23.8	24.7	26.5	28.1	26.3

Figure 5.39: UCS results for effect of TiO_2 on geopolymer reference #1, **3 days** cured, TM#18.

There is no clear trend with effect of nano titanium dioxide on the Young's modulus, as seen in Figure 5.40. However, they all showed approximately the same stiffness after 3 days curing time.



	Geopolymer reference #1	+0.10g TiO2	+0.22g TiO2	+0.33g TiO2	+0.55g TiO2
▨ std., GPa	0.07	0.02	0.03	0.09	0.01
🟨 E, GPa	1.33	1.40	1.33	1.32	1.40

Figure 5.40: Young's modulus for effect of TiO_2 on geopolymer reference #1, **3 days** cured, TM#18.

5.2.2 Portland cement for comparison with TM#20-23

It was decided to make some conventional Portland class G cement plugs to compare with the geopolymer mixtures.

5.2.2.1 Test matrix 19

Design idea: The goal was to compare the geopolymer formulations in TM#20-23 with Portland class G cement (0.44 water/solid ratio) to evaluate their properties relative to the cement.

Portland cement mixtures: The Portland class G cement mixture shown in Table 5.32 was made five times, giving 2x5=10 plugs. Two pairs of plugs were cured for 10 days and three pairs for 3 days. Then, as shown below, the plugs were cut to the same length as the respective geopolymers in TM#20-23 that they were compared with:

- 3-days cured: ~51mm (TM#23)
- 3-days cured: ~58mm (TM#22)
- 3-days cured: ~61mm (TM#20-21)
- 10-days cured: ~51mm (TM#22-23)
- 10-days cured: ~61mm (TM#20-21)

The various lengths are based on different free-water amounts on the geopolymer plugs in TM#20-23.

Table 5.32: Composition of Portland cement (two plugs), TM#19

	Portland cement Class G 0.44 water/solid ratio
Portland cement powder (g)	250
Water (g)	110
Total (g)	360

Sample preparation: Deformity, cracks and heterogeneity were observed on all the ten plugs after curing for 3 days, documented with Figure 5.41. A possible explanation is the high adhesive bonding of Portland cement to the plastic cup surface. When poured into the cups, the cement stuck to the surface, giving rise to uneven distribution. Therefore, when the ten slurries of cement were re-made, the cup's inner surface was lubricated with a thin layer of oil. A picture of the lubrication oil is shown in Figure 5.42.

For some unexplainable reason, the four Portland cement plugs in TM#8 did not show these severe fractures and heterogeneity even though the plugs were cured for 3 days at 62°C without lubrication oil. Additionally, the plugs in TM#8 achieved high (28.6±4.9) MPa strength on average.

Figure 5.41: Portland cement cured in plastic cup without lubrication oil on inner surface.

.

Figure 5.42: Lubrication oil.

Visual inspection: Figure 5.43 a) shows the Portland cement after 3 days of curing in oven at 62°C. Slightly varying in the amount of shrinkage among the four plugs depending on how much Portland cement slurry is poured above the top of plastic cup.

A minor amount of free water is shown in Figure 5.43 b). Additionally, the two plugs cut to ~58mm right in the picture in Figure 5.43 c) appeared to have more air bubbles on the top surface than the ~61mm plugs. These two unfavorable observations can give rise to greater standard deviation during the compressive strength tests.

The two plugs to the left in Figure 5.43 c) were cut to length ~61mm and compared with the 3-day cured geopolymers in TM#20-21 (also cut to ~61mm). The other two plugs to the right were cut to ~58mm and were compared with the 3-day geopolymers in TM#22 (also ~58mm in length after cut). Another two plugs of 3-day cement were made to compare with the geopolymer plugs in TM#23, and was cut to ~51mm, as seen in Figure 5.44 a). Figure 5.44 b) shows the 10-days cured ~61mm and ~51mm cement plugs that were compared with geopolymers in TM#20-21 and TM#22-23, respectively.

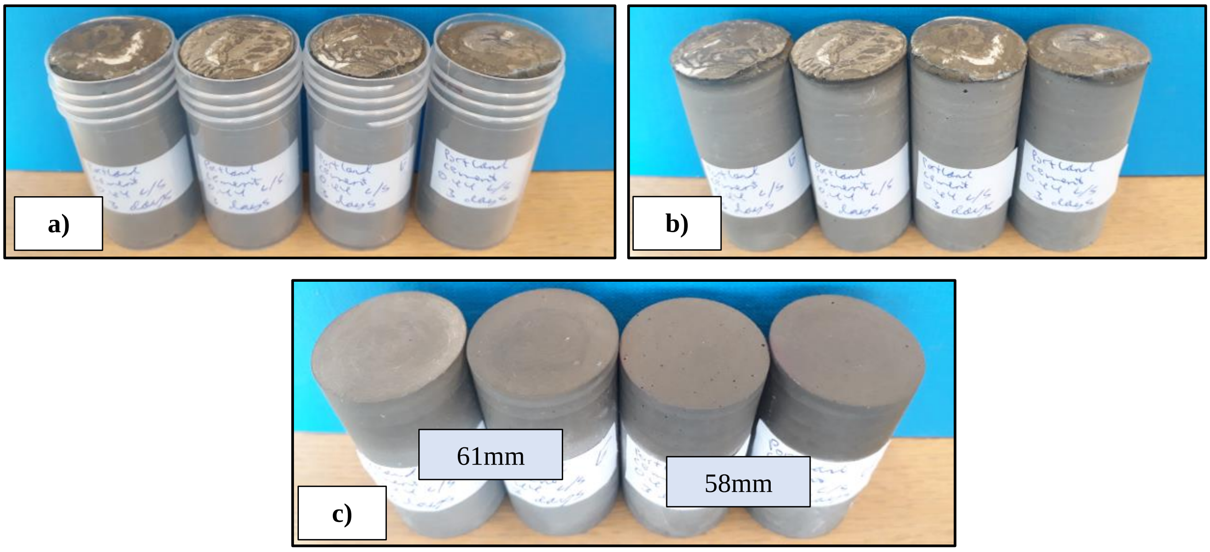


Figure 5.43: TM#19. a**) 3 days** cured Portland cement plugs. b) free water on the plugs. c) cut and polished plugs to 61mm (left two plugs) and 58mm (right two plugs).

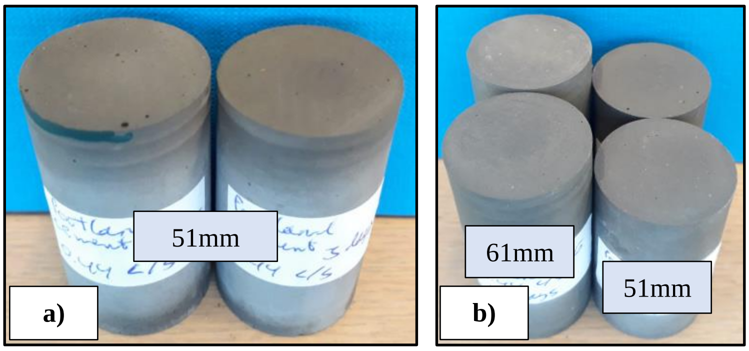


Figure 5.44: TM#19. a) **3 days** cured Portland cement plugs, cut to 51mm. b) **10 days** cured cement plugs, cut to 61mm (left two plugs) and 51mm (right two plugs).

UCS test: Figure 5.45 shows the compressive strength of the Portland cement plugs at different lengths after 3 -and 10 days curing. The decrease in UCS from 51mm to 58mm to 61mm cement plugs after 3 days curing makes sense in terms of plug length. Strength development is expected with aging time at 60°C [34]. So, it makes sense that the 61mm plugs increased in strength from 3 to 10 days curing. The situation was different for the 51mm plug, where a decrease in strength was seen. This might possibly be related to air bubble generation shown in Figure 5.43 c) and Figure 5.44 a)-b), where it can be seen that the amount of visible air bubbles on top surface varies slightly from plug to plug. Appendix A shows a few examples of the internal structure some of the Portland cement plugs after they are destructed in UCS test as well as for geopolymer reference #2 and 3. It can be observed that the visible pores are varying from plug to plug.

However, nothing seems to be abnormal with the plugs from the Modulus of Elasticity (M) shown in Appendix C. The modulus of elasticity is significantly higher than the geopolymer's in TM#20-23. This is reflected by the superior compactness and high density of the Portland cement compared to the formulated geopolymer mixtures.

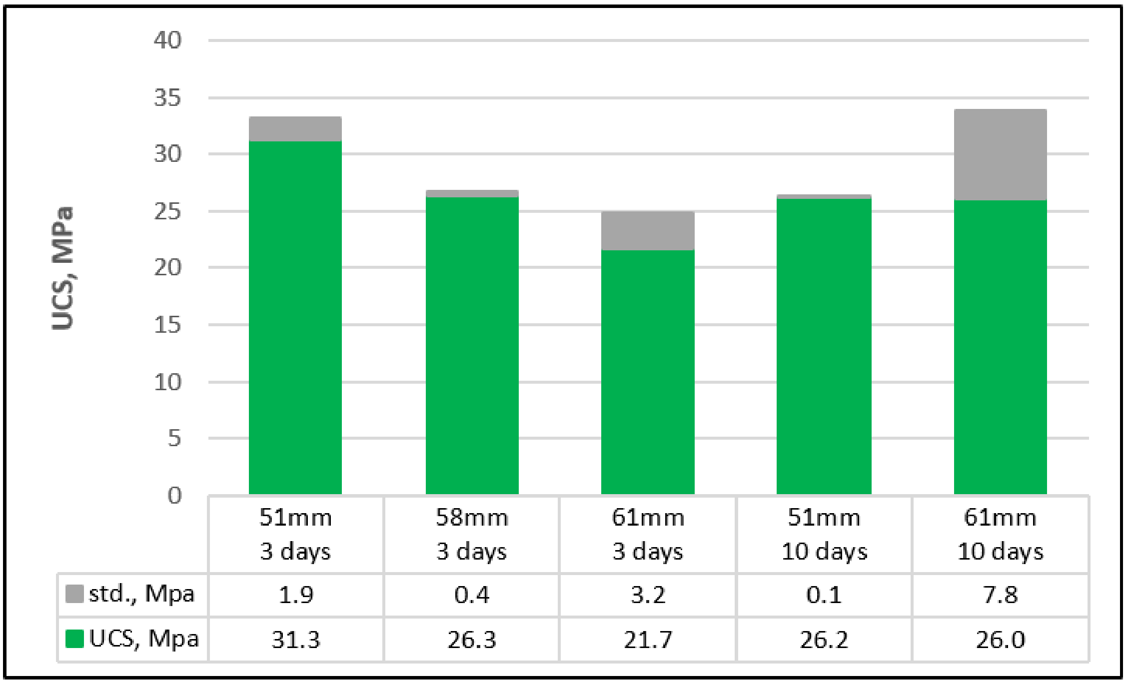


Figure 5.45: UCS of Portland cement plugs cut to different lengths, TM#19.

5.2.3 Geopolymer reference #2

In this section, the effect of nano-TiO_2 and MWCNT-COOH on geopolymer reference #2 was studied. Two test matrixes were made: one to study the effect of TiO_2 (TM#20) and one for MWCNT-COOH (TM#21). The geopolymer reference #2 can also be named based on its composition: “95/5-2.5 (30%, clear) +23g water”.

The reference for TM#20-21 was measured for rheology and is shown in TM#15. There was no time to measure the rheology for the geopolymer mixtures with nanoparticles. With added both TiO_2 and MWCNT-COOH, the rheology of slurry appeared the same, if not slightly thinner.

5.2.3.1 Test matrix 20

Design idea: The aim was to look at the effect of nanoparticle TiO_2 on geopolymer reference #2 for 3 -and 10 days curing in oven at 62°. The compressive strength was compared with Portland cement.

Geopolymer mixtures: Concentration from 0.1 to 0.4g of titanium dioxide were added to geopolymer reference #2. Table 5.33 shows the mixtures that were cured for 3 days in oven, and Table 5.34 displays the 10-days cured systems. Since it was very difficult to measure the weight of nanoparticle, we can observe a difference of 0.01g between the 3 days and the 10 days geopolymers.

Table 5.33: Geopolymer reference #2 with various concentrations of TiO_2. **3 days** cured. TM#20.

	Geopolymer reference #2	+0.10g TiO_2	+0.21g TiO_2	+0.31g TiO_2	+0.40g TiO_2
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	23	23	23	23	23
TiO_2 (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 174$				

Table 5.34: Geopolymer reference #2 with various concentrations of TiO_2. **10 days** cured. TM#20.

	Geopolymer reference #2	+0.10g TiO_2	+0.21g TiO_2	+0.31g TiO_2	+0.41g TiO_2
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	23	23	23	23	23
TiO_2 (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 174$				

The first column, with the red color marking the 3-days curing reference geopolymer in Table 5.33, means that this geopolymer is the exact same geopolymer plug made in TM#14. This was done to save time (due to COVID-19 and lab time-restrictions).

Visual inspection: There appeared to be little difference between the length of free water of the plugs cured 3 -and 10 days, comparing Figure 5.46 a)-b) with Figure 5.47 a)-b). In terms of nano-TiO_2 effect, after both 3 -and 10 days aging, there seemed to be a neglectable difference in free water length and visual crack development.

The plugs were cut to 61mm to remove the free water, and they are shown in Figure 5.46 b) and Figure 5.47 b). With the (30%) sodium metasilicate geopolymer, there seemed to be some visible air bubbles on the top surface, as seen in Figure 5.46 b). The picture in Figure 5.47 b) is of too bad resolution. However, there seemed to be no visible air bubbles related to TiO_2.

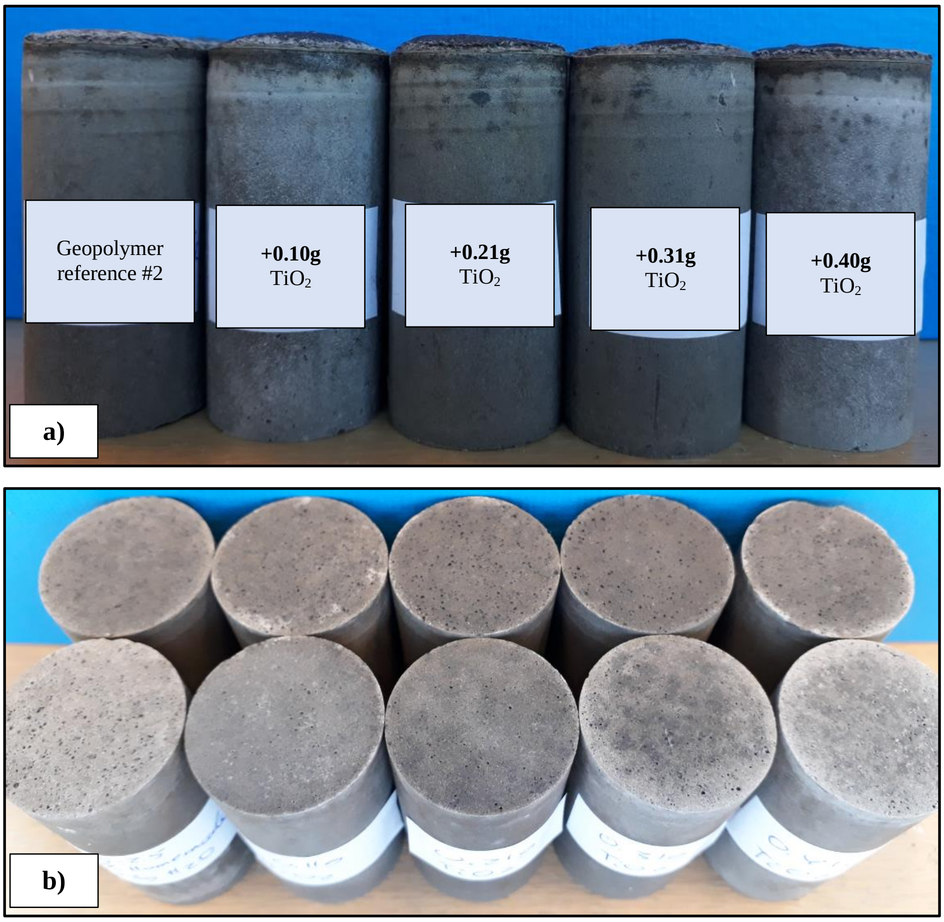


Figure 5.46: **3 days** cured, TM#20. a) showing free water of the plugs. b) plugs cut to ~61mm, below free water interface

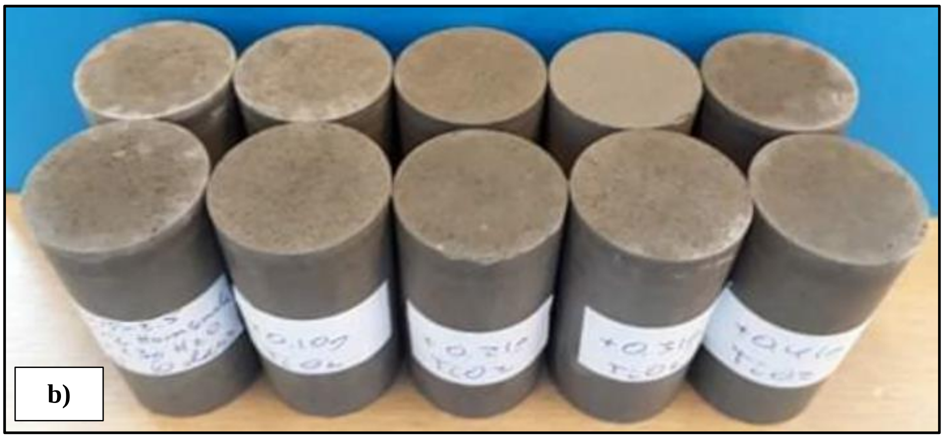
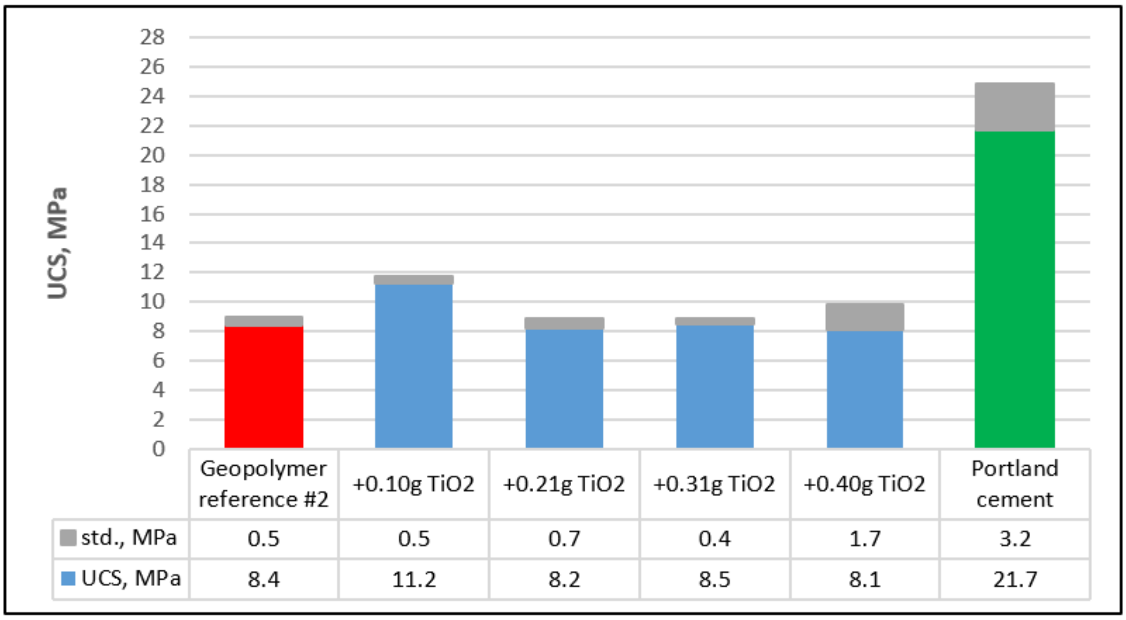


Figure 5.47: **10 days** cured, TM#20. a) showing free water of the plugs. b) plugs cut to ~61mm, below free water interface

UCS test: As shown in Figure 5.48, after 3 days of curing, all the concentrations of nano-titanium dioxide treated geopolymers seem to have approximately the same UCS, except the 0.11g TiO_2-based geopolymer. Comparing with the neat geopolymer (reference), the 0.11g TiO_2 increased the UCS by 33%. On the other hand, comparing with the Portland cement samples, 0.11g nano-TiO_2 is still 48% lower. This means that the Portland cement had a much higher early strength development.



	Geopolymer reference #2	+0.10g TiO2	+0.21g TiO2	+0.31g TiO2	+0.40g TiO2	Portland cement
▨ std., MPa	0.5	0.5	0.7	0.4	1.7	3.2
🟦 UCS, MPa	8.4	11.2	8.2	8.5	8.1	21.7

:

Figure 5.48: UCS results for effect of TiO_2 on geopolymer reference #2, **3 days** cured, TM#20.

Figure 5.49 shows the UCS after 10 days of curing. All the TiO_2-based geopolymers are nearly equal, but the neat geopolymer recorded a higher UCS value than the nano-TiO_2 systems. Reference geopolymer #2 showed 81% strength increase from 3 to 10 days curing.

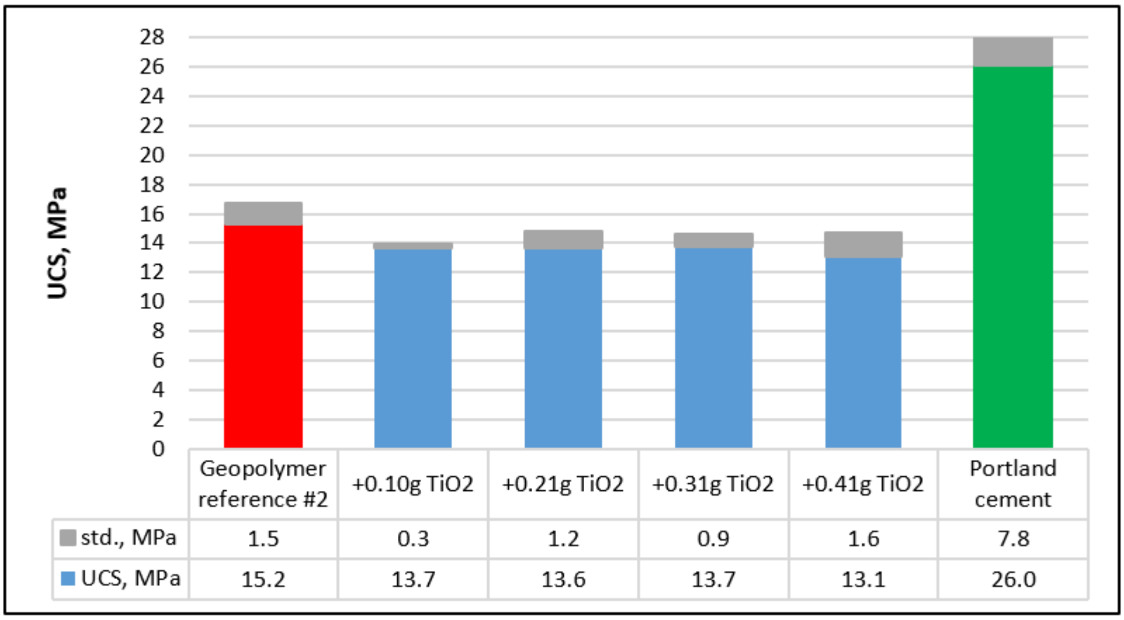


Figure 5.49: UCS results for effect of TiO_2 on geopolymer reference #2, **10 days** cured, TM#20.

5.2.3.2 Test matrix 21

Design idea: The goal was to investigate nanoparticle MWCNT-COOH on geopolymer reference #2 after 3 days and 10 days curing in oven. The UCS was compared with Portland class G cement that was cut in same length as the geopolymers.

Geopolymer mixtures: Similar to the study of TiO_2 in TM#20, the geopolymer reference #2 was first blended before the nanoparticle MWCNT-COOH was incorporated together with the extra ex-situ water. The mixtures in Table 5.35 were cured for 3 days. Then, a new batch of the same mixtures was made and cured for 10 days, shown in Table 5.36.

Table 5.35: Geopolymer reference #2 with various concentrations of MWCNT-COOH. **3 days** cured. TM#21.

	Geopolymer reference #2	+0.10g MWCNT -COOH	+0.21g MWCNT -COOH	+0.30g MWCNT -COOH	+0.40g MWCNT -COOH
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	23	23	23	23	23
MWCNT-COOH (g)	0	0.10	0.21	0.30	0.40
Viscosity	$\theta_{300} = 174$				

Table 5.36: Geopolymer reference #2 with various concentrations of MWCNT-COOH. **10 days** cured. TM#21.

	Geopolymer reference #2	+0.10g MWCNT -COOH	+0.21g MWCNT -COOH	+0.31g MWCNT -COOH	+0.40g MWCNT -COOH
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	23	23	23	23	23
MWCNT-COOH (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 174$				

Visual inspection: Comparing Figure 5.50 a)-b) with Figure 5.51 a)-b), the free water length or free water visual crack/porous development seemed not to have been affected with curing time. Moreover, there appeared to be no visual effect of MWCNT-COOH on the plugs or abnormalities before destructive test.

The plugs in Figure 5.50 b) and Figure 5.51 b) had some visible air bubbles/porosity on top surface. The (30%) sodium metasilicate liquid-geopolymers in TM#20 showed similar amount of air bubbles.

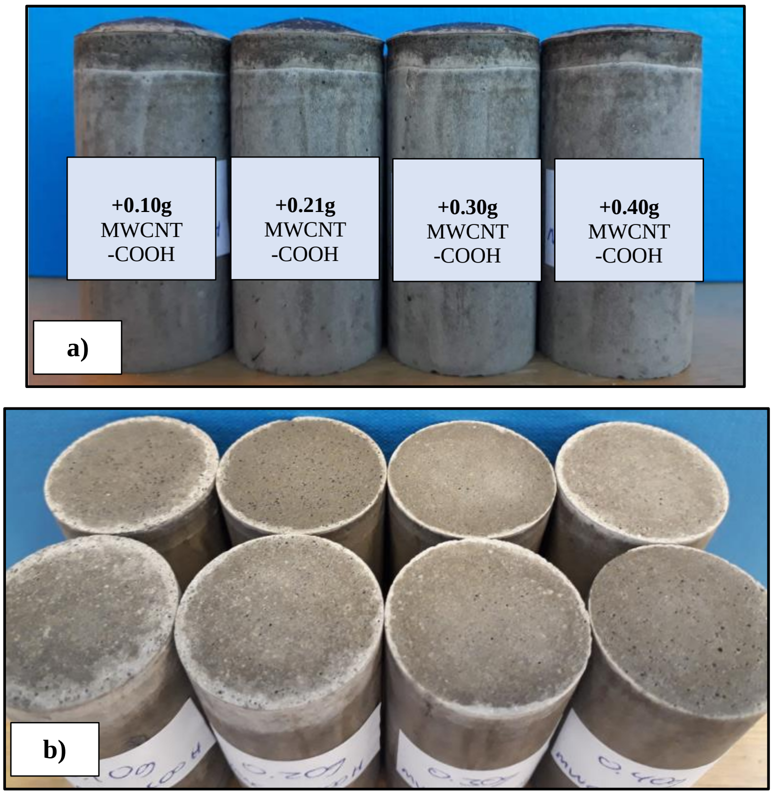


Figure 5.50: **3 days** cured, TM#21. a) showing free water of the plugs. b) plugs cut to ~61mm, below free water interface.

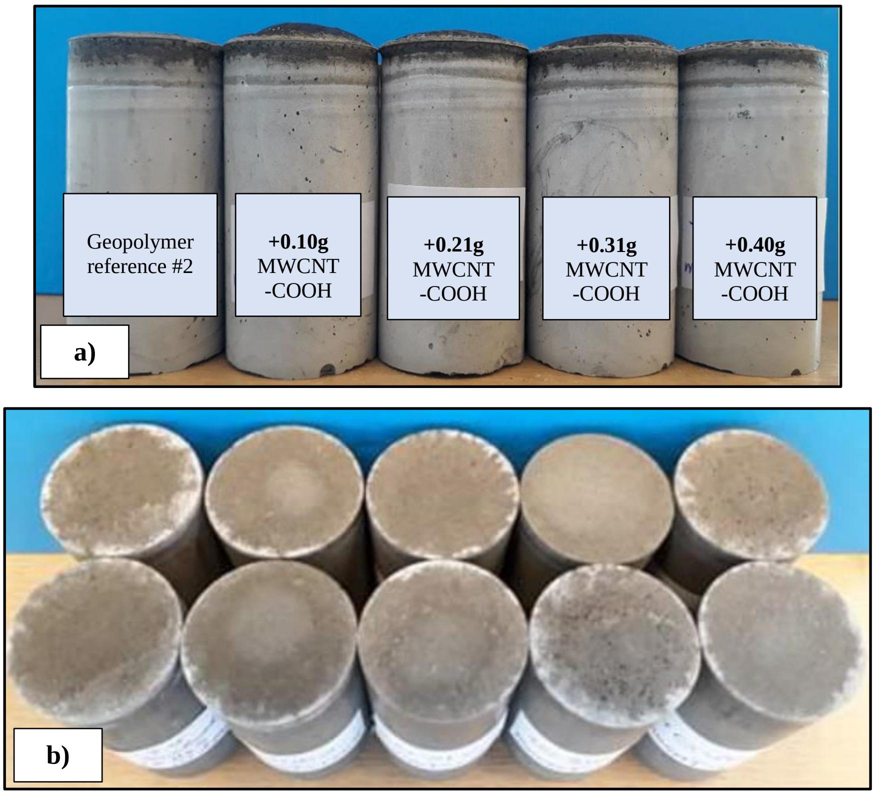
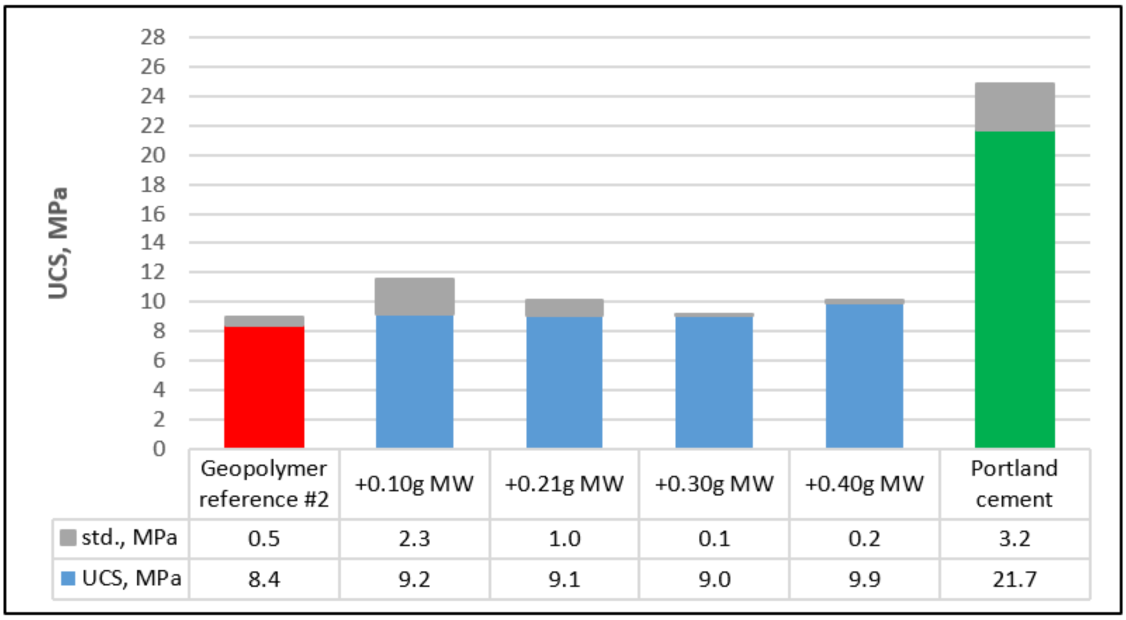


Figure 5.51: **10 days** cured, TM#21. a) showing free water of the plugs. b) plugs cut to ~61mm, below free water interface

UCS test: Figure 5.52 shows the UCS result for effect of MWCNT-COOH on reference after 3 days cured geopolymer plugs. As shown in the figure, the trend is slightly higher UCS for 0.10g, 0.21g and 0.30g MWCNT-COOH concentrations. The increase in strength with the 0.40g MWCNT-COOH showed 18% higher than the reference.



	Geopolymer reference #2	+0.10g MW	+0.21g MW	+0.30g MW	+0.40g MW	Portland cement
▨ std., MPa	0.5	2.3	1.0	0.1	0.2	3.2
■ UCS, MPa	8.4	9.2	9.1	9.0	9.9	21.7

Figure 5.52: UCS result for effect of MWNCT-COOH on geopolymer reference #2 after **3 days** cured. "MW" is abbreviation for MWCNT-COOH.

Figure 5.53 displays the UCS result for effect of MWCNT-COOH on reference after 10-days curing. Comparing the 3-days curing with the 10 days plugs, the neat geopolymer strength increased by 76%. (i.e., from 8.4 MPa to 14.8 MPa). The trend appears to be similar to TM#20, with the reference gaining the highest strength after 10 days. After 10 days curing, the 0.10, 0.20 and 0.40 g MWCNT-COOH increased the strength to approximately 11.5 MPa, whereas the 0.21g multiwall nanotube-based geopolymer gained strength to 12.6 MPa.

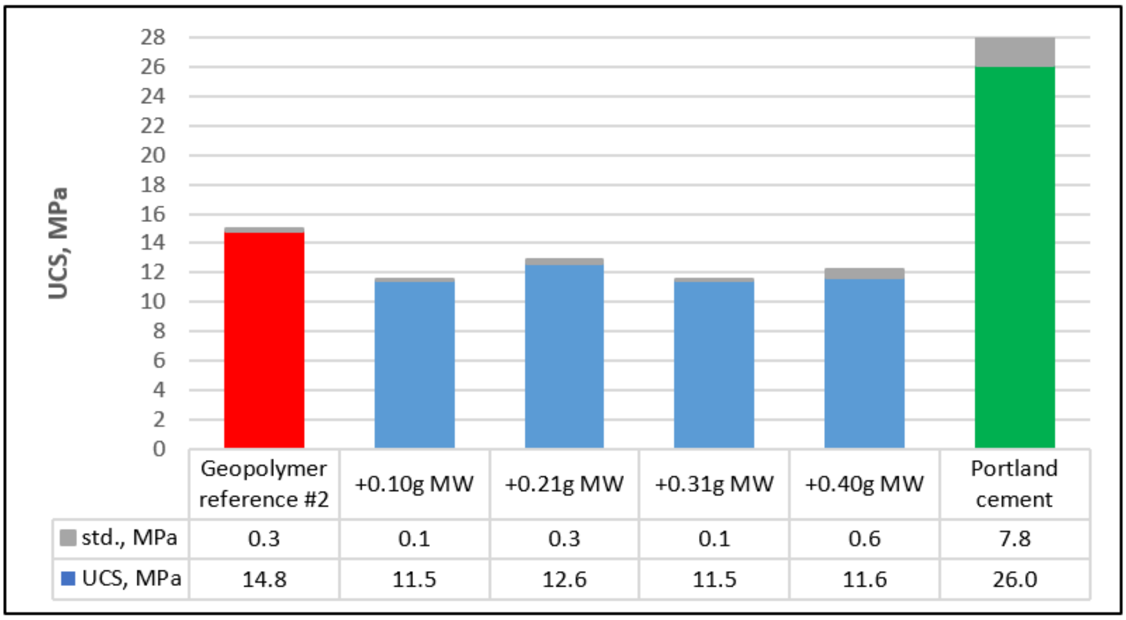


Figure 5.53: UCS result for effect of MWNCT-COOH on geopolymer reference #2 after **10 days cured**. "MW" is abbreviation for MWCNT-COOH.

5.2.4 Geopolymer reference #3

The effect of nano-TiO_2 and MWCNT-COOH nanoparticle solutions was investigated on geopolymer reference #3 found in phase 1. Geopolymer reference #3 has previously been named as "95/5-2.5 (45.1%, clear) + 40g water".

5.2.4.1 Test matrix 22

Design idea: The test matrix was designed to investigate the effect of nanoparticle TiO_2 on geopolymer reference #3 made with homemade sodium metasilicate liquid (45.1%, clear), for 3 -and 10 days curing in oven. The UCS results were compared with Portland cement.

Geopolymer mixtures: The five geopolymer mixtures for 3-days curing are shown in Table 5.37, and the systems cured for 10 days are presented in Table 5.38.

Table 5.37: Geopolymer reference #3 with various concentrations of TiO_2. **3 days** cured. TM#22.

	Geopolymer reference #3	+0.10g TiO_2	+0.21g TiO_2	+0.31g TiO_2	+0.40g TiO_2
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	40	40	40	40	40
TiO_2 (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 234$				

Table 5.38: Geopolymer reference #3 with various concentrations of TiO_2. **10 days** cured. TM#22.

	Geopolymer reference #3	+0.10g TiO_2	+0.21g TiO_2	+0.31g TiO_2	+0.40g TiO_2
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	40	40	40	40	40
TiO_2 (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 234$				

Visual inspection: Figure 5.54 a) indicates that after 3 days, there was no effect of TiO_2 on the free water. However, there seemed to be a slight difference in free water length looking at the cut plugs in Figure 5.54 b), but not severe or any trends with titanium dioxide concentration.

Figure 5.54 a) and Figure 5.55 a) show an increase in free water from 3 days to 10 days of curing for all the plugs, except 0.10g and 0.21g TiO_2, where the free water length remained about the same.

The 3-days aged plugs in Figure 5.54 b) were cut and polished to 58mm. This was the first batch to investigate the effect of nanoparticle on geopolymer reference #3, and 58mm was lower than the free water interface. But, after 10 days of aging, the plugs had more free water, so the plugs were cut to 51mm.

Note that the colors of the plugs in the pictures might vary depending on lighting when the picture was taken (i.e., time of the day and cloudy/sunny).

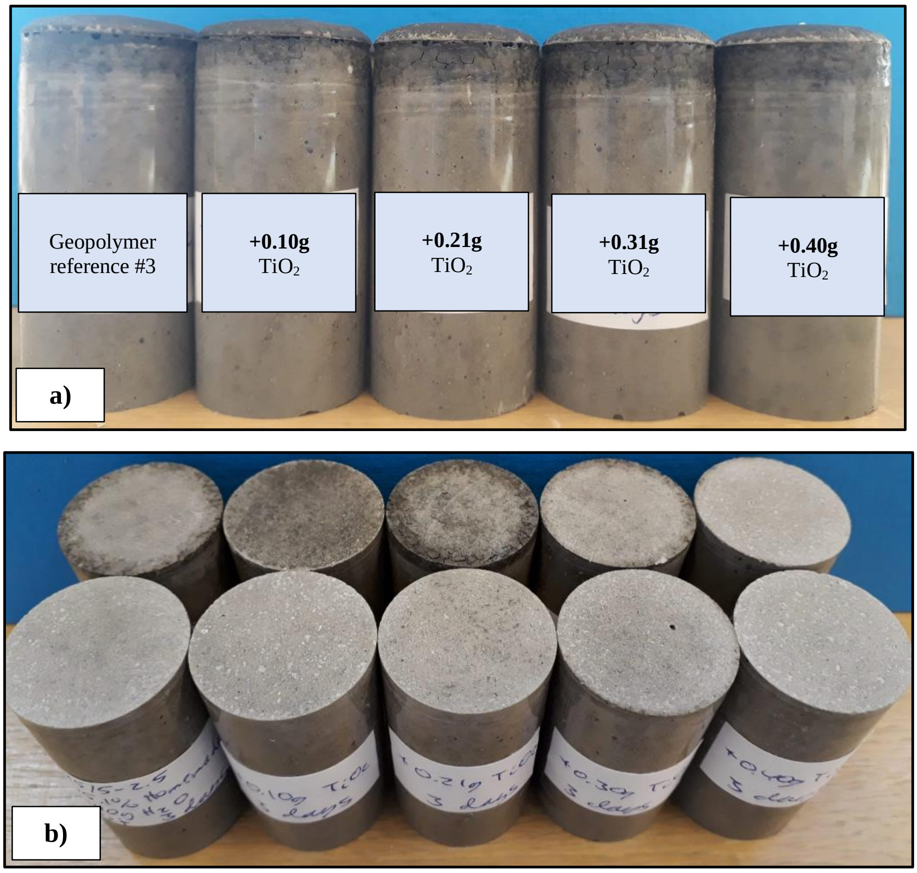


Figure 5.54: **3 days** cured, TM#22. a) showing free water of the plugs. b) plugs cut to ~58mm, below free water interface.

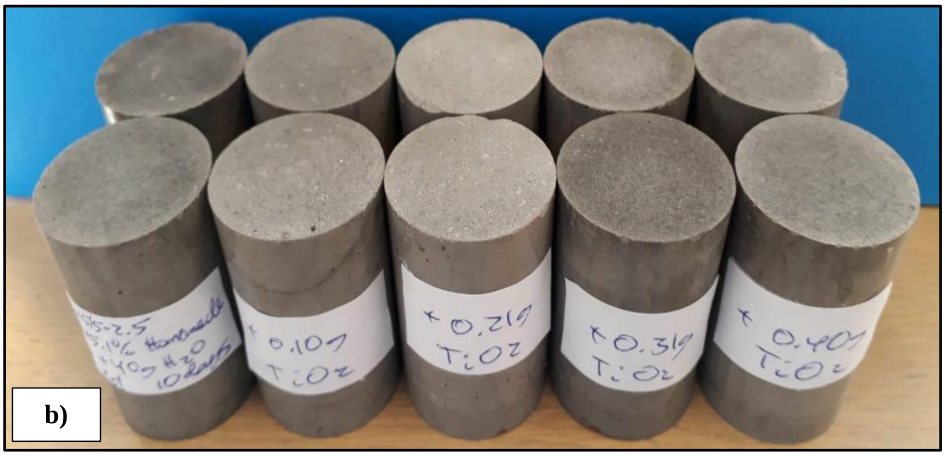
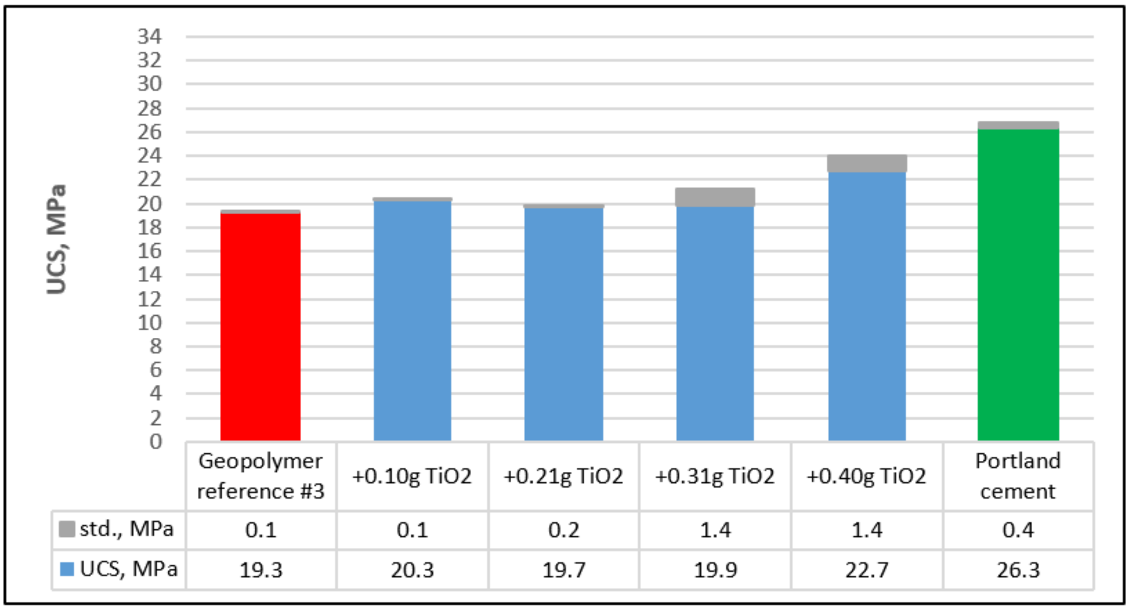


Figure 5.55: **10 days** cured, TM#22. a) showing free water of the plugs. b) plugs cut to ~51mm, below free water interface.

UCS test: The three days-batch of TiO_2-based geopolymer is shown in Figure 5.56. As displayed, the compressive strength increased with titanium dioxide concentration. The optimum was 0.40g TiO_2, with a strength of 22.7 MPa, 18% higher than the reference, and only 14% lower than the Portland cement sample plugs. The lower geopolymer reference strength compared to the TiO_2-based geopolymers hints to an improved early strength development when adding TiO_2.

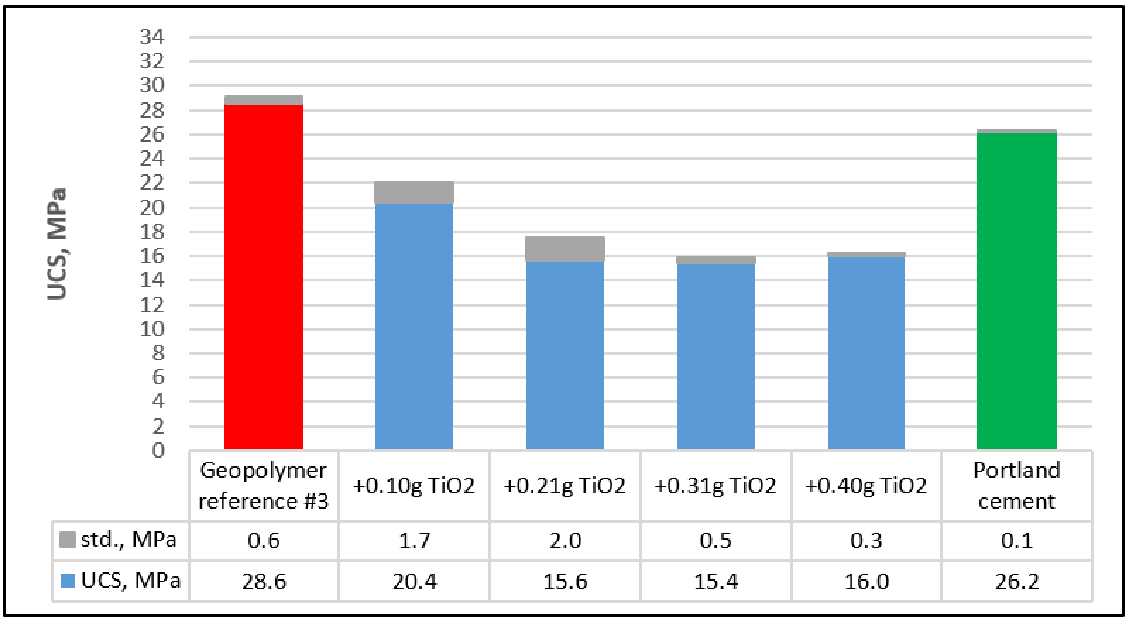


	Geopolymer reference #3	+0.10g TiO2	+0.21g TiO2	+0.31g TiO2	+0.40g TiO2	Portland cement
▨ std., MPa	0.1	0.1	0.2	1.4	1.4	0.4
🟦 UCS, MPa	19.3	20.3	19.7	19.9	22.7	26.3

Figure 5.56: UCS results for effect of TiO_2 on geopolymer reference #3, **3 days** cured, TM#22.

UCS for after 10 days curing time is shown in Figure 5.57. The trend was completely different for the 3-days cured geopolymer systems with the profile basically switched from right to left. The reference geopolymer rose 48% from 19.3 MPa, where the obtained 10-days strength of 28.6 MPa is 9% higher than that of the Portland cement sample. The 0.10g TiO_2 geopolymers showed stable UCS results from 3 to 10 days curing. Interestingly, the higher concentrations of TiO_2 suffered from a reduction in strength for 10-days curing as compared to 3-days.

There appeared to be some deformities on the cut plugs in Figure 5.55 b) that perhaps can explain the reason for the greater drop in strength from 3 to 10 days curing with increased TiO_2 concentration. The plugs with 0.31g and 0.40g TiO_2 on the back row seemed to have some pieces that fell off from top surface. The same can be seen on the 0.21g-plug on the front row. Contradicting to these visual abnormalities is the low standard deviation of the 0.31g and 0.40g titanium dioxide-based geopolymer systems.



	Geopolymer reference #3	+0.10g TiO2	+0.21g TiO2	+0.31g TiO2	+0.40g TiO2	Portland cement
▨ std., MPa	0.6	1.7	2.0	0.5	0.3	0.1
🟦 UCS, MPa	28.6	20.4	15.6	15.4	16.0	26.2

Figure 5.57: UCS results for effect of TiO_2 on geopolymer reference #3, **10 days** cured, TM#22.

Young’s modulus after 3 days of aging (Figure 5.58) basically had the same profile as the corresponding UCS data. All the geopolymer plugs showed approximately the same “stiffness”. Moreover, the Portland cement showed the steepest slope of the Standard Force vs. %Deformation slope, which is stiffer than for the geopolymer systems.

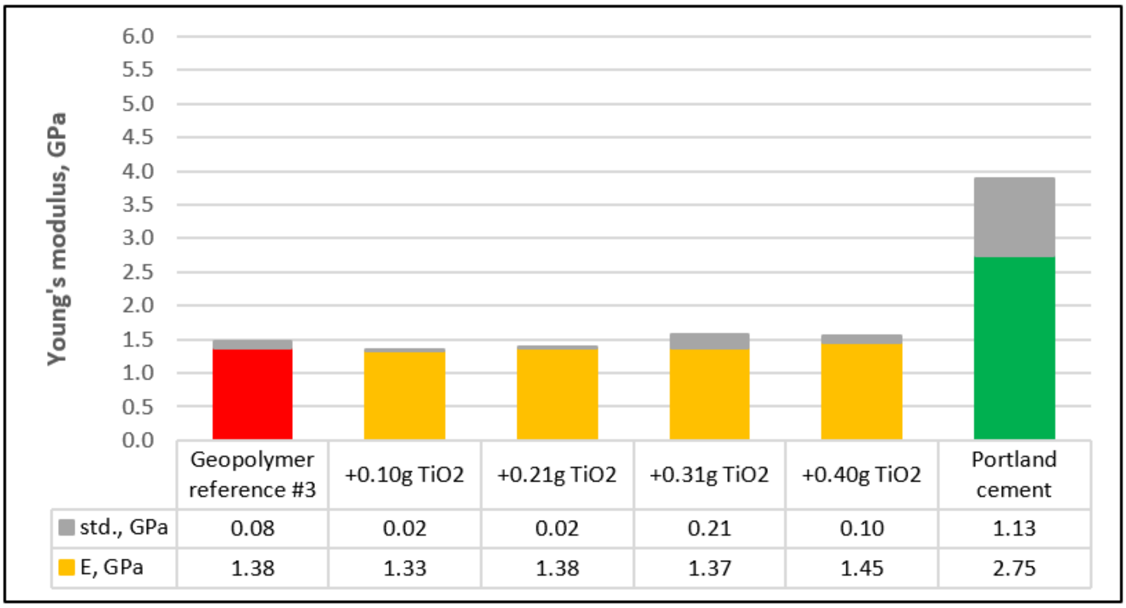


Figure 5.58: Young’s modulus for effect of TiO_2 on geopolymer reference #3, **3 days** cured, TM#22.

As the curing time increased from 3 to 10 days, the Young’s modulus increased significantly for both geopolymer and Portland cement (Figure 5.59). An outlier in this observation is the 0.10g TiO_2 geopolymer that showed no difference.

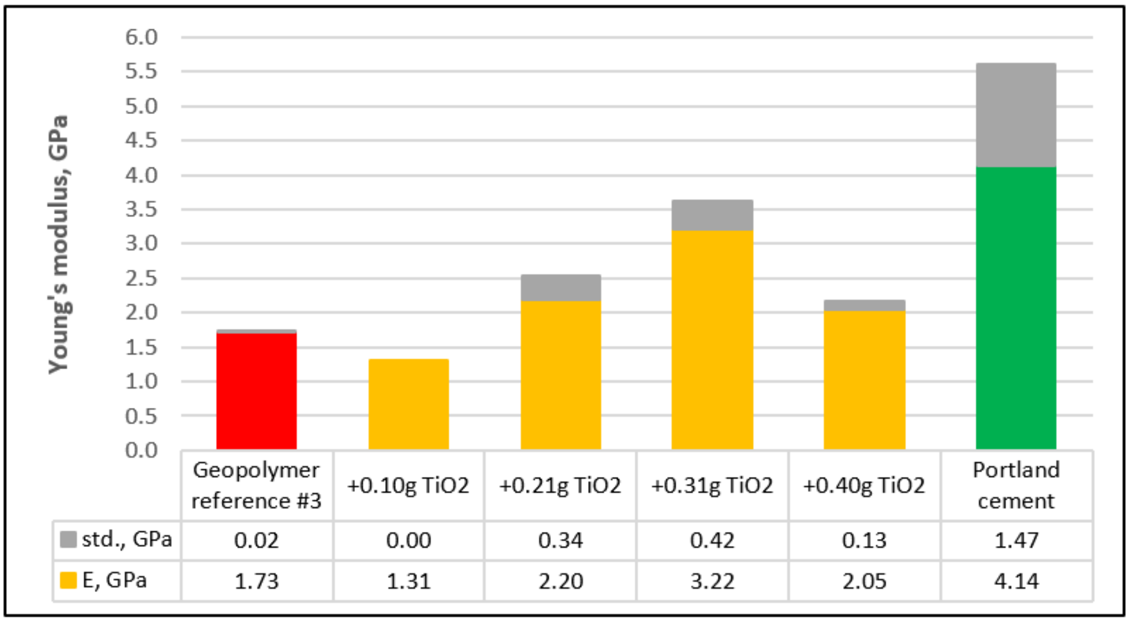


Figure 5.59: Young’s modulus for effect of TiO_2 on geopolymer reference #3, **10 days** cured, TM#22.

An interesting observation with the high-concentrated sodium metasilicate (45.1%)-based geopolymer reference #3 in TM#22 was that it exploded when maximum stress load was reached. Two sample pictures are reported in Figure 5.60. This is contrary to the softer compressing of geopolymer reference #2 in TM#20-21, as seen with the photos in Appendix

A. For that low-concentrated sodium metasilicate (30%) geopolymer, more of the plugs remained after the crushing, with a big vertically inclined crack. Nonetheless, no effect of nanoparticles was observed.

Figure 5.60: Two examples of (45.1%, clear) homemade-based geopolymer explosion when crushed.

5.2.4.2 Test matrix 23

Design idea: The goal was to investigate the effect of nanoparticle MWCNT-COOH on geopolymer reference #3 mixture from phase 1 made with homemade sodium metasilicate liquid (45.1%, clear), for 3 -and 10 days curing in oven.

Geopolymer mixtures: The sample plugs were prepared same way as in TM#22, and the mixtures are presented in Table 5.39 and Table 5.40.

Table 5.39: Geopolymer reference #3 with various concentrations of MWCNT-COOH. **3 days** cured. TM#23.

	Geopolymer reference #3	+0.10g MWCNT -COOH	+0.21g MWCNT -COOH	+0.30g MWCNT -COOH	+0.40g MWCNT -COOH
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	40	40	40	40	40
MWCNT-COOH (g)	0	0.10	0.21	0.30	0.40
Viscosity	$\theta_{300} = 234$				

Table 5.40: Geopolymer reference #3 with various concentrations of MWCNT-COOH. **10 days** cured. TM#23.

	Geopolymer reference #3	+0.10g MWCNT -COOH	+0.21g MWCNT -COOH	+0.31g MWCNT -COOH	+0.40g MWCNT -COOH
Silica fume (g)	10	10	10	10	10
Fly ash (g)	192	192	192	192	192
Total alkaline activator (g)	105	105	105	105	105
Extra ex-situ water (g)	40	40	40	40	40
MWCNT-COOH (g)	0	0.10	0.21	0.31	0.40
Viscosity	$\theta_{300} = 234$				

Visual inspection: Same as with the TiO_2-batch of geopolymers in TM#22, there can be observed an increase in free water from 3 to 10 days of curing, comparing Figure 5.61 a) with Figure 5.62 a). All the plugs, both after 3 and 10 days of aging, were cut to 51mm. Figure 5.61 b) documents that there were no abnormalities on the 3-days cured plugs after cutting. In fact, the plugs appeared to have no air bubbles on top surface. Contrary, for the 10-days cured plugs in Figure 5.62 b), one of the reference plugs had an uneven top surface with some pieces that fell off during cutting.

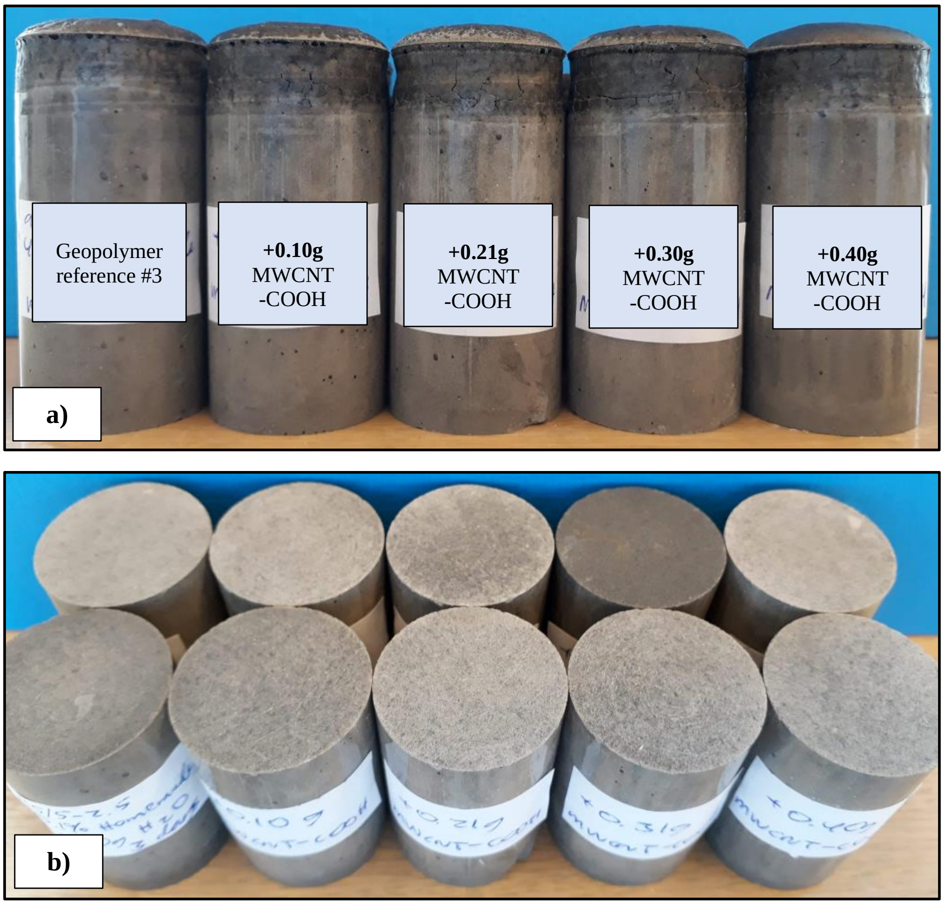


Figure 5.61: **3 days** cured, TM#23. a) showing free water of the plugs. b) plugs cut to ~51mm, below free water interface

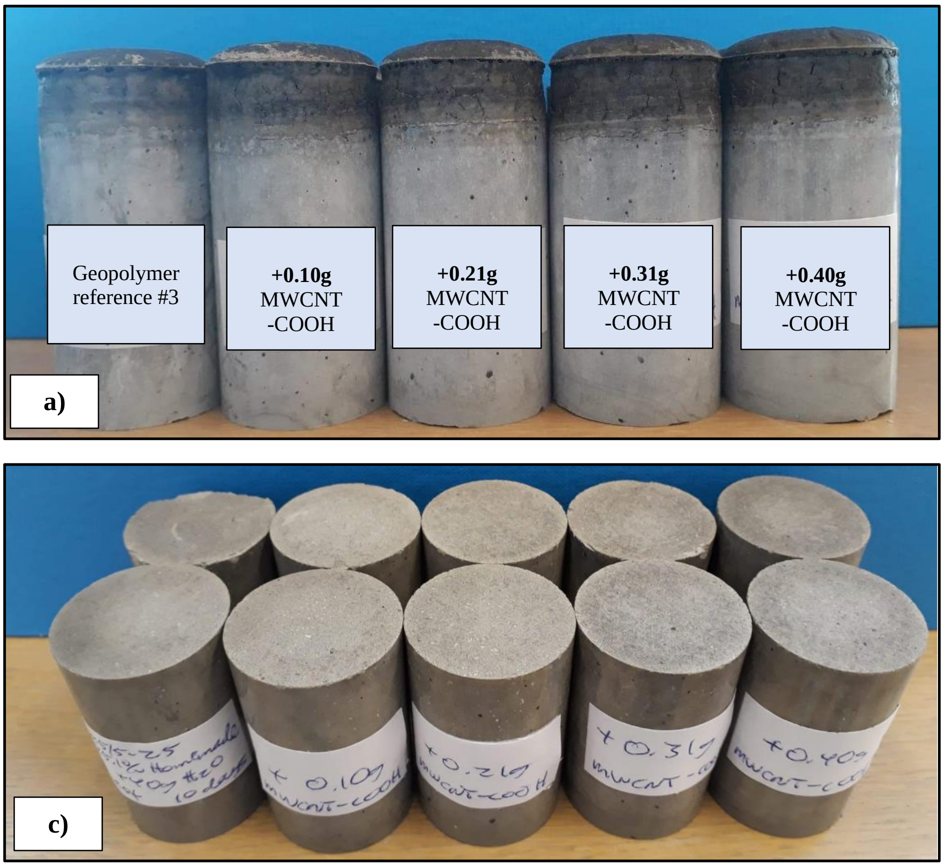
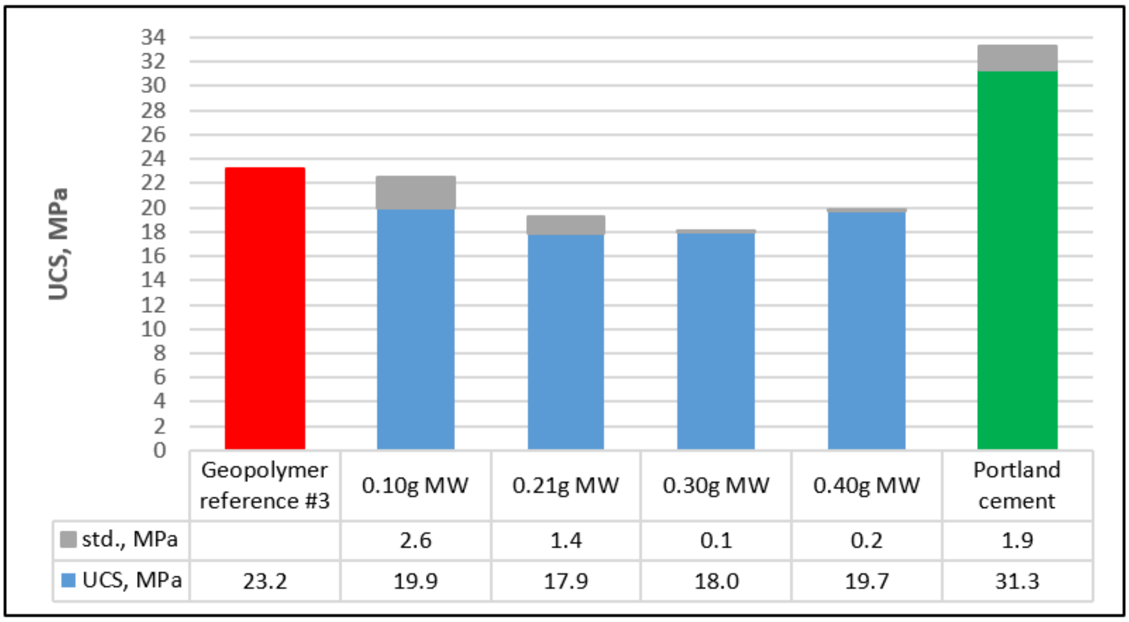


Figure 5.62: **10 days** cured, TM#23. a) showing free water of the plugs. b) plugs cut to ~51mm, below free water interface

UCS test: Based on the UCS test results displayed in Figure 5.63, the MWCNT-COOH appears to reduce the early strength development of the geopolymer. All the concentrations of nanotube showed lower strength relative to the reference. The reference geopolymer with a strength of 23.2 MPa was 17% higher than the 0.10g MWCNT-COOH-based geopolymer, which was the second strongest geopolymer. Again, the Portland cement showed the highest early strength development with 31.3 MPa. Only one of the reference plugs were detected during the UCS test because the “start” button in the computer software was not pushed for the first one.

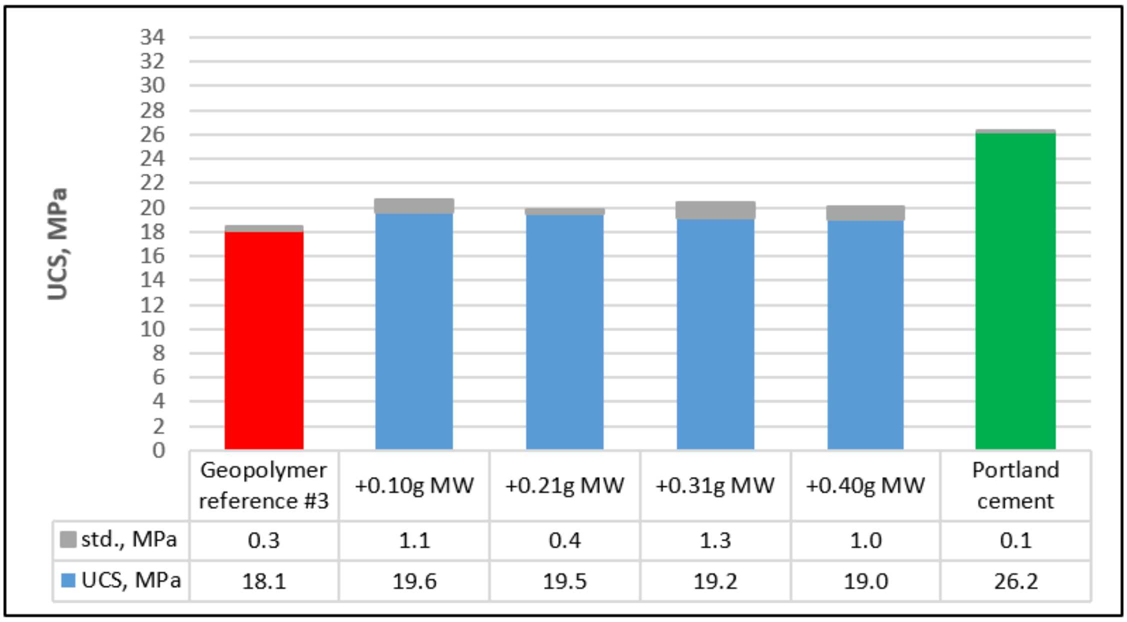


	Geopolymer reference #3	0.10g MW	0.21g MW	0.30g MW	0.40g MW	Portland cement
■ std., MPa		2.6	1.4	0.1	0.2	1.9
■ UCS, MPa	23.2	19.9	17.9	18.0	19.7	31.3

Figure 5.63: UCS results for effect of MWCNT-COOH on geopolymer reference #3, **3 days** cured, TM#23. “MW” is abbreviation of MWCNT-COOH.

After 10 days of aging, the reference geopolymer surprisingly dropped in strength with 22%, observed in Figure 5.64. As the concentrations of MWCNT-COOH increased, the strength reduced slightly, but still, the 0.40g MWCNT-COOH treated slurry (i.e., 19.0 MPa) were higher than the reference (i.e., 18.1 MPa). An observation to notice from Figure 5.62 c) is that one of the reference geopolymers lost a big piece of the top part during cutting. The defect on the reference plug might be the reason for the low UCS values presented in Figure 5.64.

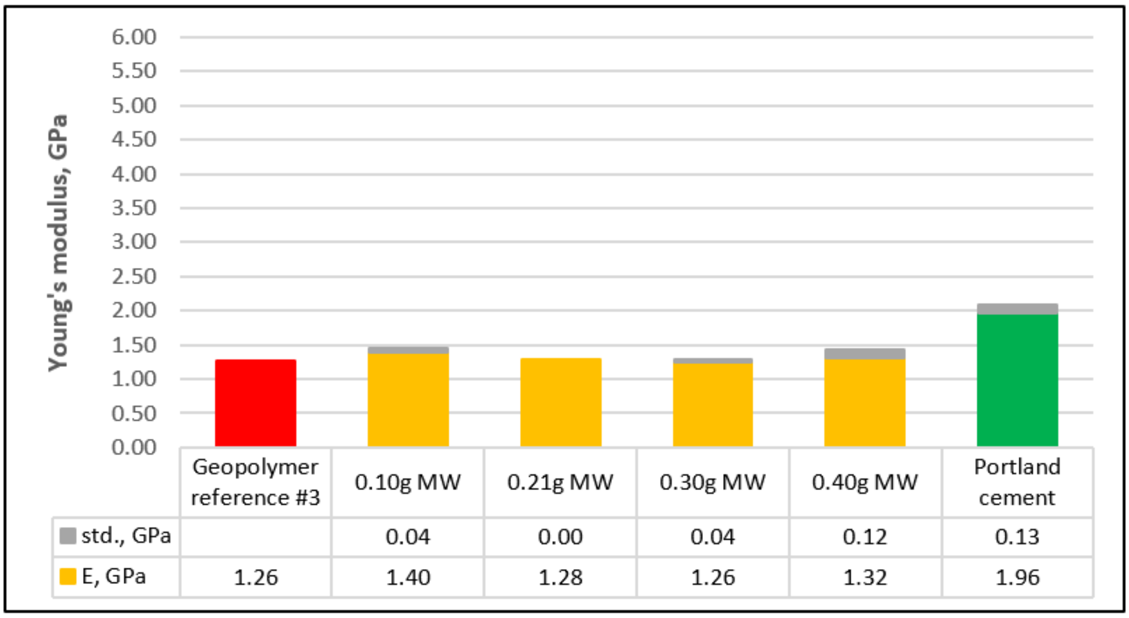
Another observation is that the Portland cement also decreased its strength (i.e., 16% from 31.3 MPa to 26.2 MPa) on the tenth day of curing. That is the same observation reported in TM#19. These unexplainable variations have occurred for both some geopolymer and Portland cement plugs. The reduction in strength could be associated with the possible internal defect or flaw in the cement plugs. A repeat and well-conditioned slurry preparation will likely reduce the uncertainty of the measurements, but due to the time lost during COVID-19 lockdown, this was unfortunately not conducted. However, future work can investigate this more.



	Geopolymer reference #3	+0.10g MW	+0.21g MW	+0.31g MW	+0.40g MW	Portland cement
▨ std., MPa	0.3	1.1	0.4	1.3	1.0	0.1
🟦 UCS, MPa	18.1	19.6	19.5	19.2	19.0	26.2

Figure 5.64: UCS results for effect of MWCNT-COOH on geopolymer reference #3, **10 days** cured, TM#23. “MW” is abbreviation of MWCNT-COOH.

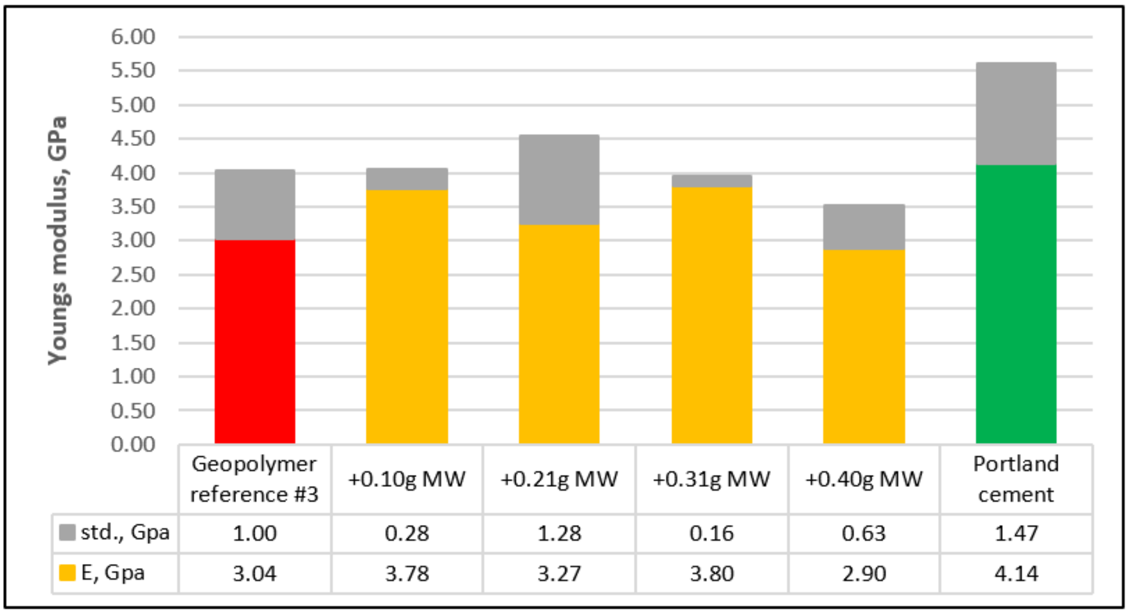
Figure 5.65 shows that the Young’s modulus for all the MWCNT-COOH concentrations is greater or equal to the reference after 3-days curing time. But, there is no clear trend with respect to multiwall carbon nanotube concentration. 0.10g MWCNT showed the highest compressive strength in Figure 5.63 among the nanotube-modified mixtures and the largest Young’s modulus in Figure 5.65.



	Geopolymer reference #3	0.10g MW	0.21g MW	0.30g MW	0.40g MW	Portland cement
▨ std., GPa		0.04	0.00	0.04	0.12	0.13
🟨 E, GPa	1.26	1.40	1.28	1.26	1.32	1.96

Figure 5.65: Young’s modulus for effect of TiO_2 on geopolymer reference #3, **3 days** cured, TM#23. “MW” is abbreviation of MWCNT-COOH.

After 10 days of curing, the Young’s modulus of all geopolymers and also the Portland cement had risen abruptly, seen in Figure 5.66. However, no clear trend can be seen, partly because the 0.21g MWCNT-COOH is so low compared to the other CNT concentrations. The 0.21g also had a high standard deviation that comes from large spreading of Young’s modulus for the two plugs. One plug showed E = 4.17 GPa and the other E = 2.36 GPa. Despite that, the standard deviation for UCS was only 0.4 MPa. The Portland cement also showed large spreading of Young’s modulus with 1.47 GPa standard deviation, with very low 0.1 MPa std. for UCS.



	Geopolymer reference #3	+0.10g MW	+0.21g MW	+0.31g MW	+0.40g MW	Portland cement
▨ std., Gpa	1.00	0.28	1.28	0.16	0.63	1.47
🟨 E, Gpa	3.04	3.78	3.27	3.80	2.90	4.14

Figure 5.66: Young’s modulus for effect of TiO_2 on geopolymer reference #3, **10 days** cured, TM#23. “MW” is abbreviation of MWCNT-COOH.

5.3 Uncertainties with the experimental work

Here will the known uncertainties with the experimental work in this MSc project be presented.

Inclined top surface of plug

Polishing the geopolymer and cement plugs with sandpaper and using water leveler were two techniques to make the top surface as horizontal as possible to avoid point load during UCS test, but deviations may of course occur.

Inclined bottom and/or top plate

A water leveler was used to make sure the bottom plate of the UCS machines was horizontal. Had top surface been completely horizontal for both top -and bottom plates and the plugs, more interesting test results would have been obtained.

Air bubbles in slurries

Since the geopolymer and cement were cured at ambient pressure, they are more prone to air bubble generation. While stirring the slurry mix, air bubbles might form. The effect of this was reduced by stirring slowly before pouring the slurry into the molding cups while vibrating the precast cup. Had the air bubbles been removed, more interesting test results would have been obtained.

Free water in slurry

With very thin slurries, there can perhaps be a risk that unevenly more free water in the slurry ends up in one of the cups, and thereby the plugs will have a higher amount of free water from the slurry. More interesting results could have been obtained using larger precast cups (i.e., 100mm length and 50mm diameter) with likely less proneness to free water.

Dispersion of the nanoparticles

The nanoparticles were in solution form and were dispersed in the water very well. However, the mixture of the nanofluid with the slurry was conducted by hand. The homogeneity of the nanofluid dispersion in the slurry is expected to be not very uniform. Had the slurry been conditioned with lower RPM for some minutes, the degree of homogenous distribution of the nanoparticles in the slurry would have increased. Due to hand mixing, the effect of nanoparticles in the slurry test results would therefore vary because of the different uniformity of nanoparticle in the slurry.

Repeated measurements

In this work, two plugs were made for each geopolymer and Portland cement mixture. For better statistical credibility and to be able to make conclusions, it is beneficial with more sample plugs of the same mixture to be synthesized and repeat the tests.

6 Summary and discussion

The overall results and most important findings of experimental works will be discussed in this chapter. The discussion is divided into two parts: phase 1 and phase 2 of experimental works.

6.1 Phase #1: Formulation geopolymer reference mixture

As illustrated with blue arrows in Figure 1.5, three geopolymer reference mixtures were successfully formulated that passed the pre-defined criteria. Phase 1 of experimental works was a screening process by trial/error. Many test matrixes and experimental tests were conducted with the goal of formulating a geopolymer mixture with UCS close to the strength of Portland cement and a good workability for oil well cementing operations (300rpm reading criteria). However, please note that the systems were categorized as fail for the oil well if they had too high viscosity but were suggested to be used for civil construction works if they had strong compressive strength.

The test matrix designs are formulated based on the results obtained from the previous test matrix. The screening procedure base for an oil well application defined in this thesis work are:

a) Trying to formulate geopolymer as strong as Portland cement.
b) Trying to make sure that the slurry’s workability is good enough such that the 300RPM value should not be beyond the maximum limit.
c) Trying to make sure that the free water amount on the top part of plug is low and not porous as well as not highly fractured.

Please note that the formulated geopolymers in this thesis work are under worst case scenario. This means that the slurry was not very well conditioned to remove the air from the system, and the slurry was not cured at higher pressure. However, under these worst-case scenarios, the results obtained from phase 1 were satisfactory because three novel geopolymer mixtures were formulated.

The following discusses the overall results from phase 1 by systematically addressing the issues stated in chapter 1.2.

6.1.1 Geopolymer systems chosen as reference

Through the screening process pre-defined in this thesis work, three novel formulated geopolymer mixtures were selected as reference to study the impact of nanoparticles. Their composition and characteristics are summarized below:

Geopolymer formulation reference #1

- 95/5 wt% fly ash / silica fume
- 2.5 ratio of homemade sodium metasilicate liquid (45.1%, milky) / 10M NaOH
- 0.52 alkaline liquid / solids ratio
- +30g extra ex-situ water (0.15 water / solids ratio)
- Viscometer 300RPM reading of $\theta_{300} > 300$ (thick slurry so not measured)
- After 3 days of 62°C curing + 1 day resting at room temperature, and cut to 53mm:
    - MWCNT-COOH batch
        - 23.1 MPa uniaxial compressive strength
        - 1.39 GPa Young's modulus
    - TiO_2 batch
        - 23.8 ± 3.3 MPa uniaxial compressive strength
        - 1.33 ± 0.07 GPa Young's modulus

Geopolymer formulation reference #2

- 95/5 wt% fly ash / silica fume
- 2.5 ratio of homemade sodium metasilicate liquid (30%, clear) / 10M NaOH
- 0.52 alkaline liquid / solids ratio
- +23g extra ex-situ water (0.11 water / solids ratio)
- Viscometer 300RPM reading of $\theta_{300} = 176$
- After 3 days of 62°C curing + 1 day resting at room temperature, and cut to 61mm:
    - 8.4 ± 0.5 MPa uniaxial compressive strength

Geopolymer formulation reference #3

- 95/5 wt% fly ash / silica fume
- 2.5 ratio of homemade sodium metasilicate liquid (45.1%, clear) / 10M NaOH
- 0.52 alkaline liquid / solids ratio
- +40g extra ex-situ water (0.20 water / solids ratio)
- Viscometer 300RPM reading of θ_{300} = 234
- After 3 days of 62°C curing + 1 day resting at room temperature:
    - TiO_2 batch (cut to 58mm)
        - 19.3 ± 0.1 MPa uniaxial compressive strength
        - 1.38 ± 0.08 GPa Young’s modulus
    - MWCNT-COOH batch (cut to 51mm)
        - 23.2 MPa uniaxial compressive strength
        - 1.26 GPa Young’s modulus

6.1.2 The solids ratio (fly ash / silica fume)

As the starting point, the first geopolymer was made with the 70/30 FA/SF solid ratio, which was taken from Ridha et al. (2015) [19]. The results showed very week geopolymer, and it was screened out with visual inspection and water absorption test. Further investigation was conducted to optimize the combination of FA/SF. Finally, 95/5 was found to have the highest compressive strength. All the further geopolymers in this thesis were then based on this ratio.

It was with TM#1-3 found that increasing silica fume required more extra ex-situ water added and showed more expansion.

6.1.3 Alkaline activator solution ratio (silicate / sodium hydroxide)

In the TM#4 design, the 2.5 silicate / sodium hydroxide ratio based geopolymer showed 22% higher compressive strength (i.e., 21.7 MPa) than geopolymer with 2.0-ratio.

6.1.4 Homemade sodium metasilicate alkaline activator material

In this thesis, five different homemade sodium metasilicate liquids were synthesized and mixed with constant 10M NaOH as alkaline activator as part of screening process of searching for a neat geopolymer.

6.1.4.1 45.1%, milky color

The first solution synthesized, was 45.1% concentration of sodium metasilicate in water. The particles were not completely dissolved, and hence, the color was white/milky. The solution was therefore named as (45.1%, milky). With this alkaline solution, geopolymer systems were synthesized, and the resulting slurry was thick and viscous. The UCS was high after 3 days of curing in oven and being exposed 1 day to air, with 21.7 MPa (TM#4) and 23.1-23.8 MPa (TM#17-18).

6.1.4.2 37.1%, clear color

The second type of homemade sodium metasilicate liquid had 37.1% concentration, where the particles were dissolved until clear water glass color. The geopolymer formulated with this solution provided a strength of 13.6 MPa after 3 days of curing and one resting day (TM#5), which is lower than the 45.1% milky-based geopolymer. The main reason partly because of lower sodium metasilicate concentration but likely also due still some free water/porous on top even though the top layer was removed. With the 2.3g extra water in TM#5, it was too viscous to be measured by viscometer.

6.1.4.3 30%, clear color

Thirdly, the synthesis of 30% concentration homemade sodium metasilicate solution concentration. Since all the particles were dissolved, the solution was clear as water glass. In TM#9, with no additional water, this silicate-type resulted in a strong geopolymer with 24.2 MPa strength (after 3 days of curing at 62°C and 56 days of resting at room temperature). 23g extra ex-situ water was added in order to improve its workability to $\theta_{300} < 300$ from viscometer measurement (TM#15). The extra water and the less time being exposed to ambient air (1 day) decreased the UCS significantly to 8.4 MPa.

6.1.4.4 20%, clear color

Furthermore, 20%-based geopolymers were formulated. However, with 4g extra ex-situ water added, the results were very weak compressive strength of 4.6 MPa after 3 days and 52 days exposed to room temperature (TM#12).

6.1.4.5 45.1%, clear color

The fifth silicate type that was made in the lab consisted of a sodium metasilicate liquid of 45.1% concentration with clear water glass color. Here, more energy was used to make the solution as clear as possible. This novel geopolymer mixture was designed for oil well operations by having thin enough slurry ($\theta_{300} < 300$) and showing strong UCS. After 3 days of curing and 1 day of resting in ambient temperature, it showed compressive strength of 20.4 MPa (test matrix 16).

6.1.5 Commercial sodium silicate alkaline activator performance

From visual inspection, the commercial silicate-based showed the highest free water content of all the geopolymers formulated in this thesis (TM#13). 20g of water was added so that the rheology $\theta_{300} < 300$ viscometer criteria was fulfilled. However, even with that much free water and visible pores and cracks, it showed a UCS of 14.4 MPa after 3 days of curing at 62°C and being exposed for 48 days in air at room temperature.

6.1.6 Compressive strength and workability

The overall trend is that higher concentration of sodium metasilicate particles in the home-made sodium metasilicate liquid increased uniaxial compressive strength and reduced workability. This is likely because more activator is available to react with the aluminosilicate compounds in the solid fly ash and silica fume source material.

6.1.7 Visual inspection

The formulated geopolymer mixtures showed different appearance, which depends on the ingredients type, amounts and activator ratio as well as concentrations. The common observation for all is that that they had some amount of free water on the top, which is expected as the particles settled down during hydration process. Generally, the amount of free water on the plugs increased with higher volume of extra ex-situ water added.

The free water affects the compressive strength highly because it can induce high local stress concentration, which gives rise to an early rupture and failure. The free water generally looked very porous, fractured, brittle and poorly geopolymerised. Therefore, cutting the geopolymers below the free water interface was seen essential in order to get an idea of its strength. However, in phase 1 (TM#7-13), it was decided to cut the geopolymers at a 64mm length, which was the average length after shrinkage of four sample Portland cement plugs. For that reason, some of the geopolymer plugs still had free water at 64mm length and a resulting poor UCS.

Another finding from visual inspection was that geopolymers made with higher concentrated sodium metasilicate liquids, for example 45.1% compared to 30%, showed less air bubbles on top surface before UCS test and internally after observing the samples post to crushing. The main reason for this is perhaps that the 45.1 % alkaline solution provided a higher viscous slurry, stronger alkali activation, and reduced the particle settling.

6.1.8 Lignosulfonate admixture

Different concentrations of lignosulfonate were blended with the homemade metasilicate-geopolymer mixtures. For the 37.1% concentration based geopolymer, the mixture of lignosulfonate up to 1.5% by weight of solids reduced the amount of free water in plugs significantly, and the workability was highly improved, as expected from literature study [50]. However, when it comes to the UCS, for geopolymer formulated with 7.5-ratio of Na_2SiO_3 to NaOH (TM#6), the strength reduced by 23% at maximum. The lignosulfonate of concentrations 0.54wt% and 0.83wt% blended with 2.5-ratio based geopolymer (TM#5) did not alter the UCS.

Lower concentrated homemade sodium metasilicate liquid (i.e., 30% and 20%)-based geopolymer showed reducing strength with increasing amount of lignosulfonate. Moreover, too high concentrations of the disperser resulted in too large volume of free water. For instance, the 1.5wt% lignosulfonate added to the (30%) homemade sodium metasilicate-based geopolymer in TM#10. The resulting slurry was extra thin, illustrating that the dispersing impact of lignosulfonate was too high in that case. Ultimately, the lignosulfonate for high-concentrated sodium metasilicate liquid did not alter the strength that much, and the free water was reduced. The possible explanation for this observation is that first, the activator concentration is lower as well as the presence of lignosulfonate dispersant increases the repulsive force among the solids. As a result, the binding strength of the geopolymer is reduced. On the other hand, in the high-concentrated metasilicate solution, the impact of dispersant on the binding effect is not as that of the lower concentration. However, since the presence of lignosulfonate created more air bubbles in the system, conditioning the slurry by removing the bubbles would likely enhance the mechanical strength of the geopolymer.

6.1.9 Shrinkage / expansion

All the geopolymers formulated in this thesis work did not show shrinkage after 3-and 10 days curing at 62°C. The evaluation for the lateral shrinkage was by visual inspection of the plugs-plastic molding integrity. The plugs were not easily detached from the cup due to the tight bonding. In fact, they showed expansion on the top part, which is mainly associated with free water dominated layers. However, the layer contained more air bubbles, and the expansion may be due to the trapped air. Similar observations have been reported by several researchers, as geopolymer exhibited low shrinkage potential [69]. On the other hand, the Portland cement-based plugs showed shrinkage issues with free water on the top, which is due to the particle settling.

6.2 Phase #2: Effect of nanoparticles on neat geopolymer

The goal with phase two of experimental works was to investigate the effect of nanoparticles nano-TiO_2 and MWCNT-COOH on the three geopolymer references obtained from phase 1. The idea here was to incorporate the positive impacts of the nanoparticles on the neat geopolymer formulation. The mechanism for the positive effect is that the nanoparticles may improve the pore filling of the neat geopolymer and might undergo chemical reaction enhancing geopolymerisation process. The effect depends on the concentration and the surface charge of the nanoparticles, as well as the pH of the systems after the nanoparticles have been blended. The idea was tested through experiments.

The results from phase 1 were positive, but the impression of phase 2 was different because the nanoparticles showed little trend on the reference. Both nano-TiO_2 and MWCNT-COOH showed positive and negative impacts on the neat reference systems. The Portland cement also showed varying strength development. Hence, there are some unexplainable factors that make it necessary to do more experimental works on the geopolymer systems to conclude the positive and negative impacts of the nanoparticles. The positive and negative impact results have also been documented by several investigators [53], [58].

Nevertheless, the major findings will be discussed in the following section.

6.2.1 Geopolymer reference #1

This geopolymer formulation was suggested for construction works because of its high strength and viscous slurry. All the plugs were cured for 3 days at 62^{o}C and exposed in air for 1 day at room temperature before testing. The geopolymers were synthesized with the high-concentrated sodium metasilicate liquid (45.1%), characterized by milky color.

6.2.1.1 Effect of MWCNT-COOH

All concentrations of MWCNT-COOH (0.050g, 0.10g, 0.22g and 0.33g) resulted in **higher compressive strength**. The optimum concentration for MWCNT-COOH was seen to be 0.10g with UCS of 26.4 MPa. That accounted for a 14% increase relative to the reference. Besides, the stiffness of the MWCNT-COOH-based geopolymers was lower than the reference.

6.2.1.2 Effect of TiO_2

Incorporating TiO_2 into the geopolymer slurry resulted in a similar trend as for MWCNT-COOH, also a **greater compressive strength**. The optimum concentration was for 0.33g TiO_2 with increased strength of 18% relative to reference (i.e., 28.1 MPa). The stress–strain curve obtained from the plugs showed ductile type with lower gradient for all the nano-particle blending, which resulted in a lower stiffness (i.e., lower Young's modulus).

6.2.2 Geopolymer reference #2

This geopolymer system was made of homemade sodium metasilicate liquid of 30% concentration, which had clear water glass color. The samples were cured for 3 -and 10 days at 62°C and exposed in air for 1 day at room temperature.

6.2.2.1 Effect of TiO_2

Results showed that the 0.11g TiO_2 recorded the UCS of 11.1 MPa after 3 days of curing, but **no clear trend** could be seen. On the other hand, both the reference and the other TiO_2 concentrations had compressive strength of approximately 8.4 MPa.

After 10 days of aging, the UCS increased greatly for all the mixtures. Then the reference had increased to a strength of 15.2 MPa. The strength of the TiO_2-based geopolymers was approximately 10% lower.

Despite this increased strength development after 10 days of curing relative to 3 days, the compressive strength of the Portland cement increased by 20% (i.e., 21.7 to 26.0 MPa). However, more investigation is required before making any conclusion here. The internal structure of the plugs should be analyzed under Scan Electron Microscope if the TiO_2 system had been degraded or not under the 10 days curing. This will be investigated in the future work.

6.2.2.2 Effect of MWCNT-COOH

Similar to the TiO_2-batches, after 3 days of curing, **no clear trend** of the UCS data could be observed. Both the reference and addition of MWCNT-COOH showed strength in range 8.4 – 9.9, MPa with the reference the lowest, and 0.40g MWCNT-COOH the highest.

After 10 days of curing, the trend for UCS reminded about the same as the TiO_2-blended systems. All the geopolymer mixtures showed an increase in UCS, with the greatest increase for the neat reference geopolymer by 76% (i.e., up to 14.8 MPa). For that case, the 0.22g MWCNT-COOH resulted in the highest UCS with 12.6 MPa among the nanotube concentrations, but relative to the other concentrations, there was no clear trend.

6.2.3 Geopolymer reference #3

The neat reference #3 geopolymer was formulated with a 45.1% concentrated homemade sodium metasilicate liquid (i.e., clear water glass color).

6.2.3.1 Effect of TiO_2

After 3 days of curing, the geopolymers showed **strength increase** with increasing nano-TiO_2 concentration. Out of the considered concentrations, the 0.4g TiO_2 recorded the highest strength, increasing the UCS of the neat geopolymer by 18%. However, comparing the strength, it was 14% lower than the Portland cement sample. Please note that the fluid to solid ratio in the cement (0.44 water to solid ratio) is lower than that of the geopolymer systems (0.52 alkaline liquid to solid ratio).

After 10 days of curing, the UCS-trend varied non-linearly with the concentrations. Comparing with the 3-days curing, the neat geopolymer increased by 48%, whereas the TiO_2-geopolymers degraded its strength. For instance, the strength of 0.1g TiO_2-geopolymer remained stable, while the 0.4g TiO_2-geopolymer reduced the strength by 30%. The geopolymer reference showed 9% higher UCS than the Portland cement after 10 days aging. It is important to note that the length of the plugs of the 3-days and 10-days are not the same, and the degree of the homogeneity of the plugs are different. The reason for the different results could have been answered by analyzing the internal structure of the plugs under the Scan Electron Microscope as well as quantifying the element analysis. This was not conducted due to the COVID-19 limited laboratory access.

6.2.3.2 Effect of MWCNT-COOH

Comparing the batch of geopolymer incorporated with MWCNT-COOH with the TiO_2-batch, it was **not easy to find a good trend** and explanation. This was because the reference for the MWCNT-COOH-batch decreased the strength by 22% to 18.1 MPa after 10 days curing time relative to the 3-days strength. On the other hand, for the titanium dioxide-batch, there was a 48% increase for the reference. Ideally, since it is theoretically the exact same reference mixture, it should give approximately the same UCS. A possible uncertainty with this observation was thought to be related to the visually observed deformity (pieces of the top fell off) on one of the 10-days cured reference plugs as well as internal air bubbles.

7 Conclusion

The main focus of the experimental works was to formulate a novel geopolymer mixture based on a homemade sodium metasilicate liquid and compare with the commercial ready-made sodium silicate. The word "homemade" used in this thesis is to represent that the sodium metasilicate alkaline solution was prepared in the laboratory. Moreover, the effect of TiO_2 and MWCNT-COOH nanoparticle solutions on the neat geopolymer was investigated.

The overall results showed that:

- Based on the established pass/fail screening criteria, three neat geopolymer mixtures were formulated, each from sodium metasilicate alkaline solution of different concentrations.

- As the concentration of the metasilicate concentration increased,
    - The geopolymer compressive strength increased.
    - Lower amount of air bubbles in the slurry was observed, which created less pores in the core plugs.
    - The workability was reduced due to higher viscosity and more extra water required.
    - The opposite was true when the concentration reduced.

- Effect of nanoparticles on the three neat geopolymers:
    - Both TiO_2 and MWCNT-COOH increased the UCS to an optimum of the 3-days cured geopolymer formulated with the (45.1%, milky)-based sodium metasilicate.
    - Both particles showed a non-linear effect on the strength of the geopolymer synthesized with the (45.1%, clear) sodium metasilicate liquid. The results were varying and there was no clear trend. However, it was observed that one of the geopolymers showed a higher strength than the Portland cement sample. Also, the Young's modulus and modulus of elasticity increased with curing time.
    - The nanoparticles did not show any impact on the (30%, clear) sodium metasilicate liquid-based geopolymer. However, the system showed a higher strength and modulus of elasticity as the curing days increased.

At this level of research, the failure mechanisms for the plugs are not fully understood. More experimental tests must be conducted to have better statistical data to conclude the effect of nanoparticles and as well to understand the variations in the reference system from 3 to 10 days of curing. It would have been beneficial with a Scan Electron Microscope and element analysis as well to analyze the internal structure of the geo-polymer.

Table 7.1 summarizes the UCS test results for the best geopolymer systems for each test matrix formulated throughout this MSc work in phase 1. The mixtures that were screened out from visual inspection are not included. The Portland cement plugs are also shown for comparison. The UCS test results obtained from the effect of nanoparticles on the three neat geopolymer references in phase 2 are summarized in Table 7.2.

Table 7.1: Summary of the formulated geopolymer mixtures in phase 1.

Test matrix	FA/ SF	Na_2SiO_3	Na_2SiO_3 / NaOH	AA/ S	Ligno (g)	Water (g)	UCS (MPa)	E (GPa)	Curing time (days)	Air time (days)	≈ L (mm)
Effect of homemade sodium metasilicate liquid (45.1%, milky)											
TM#4	95/5	(45.1%,milky)	2.5	0.52	0	9	21.7	0.57	3	1	68
	100/0					6	20.3	0.44			
	95/5		2.0			6	17.8	0.53			
Effect of homemade sodium metasilicate liquid (37.1%, clear)											
TM#5	95/5	(37.1%, clear)	2.5	0.52	0	2.3	13.6	1.36	3	1	68
					1.1		13.3	1.18			
					1.7		13.8	1.23			
TM#6	95/5	(37.1%, clear)	2.5	0.52	0	15	21.8	1.63	3	1	68
					0.51		16.8	1.52			
					1.01		19.5	1.51			
					2.02		19.3	1.44			
					3.03		17.7	1.44			
TM#7	95/5	(37.1%, clear)	2.5	0.55	0	0	31.7	-	3	57	64
				0.52			27.2				
Comparing geopolymer systems in TM#7-13 with Portland cement											
TM#8	Portland cement class G, 0.44 water to solid ratio						28.5	-	3	56	64
Effect of homemade sodium metasilicate liquid (30%, clear)											
TM#9	95/5	(30%, clear)	2.5	0.52	0	0	24.2	-	3	56	64
					0.75	23	13.8				
TM#10	95/5	(30%, clear)	2.5	0.52	1.2	18	10.9	-	3	53	64
TM#11	95/5	(30%, clear)	2.5	0.52	0.75	23	7.5	-	3	50	64
Effect of homemade sodium metasilicate liquid (20%, clear)											
TM#12	95/5	(20%, clear)	2.5	0.52	0	4	4.5	-	3	52	64
					0.25		3.9		3	52	
					0		5.9		7	48	
					0.25		5.5		7	48	

Effect of commercial sodium silicate liquid (37.1%)											
TM#13	95/5	Commercial	2.5	0.52	0	20	14.4	-	3	48	64
					0.6		12.2				
Selection of the three geopolymer references											
TM#14	95/5	(45.1%, milky)	2.5	0.52	0	30	See TM#17-18		3	1	53
TM#15	95/5	(30%, clear)	2.5	0.52	0	23	See TM#20-21		3/10	1	61
TM#16	95/5	(45.1%, clear)	2.5	0.52	0	40	15.3	-	1.5	1	60
							20.4		3		60

Table 7.2: Summary of the study of effect of nanoparticles on the three geopolymer references in phase 2. All formulated with fly ash to silica fume ratio of 95/5, $Na_2SiO_3/NaOH = 2.5$ and alkaline activator / solids = 0.52.

Test matrix	Na_2SiO_3	TiO_2 (g)	MWCNT-COOH (g)	Water (g)	UCS (MPa)	E (GPa)	Curing time (d)	Air time (d)	≈ L (mm)
Geopolymer reference #1									
TM#17	(45.1%,milky)	-	0	30	23.1	1.39	3	1	53
			0.050		23.8	1.14			
			0.10		26.4	1.31			
			0.15		23.4	1.25			
			0.20		23.9	1.21			
TM#18	(45.1%,milky)	0	-	30	23.8	1.33	3	1	53
		0.10			24.7	1.40			
		0.22			26.5	1.33			
		0.33			28.1	1.32			
		0.55			26.3	1.40			
Portland cement for comparison with TM#20-23									
TM#19	Portland cement class G, 0.44 water to solid ratio				31.3	1.96	3	1	51
					26.3	2.75			58
					21.7	-			61
					26.2	4.14	10		51
					26.0	-			61
Geopolymer reference #2									
TM#20	(30%, clear)	0	-	23	8.4	-	3	1	61
		0.10			11.2				
		0.21			8.2				
		0.31			8.5				
		0.40			8.1				
TM#20	(30%, clear)	0	-	23	15.2	-	10	1	61
		0.10			13.7				
		0.21			13.6				
		0.31			13.7				
		0.41			13.1				
TM#21	(30%, clear)	-	0	23	8.4	-	3	1	61
			0.10		9.2				
			0.21		9.1				
			0.30		9.0				
			0.40		9.9				

TM#21	(30%, clear)	-	0	23	14.8	-	10	1	61
			0.10		11.5				
			0.21		12.6				
			0.31		11.5				
			0.40		11.6				
Geopolymer reference #3									
TM#22	(45.1%, clear)	0	-	40	19.3	1.38	3	1	58
		0.10			20.3	1.33			
		0.21			19.7	1.38			
		0.31			19.9	1.37			
		0.40			22.7	1.45			
TM#22	(45.1%, clear)	0	-	40	28.6	1.73	10	1	51
		0.10			20.4	1.31			
		0.21			15.6	2.20			
		0.31			15.4	3.22			
		0.40			16.0	2.05			
TM#23	(45.1%, clear)	-	0	40	23.2	1.26	3	1	51
			0.10		19.9	1.40			
			0.21		17.9	1.28			
			0.30		18.0	1.26			
			0.40		19.7	1.32			
TM#23	(45.1%, clear)	-	0	40	18.1	3.04	10	1	51
			0.10		19.6	3.78			
			0.21		19.5	3.27			
			0.31		19.2	3.80			
			0.40		19.0	2.90			

Description of symbols, words and abbreviations in Table 7.1 and Table 7.2:

- FA/SF = fly ash to silica fume ratio
- Na_2SiO_3/NaOH = homemade sodium metasilicate (OR commercial sodium silicate) / 10M NaOH ratio
- AA/S = alkaline activator / solids
- Ligno = grams of lignosulfonate powder dispersed in the corresponding ex-situ water. Except in TM#9, where the lignosulfonate was added as powder to the slurry
- Water = extra ex-situ added water
- UCS = uniaxial compressive strength (average of two plugs)
- E = Young’s modulus (average of two plugs)
- Curing time = curing time at 62°C
- Air time = time the plugs were exposed to ambient conditions after curing in oven and before UCS test.
- d = days

- L = length of the plugs after cut and polished with sandpaper, before UCS test
- wt% = weight percentage of solids
- Total solids in the geopolymer mixtures are 202g (fly ash + silica fume), so i.e., 0.1g nanoparticles = 0.05wt%, 0.2g = 0.10wt%, 0.3g = 0.15wt% and 0.4g = 0.20wt%.

8 Future works

The author suggests the following lists as future works:

Pressurized system

Nelson & Guillot (2006) writes in their well cementing book that the cement system should be cured in a pressurized chamber to eliminate the effects of entrained air. They also state that if pressure chamber is not available, the cement slurry should be degassed by stirring it gently under vacuum [8, p. 646].

In this work, the samples were cured at ambient pressure. It would have been interesting to see the effect of curing the geopolymer plugs in pressurized chamber or with stirring under vacuum in order to reduce the air from the slurry.

Different curing temperatures

The mixtures were in this study cured at 62°C. Finding the optimum curing temperature for the novel formulated geopolymers is of interest.

Increase the size of the plugs

It would have been interesting to make a big plug (50x100 size for example).

Ground granulated blast furnace slag (GGBFS)

GGBFS is another type of aluminosilicate source like fly ash and silica fume. Almufarji et al. (2019) reported that combined with fly ash in a geopolymer mixture, it increased early strength development and gave a slight increase after 28 days [70].

Especially for the homemade sodium metasilicate (30%, clear)-based geopolymer it would have been captivating to modify with GGBFS to try to enhance the geopolymerisation process.

Hybrid system

The Portland cement showed higher compressive strength, higher density and modulus of elasticity, and lower sonic measurement. Beneficially, the formulated geopolymers showed lower Young's modulus. Therefore, it would have been interesting to formulate a hybrid system consisting of Portland cement and geopolymer chemicals.

Repeat the experiments

For better statistics and to be able to conclude the results, several tests should be repeated.

Bonding to casing and rock formation

For the geopolymer to be an alternative for the Portland cement in oil well applications and form strong durable zone isolation, there must be strong casing-geopolymer and formation-geopolymer bonding. There was no time to conduct such an experiment.

Scan Electron Microscope

It would have helped to use a Scan Electron Microscope to see the internal microstructure of the geopolymers. That way the process of geopolymerisation can be more understood, and the rupture reason at maximum compressional force load can perhaps be understood (i.e., degradation).

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Appendix

Appendix A: Visual inspection

Test matrix 19

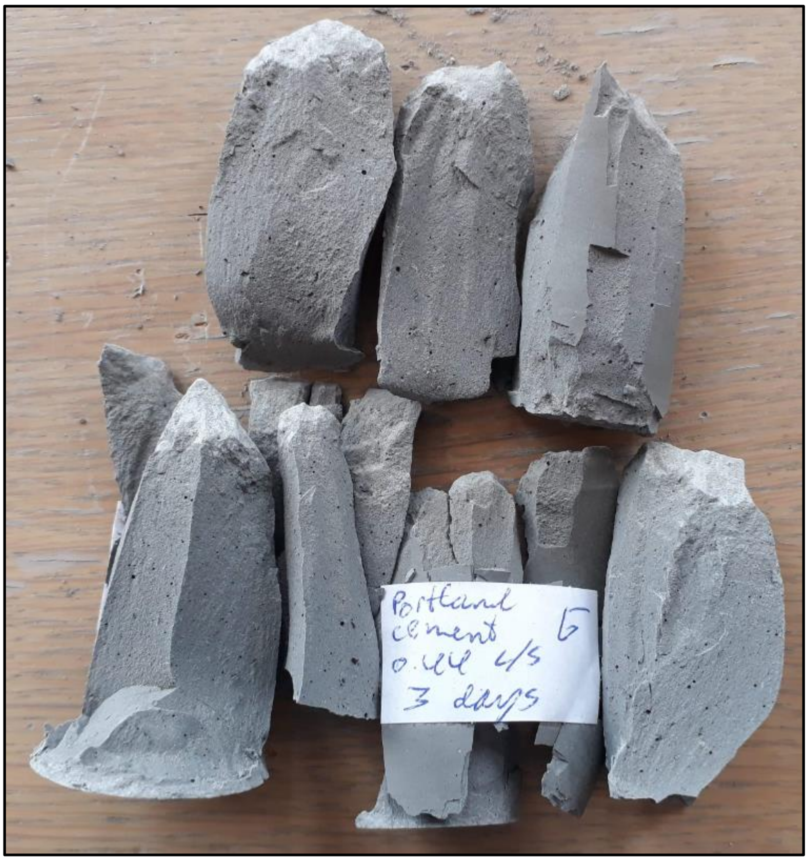


Figure Apx.1: A few pieces of the Portland cement plugs after UCS test, showing that internal visible pores exist.

Test matrix 20

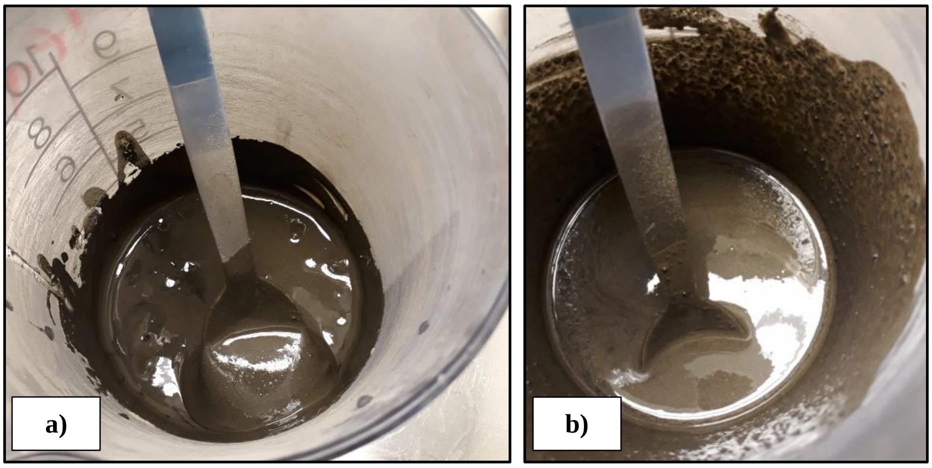


Figure Apx.2: Geopolymer based on homemade sodium metasilicate liquid (30%, clear). a) mixing of solids and alkaline activator **before** adding extra ex-situ water. b) mixing of solids and alkaline activator **after** adding 23g extra ex-situ water.

Figure Apx.3: Two examples of (30%, clear) homemade-based geopolymer when crushed.

Test matrix 21

Figure Apx.4: A few pieces of the geopolymer reference #2 + MWCNT-COOH plugs after UCS test, showing that internal visible pores exist.

Test matrix 22

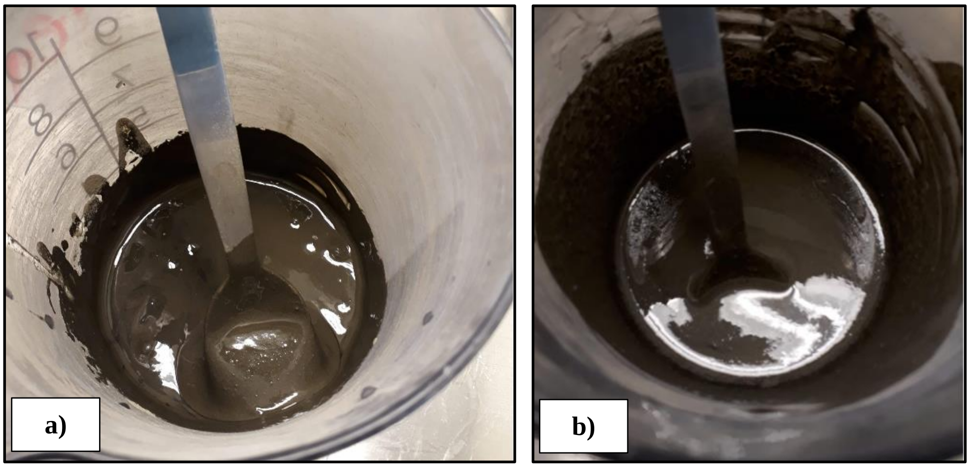


Figure Apx.5: Geopolymer based on homemade sodium metasilicate liquid (45.1%, clear). a) mixing of solids and alkaline activator **before** adding extra ex-situ water. b) mixing of solids and alkaline activator **after** adding 40g extra ex-situ water.

Figure Apx.6: A few pieces of the geopolymer reference #3 + TiO_2 plugs after UCS test, showing that internal visible pores exist.

Appendix B: Force vs. %Deformation plots

Test matrix 4

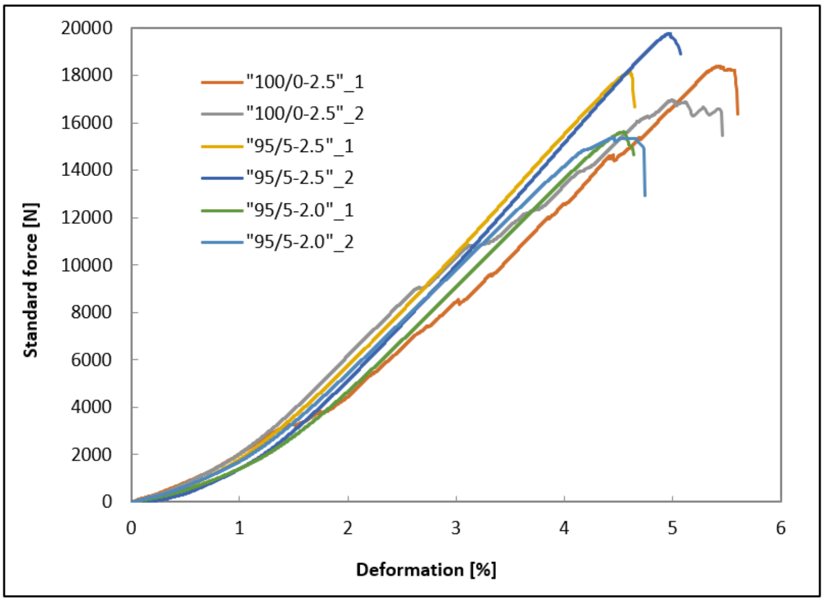


Figure Apx.7: Geopolymer made with homemade sodium metasilicate liquid (45.1%, milky), TM#4. Zwick/Roell Z020.

Test matrix 5

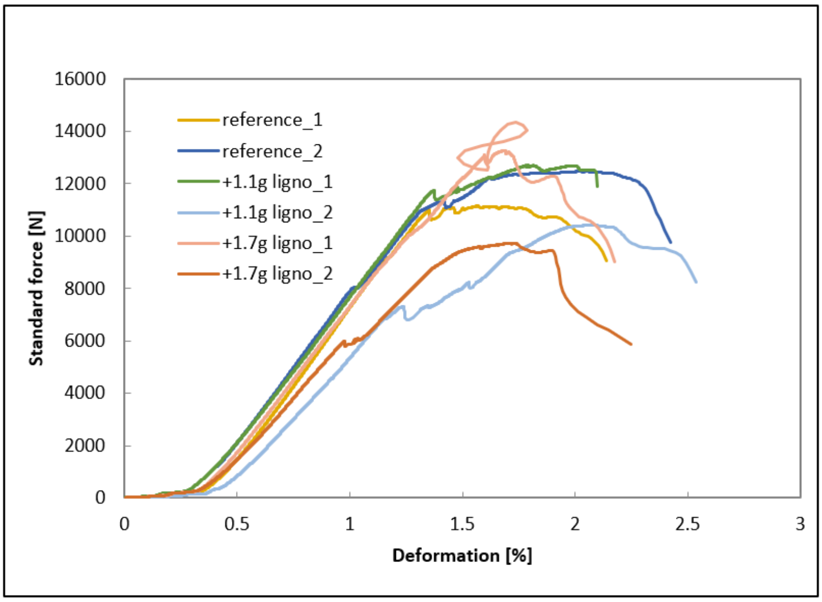


Figure Apx.8: Geopolymer made with homemade sodium metasilicate liquid (37.1%, clear), TM#5. Zwick/Roell Z050.

Test matrix 6

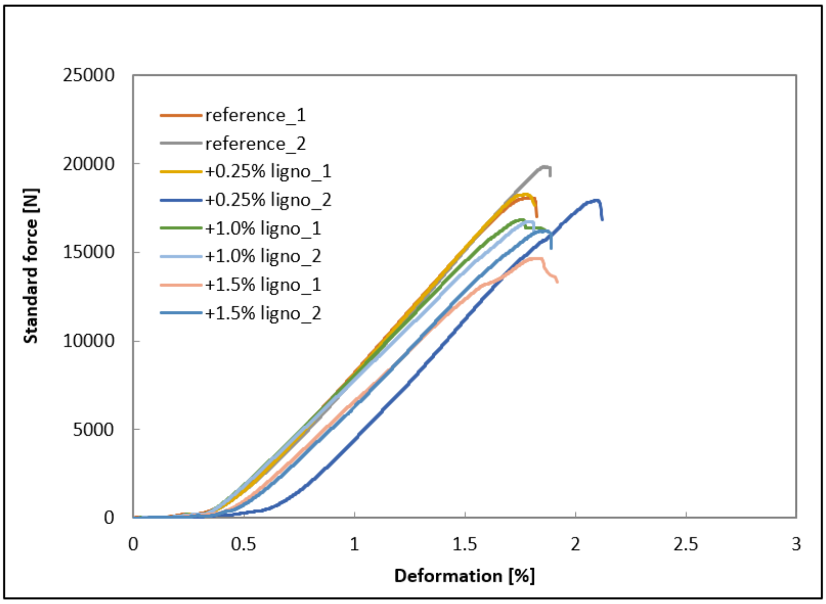


Figure Apx.9: Geopolymer made with homemade sodium metasilicate liquid (37.1%, clear), TM#6. Zwick/Roell Z050.

Test matrix 7

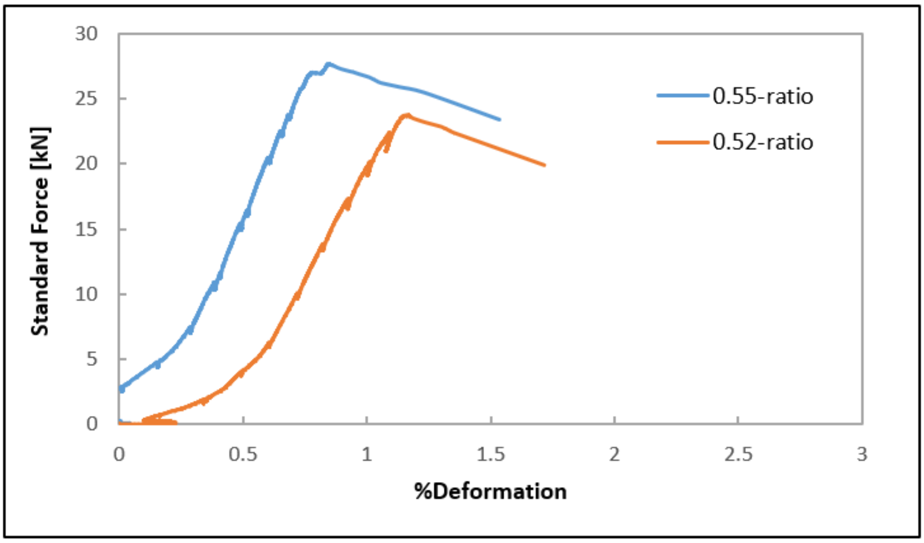


Figure Apx.10: Geopolymer made with homemade sodium metasilicate liquid (37.1%, clear), TM#7. Manual operated UCS machine.

Test matrix 8

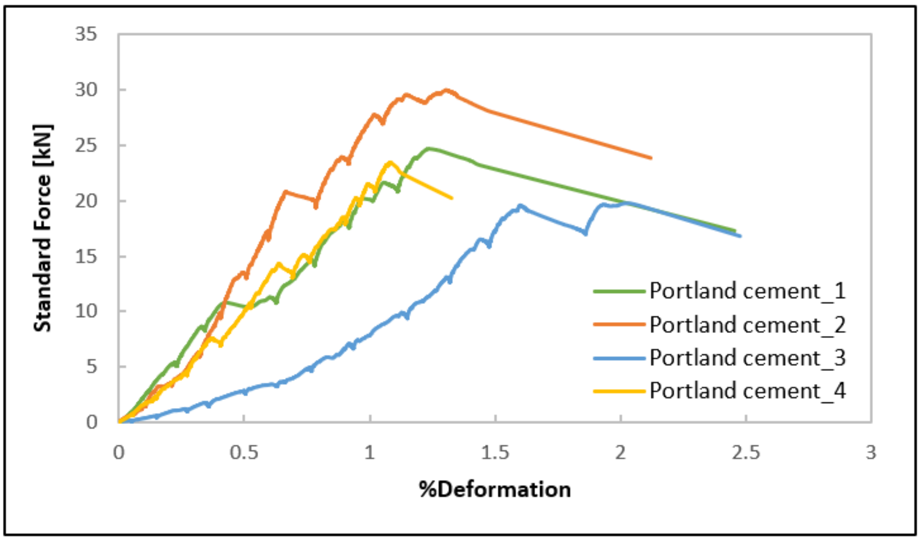


Figure Apx.11: Portland cement class G for comparison, TM#8. Manual operated UCS machine.

Test matrix 9

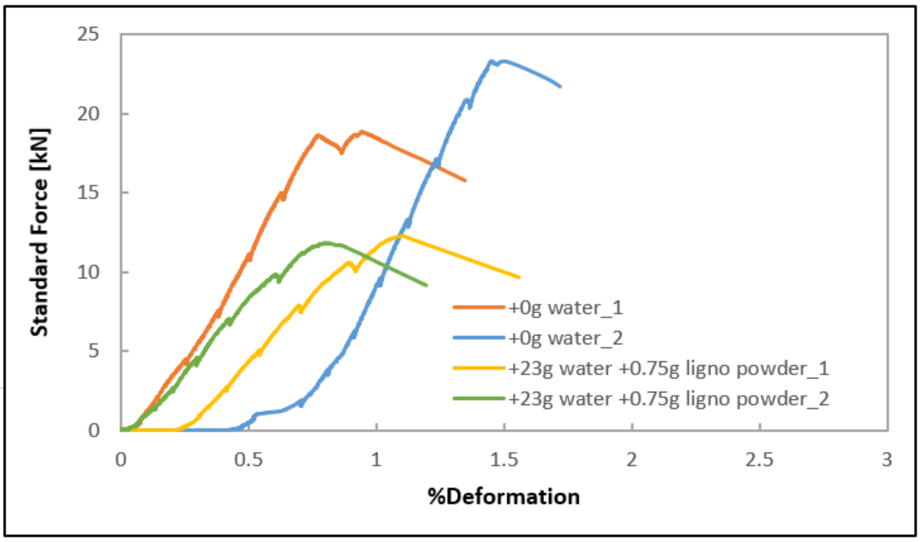


Figure Apx.12: Geopolymer made with homemade sodium metasilicate liquid (30%, clear), TM#9. Manual operated UCS machine.

Test matrix 10

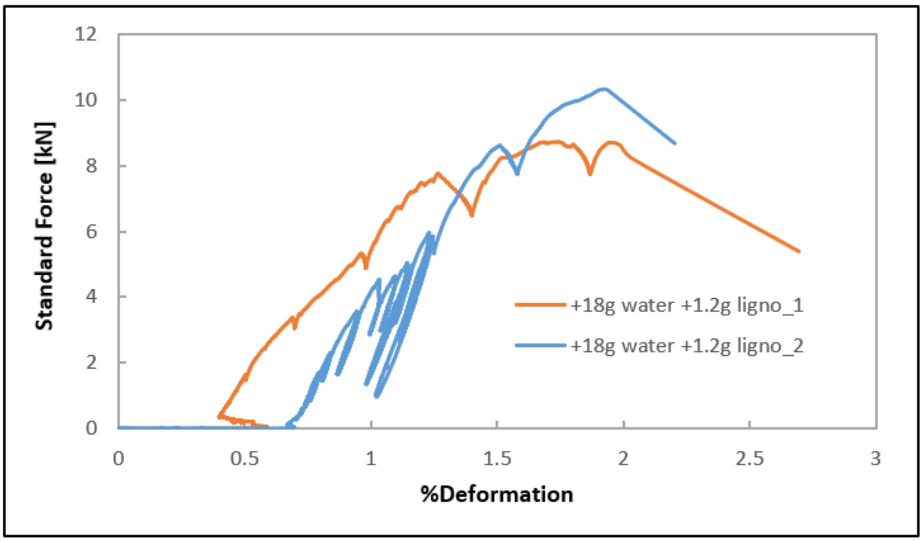


Figure Apx.13: Geopolymer made with homemade sodium metasilicate liquid (30%, clear), TM#10. Manual operated UCS machine.

Test matrix 11

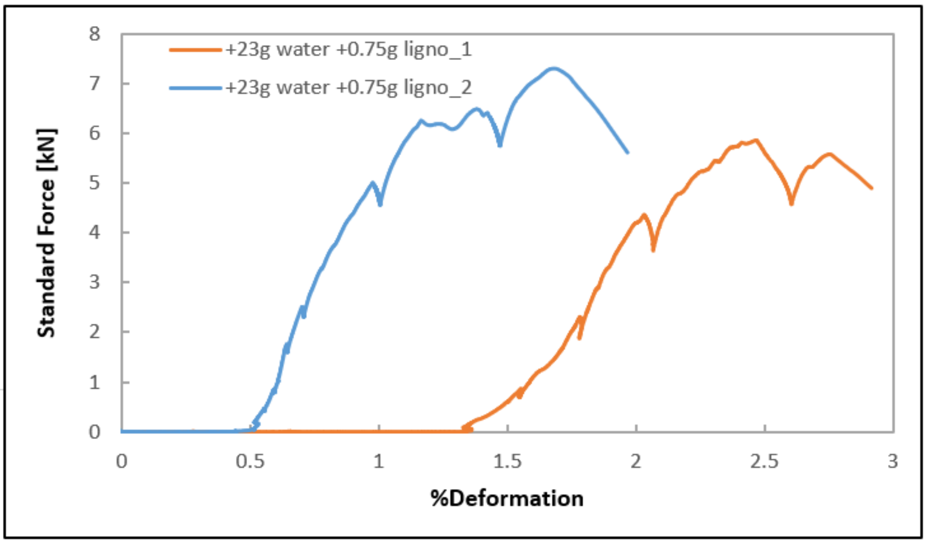


Figure Apx.14: Geopolymer made with homemade sodium metasilicate liquid (30%, clear), TM#11. Manual operated UCS machine.

Test matrix 12

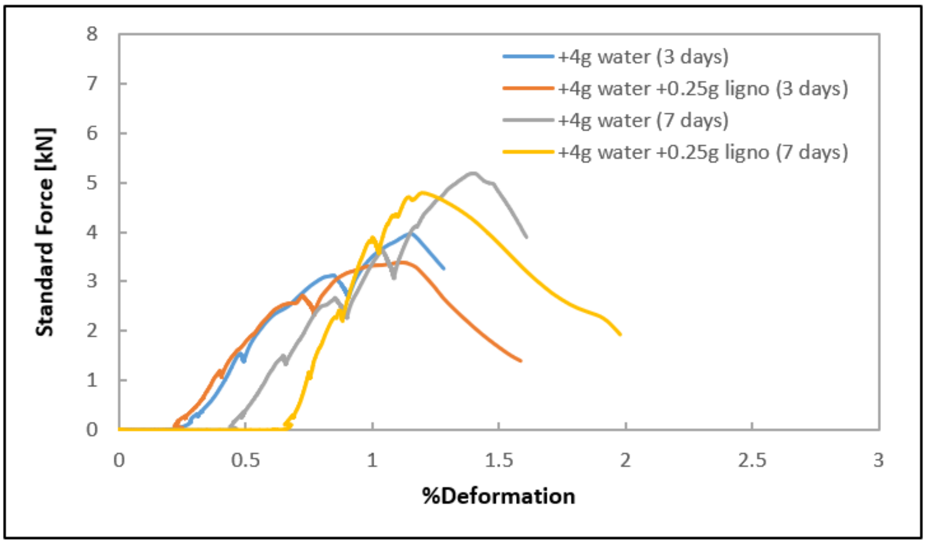


Figure Apx.15: Geopolymer made with homemade sodium metasilicate liquid (20%, clear), TM#12. Manual operated UCS machine.

Test matrix 13

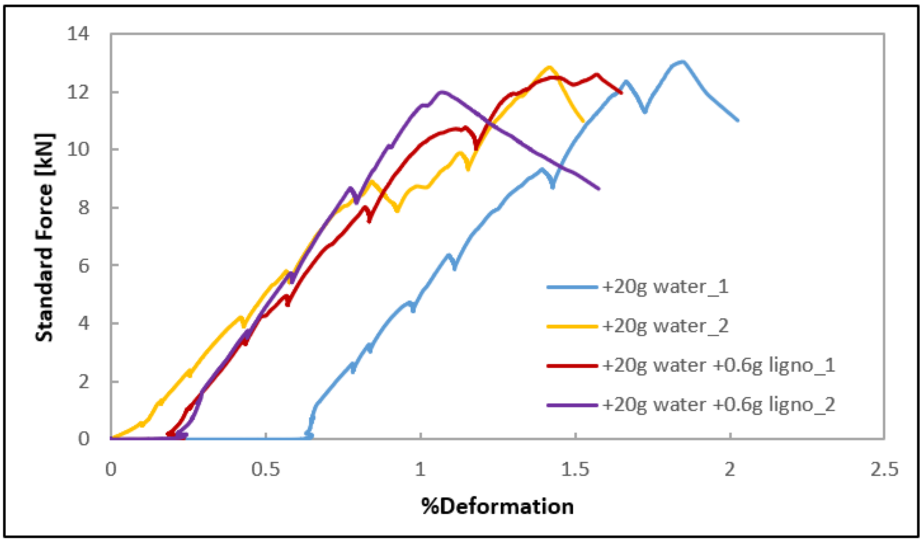


Figure Apx.16: Commercial silicate-based geopolymer, TM#13. Manual operated UCS machine.

Test matrix 16

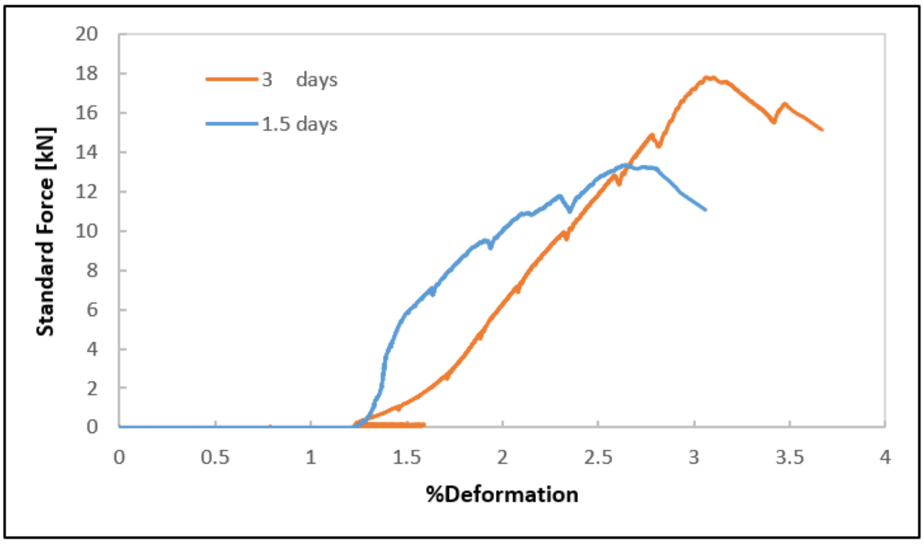


Figure Apx.17: Geopolymer made with homemade sodium metasilicate (45.1%, clear), TM#16. Manual operated UCS machine.

Test matrix 17

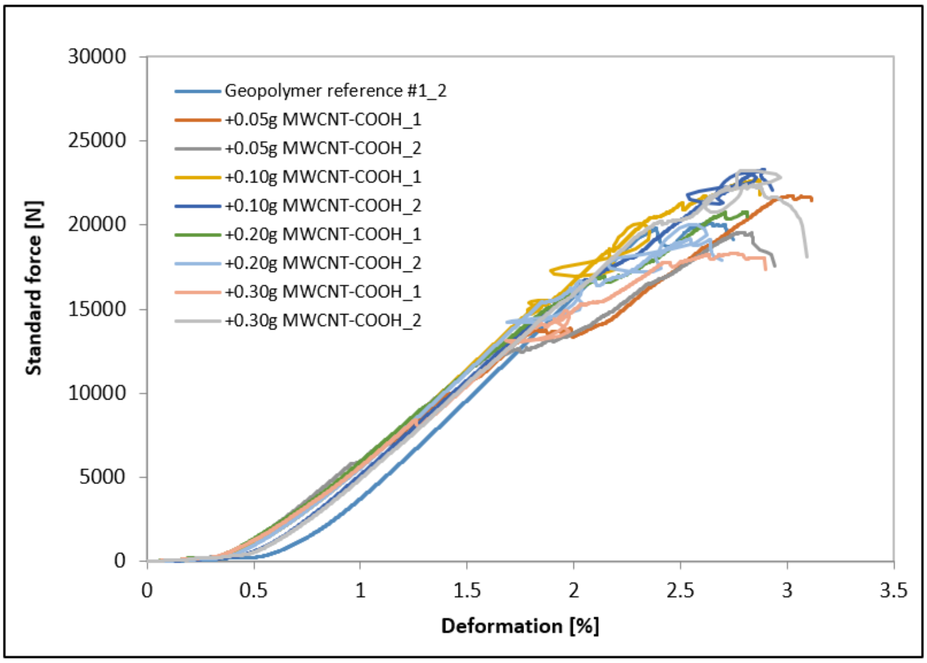


Figure Apx.18: Effect of MWCNT-COOH on geopolymer reference #1, TM#17. Zwick/Roell Z050.

Test matrix 18

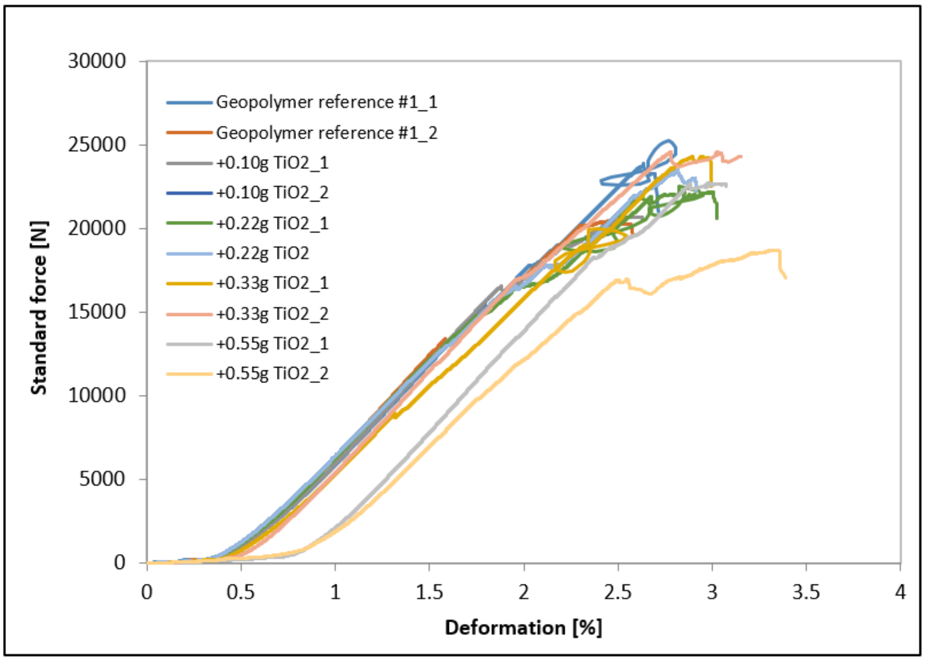


Figure Apx.19: Effect of TiO_2 on geopolymer reference #1, TM#18. Zwick/Roell Z050.

Test matrix 19

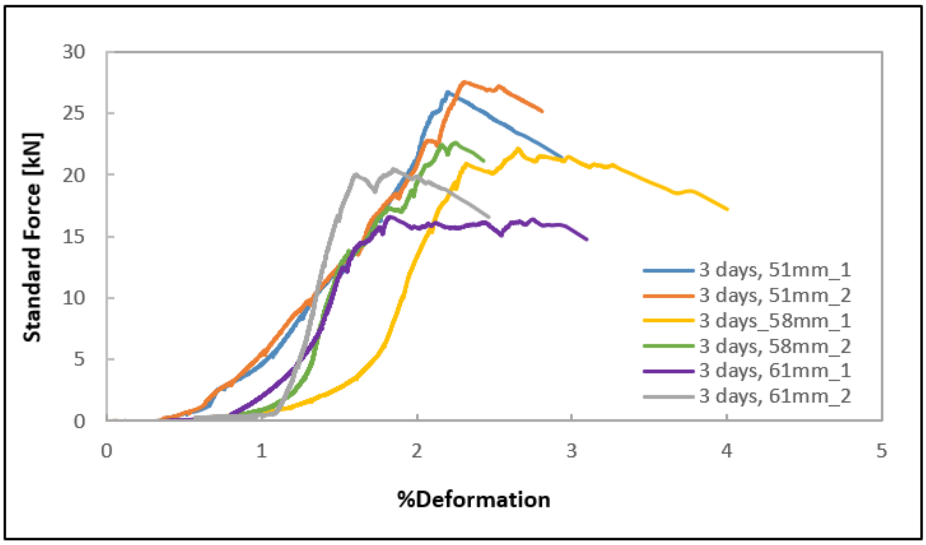


Figure Apx.20: **3 days** cured Portland cement, TM#19. Manual operated UCS machine.

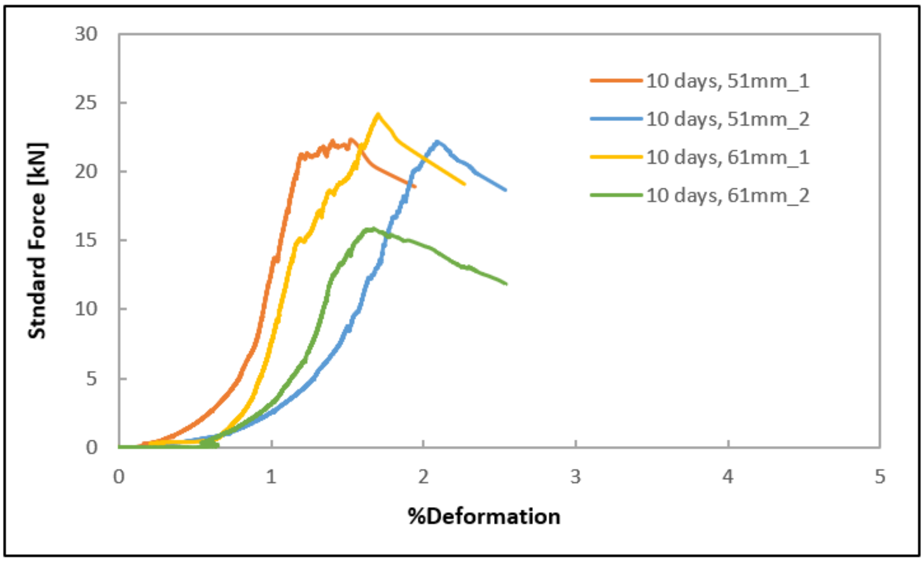


Figure Apx.21: **10 days** cured Portland cement, TM#19. Manual operated UCS machine.

Test matrix 20

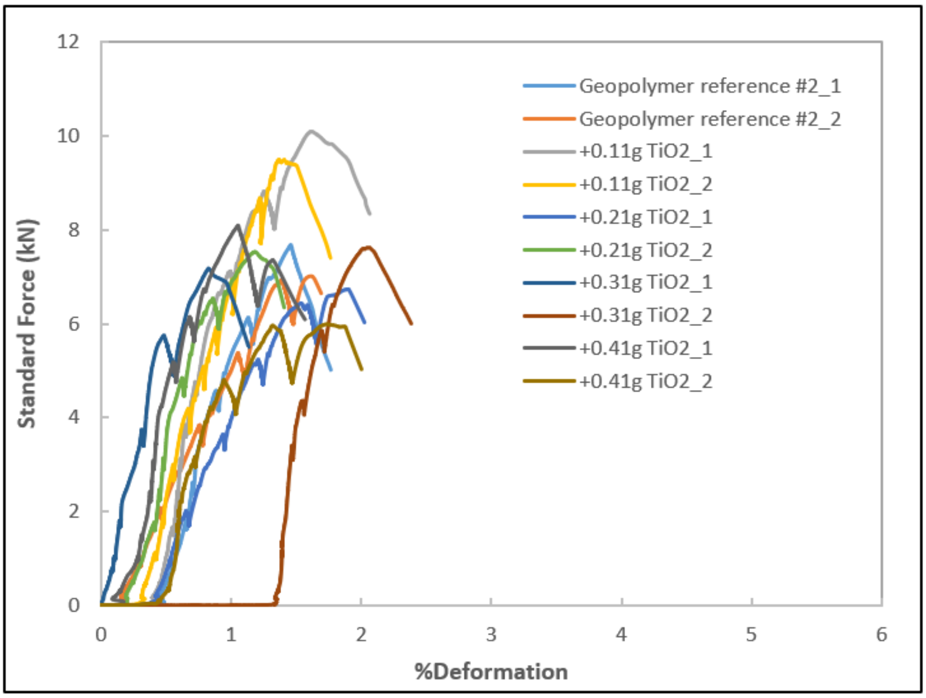


Figure Apx.22: Effect of TiO_2 on geopolymer reference #2, **3 days** cured. TM#20. Manual operated UCS machine.

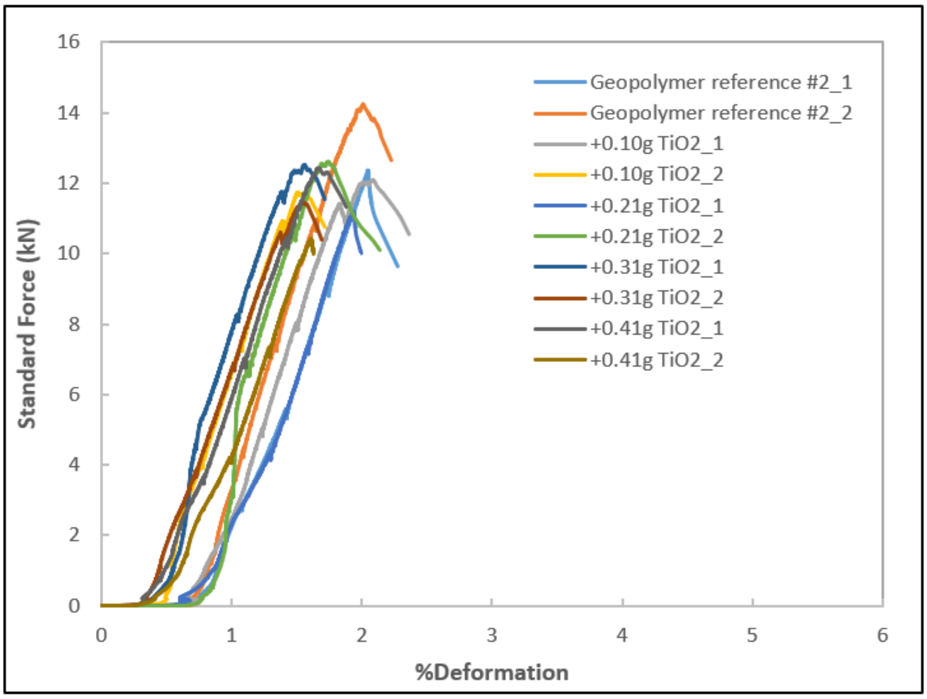


Figure Apx.23: Effect of TiO_2 on geopolymer reference #2, **10 days** cured, TM#20. Manual operated UCS machine.

Test matrix 21

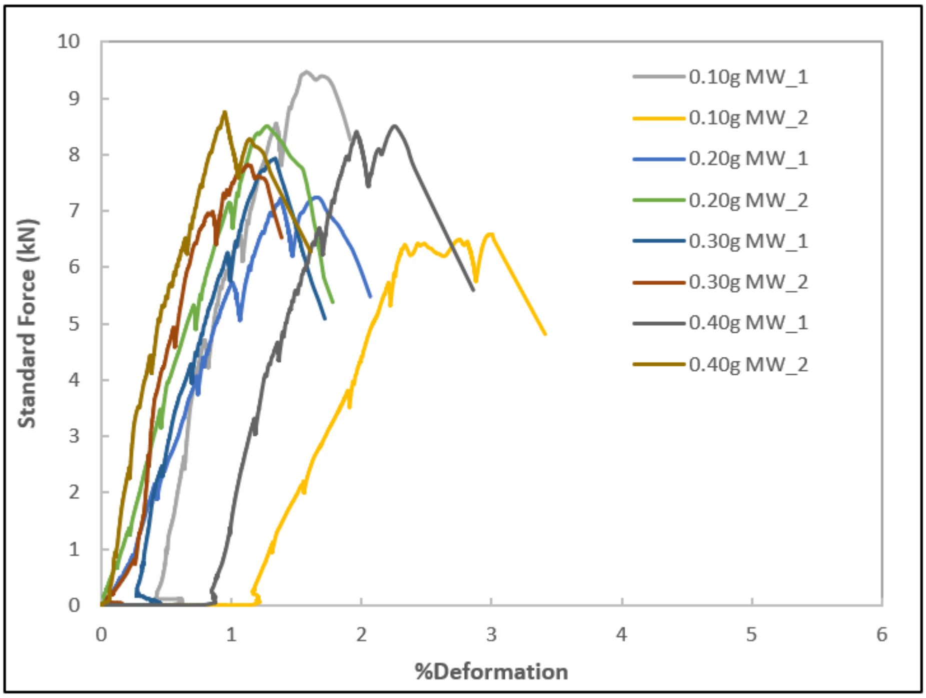


Figure Apx.24: Effect of MWCNT-COOH on geopolymer reference #2, **3 days** cured, TM#21. “MW” is abbreviation for MWCNT-COOH. Manual operated UCS machine.

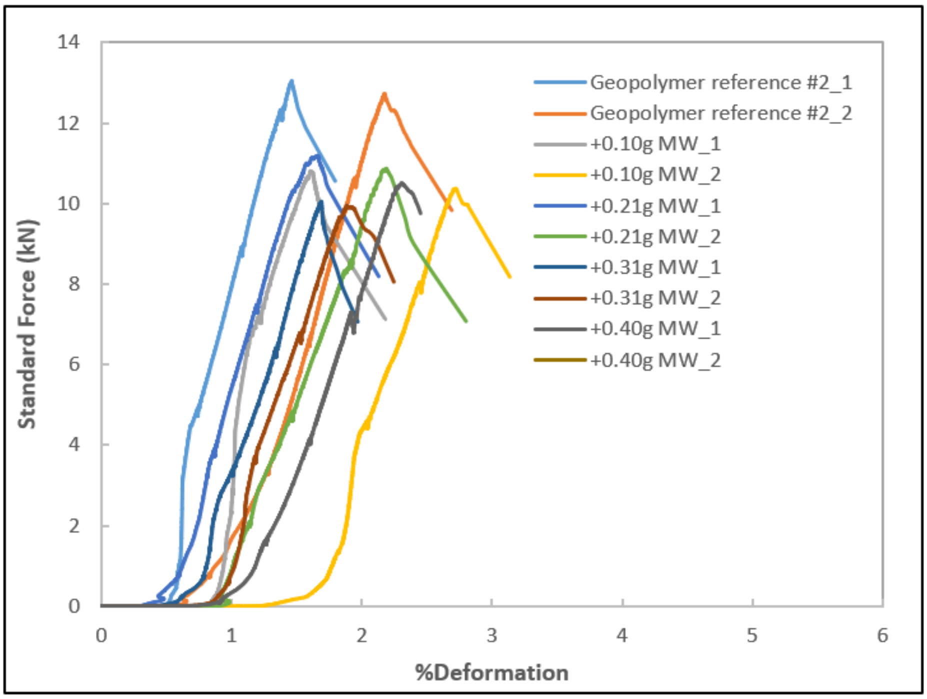


Figure Apx.25: Effect of MWCNT-COOH on geopolymer reference #2, **10 days** cured, TM#21. "MW" is abbreviation for MWCNT-COOH. Manual operated UCS machine.

Test matrix 22

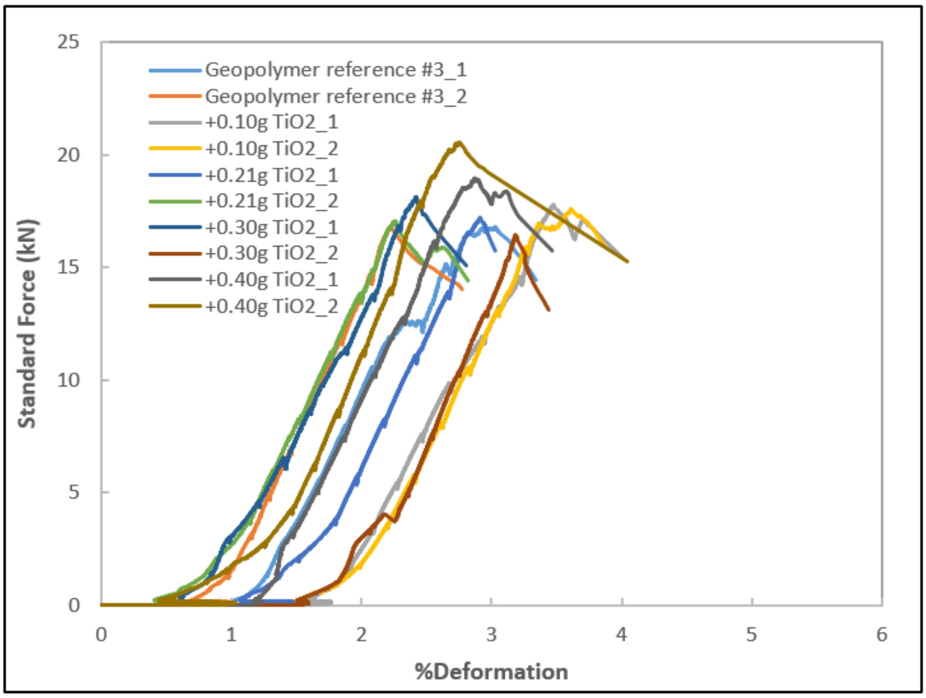


Figure Apx.26: Effect of TiO_2 on geopolymer reference #3, **3 days** cured, TM#22. Manual operated UCS machine.

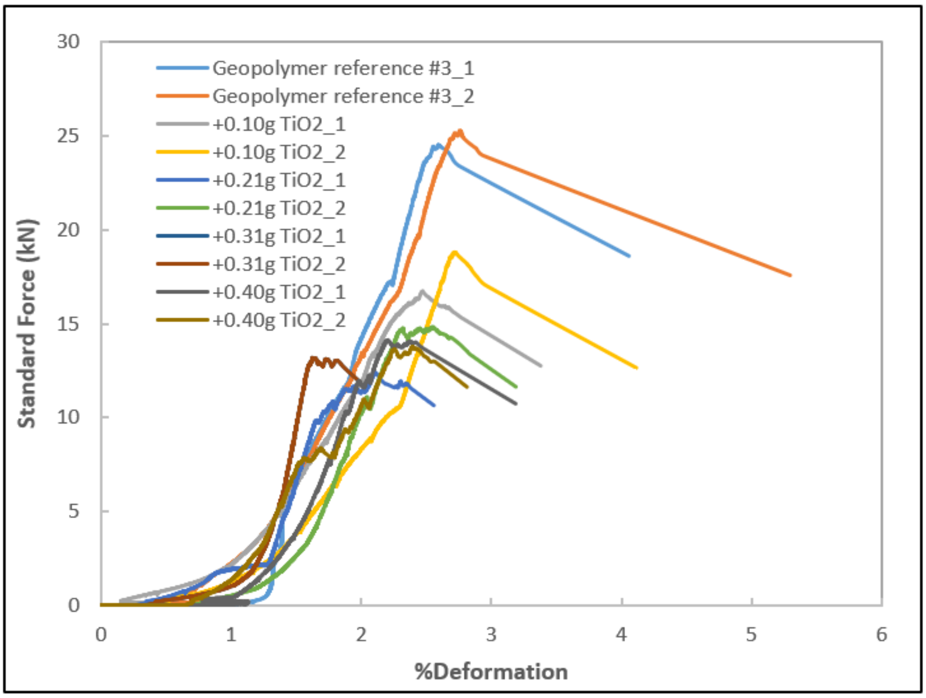


Figure Apx.27: Effect of TiO_2 on geopolymer reference #3, **10 days** cured, TM#22. Manual operated UCS machine.

Test matrix 23

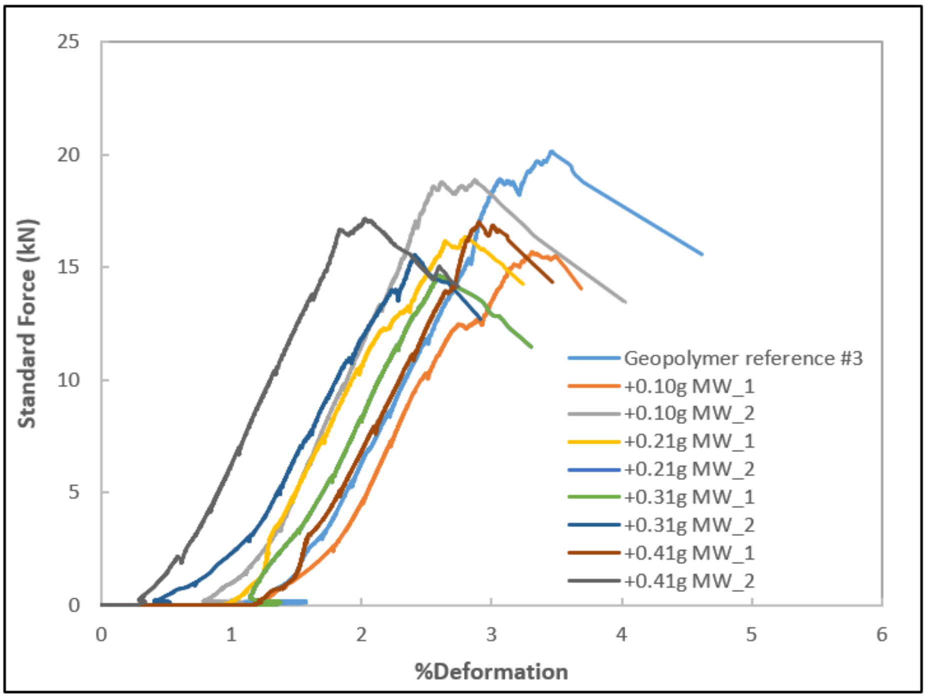


Figure Apx.28: Effect of MWCNT-COOH on geopolymer reference #3, **3 days** cured, TM#23. “MW” is abbreviation for MWCNT-COOH. Manual operated UCS machine.

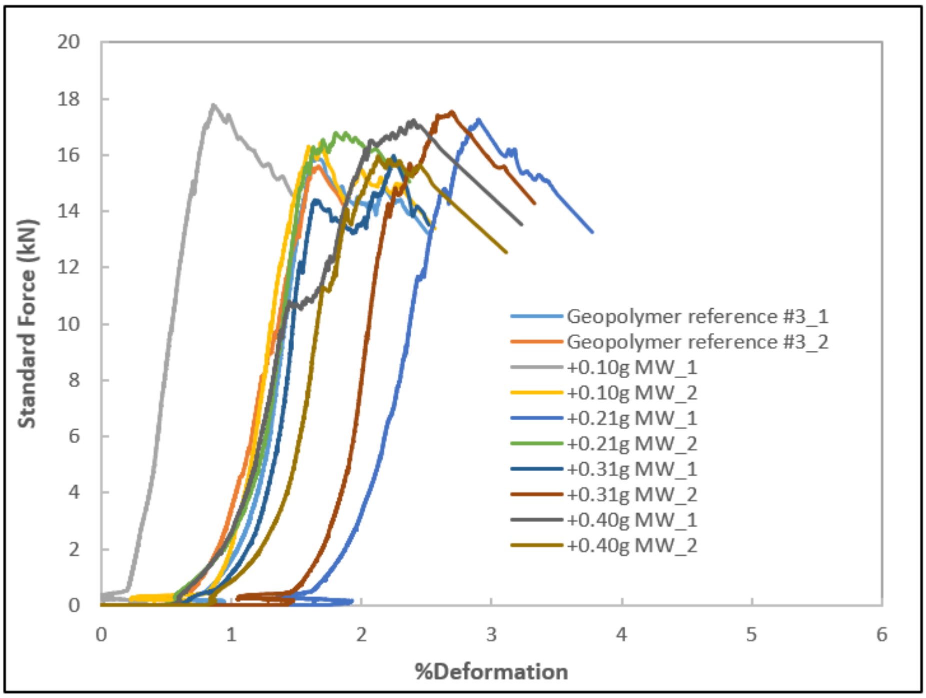


Figure Apx.29: Effect of MWCNT-COOH on geopolymer reference #3, **10 days** cured, TM#23. “MW” is abbreviation for MWCNT-COOH. Manual operated UCS machine.

Appendix C: Measured diameter, length, mass and sonic

TM#4

Table Apx.1: Measured diameter, length, mass and sonic before immerged in water. Geopolymers in TM#4.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
“70/30-2.5 (45.1%, milky) +25g water”_1	32.87	68.24	85.404	58.8
“70/30-2.5 (45.1%, milky) +25g water”_2	32.80	68.47	85.467	58.8
“95/5-2.5 (45.1%, milky) +9g water”_1	33.32	67.90	101.378	27.6
“95/5-2.5 (45.1%, milky) +9g water”_2	33.26	68.08	101.777	26.6
“100/0-2.5 (45.1%, milky) +6g water”_1	33.05	68.06	104.722	22.1
“100/0-2.5 (45.1%, milky) +6g water”_2	33.32	67.73	104.662	22.2
“95/5-2.0 (45.1%, milky) +6g water”_1	33.30	68.21	100.151	29.4
“95/5-2.0 (45.1%, milky) +6g water”_2	33.42	68.11	100.284	29.1

Table Apx.2: Measured diameter, length, mass and sonic after 24h immerged in water. Geopolymers in TM#4.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
“70/30-2.5 (45.1%, milky) +25g water”_1	Failed visual inspection and water absorption test			
“70/30-2.5 (45.1%, milky) +25g water”_2	Failed visual inspection and water absorption test			
“95/5-2.5 (45.1%, milky) +9g water”_1	33.32	67.90	105.839	28.4
“95/5-2.5 (45.1%, milky) +9g water”_2	33.26	68.08	106.154	28.7
“100/0-2.5 (45.1%, milky) +6g water”_1	33.05	68.06	109.488	22.0
“100/0-2.5 (45.1%, milky) +6g water”_2	33.32	67.73	109.416	22.5
“95/5-2.0 (45.1%, milky) +6g water”_1	33.30	68.21	104.342	31.5
“95/5-2.0 (45.1%, milky) +6g water”_2	33.42	68.11	104.466	30.1

Table Apx.3: Measured diameter, length, mass and sonic after 48h immerged in water. Geopolymers in TM#4.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
“70/30-2.5 (45.1%, milky) +25g water”_1	Failed visual inspection and water absorption test			
“70/30-2.5 (45.1%, milky) +25g water”_2	Failed visual inspection and water absorption test			
“95/5-2.5 (45.1%, milky) +9g water”_1	33.32	67.90	105.790	28.2
“95/5-2.5 (45.1%, milky) +9g water”_2	33.26	68.08	106.112	28.2
“100/0-2.5 (45.1%, milky) +6g water”_1	33.05	68.06	109.446	22.2
“100/0-2.5 (45.1%, milky) +6g water”_2	33.32	67.73	109.399	22.3
“95/5-2.0 (45.1%, milky) +6g water”_1	33.30	68.21	104.151	31.9
“95/5-2.0 (45.1%, milky) +6g water”_2	33.42	68.11	104.270	30.1

Table Apx.4: Measured diameter, length, mass and sonic after additional 36h exposed to ambient air. Geopolymers, TM#4.

Plug #	**OD, mm**	**Length, mm**	**Mass, g**	**Sonic, µs**
“70/30-2.5 (45.1%, milky) +25g water”_1	Failed visual inspection and water absorption test			
“70/30-2.5 (45.1%, milky) +25g water”_2	Failed visual inspection and water absorption test			
“95/5-2.5 (45.1%, milky) +9g water”_1	33.32	67.90	97.363	29.5
“95/5-2.5 (45.1%, milky) +9g water”_2	33.26	68.08	96.937	29.7
“100/0-2.5 (45.1%, milky) +6g water”_1	33.05	68.06	102.247	22.7
“100/0-2.5 (45.1%, milky) +6g water”_2	33.32	67.73	102.130	23.0
“95/5-2.0 (45.1%, milky) +6g water”_1	33.30	68.21	93.522	32.1
“95/5-2.0 (45.1%, milky) +6g water”_2	33.42	68.11	94.389	30.9

TM#5

Table Apx.5: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 1d. Geopolymers, TM#5.

Plug #	**OD, mm**	**Length, mm**	**Mass, g**	**Sonic, µs**
“95/5-2.5 (37.1%, clear) +2.3g water ”_1	33.18	68.33	104.848	25.5
“95/5-2.5 (37.1%, clear) +2.3g water”_2	33.18	68.50	105.140	26.1
+1.1g lignosulfonate_1	33.20	68.24	102.539	26.0
+1.1g lignosulfonate_2	33.19	68.23	102.458	26.0
+1.7g lignosulfonate_1	33.18	68.26	102.387	25.8
+1.7g lignosulfonate_2	33.20	68.29	102.284	26.8

TM#6

Table Apx.6: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 1d. Geopolymers, TM#6.

Plug #	**OD, mm**	**Length, mm**	**Mass, g**	**Sonic, µs**
“95/5-7.5 (37.1%, clear) +2.3g water ”_1	33.24	67.76	99.089	31.0
“95/5-7.5 (37.1%, clear) +2.3g water”_2	33.23	67.63	100.005	31.3
+0.25wt% ligno_1	33.24	67.65	99.531	31.1
+0.25wt% ligno_2	33.27	67.78	101.237	29.8
+0.50wt% ligno_1	33.23	67.80	99.939	31.0
+0.50wt% ligno_2	33.24	68.02	100.800	30.4
+1.00wt% ligno_1	33.22	67.56	101.111	29.2
+1.00wt% ligno_2	33.24	67.75	99.878	30.6
+1.50wt% ligno_1	33.22	67.72	101.568	29.4
+1.50wt% ligno_2	33.24	67.75	101.518	29.8

TM#7

Table Apx.7: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 57d. Geopolymers, TM#7.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
“95/5-7.5 (37.1%, clear), 0.55-ratio”_1	33.20	63.58	87.518	22.4
“95/5-7.5 (37.1%, clear), 0.55-ratio”_2	Not poured in mold cup because too thick slurry			
“95/5-7.5 (37.1%, clear), 0.52-ratio”_1	33.24	64.41	86.195	25.3
“95/5-7.5 (37.1%, clear), 0.52-ratio”_2	Not poured in mold cup because too thick slurry			

TM#8

Table Apx.8: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 56d. Portland cement, TM#8.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Portland class G cement_1	32.85	64.04	99.591	19.4
Portland class G cement_2	32.95	64.41	97.399	19.8
Portland class G cement_3	32.96	63.51	95.991	18.9
Portland class G cement_4	32.74	64.37	96.675	18.8

TM#9

Table Apx.9: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 56d. Geopolymers, TM#9.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
“95/5-2.5 (30%, clear)”_1	33.31	64.42	85.731	27.4
“95/5-2.5 (30%, clear)”_1	33.39	64.02	86.643	27.0
+23g water + 0.75g ligno powder_1	33.29	63.87	78.886	35.2
+23g water + 0.75g ligno powder_2	33.38	63.83	79.225	33.0

TM#10

Table Apx.10: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 53d. Geopolymers, TM#10.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (30%, clear) +23g water + 3.1g ligno"_1	Failed visual inspection			
"95/5-2.5 (30%, clear) +23g water + 3.1g ligno"_2	Failed visual inspection			
"95/5-2.5 (30%, clear) +23g water + 1.2g ligno"_1	Failed visual inspection			
"95/5-2.5 (30%, clear) +23g water + 1.2g ligno"_2	Failed visual inspection			
"95/5-2.5 (30%, clear) +18g water + 1.2g ligno"_1	33.24	63.97	31.0	29.1
"95/5-2.5 (30%, clear) +18g water + 1.2g ligno"_2	33.27	64.26	30.5	29.7

TM#11

Table Apx.11: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 50d. Geopolymers, TM#11.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (30%, clear) +23g water + 0.75g ligno"_1	33.29	63.89	79.353	34.7
"95/5-2.5 (30%, clear) +23g water + 0.75g ligno"_2	33.27	63.78	78.840	31.1
"95/5-2.5 (30%, clear) +23g water + 1.0g ligno"_1	Failed visual inspection			
"95/5-2.5 (30%, clear) +23g water + 1.0g ligno"_2	Failed visual inspection			

TM#12

Table Apx.12: Measured diameter, length, mass and sonic after 3 -and 7d curing and exposed to room T for 52 -and 48d. Geopolymers, TM#12.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (20%, clear) +4g water, 3 days"	33.34	64.31	87.69	27.2
"95/5-2.5 (20%, clear) +4g water, 7 days"	33.24	64.42	86.64	24.3
"95/5-2.5 (20%, clear) +4g water + 0.25g ligno, 3 days"	33.35	63.70	82.594	43.5
"95/5-2.5 (20%, clear) +4g water + 0.25g ligno, 7 days"	33.30	64.21	81.566	36.6

TM#13

Table Apx.13: Measured diameter, length, mass and sonic after 3d curing and exposed to room T for 48d. Geopolymers, TM#13.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (37.1%, commercial) +20g water + 0.6g ligno"_1	33.09	64.05	82.997	35.9
"95/5-2.5 (37.1%, commercial) +20g water + 0.6g ligno"_2	33.08	64.16	83.208	37.4
"95/5-2.5 (37.1%, commercial) +20g water"_1	33.13	64.26	83.666	35.7
"95/5-2.5 (37.1%, commercial) +20g water"_2	33.17	64.01	83.809	35.0

TM#14

Table Apx.14: Measured diameter, length, mass and sonic for geopolymer reference #1, TM#14.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (45.1%, milky) +30g water"_1	Made in TM#17-18			
"95/5-2.5 (45.1%, milky) +30g water"_2	Made in TM#17-18			

TM#15

Table Apx.15: Measured diameter, length, mass and sonic for geopolymer reference #2, TM#15.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (30%, clear) +23g water"_1	Made in TM#20-21			
"95/5-2.5 (30%, clear) +23g water"_2	Made in TM#20-21			

TM#16

Table Apx.16: Measured diameter, length, mass and sonic for geopolymer reference #3, TM#16.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
"95/5-2.5 (45.1%, clear) +40g water, 1.5 days"_1	33.38	60.35	93.217	30.3
"95/5-2.5 45.1%, clear) +40g water, 3 days"_2	33.36	60.12	80.009	27.4

TM#17

Table Apx.17: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#17.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, μs
Geopolymer ref #1_1	33.29	53.18	76.922	22.0
Geopolymer ref #1_2	33.19	53.52	75.768	21.8
+0.05g MWCNT_1	33.24	53.11	77.260	21.7
+0.05g MWCNT_2	33.23	53.15	77.482	22.0
+0.10g MWCNT_1	33.18	53.07	76.479	22.0
+0.10g MWCNT_2	33.25	52.72	75.369	21.9
+0.22g MWCNT_1	33.23	53.52	76.351	22.7
+0.22g MWCNT_2	33.29	53.06	75.486	22.5
+0.33g MWCNT_1	33.28	53.14	75.118	22.1
+0.33g MWCNT_2	33.24	52.44	74.091	22.0

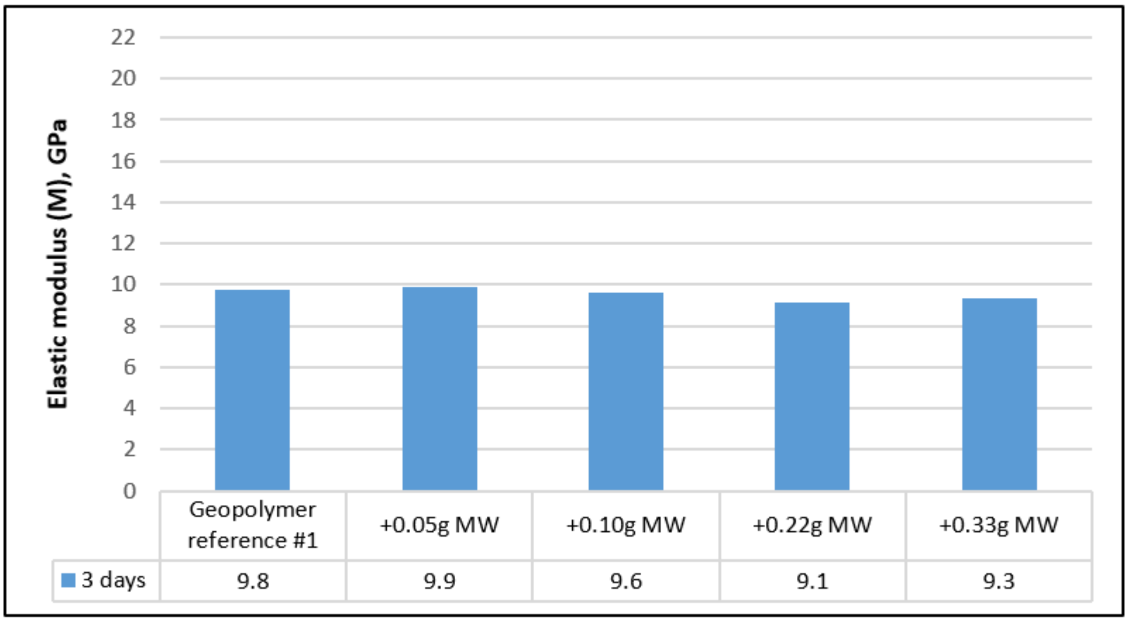


Figure Apx.30: Modulus of elasticity for geopolymer in TM#17.

TM#18

Table Apx.18: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#18.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref#1_1	33.20	52.64	75.019	21.4
Geopolymer ref #1_2	33.21	53.12	75.589	21.7
+0.10g TiO_2_1	33.27	52.92	75.220	21.8
+0.10g TiO_2_2	33.30	52.64	74.935	21.3
+0.20g TiO_2_1	33.24	53.11	76.152	21.5
+0.20g TiO_2_2	33.25	52.67	75.151	20.9
+0.33g TiO_2_1	33.19	52.92	74.759	20.9
+0.33g TiO_2_2	33.31	52.90	75.391	21.3
+0.55g TiO_2_1	33.23	52.75	74.450	21.0
+0.55g TiO_2_2	33.24	52.73	74.543	21.2

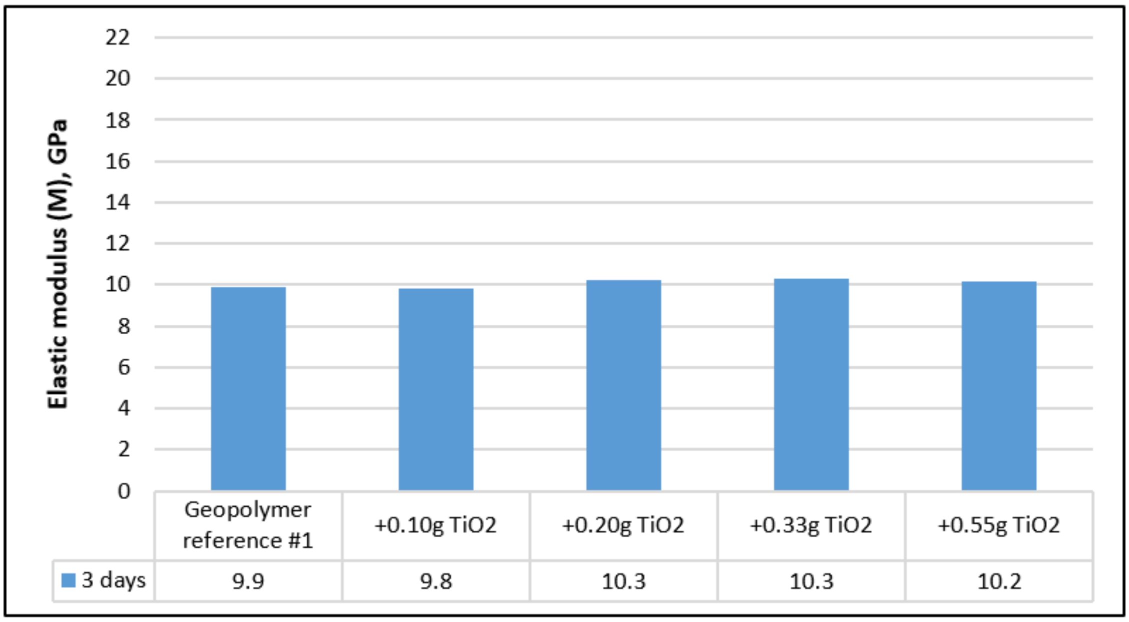


Figure Apx.31: Modulus of elasticity for geopolymer in TM#18.

TM#19

Measured diameter, length, mass and sonic data for Portland cement are shown in TM#20-23 for comparison with geopolymer.

TM#20

Table Apx.19: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#20 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #2_1	33.32	61.23	87.056	36.6
Geopolymer ref #2_2	33.34	60.50	87.306	36.7
+0.10g TiO_2_1	33.30	60.85	90.939	35.3
+0.10g TiO_2_2	33.34	60.86	90.311	35.7
+0.21g TiO_2_1	33.30	60.86	87.717	36.0
+0.21g TiO_2_2	33.28	61.45	89.835	35.4
+0.31g TiO_2_1	33.31	60.90	86.114	36.7
+0.31g TiO_2_2	33.32	60.95	88.676	37.6
+0.40g TiO_2_1	33.29	60.83	88.310	38.2
+0.40g TiO_2_2	33.35	60.79	89.915	37.7
Portland cement_1	32.94	60.80	92.382	19.9
Portland cement_2	32.96	60.84	93.174	19.3

Table Apx.20: **10 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#20 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #2_1	33.32	61.72	88.908	32.1
Geopolymer ref #2_2	33.33	61.44	87.909	32.1
+0.10g TiO_2_1	33.29	61.47	88.803	32.2
+0.10g TiO_2_2	33.28	61.25	86.871	32.3
+0.21g TiO_2_1	33.29	60.31	86.867	32.3
+0.21g TiO_2_2	33.32	61.31	87.586	32.6
+0.31g TiO_2_1	33.33	61.32	87.225	32.6
+0.31g TiO_2_2	33.32	61.20	87.805	32.5
+0.41g TiO_2_1	33.30	60.44	86.671	32.9
+0.41g TiO_2_2	33.31	61.65	88.706	32.9
Portland cement_1	32.85	61.58	96.048	19.4
Portland cement_2	32.93	61.16	93.878	18.9

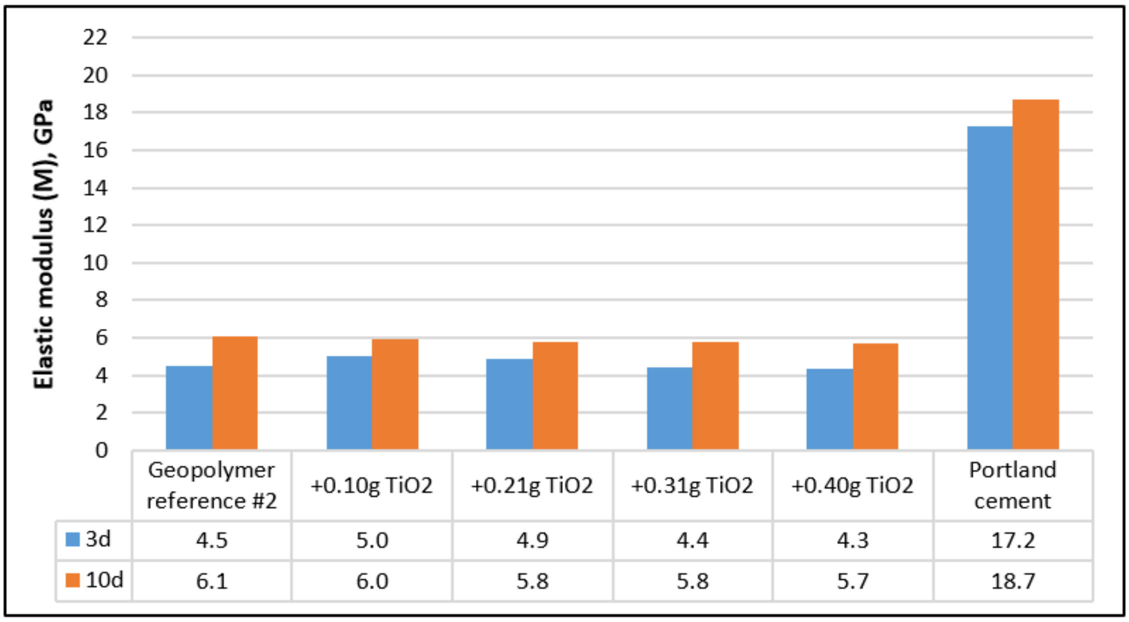


Figure Apx.32: Modulus of elasticity for geopolymer in TM#20 + Portland cement from TM#19.

TM#21

Table Apx.21: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#21 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #2_1	33.32	61.23	87.056	36.6
Geopolymer ref #2_2	33.34	60.50	87.306	36.7
+0.10g MWCNT_1	33.35	61.19	88.586	38.6
+0.10g MWCNT_2	33.38	60.33	89.79	37.7
+0.21g MWCNT_1	33.30	61.06	89.162	38.7
+0.21g MWCNT_2	33.26	61.07	90.933	37.2
+0.30g MWCNT_1	33.34	60.04	89.111	39.9
+0.30g MWCNT_2	33.28	60.05	89.644	40.4
+0.40g MWCNT_1	33.28	60.87	89.493	38.6
+0.40g MWCNT_2	33.25	61.40	88.272	39.2
Portland cement_1	32.94	60.80	92.382	19.9
Portland cement_2	32.96	60.84	93.174	19.3

Table Apx.22: **10 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#21 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #2_1	33.29	61.62	89.165	35.8
Geopolymer ref #2_2	33.31	60.48	89.071	35.6
+0.10g MWCNT_1	33.29	60.80	89.755	35.1
+0.10g MWCNT_2	33.30	60.31	89.355	34.3
+0.21g MWCNT_1	33.33	61.57	90.503	35.2
+0.21g MWCNT_2	33.33	61.33	90.410	34.9
+0.31g MWCNT_1	33.28	61.24	90.127	32.5
+0.31g MWCNT_2	33.29	60.49	89.734	32.2
+0.40g MWCNT_1	33.33	61.32	90.006	33.0
+0.40g MWCNT_2	33.32	61.71	90.379	33.3
Portland cement_1	33.29	61.58	96.048	19.4
Portland cement_2	33.29	61.16	93.878	18.9

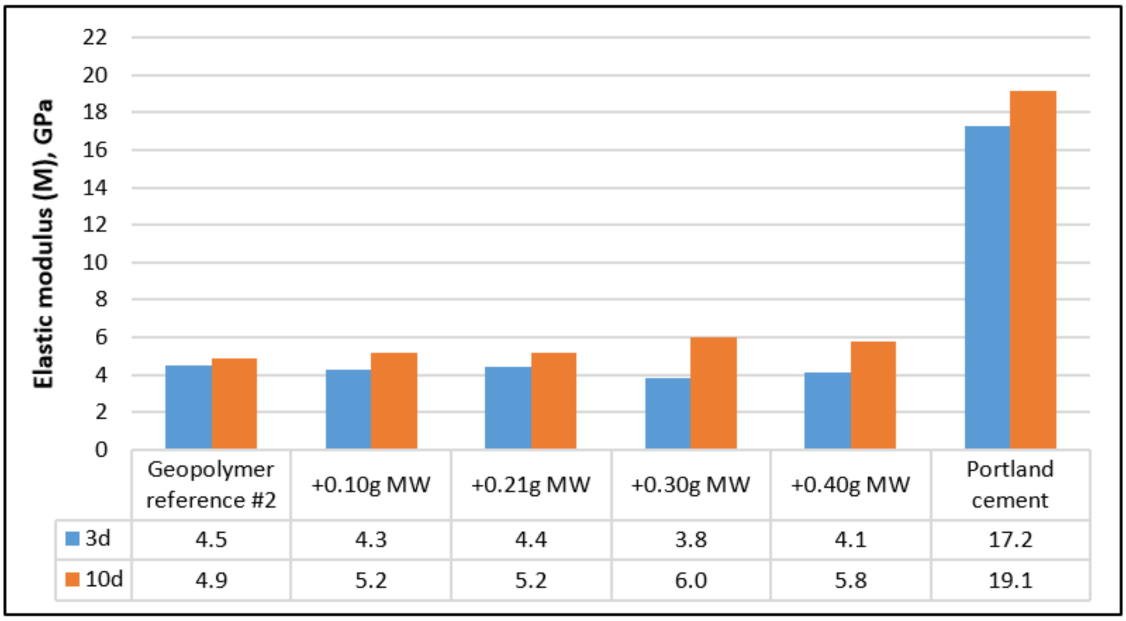


Figure Apx.33: Modulus of elasticity for geopolymer in TM#21 + Portland cement from TM#19.

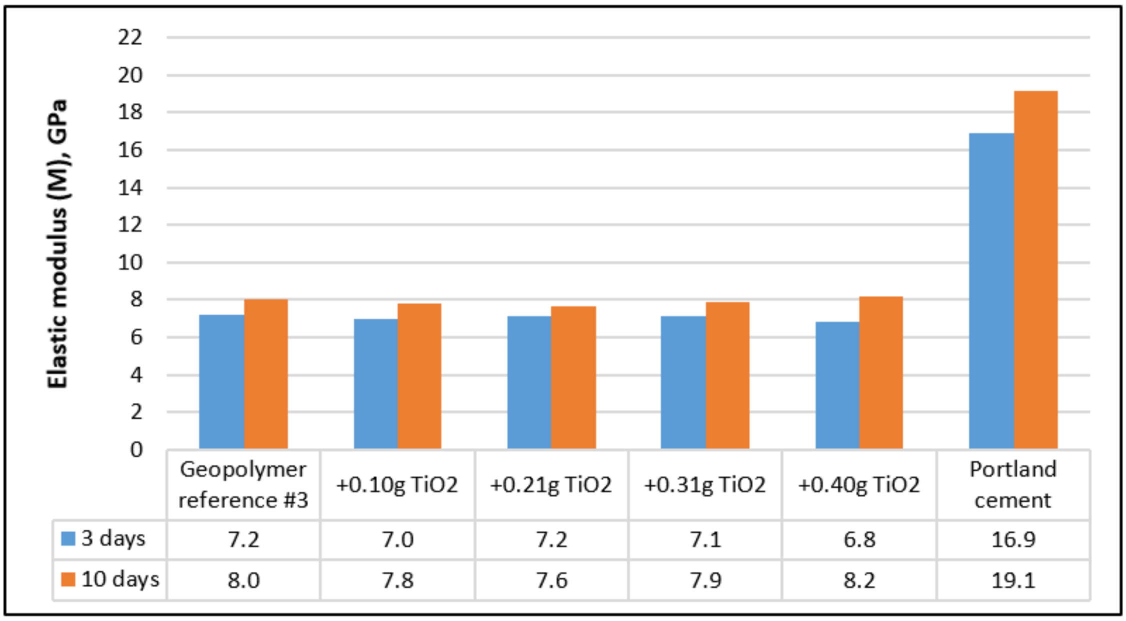
TM#22

Table Apx.23: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#22 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #3_1	33.27	58.36	82.669	27.6
Geopolymer ref #3_2	33.34	58.64	83.063	28.1
+0.10g TiO_2_1	33.31	58.33	84.692	28.3
+0.10g TiO_2_2	33.27	58.79	81.590	28.2
+0.21g TiO_2_1	33.29	58.43	82.428	28.0
+0.21g TiO_2_2	33.33	58.22	84.019	27.8
+0.31g TiO_2_1	33.29	58.41	82.352	27.9
+0.31g TiO_2_2	33.28	58.15	82.732	27.9
+0.40g TiO_2_1	33.35	57.92	80.762	28.1
+0.40g TiO_2_2	33.27	58.67	81.142	28.2
Portland cement_1	32.99	58.52	90.036	19.2
Portland cement_2	32.97	58.39	92.129	19.2

Table Apx.24: **10 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#22 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #3_1	33.28	51.14	73.032	22.7
Geopolymer ref #3_2	33.24	51.09	73.412	23.7
+0.10g TiO_2_1	33.27	50.89	68.381	22.7
+0.10g TiO_2_2	33.32	51.05	68.459	22.6
+0.21g TiO_2_1	33.33	51.15	68.64	22.9
+0.21g TiO_2_2	33.24	50.95	68.034	22.9
+0.31g TiO_2_1	33.33	51.16	73.801	23.5
+0.31g TiO_2_2	33.27	51.05	71.682	23.0
+0.40g TiO_2_1	33.30	50.93	70.721	22.6
+0.40g TiO_2_2	33.26	51.02	71.548	22.6
Portland cement_1	32.41	51.03	80.247	16.3
Portland cement_2	32.35	50.99	79.487	16.1



	Geopolymer reference #3	+0.10g TiO2	+0.21g TiO2	+0.31g TiO2	+0.40g TiO2	Portland cement
🟦 3 days	7.2	7.0	7.2	7.1	6.8	16.9
🟧 10 days	8.0	7.8	7.6	7.9	8.2	19.1

Figure Apx.34: Modulus of elasticity for geopolymer in TM#22 + Portland cement from TM#19.

TM#23

Table Apx.25: **3 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#23 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #3_1	33.29	50.39	70.815	24.2
Geopolymer ref #3_2	33.22	50.38	71.467	24.1
+0.10g MWCNT_1	33.29	50.46	72.261	24.5
+0.10g MWCNT_2	33.33	50.34	72.308	24.2
+0.21g MWCNT_1	33.34	50.49	72.332	24.6
+0.21g MWCNT_2	33.33	50.51	73.283	24.5
+0.30g MWCNT_1	33.28	50.28	72.042	24.2
+0.30g MWCNT_2	33.29	50.02	74.714	24.6
+0.40g MWCNT_1	33.29	50.42	72.187	24.4
+0.40g MWCNT_2	33.30	50.41	72.359	24.7
Portland cement_1	32.56	50.78	78.304	15.6
Portland cement_2	32.57	50.29	77.356	16.2

Table Apx.26: **10 days**. Measured diameter, length, mass and sonic. Geopolymers in TM#23 + Portland cement in TM#19.

Plug #	OD, mm	Length, mm	Mass, g	Sonic, µs
Geopolymer ref #3_1	33.01	51.04	71.174	22.7
Geopolymer ref #3_2	33.07	50.02	72.033	22.6
+0.10g MWCNT_1	33.07	51.36	71.847	22.8
+0.10g MWCNT_2	33.08	51.29	72.135	22.6
+0.21g MWCNT_1	33.03	51.13	71.152	22.4
+0.21g MWCNT_2	33.05	51.17	72.103	22.2
+0.31g MWCNT_1	33.02	51.21	71.891	22.7
+0.31g MWCNT_2	32.91	51.1	69.901	22.9
+0.40g MWCNT_1	33.06	50.94	71.494	22.8
+0.40g MWCNT_2	33.0	51.33	72.738	22.9
Portland cement_1	32.41	51.03	80.247	16.3
Portland cement_2	32.35	50.99	79.487	16.1

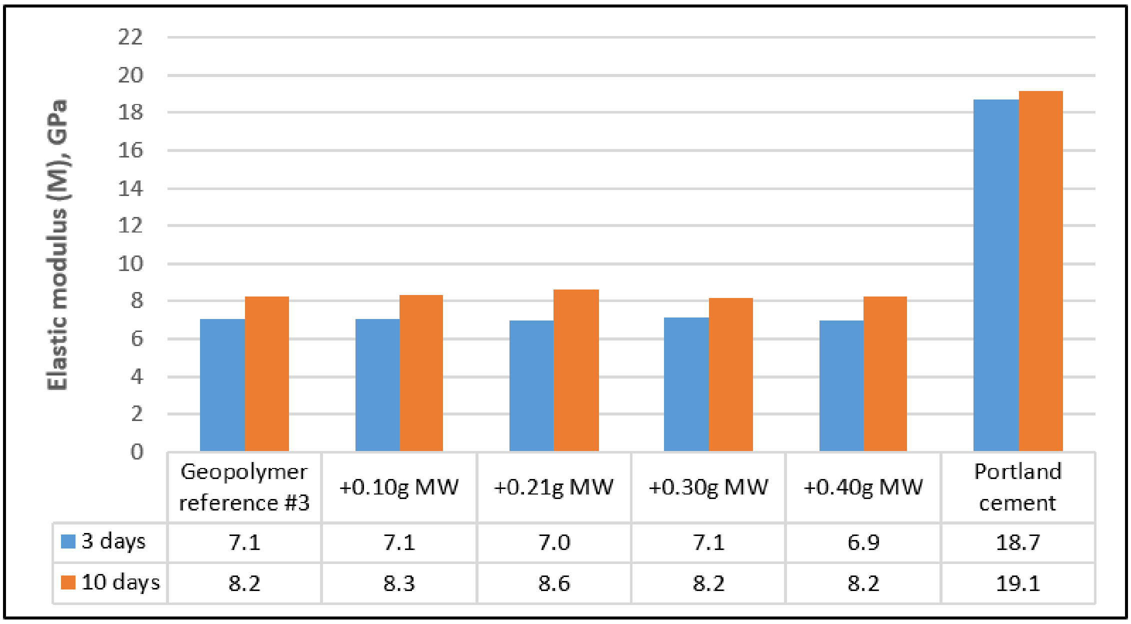


Figure Apx.35: Modulus of elasticity for geopolymer in TM#23 + Portland cement from TM#19.