

Green Cement with Enhanced Mechanical Properties

by

Mohamad Shamsuri bin Mahussin

13550

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
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in partial fulfilment of the requirement for the
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Approved by,

DR SYAHRIR RIDHA

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own concept as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMAD SHAMSURI MAHUSSIN

ABSTRACT

In the midst of increasing awareness of global warming, geopolymer-based cement has been recognized as one of the feasible solutions in reducing the emission of CO₂ contributed by oil well cementing. Nevertheless, it is important for the developed geopolymer cement to possess specific oil well requirement and durable in extreme condition in order to substitute the conventional Portland cement. The use of geopolymer in cement system was widely tested and claimed to be an ideal alternative. However, this new cement system needs comprehensive study to yield better advantages of it. In this research, the main objective was to evaluate the geopolymer cement performance in terms of mechanical properties under extreme wellbore condition, as well as rheological behaviour, density and filtration loss. This research utilized the combination of low calcium (ASTM class F) fly ash and silica fume as the main substitute materials varying in terms of mix proportion. The base case and five samples were cured at 120°C and at 4000 psi pressure to simulate wellbore condition. The results indicate a significant pattern in geopolymer cement strength development with increasing curing time ideally with 40% fly ash and 60% silica fume while standard cement degrades. The higher silica fume content provides early and greater strength attainment. Geopolymer cements lies in ideal plastic viscosity range with sample D (40% fly ash, 60% silica fume) exhibit comparable high yield point to standard G cement. The pattern in density measurement meanwhile shows that the incorporation of silica fume helps in producing lower density slurry. All geopolymer cements show better fluid loss properties. Overall, geopolymer cement exhibit significant strength development and better properties compared to conventional cement but special consideration must be made in elevated curing temperature.

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ABBREVIATIONS AND NONMENCLATURES

API	American Petroleum Institute
ASTM	American Society of Testing and Materials
BHCP	Bottom hole Circulating Pressure
CaCO ₃	Calcium Carbonate
CO ₂	Carbon dioxide
CaO	Calcium Oxide
C ₂ S	Dicalcium Silicate
C ₃ S	Tricalcium Silicate
C ₃ F	Tricalcium Ferrite
C ₄ AF	Tetracalcium Aluminoferrite
GHG	Green House Gases
ISO	International Organization for Standardization
NaOH	Sodium hydroxide
Na ₂ SiO ₃	Sodium silicate
TOC	Top of Cement
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Cement in general can be defined as the binding materials grinded into fine powder, which can be mixed with water and once set, will form a solid mass. This binder when sets, it will harden independently and has the ability to bind other materials together. In oil and gas industry, cement is used widely in cementing jobs for drilling well, where cementing is a crucial step in completion. Well cementing is the procedure of circulating cement slurry inside out of the casing shoe into the annulus between the formation and casing. In general, cement functions are as follows:

1. Restriction of fluid movement between permeable zone
2. Provision of mechanical support of the casing string
3. Protection of casing from corrosion
4. Support of the well bore walls from collapse

The main function of the cement is to mitigate and block fluid communication between the formations to attain long-term zonal barrier throughout the well life and also after its abandonment. The effective isolation between formation zones will boost the production in a safe manner and economically. Besides, cementing strengthens and keeps the borehole integrity from collapsing, mitigate corrosion and seals off problematic zones. To achieve this, once set in place, cement should conform to both short-term and long-term specification to safeguard well operation. The standard properties required are as shown in Table 1.1:

TABLE 1.1: Cement attributes (Short and Long-term)

Cement Slurry (Short Term)	Cement Sheath (Long-Term)
High environmental consideration	Thermally resistant under down-hole pressure and temperature Mechanical properties to resist various downhole stresses and provide zonal isolation throughout the well life.
Mixable at surface	
Non-settling (no free water)	
Optimum density & thickening time	
Optimum fluid loss & strength development	
Effective slurry placement	
Withstand influx of well fluid	

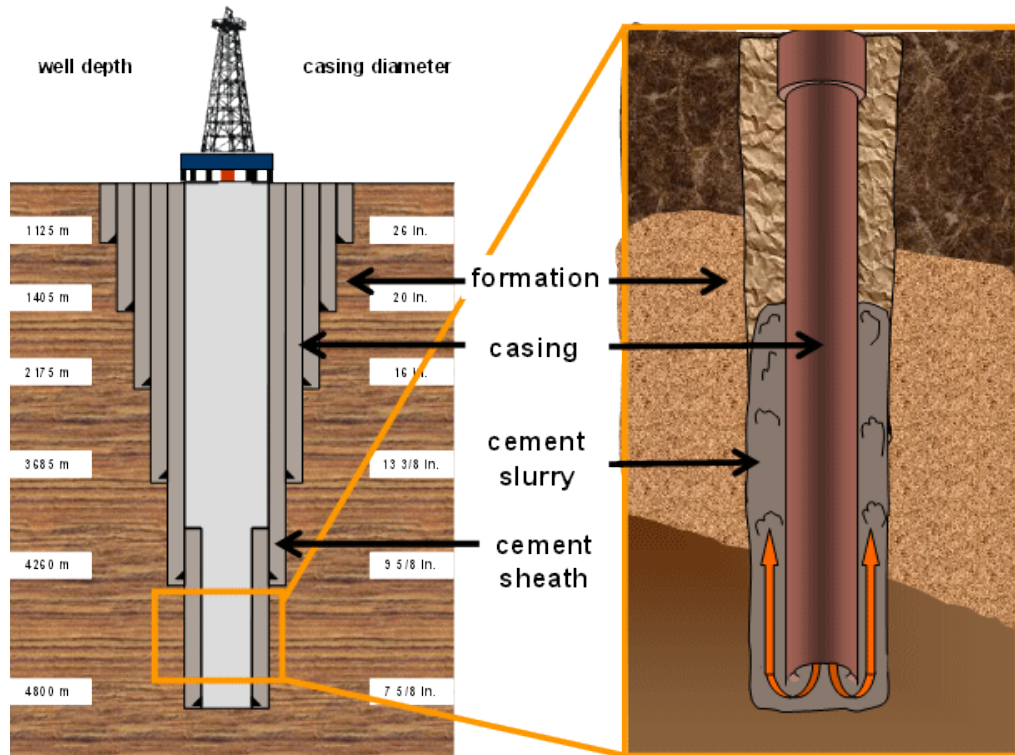


FIGURE 1.1: Schematic of cemented oil well (left); principle of cement placement (right)

The typical oil or gas well can be drilled up to several thousand meters in depth, less than a meter in diameter. As referred to Figure 1.1, cement slurry will be pumped down the wellbore to a depth exceeding 20000 ft where it will be subjected to extreme condition; temperature may increase to 205°C and pressure exceeding 30000 psi. However, the circulation of cooler drilling mud will reduce the effect of high temperature. Thus, the cementing work on surface would definitely differ to how it is done underground, with additional challenges, restrictions and uncertainties. After drilling to a desired depth, drill pipe will be removed and a longer casing string will be lowered. Cementing takes place when the slurry is deployed via pumps, displacing the drilling fluid inside the casing and forced it up the annular between outer casing wall and wellbore. This forms a seal from outside materials as well as permanently positions the casing in place.

The Portland cement, the most commonly used in oil and gas industry is produced from limestone and either clay or shale and heated up to 1649 °C to form a material called cement clinker. The product were then ground to a size specified by the cement grade in which it has direct relation to how much water is required for mixing. To suit with wellbore requirement, Portland cement is calibrated with additives to form nine different API classes of cement. Each class is exclusive to a certain range

of depth and properties where Class G cement is the most commonly used. The Class G cement features which were used as a benchmark are defined as in Table 1.2:

TABLE 1.2: Cement Class G features

Cement Class	G
Recommended w/c, % mass fraction of cement	44
Range of depth, m (ft)	0 to 2440 (0 to 8000)
Availability	Moderate-sulphate resistant & High-sulphate resistant grades
Other features	<ol style="list-style-type: none"> 1. Basic well cement 2. Thickening time controllable using additives to prevent loss of circulation up to 120°C

The issue of cement strength has always been of interest since an ideal well cementing need to develop considerably high strength throughout the well life, provide strong support to the casing, effectively isolate downhole formations and also durable to highly intense reservoir conditions.

1.2 PROBLEM STATEMENT

The low cost and widespread availability of raw materials contributes to the extensive usage of Portland cement in well cementing operation. Nevertheless, the main setback is that this standard cement is prone to failure of mechanical strength as the function of time, experience degradation when subjected to extreme wellbore condition and contributes to the abundant CO₂ emission through its manufacturing process.

Mechanical Failure

Previous experimental study in substituting standard Portland Class G cement with geopolymer cement resulted in the less desirable performance in strength profile build-up. Although proven to be greater in strength, but geopolymer cement exhibits lower performance in terms of Waiting on Cement (WOC) compared to Class G cement. It takes slightly longer period for cement slurry to retain compressive strength once set. Early strength build-up is very crucial to effectively perform zonal isolation and proceeding drilling activities to a greater depth. Therefore, the ideal

formulation of cement slurry needs to achieve a faster and even higher compressive strength build-up for a successful cementing job.

On the other hand, cement degradation indicates the failure in cement body itself whether during pre-production phase or production phase. This occurs when cement bonds weaken as a function of time. This explains the need for remedial cementing job during productive well life, causing difficulties and costly. The major factor leading to degradation is because of the well exposure to extreme temperature and pressure cycles. As a result, cement sheath will no more effective in sealing and supporting the well. Defective cement bond can occur as tensile failure, debonding or shear failure as illustrated in Figure 1.2. Tensile failure is caused by high internal pressure of the casing, which exceeds tensile stress and causes cement crack. Debonding occurs between cement and casing contacts. Excessive internal pressure causes casing to deform and lost contact, thus creating micro-annulus. Shear failure meanwhile occurs when cement is subjected to high formation pressure. This exceeded cement compressive strength and the material will crush.

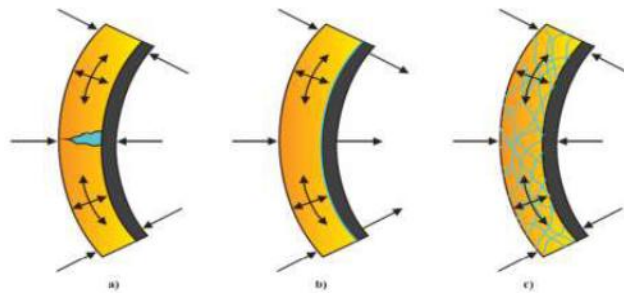
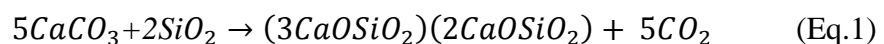


FIGURE 1.2: Types of mechanical failure in cement i) Radial crack ii) Debonding iii) Shear failure

Carbon Dioxide Emission

The worldwide conventional cement industry contributes to severe greenhouse gases emission. The industry emits nearly 900 kg of CO₂ for every 1000 kg of cements produced [11]. The manufacturing of Portland cement clinker involves the calcinations of calcium carbonate according to Equation 1:



The release of carbon dioxide to the atmosphere subsequently leads to the global warming. Portland cement production is estimated to contribute to 7% of global carbon dioxide emission [1] besides consume high energy during its manufacturing. Geopolymer is seen to be a viable option to combat this sustainability problem.

1.3 OBJECTIVE AND SCOPE OF STUDY

This project on well cementing system will focus on few quantifiable aspects as follows:

1. To developed geopolymer cement with enhanced mechanical properties using industrial by-products.
2. To compare the performance of the developed geopolymer cements which varied by different compositions and standard Class G cement.

The scope of study includes:

1. The development of the geopolymer oil well cementing system using combined low calcium (ASTM Class F) fly ash and silica fume. The high amount of calcium might hinder polymerization process and make changes in microstructure [16].
 - Preparing the respective amount of slurry composition in accordance to “API Specification 10A/ISO 10426-1:2000 Specification for Cements and Materials for Well Cementing”.
 - Alteration in the chemical compositions and their respective amount required to develop the geopolymer oil well cementing.
2. Testing the cement quality in terms of physical and mechanical properties:
 - Rheological properties
 - Filtration loss
 - Compressive strength
3. Analyze the performance between the developed geopolymer cements which are varied by different composition and standard cement.
4. Identifying the optimum geopolymer cement mixture that provides the best performance and quality.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 LITERATURE REVIEW

Ensuring zonal isolation throughout the well life to allow safe and economic hydrocarbon production is the main purpose of oil well cementing. It is important to be achieved during the life of the well to maintain well integrity and ensure effective production. However, this isolation can be compromised due to various factors during operative life of the well. Such factors may be in the form of thermal and pressure loads generally regarded as high pressure-high temperature (HPHT), inducing possibilities of cement failure. Various experimental works suggest that under elevated pressure and temperature, cement compressive and tensile strength clearly degraded.

Ordinary Portland Cement (OPC) which was globally used in well cementing job also poses problems in durability [4,9,18-19] as well as carbon dioxide emission. [4,8-9,11-13,20] OPC emits CO₂ ranging from 0.66 to 0.82 kg for every kilogram it was produced and also contributed to 5-7% of global anthropogenic CO₂ emission, caused by calcinations on limestone [12-13]. Some other studies suggested OPC manufacturing releases approximately 10% of global anthropogenic CO₂ emission, accounted for 82% [8] and 64% [9] in total of greenhouse gases (GHG) globally. Cement production releases CO₂ in two ways: the conversion of calcium carbonate to calcium oxide inside the kilns, and by burning large quantities of fossil fuels to up to 1450°C necessary for roasting limestone.

Generally, to manufacture one ton of Portland cement requires approximately 2.8 ton raw materials. This includes fuel and other components which eventually generates 5-10% of dusts. Entirely, for every ton of cement manufactured, 6000-14000 m³ dust-bearing air streams are generated. This is equivalent to 0.7 to 800 g/m³ of dusts which accounts for about a ton of CO₂ discharged into the atmosphere [11] as a result of aforementioned chemical reaction in Equation 1. Thus, geopolymers emerged as a possible solution to counteract the environmental effects of cement manufacturing.

According to Mahmoudkhani et. al [8] their research suggests geopolymer application in low or high density cement system as it possess better mechanical properties besides being chemical-resistant suitable for cementing job in oil and gas well. The robustness and versatilities of amorphous aluminosilicate seems to be an ideal alternative that gives good performance and environmental benefits at low cost. Other researches also concluded that geopolymer-based materials possess low shrinkage and early strength. It also has high resistance to freezing and thawing, sulphate attack and corrosion [1-3].

Research about fly ash with silica fume effects on cement hydration provides an insightful result on incorporation of both materials in cementing. The experiment however shows that fly ash exhibit slow strength development even though it is stronger and durable in longer term. By incorporating fly ash with silica fume together, the cement hydration is significantly retarded. Silica fume early reactivity is hindered, heat of hydration decreases and accelerating effect of silica fume is delayed. [5]

Similarly in other study, fly ash concrete slow early strength development is claimed to be caused by the assemblage of reactive silica within the particle's interior part [15]. Silica fume with higher surface area and greater SiO_2 content, is found more reactive than fly ash, therefore combined together to substitute Portland cement [5]. In silica fume, the extremely fine particles elevate pozzolanic reaction between SiO_2 particles in it and CaOH_2 of hydration products. These fine particles were said to produce "micro-filler effect" that gives strength in the interfacial transition zone of concrete [15].

Oil well cement composed of mainly four (4) phases namely C_3F , C_4AF , C_3S , and C_2S where C_2S and C_3S stated to be responsible for compressive strength. When they react with water, C-S-H gel and calcium hydroxide are formed, which acts as cement binder. It subsequently consolidates the cement matrix, thus improving cement strength. The incorporation of silica particles will also help to gain earlier strength, filling voids between particles, creating dense solid matrix even before chemical reaction starts to occur [23].

Consistent with the laboratory works done to evaluate cement properties used in Saudi Oil Field under HPHT condition, the addition of silica flour resulted in a substantial increase in compressive strength as compared to Class G slurry. The XRD analysis done also shows that C-H phase has transformed to calcium silicate hydrate and tobermorite at elevated temperature. This prevents strength degeneration and lowers the permeability [23].

Dolezal et. al [6] stated that pore size and permeability will reduce as the percentage of Na_2O increases,. This is advantageous when applied in HPHT deep well condition. Higher pressure will shrink the porosity thus providing better geopolymer matrix with lower permeability. In ensuring proper zonal isolation, other attainment through research has been studied as well, using geopolymer-based pills [7].

From their research entitled the development of a geopolymer-based pill as an engineered solution to lost circulation, they stated that sodium silicate has been classified as chemical sealant and developed to hinder seepage into high permeable zones or block minor fractures. Its attractive features in mitigating loss circulation include nano size molecule, low viscosity, excellent thermal and chemical stability, environmental friendly and cost effective [7].

Besides, cement mechanical properties are not only dependable on additives, but on density as well. Hence, additives known to improve strength in cement in low to medium density systems are less effective in higher density system [24]. The industry in present is shifting into lightweight cement for a broader application and advantages it offers, without the need of sacrificing the qualities. Standard cement (15.6 to 16.4 lb/gal) cannot be used in weak or depleted zoned as bottomhole circulating pressure (BHCP) will exceed rock strength, causes cement loss and reduces top of cement (TOC) [16].

2.2 THEORY

Geopolymer cement is the alternative substitutes of Portland cement where geopolymerization is defined as a geosynthesis (reaction that chemically integrates minerals) involving naturally-occurring silico-aluminates [11]. It relies on minimally processed natural materials or industrial by-products to reduce carbon footprint, while possessing favourable qualities including resistive to durability problems. Geopolymer comes from pozzolanic materials that react with alkaline to form a cementitious material.

Pozzolanic compound or source of silica and alumina in the presence of alkaline solution, acts as a source of geopolymer precursor. This alkali activator comes from the element in the first group of periodic table, thus called as alkali activated aluminosilicate binders or alkali activated cementitious material [11]. The alkali activator will therefore activate the raw geopolymer to take part in polymerization process, activating Si and Al to form a compacted composite. It was also defined as class of aluminosilicates formed when alkali silicate solution reacts with dehydroxylated clay in the presence of highly alkaline conditions [13].

The geopolymeric reaction occurs when alumina silicates reacts with alkali and soluble alkali polysilicates. The resulting reactions are in the form of silica oxide and aluminium oxide tetrahedral linked shared by oxygen atoms. There is a mild exothermic reaction in alkali activated mixture, accompanied by hardening and polycondensation. This geopolymer, after long curing period at designated pressure and temperature, will transform from amorphous solid phase into semi-crystalline phase [8]. The simplified processes are illustrated in the Figure 2.1.

The primary advantages of geopolymers over conventional cement from environmental perspective is definitely due to much lower CO₂ produced from geopolymer manufacture compared to Portland cement process. The main reason is due to the absence of high-temperature calcinations of cement clinker where the step did not only consume a large amount of fossil fuels-driven energy, but also emitted abundant of CO₂ as the reaction products.

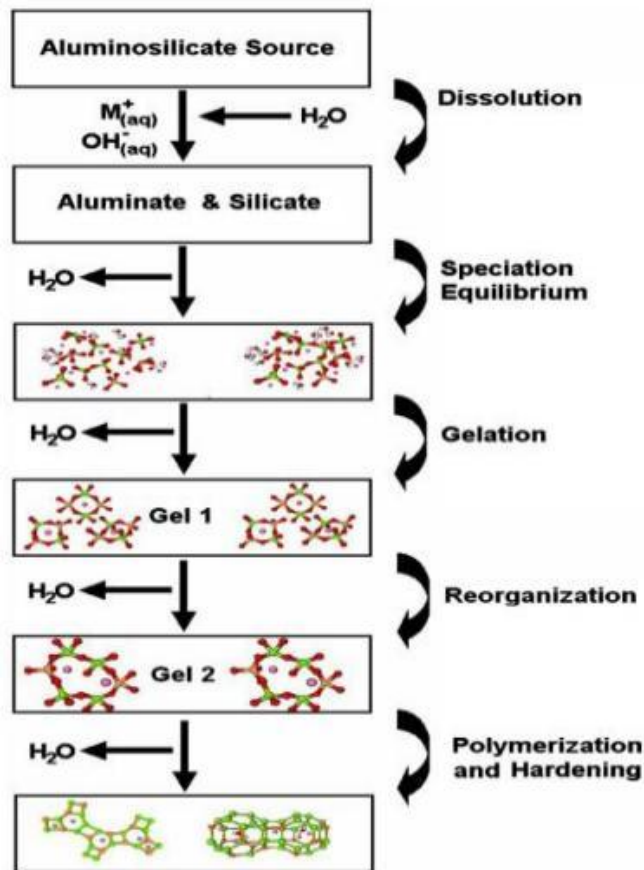


FIGURE 2.1: Concept of geopolymerization [27]

Most of the processes illustrated in forming geopolymer happened at the same time. Dissolution takes place by alkaline hydrolysis (intake water), forming aluminate and silicate. Once released by dissolution, they are incorporated into aqueous phase, and then form a complex mixture of silicate, aluminate and aluminosilicate. In alkaline nature, gelation takes place forming large networks by condensation followed by the release of water. The system continues to restructure as the connectivity of the gel network increases, forming three-dimensional aluminosilicate network which is attributed as geopolymer [27].

Besides greater strength exhibited by geopolymer-based cement, if the two cements be compared, geopolymer-based has the following advantages:

1. The alumina silicate materials present in geopolymer better enhance the cement to withstand chemical attack.
2. There will be no release of CO_2 due to the absence of calcinations step.
3. Total consumption of energy for production is lower than Ordinary Portland Cement. [9]

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 RESEARCH METHODOLOGY

In accomplishing the project objectives, the method used is through various experimental works and analyses. They are divided into several phases for a clearer flow of project work.

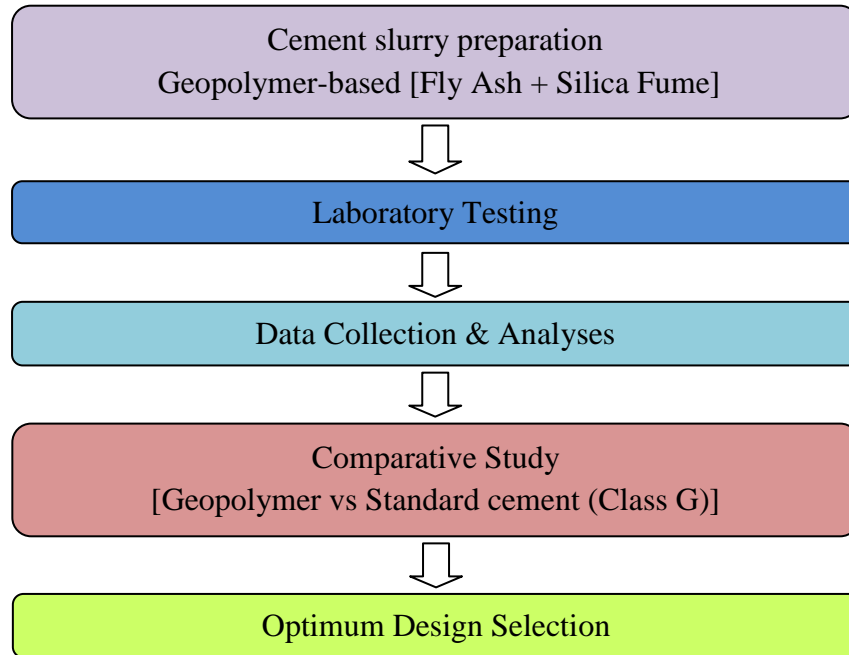


FIGURE 3.1: Research methodology

3.2 PROJECT ACTIVITIES

3.2.1 Preparation of Cement Slurry

Materials and Equipments

The equipments and materials used for the project are listed in Table 3.1:

TABLE 3.1: Materials and equipment for cement preparation

Materials	Equipments	
Class G cement	Electronic balance	Static Fluid Loss Tester
Fly Ash (ASTM Class F)	Constant speed mixer	HPHT Curing Chamber
Silica Fume	Magnetic stirrer	Compressive Strength Tester
Sodium Silicate	Baroid mud balance	
Sodium Hydroxide	HPHT Consistometer	
Water	Viscometer	

Two main components that made up geopolymers are the source material and alkaline liquid. The materials should be rich in silicon (Si) and aluminium (Al). This project will utilize industrial by-products, which are fly ash and silica fume as the substitutes for Class G cement. In geopolymer slurry, for polymerization to occur, the alkaline liquids used are sodium-based, utilizing the most common combination of sodium hydroxide and sodium silicate solution. They will act as activator to initiate and speed up polymerization process.

The equipments and test apparatus were to serve different functions in testing the developed cement properties and performance as illustrated in Figure 3.2. Some of the test will be carried out while cement was still in slurry state, while some after the hardened cement subjected to several curing conditions which will be further elaborated in the next sections.



FIGURE 3.2: Equipments for slurry preparation

3.2.2 Slurry Mixing

For benchmarking, mixing quantities of cement slurry for Class G was prepared using a standard procedure and specifications outlined by “API Specification 10A/ISO 10426-1:2000” before proceeding to formulate compositions for geopolymer slurries. The mixing proportions or known as ‘Water-Cement Ratio’ of Class G is referred to the following Table 3.2:

TABLE 3.2: API Specification for water-cement ratio

Components	Classed A and B (g)	Class C (g)	Classes D,E,F,H (g)	Class G (g)
Mix water	355 ± 0.5	383 ± 0.5	327 ± 0.5	349 ± 0.5
Cement	772 ± 0.5	684 ± 0.5	860 ± 0.5	792 ± 0.5

Too much mix water can result in failure of the cement to set into a strong, impermeable cement barrier, while too little mix water will increase slurry density and viscosity, decrease pumpability and workability of slurries for testing.

The mix ratio used was 0.44, where 349 g and 792 g were measured respectively for water and cement. The ratio was expected to be constant for alternative materials used later to prepare geopolymer-based slurry. For the mixture, in the base case using Class G, it was composed of only pure cement and distilled water, without any chemicals or additives. This is to observe the properties and performance of the basic standard cement.

Consecutively, another five (5) sets of cement slurries were prepared for geopolymer-based, each containing composition with various proportions:

Base case: 100% Class G cement + Water

Slurry A : 90% Fly Ash + 10% Silica Fume + NaOH + Na₂SiO₃ + Water

Slurry B : 80% Fly Ash + 20% Silica Fume + NaOH + Na₂SiO₃ + Water

Slurry C : 60% Fly Ash + 40% Silica Fume + NaOH + Na₂SiO₃ + Water

Slurry D : 40% Fly Ash + 60% Silica Fume + NaOH + Na₂SiO₃ + Water

Slurry E : 100% Fly Ash+ NaOH + Na₂SiO₃ + Water

3.2.3 Geopolymer Mixing Proportion

For geopolymer-cement mixture, there is a parameter called ‘water to geopolymer solid ratio’ devised to assist the design of low calcium fly ash [21]. Total mass of water is the sum of water in Na_2SiO_3 solution, the mass of water in NaOH solution and the mass of excess water present in the mixture, if any. The mass of geopolymer solid is the sum of the substitute material mass (fly ash and silica fume), the mass of solids in Na_2SiO_3 solution and the mass of NaOH solids. Both water and geopolymer formulations are shown in Equation 2 and Equation 3:

$$\text{Water(g)} = \text{Na}_2\text{SiO}_3 (\text{water}) + \text{NaOH}(\text{water}) + \text{Excess water (if any)} \quad (\text{Eq.2})$$

$$\text{Geopolymer solid(g)} = [\text{FA} + \text{SF}] + \text{Na}_2\text{SiO}_3 (\text{solid}) + \text{NaOH}(\text{solid}) \quad (\text{Eq.3})$$

As the geopolymer-based was to be compared with G cement, the ratio of water to geopolymer solid has been made constant as standard Class G cement outlined in API standard which is 0.44. The ratio of Na_2SiO_3 solution to NaOH solution is taken approximately as 2.5 based on suggested laboratory experience [21].

The geopolymer was prepared using ASTM class F (low calcium) fly ash, while alkaline liquid used was the mixture of 12M NaOH and Na_2SiO_3 . The NaOH, composed of 40% of solid and 60% of water was mixed with Na_2SiO_3 solution with the ratio of 2.5. The mixtures were then mixed to form cement slurries as the following procedures:

1. The amount of materials needed to prepare each type of cement slurries was calculated and measured using electronic balance.
2. All the materials were mixed using constant speed mixer Model 3060 from Chandler Engineering following API mixing procedure.
3. The slurry mixing procedure was explained as below:
 - I. Distilled water was filled up in the mixer and agitated with 4000 rpm for 15 seconds. Cement powder should be poured bit by bit.
 - II. Na_2SiO_3 and NaOH were added into the mixer.
 - III. Materials in powder and pellet forms were added into the mixer.
 - IV. The mixer speed was increased to 12000 rpm and run for 35 seconds.

Instantly after the mixture was readily mixed, the density of the slurry formed will be measured using Baroid mud balance and recorded. The designed cement slurry for Class G cement should be consistent with API standard of 15.8 ppg. The density of geopolymer slurry on the other hand might vary.

Density measuring procedures are as follows:

1. The lid was removed from the cup and it was then filled completely with cement slurry until overflow.
2. The lid was re-placed and rotated until firmly seated, making sure that some cement slurry was expelled through the hole on the lid. (Air bubbles should be removed before closing the lid)
3. The balance arm was placed on the base, with the knife-edge resting on the fulcrum.
4. The rider was adjusted until the arm was levelled, as indicated by the level vial on the beam.
5. At the left-hand edge of the rider, the density was read on either side of the lever without disturbing the rider.

3.2.4 Laboratory Tests on Cement Slurries

After the preparation of slurries was completed, a series of laboratory testing will be conducted to examine the properties and performance of the developed cement, as shown in Table 3.3:

TABLE 3.3: Type of laboratory testing

No.	Test	Purpose
1	Cement Rheology Test	To test for cement rheological properties (plastic viscosity and yield point)
2	Filtration Loss Test	To determine the relative effectiveness of cement slurries of losing its water phase as a filtrate.
4	Compressive Strength Test	A non-destructive method to test strength development of the cement slurries under down-hole pressure and temperature condition.

The procedural steps in preparing these tests will follow “API Recommended Practice 10B-2/ISO 10426-2” (*Appendix A*). Rheology Test and Fluid Loss Test were all conducted when the cement was still in the slurry form whereas Compressive Strength Test were done after the cement had been cured under elevated pressure and temperature illustrated in the following Table 3.4:

TABLE 3.4: Cement testing with designated curing condition

Cement slurry	Composition								Curing Condition	
	Fly Ash	Silica Fume	NaOH & Na ₂ SiO ₃	Distilled water	Rheology test	Fluid loss test	Thickening time test	Comp. Strength Tester	4000psi & 120Celsius	
									Hydration time	Compressive Strength
G	0%	0%	0%	/					1 day	
	0%	0%	0%	/					3 days	
	0%	0%	0%	/					5 days	
A	90%	10%	/	/					1 day	
	90%	10%	/	/					3 days	
	90%	10%	/	/					5 days	
B	80%	20%	/	/					1 day	
	80%	20%	/	/					3 days	
	80%	20%	/	/					5 days	
C	60%	40%	/	/					1 day	
	60%	40%	/	/					3 days	
	60%	40%	/	/					5 days	
D	40%	60%	/	/					1 day	
	40%	60%	/	/					3 days	
	40%	60%	/	/					5 days	
E	100%	0%	/	/					1 day	
	100%	0%	/	/					3 days	
	100%	0%	/	/					5 days	

3.2.5 Tabulation and Interpretation of Laboratory Tests Data

The results are tabulated and interpreted to analyze the mechanical performance of cement slurries and to compare the geopolymers cement with alteration in compositions with conventional Class G cement. These will determine the success of pre-defined project objectives. The results are also to be used to deduce the type of well application in which the developed geopolymers cements are suitable in. Recommendations will be made by analyzing the performance of cement through various tests done. All the tabulation and interpretation of data were documented in the next chapter.

3.3 GANTT CHART

 Process  Key Milestones

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topics														
2	Preliminary Research Work														
3	Laboratory Work Arrangement - Cement Test Equipment booking - Preparation of geopolymer-material (Silica Fume and Fly Ash)														
4	Proposal Defence														
5	Project Work continues - Arrangement of material purchasing - Avantis Laboratory (Na ₂ SiO ₃)														
6	Performing Test Run on HPHT Curing Chamber using G cement.														
7	Performing Test Run on HPHT Consistometer														

TABLE 3.5: FYP1 Gantt Chart

 Process
  Key Milestones

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Project Work Continues - Preparation of Alkali activator solution (12M) - 2 nd Test run of HPHT Curing Chamber	Process	Process														
2	Cement slurry preparation trial run and adjustment to obtain the optimum mix design.			Key Milestones													
3	Preparation of Base Case (Class G cement) - Rheology Test - Fluid Loss Test - Curing for 1 day				Key Milestones	Key Milestones											
4	Curing for cement samples (G, A, and B) - 1, 3 and 5 days curing period						Process	Process	Process								
5	Curing for cement samples (C, D, and E) - 1, 3 and 5 days curing period								Process	Process	Process						
6	Completing Rheology Test and Fluid Loss Test for all cement samples.									Key Milestones	Key Milestones	Key Milestones	Key Milestones				
7	Strength Test Evaluation (Control + 5 cement samples)											Key Milestones	Key Milestones	Key Milestones			
8	Data analysis and additional research references with other published work.											Process	Process	Process	Process		
9	Viva																Key Milestones

TABLE 3.6: FYP2 Gantt Chart

3.4 PROJECT KEY MILESTONES

- [Week 1]-Selection of Project Topics
Green Cement for Zonal Isolation with Enhanced Mechanical Properties
- [Week 6]-Obtain required materials
The amount of fly ash and silica fume needed was determined to prepare for four desired samples.
- [Week 8]- Proposal Defence
- [Week 13]-Preliminary laboratory testing on G-cement (base case)
Class G cement was tested for benchmarking; undergo curing in High Pressure and High Temperature (HPHT) condition.
- [Week 17]-Finalize mix design for geopolymer cement slurry
Trial run and adjustments were done to obtain optimum slurry mix design.
- [Week 18]-Laboratory testing on Base Case
Rheology Test, Fluid Loss Test and cement curing were done.
- [Week 23]-Completing Rheological and Fluid Loss test of all samples
All tests in slurry condition were done covering all 6 cement samples before proceeding to strength test.
- [Week 25]-Compressive Strength Evaluation
The cement cubes were tested for strength development after subjected to curing conditions.
- Data gathering and analysis
The resulting data were collected and comparative analyses were done to study the performance of newly developed cement.
- [Week 30]- Viva

CHAPTER 4

RESULT AND DISCUSSION

4.1 DATA GATHERING AND ANALYSIS

Rheology test, filtration loss test and compressive strength test had been carried out on all types of cement slurry, namely standard Class G cement, geopolymer A, geopolymer B, geopolymer C, geopolymer D and geopolymer E. All test results are discussed in the following section:

4.1.2 Rheology Test

The density of the base case (Class G) according to API standard is 15.8 ppg. The comparative values of other samples were tabulated in the following table. Table 4.1 shows the viscometer reading of different cement slurries.

TABLE 4.1: Revolution per minute (RPM) of cement slurries

SAMPLE	θ_{600}	θ_{300}	θ_{200}	θ_{100}	θ_6	θ_3
G	165	124	124	100	25	15
A	141	72	53	25	3	1
B	175	97	69	35	4	2
C	190	120	113	61	12	8
D	210	143	260	162	40	32
E	110	46	39	16	2	1

TABLE 4.2: Rheological properties of cement samples

Properties	G	A	B	C	D	E
Density (ppg)	15.69	14.80	14.85	14.43	14.10	14.10
Rheology						
Shear rate (600 RPM)	165	141	175	190	210	110
Shear rate (300 RPM)	124	72	97	120	143	46
Plastic Viscosity (cp)	41	69	78	70	67	64
Apparent Viscosity (cp)	82.5	70.5	87.5	95.0	105.0	55.0
Yield Point (lb/ft2)	83	3	19	50	76	-18

Rheology can be defined as the deformation and flow behaviour of all forms of matter. Rheological measurement made on fluid; viscosity and yield point aid in determining how the fluid will flow under different conditions. Thus, a comprehensive study on rheological properties of cement slurry will help to overcome difficulties in cementing operation such as rapid loss of workability, problems in pumping and acceleration in cement hydration. The dependability of slurry to temperature is also an important aspect to be investigated; however this paper will only cover the rheological behaviour of different geopolymers cement sample in ambient temperature.

Table 4.1 shows the readings under different RPM (revolution per minutes) of all slurry samples at ambient temperature while Table 4.2 shows the rheological properties of slurries such as density, viscosity, yield point and gel strength which varies throughout the samples. Plastic viscosity and yield point are the parameters to be focused on in this paper.

Plastic viscosity

It is the resistance of fluid to flow. A low value indicates that the slurry has a good mixability and can be pumped smoothly into the well because of low slurry viscosity exiting at the bit. It is observed that Geopolymer B exhibit highest plastic viscosity of 78 cp while other geopolymers are only a bit difference. There is no direct relationship noticed between the silica fume percentage and the values of plastic viscosity. Nevertheless, all slurries regardless the amount of silica fume mixed in it have plastic viscosity less than 100 cp which is considered good for cement slurry.

Yield Point

Following the Bingham plastic model, yield point is used to evaluate the cement slurry ability to lift cuttings out of the annulus. High value indicates a non-Newtonian fluid (plastic fluids where the viscosity is not constant), one that carries cuttings better than a fluid of similar density but lower yield point. The data shows that standard G cement stands out better than geopolymer slurries but geopolymer D has slightly similar value. Whereas geopolymer E (100% fly ash constituent) shows undesirable value, indicating that pure geopolymer slurry with the absence of silica fume is not ideal for wellbore cleaning from cuttings.

In short, for plastic viscosity all geopolymers exhibit relatively good performance while for yield point, geopolymer D shows a desirable capacity as class G cement to lift cuttings out of the annulus. The absence of silica fume in cement slurry (Geopolymer E) gives unwanted effect on yield point values.

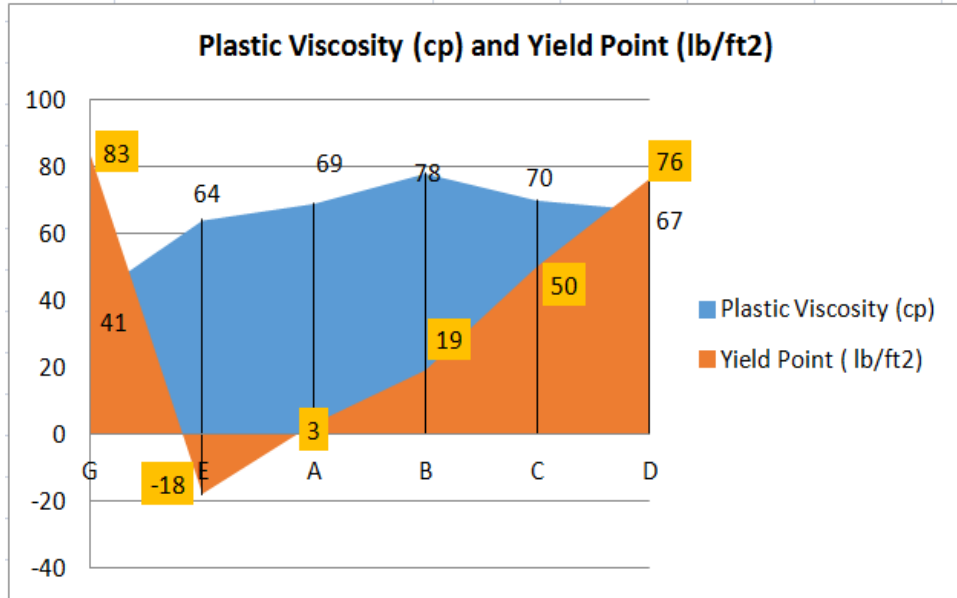


FIGURE 4.1: Plastic viscosity and yield point of slurries

4.1.3 Density

The density explains the hydrostatic head of cement slurry in a well. After conditioning, slurry was poured into Baroid mud balance to get its density. The values were tabulated and illustrated in Table 4.3 and Figure 4.2 respectively:

TABLE 4.3: Density of cement samples

Samples	G	E	A	B	C	D
Density (ppg)	15.69	14.10	14.80	14.85	14.43	14.10

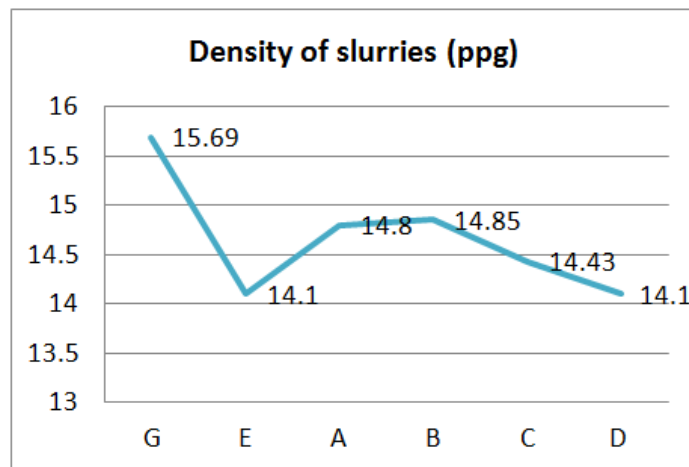


FIGURE 4.2: Density of slurries

It can be observed that out of all samples, standard G cement exhibit highest density and generally when the composition of fly ash and silica fume are altered in the decreasing and increasing order respectively, the density are lowered until 14.1 ppg. The less dense cement can be beneficial as well as a denser one depending on the requirement of different drilling condition. As the industry is moving into more challenging environment, numerous ultra lightweight cements has been studied and applied in live well over the years. In application, when encounter depleted or weak zones, higher density cement will cause cement loss to the formation, as bottom hole circulating pressure is exceeding the rock strength. The density must be reduced to a point where the summation of frictional force and hydrostatic pressure will not exceed fracture gradient [16].

The trending showed through the combination of geopolymer in this paper gives an insight of density alteration without compromising on mechanical properties. This is important due to the fact that the reduction of density achieved through the addition of extra water alone will result in severe dilution effect. The compressive strength of cement appears to be too low that it can no longer serve as annular sealant in both oil and gas well [16].

4.1.4 Filtration Loss Test

Filtration loss can be defined as the leakage of liquid phase of cement slurry into the formation matrix. Excessive loss may cause cement degradation thus endanger well integrity. The less the recorded volume of fluid loss, the better will be the cement slurry performance. The base parameter of API standard is 50 ml/30 minutes of fluid loss [25]. Thus, good slurry shall not exceed the base value.

TABLE 4.4: Fluid loss reading of different cement samples

Samples	Fluid Loss (ml)					
	5 min	10 min	15 min	20min	25 min	30 min
G	76	78	83	87	93	94
E	2	4	6	8	9	9
A	2	3	5	5	6	6
B	1	2.5	3	3	3	3
C	<1	<1	<1	<2	<2	<2
D	<1	<1	<1	<2	<2	<2

The fluid loss test was carried out at 65°C and 500 psia using static fluid loss tester. Based on the data obtained, it gives clear indication of fluid loss experienced by standard G cement within 30 minutes which is 94 ml in total. The value is considerably high, recording almost double the base parameter outlined by API. The variance might take into account the discrepancies during lab testing and the fact that the sample is a neat sample with no additives to rectify the performance to a desired value, however the data for other samples tested were smooth and highly reliable.

All geopolymer samples record excellent performance with favourably low fluid loss with the highest reading was approximately 80% lower than the API standard fluid loss. As the percentage of silica fume combined into the cement mixture increases, the lower the fluid loss volume being observed. For geopolymer C and D, with the percentage of silica fume of 40% and 60% respectively, both samples exhibit extremely low fluid loss value reflected by the lowest amount of filtrate collected.

The low volumes recorded in geopolymer sample are expected when incorporating silica fume as cement substitute because of the high specific surface area of silica fume particles with an average diameter of 0.15 to 0.3 µm. (100 times finer than cement particle). Bleeding was significantly reduced by silica fume because free water is consumed in wetting of the large area made up by silica fume. Thus, free water in slurries expected for bleeding also decrease significantly [25]. Cement slurries with the combination of silica fume therefore show better fluid loss properties compared to standard G cement.

4.1.5 Compressive Strength Test

The compressive strength property is the maximum stress a material can sustain under load crushing and indicates the integrity of cement to bear long term imposed stresses. This paper presented the cement strength properties of cured cement moulds through destructive testing using Compressive Strength Tester. The poor compressive strength can lead to structural failure and results in serious safety issues.

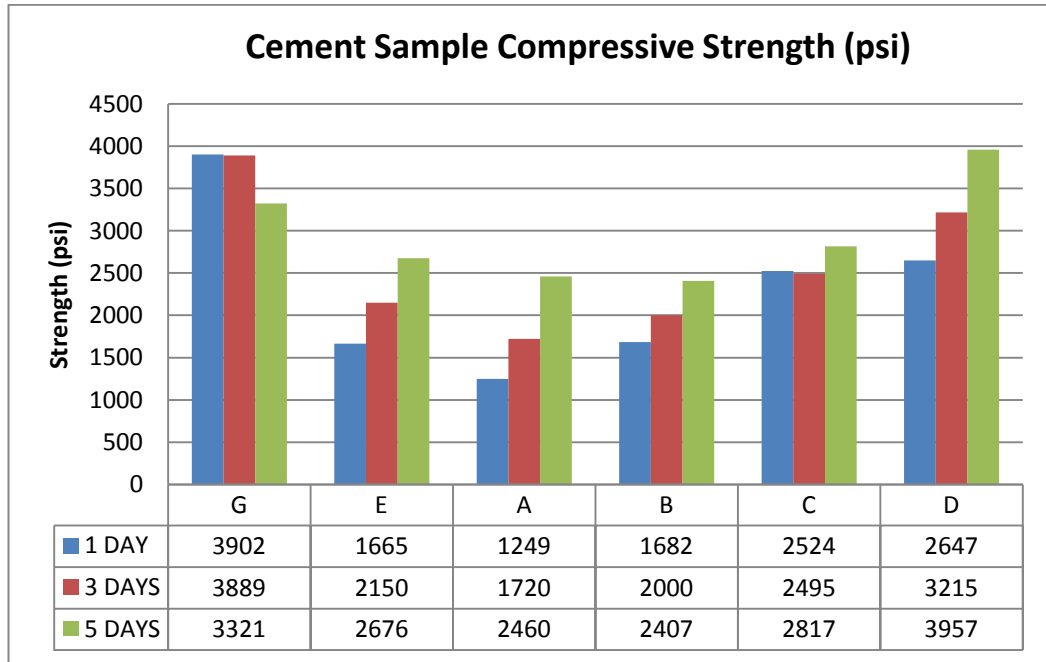


FIGURE 4.3: Cement sample compressive strength

TABLE 4.5: Compressive strength under different curing time

Curing Time (days)	Strength of samples (psi)					
	G	E	A	B	C	D
1	3902	1665	1249	1682	2524	2647
3	3889	2150	1720	2000	2495	3215
5	3321	2676	2460	2407	2817	3957

Geopolymer cement slurry composition:

- Sample E : 100% Fly Ash
- Sample A : 90% Fly Ash 10% Silica Fume
- Sample B : 80% Fly Ash 20% Silica Fume
- Sample C : 60% Fly Ash 40% Silica Fume
- Sample D : 40% Fly Ash 60% Silica Fume
- Curing condition : **120°C, 4000 psi**

The graph in Figure 4.4 projected the trend of compressive strength exhibited by all six (6) cement composition which varies in terms of geopolymer-substitute materials' percentage. Whereas, Table 4.5 presented compressive strength values of different curing days. This includes the base case of standard Class G cement and also sample E which constitutes fully fly ash for extensive interpretation.

The obvious trend shows that for Class G cement, it is proven to have a considerably high compressive strength recorded after 1 day curing time with 3902 psi. However, the highest strength was recorded by geopolymer D under elevated curing condition after 5 days, which is 3957 psi. The important properties shown by this standard cement is that, the strength gradually degrades with the increasing curing time. On the contrary, the general trend shows by geopolymer cement is favourable because as curing time increases, the cement strength develops higher.

There is no conclusive summary on the trend based on this paper alone as there is no further extension of HPHT curing condition. The increasing strength might continue and might as well degrade. Various comparative studies suggested that both geopolymer and Class G cements develop strength with the curing temperature up to the optimum value [20]. This indicates that the decreasing trend in Class G is due to the effect of elevated temperature in which the cement starts to degrade. This is inferred to the loss of silica at higher temperature [20].

However, all geopolymer cement increases in compressive strength values as Si and Al form source materials have readily dissolves [20]. Nevertheless, it must be noted that the developed geopolymer cement for this paper was cured under elevated condition. This would adversely affect the intergranular structure of geopolymer when the temperature is in very high range. ($> 100^{\circ}\text{C}$) The possibility of breaking up will lead to strength reduction [20].

In addition, when subjected to temperature in excess of 110°C , C-S-H phase undergoes transformation that alters mechanical strength, gives high permeability and strength retrogression [19]. Comparing to the data obtained in regards to geopolymer cement, it is contradict as the strength keeps developing with the elongated curing time. This however can be inferred that the pure geopolymer cement composition used has not yet achieved their optimal values. If the curing time is extended, the increments in strength will still be expected which is very favourable.

To obtain a clearer view of the effect of temperature on geopolymer cement, another comparative study with other published work was done as illustrated in the following Figure 4.5:

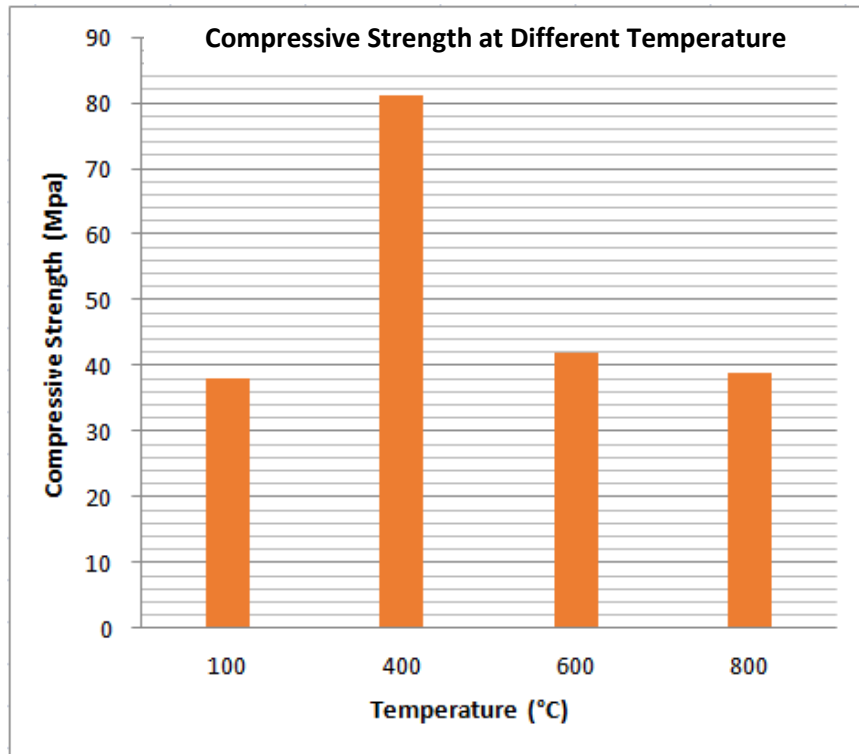


FIGURE 4.4: Geopolymer cement strength at different curing temperature [26]

The above chart shows a relative study of other author incorporating fly ash as geopolymer cement. This shows a clear trend of geopolymer behaviour with respect to temperature elevation for the cross-reference as this paper only focuses on a specific pressure and temperature values. (120°C and 4000 psi)

It is observed that geopolymer cement is capable of sustaining even higher temperature than what is being presented in this paper. While G cement degrades, geopolymer on the other hand can maintain a higher compressive strength even at 400 centigrade. This justifies the increment in strength in all geopolymer samples (A,B,C,D and E) which are expected to go higher if the experiment is to be extended at elevated temperature. However as various studies [19-20] suggest, the strength will degrade at a certain temperature limit.

In this author's work, the strength drops when exceeding 400°C suggesting the breaking up of the intergranular structures. However, in real application these ultra HPHT temperature range is not widely explored due to many limitations and questionable hydrocarbon source in that particular extreme environment.

In overall, geopolymer exhibit excellent strength development compared to cement G; however it is dependable on curing temperature. It can therefore be concluded that geopolymer cement will degrade under elevated temperature condition. A more desirable value can possibly be obtained with the usage of additives, however this paper is based on pure composition with no additional additives.

Comparing all geopolymer samples, geopolymer D exhibit the best performance in term of strength development with a value of 3957 psi when cured under elevated condition for 5 days. The strength observed is comparable to the standard G cement. This is due to the high amount of silica fume incorporated in it, in which high degree of pozzolanic reaction induces higher compressive strength development [22]. The fineness of silica fume forms dense matrixes that enhance the bonding and thus gave strength to cement [19].

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The paper provides a data inventory for standard G cement as a benchmark with the comparative analysis of geopolymer cement samples that can be used for interpreting cement mechanical properties.

Based on the experimental work's findings, the following conclusions are drawn:

1. Plastic viscosity of all geopolymer sample exhibit relatively good performance while for yield point, geopolymer D (40% fly ash, 60% silica fume) shows a desirable capacity as standard G cement. The combination with silica fume in cement slurry improves the performance.
2. All geopolymer sample exhibit lower density slurry which can be further explored to be ultra lightweight cementing option.
3. Cement slurries with the combination of silica fume shows better fluid loss properties compared to standard G cement. Geopolymer C (60% fly ash, 40% silica fume) and geopolymer D (40% fly ash, 60% silica fume) exhibit the lowest fluid loss reading.
4. The increasing percentage of silica fume combined with fly ash shows substantial increase in compressive strength.
5. Geopolymer cement will undergo degradation when subjected to elevated temperature over its optimum value.
6. Geopolymer cement exhibits better physical and mechanical properties compared to standard Class G cement.

5.2 RECOMMENDATION

Due to expected long testing phase, it is recommended to have systematic planning and to run the experiment earlier than expected target period and systematically. Pros and cons from studies show the capacity of geopolymer cement as an alternative option for Portland cement substitute in the near future. Further improvement can be made in these areas:

- Geopolymer material

The research by utilizing a wider range of geopolymer materials shall be performed instead of using only fly ash and silica fume. The results will be more reliable and impactful. The choices of materials could be rice husk ash, wood ash and metakaolin.

- Pressure and temperature variation

This research is limited to only one elevated pressure and temperature condition. (120°C, 4000 psia). A wider range of temperature and pressure condition should be explored to get the optimum performance of geopolymer cement. The curing condition may be tested to HPHT (177°C), Ultra HPHT (204°C) or Extreme HPHT (260°C) conditions.

- Strength evaluation

In density measurement, this research was done on the basis of investigating the effects of using geopolymer in cement system. This explains the various density reading because of the amount of aluminosilicate materials used was made constant. Hence, from industrial view point it is unfair to perform a direct comparison on strength when the samples are of different density which suggests a different compactness. From the compressive strength analysis, the performance of geopolymer cement with a lower density is not representative although it already exhibits a higher compressive strength value. The geopolymer cement strength will theoretically be a lot greater than what was achieved in this paper. Thus for extension of the project, the density of slurry shall be designed to a constant value for a more significant result of cement strength.

- Feasibility

In adopting green cement technology, a projected economic model should be designed so that a clear view on industrial scale production can be established. In relatively small scale, the industrial by-products utilization was an excellent option with proven end product quality. However, the feasibility of green cement production for worldwide scale can only be justified with a good economic projection in place and favourable green cement supply and demand from the industry.

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APPENDICES

APPENDIX A

Recommended Practice for Testing Well Cements

ANSI/API RECOMMENDED PRACTICE 10B-2
FIRST EDITION, JULY 2005

ERRATA 1, JUNE 2006
ERRATA 2, JANUARY 2007

REAFFIRMED, JULY 2010

**ISO 10426-2:2003 (Identical), Petroleum and natural
gas industries—Cements and materials for well
cementing—Part 2: Testing of well cements**

AMENDMENT 1: Water-wetting capability testing



AMERICAN PETROLEUM INSTITUTE

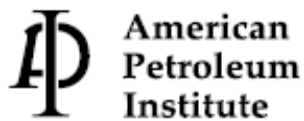


Specification for Cements and Materials for Well Cementing

API Specification 10A
Twenty-third Edition, April 2002
ANSI/API 10A/ISO 10426-1-2001

Effective Date: October 1, 2002

ISO 10426-1:2000
Petroleum and natural gas industries—
Cements and materials for well cementing—
Part 1: Specification



**Helping You
Get The Job
Done Right.™**



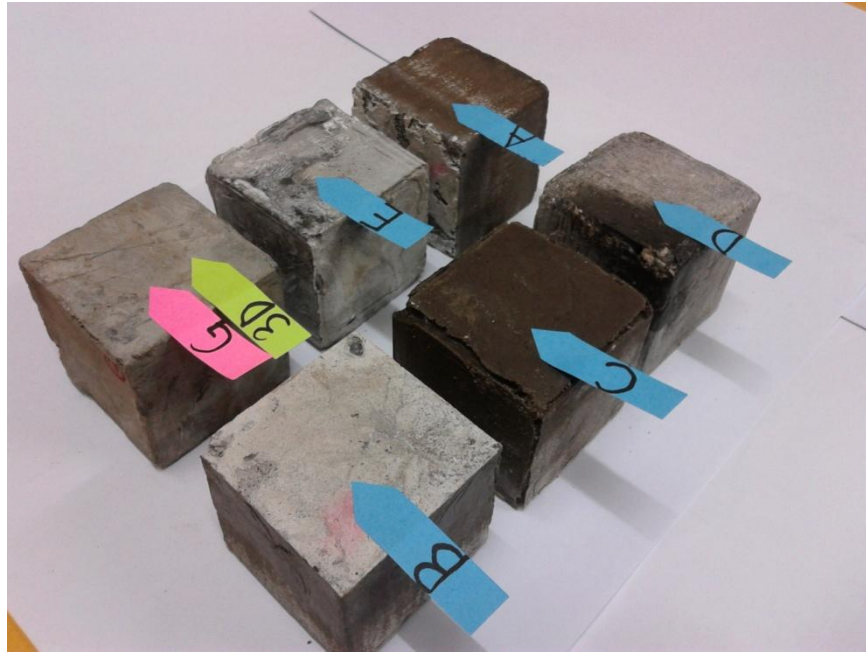
APPENDIX C

Table 2.1 Key features of API Oil Well Cement (API Specification 10A, 2002; Nelson and Michaux, 2006; Lafarge, 2009; Halliburton, 2009)

Cement Class	A	B	C	D	E	F	G	H
Recommended w/c, % mass fraction of cement	46	46	56	38	38	38	44	38
Recommended range of depth, m (ft)	0 to 1830 (0 to 6000)	0 to 1830 (0 to 6000)	0 to 1830 (0 to 6000)	1830 to 3050 (6000 to 10000)	3050 to 4270 (10000 to 14000)	3050 to 4880 (10000 to 16000)	0 to 2440 (0 to 8000)	0 to 2440 (0 to 8000)
Availability	O [*] grade, compatible with ASTM C 150, Type I Portland Cement	MSR ^{**} and HSR ^{***} grades, Comparable with ASTM C 150, Type II	O [*] , MSR ^{**} and HSR ^{***} grades, similar to ASTM C 150, Type III	MSR ^{**} and HSR ^{***} grades	MSR ^{**} and HSR ^{***} grades	MSR ^{**} and HSR ^{***} grades	MSR ^{**} and HSR ^{***} grades	MSR ^{**} and HSR ^{***} grades
Cost	Lower cost	Lower cost	More costly than ordinary portland cement	More costly than ordinary portland cement	More costly than ordinary portland cement	More costly than ordinary portland cement
Other features	Intended for use when special properties are not required	(1) Intended for use when conditions require moderate or high sulphate-resistance (2) lower C ₃ A content than Class A	(1) Intended for use when conditions require high early strength (2) The C ₃ S content and surface area are relatively high	(1) Required under conditions of moderately high temperatures and pressure (2) Retarded cement and retardation is achieved by reducing C ₃ S and C ₃ A, and increasing the particle size of the cement grains.	(1) Required under conditions of high temperatures and pressure (2) Retarded cement and retardation is achieved by reducing C ₃ S and C ₃ A, and increasing the particle size of the cement grains.	(1) Required under conditions of extremely high temperatures and pressures (2) Retarded cement and retardation is achieved by reducing C ₃ S and C ₃ A, and increasing the particle size of the cement grains.	(1) Basic well cement. (2) Thickening Times controllable with additives to prevent loss of circulation up to 250° F (~120° C)	(1) Basic well cement (2) Surface area is coarser than that of Class G (3) Thickening Times controllable with additives to prevent loss of circulation up to 450° F (~230° C)

*O: ordinary, **MSR: moderate sulphate resistant, ***HSR: high sulphate-resistant

APPENDIX D



Cement Samples after Curing



Compressive Strength Tester (left); Crushing of Cement Sample (right)