STUDY ON THE EFFECT OF SILICA FUME WITH LOW CALCIUM FLY ASH IN GEOPOLYMER PROPERTIES FOR OIL WELL CEMENTING

By

Maheswaren Sugumaran

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

JANUARY 2015

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CERTIFICATION OF APPROVAL

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Approved by,

………………………………
(Raja Rajeswary Suppiah)

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TRONOH, PERAK
JANUARY 2015

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 except 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.

MAHESWAREN SUGUMARAN

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ABSTRACT

Increasing concern of greenhouse gas emission had been a chief highlight in inducing global warming. Application of Ordinary Portland Cement (OPC) for oil well cementing contributes a large portion for these gases, and therefore, geopolymeric technology is proposed to help curb down CO_2 emission by replacing OPC. However, enough justification has to be shown to ensure the new technology is reliable enough to replace OPC for oil well cementing. This study aims to study the effect of silica fume addition to low calcium fly ash geopolymer cement by focusing on compressive strength and other properties such as thickening time, fluid loss and acid resistance test. Low calcium fly ash pose geopolymeric properties besides having a very low utilization rate which justify fly ash as our base material. Five different composition of varying silica fume (SF) content (0, 5, 10, 15 and 20%) was prepared and cured under wellbore condition (3000 psi and 200 F) under two curing time;8 hour and 24 hours, before being tested for compressive strength. Composition with 15% SF posed highest compressive strength of 5.6MPa (8 hours time) and 11.6MPa (24 hours time). Acid resistance test was conducted by immersing the 15% SF mould in 4 different HCl and 35% reduction of strength was observed for both mould cured at different time. Thickening time of 15% SF slurry was 21minutes (static) and 36minutes (dynamic) and fluid loss rate 32 ml. Further analysis on structure of cement was done via FTIR, EDX and FESEM studies. Geopolymer cement has good resistance up to 10% HCl enough to withstand acidizing operations in wellbore. However, higher amount fly ash shall be added to enhance the physical durability of cement, or else there will be a chance for formation gas to migrate through the annulus of the wellbore. Compared to Class G cement (without addictive), geopolymer cement pose higher compressive strength and lower thickening time with high fluid loss rate. Thus, it's proven that geopolymer cement can be applicable as a replacement material for Class G cement from a shallow to medium depth cementing process. It helps to reduce greenhouse gas emissions, reduces landfill dumping issues and saves cost. With available material and equipment, further study on this topic is recommended. Thus, the objectives of this project have been achieved.

Chapter 1

INTRODUCTION

1.1 Background of Study

Well cementing is a vital procedure in drilling which requires supervision in order to maintain the well integrity. Some of objectives for well cementing are to seal off the wellbore, and to reduce water breakthrough in wellbore. In some concern, it's used to geo-sequestration of carbon dioxide (CO_2). Cementing can be explained as a method of pumping cement slurry downhole to fill the annular space between casing and formation.

As present, Ordinary Portland Cement (OPC) is used as the common cement slurry in oil and gas industry. However, the Government of Canada indicated the implementation of OPC has generated to the largest volume of greenhouse gases. Carbon dioxide (CO_2) which is one of the major greenhouse gasses, actually accounts for 82% of the total. Yang (2009) further highlighted that 1 tonne of CO_2 is emitted by producing 1 tonne of OPC which accounts for greenhouse gas emissions. It was suggested that the most effective means to reduce carbon dioxide is to replace the OPC with material that has the similar performance which ranges from fly ash, silica fumes, blast furnace slag and rice husk. The replacement materials accounts for geopolymeric cement system, which contains high naturally occurring aluminosilicate materials It was mentioned that the geopolymeric materials contribute to the cost saving;10-30% less than OPC (Amir H. M, 2008).

Further study of geopolymer cement is crucial as it offers a number of advantages over the traditional technology. Geopolymer cement can be used to completely or partly replace OPC as it depends on industrial by-products (Dam,2010) Implications of geopolymer technology provide significant improvements in mechanical properties of the blend. To enhance the ideal performance of geopolymer cement, studies need to be done to understand its properties (Seabrook P., 2003). This research will zoom on the outcome of low calcium fly ash geopolymer properties with different value of silica fume. Experimental work will be carried out and testing will be done in order to identify the compressive strength, fluid loss level and thickening time of the cement slurry. This will be vital to ensure it is compatible for downhole oil well cementing.

1.2 Problem Statement

1.2.1 Problem Identification

Ordinary Portland Cement (OPC) the current conventional cement slurry used which releases tremendous amount of CO_2. It was reported that production of one tonne of OPC releases one tonne of CO_2 (Yang et al., 2009). Besides, OPC undergoes strength retrodegradation under acidic bottomhole environment. Duguid (2009) highlighted OPC undergoes depletion and lost all its sealing capability when tested with calcium hydroxide and calcium silicate hydrate. OPC requires high water content for mixing therefore reducing its workability approximately 5.5 gallons of water per sack. Besides, OPC is that is poses settling and plugging issue since sometimes bentonite or other addictives are not properly mixed. (Khalifeh et al.,2014). OPC provokes lower compressive strength at high temperature (140 bars) and high temperature (120°C) exposure (Arina B, 2010). This is because heat is generated during setting process. Therefore, most of the heat is transferred to the formation and mud since the temperature of cement is higher than the formation temperature. Insufficient heat causes a partial chemical reaction reducing large temperature anomalies and reduced mechanical strength or which we refer as strength retrodegradation. Thus, geopolymer is being considered as the best replacement for OPC, mainly due its low CO_2 emission as compared to OPC. Fly ash was considered as a good replacement for OPC due its mass production from coal burning in power plant. Ahmaruzzaman (2010) mentioned that the present utilization of fly ash ranges from 3% to 57% only, where remaining substantial amounts are disposed in landfill. Fly ash pose a hazardous threat to the environment as it has no ability to decompose. At the same time, fly ash geopolymer cement can give compressive strength around 50-80 MPa with a low water requirement (Andri Kusbiantoro,2012). On the other hand, silica fumes are always considered to be a good aluminosilicate source to optimize the compressive strength obtained from the geopolymer cement with fly ash only. (Duguid, 2009). This experimental study will try to optimize the compressive strength of fly ash with addition of silica fume.

In summary, problems are:

- Fly ash cannot be recycled and has very low utilization rate.
- OPC is emits high CO_2 and highly exothermic in reaction.
- OPC requires high water content for mixing and pose settling issue when not mixed properly.
- Compressive strength of geopolymer itself is low.

1.2.2 Significance of the Project

Replacement of current conventional cement slurry system with fly ash based geopolymer cement with various silica fume content in oil well cementing will reduce the emissions of greenhouse gases, and diminish the amount of energy required to manufacture the cement. Uehara (2010) tested OPC and geopolymer cement in acidic environment by submerging in 10% H_2SO_4 and proved OPC failed after 4 months and geopolymer with no major changes. Geopolymer CO_2 emission is 90% lower compared to OPC and less 50% energy required for production due to low process temperature (Hewayde et al,.2006). Fly ash was used as based material as it is capable of increasing the compressive strength and durability of cement. BAadur(2008) mentioned fly ash also increases the workability, resistance towards acid and reduces permeability and water ratio requirement. Silica fume will be to further add to enhance and optimize the compressive strength of the geopolymer cement. Silica fumes being industrial by-product with relative low utilization is also used to enhance it utilization level and compressive strength. Ubolluk (2010) mentioned that silica fumes enhance the bond strength and abrasion resistance therefore reduces permeability which helps much in gas-tight reservoirs.

1.3 Objective and Scope of Project

1.3.1 Objective

The study aims to assess the effect of silica fume addition to fly ash based geopolymer cement in improving the cement properties in terms of compressive strength primarily. The study will then focus on testing the thickening time, fluid loss and acid resistance on the cement slurry which produces the highest compressive strength. Further study such as viscosity and density might be also measured to validate the result compared to OPC slurry. Besides that, the advantages of using fly ash as base material and the best ratio of silica fume to enhance compressive strength will be identified and recommended for future improvement.

1.3.2 Scope of Project

The project is focused on designation of fly ash geopolymer cement in varies value content of silica fume to get the best compressive strength primarily. Testing of the cement will be done following the guideline of American Petroleum Institute API-RB-10B. The results will be compared to conventional OPC. It covers; (i) Fly ash cement with different silica fume value content; (ii) Testing of geopolymer cement properties such as compressive strength, thickening time, fluid loss and acid resistance; (iii) Comparison of fly ash based geopolymer with OPC for oil well cementing.

1.4 Relevancy of Project

The study of fly ash, silica fume and composition of geopolymer cement are relevant as it has been covered in the drilling subjects in prior years. Fly ash geopolymer cement poses the advantage of being environmental friendly and green cement. Besides, it reduces the CO_2 emission and drastically minimizing dumpsite issues. Silica fume helps to enhance the bond strength due to its high pozzolanic properties. As the industry is always looking for better alternative, geopolymer cement would be a relevant study to focus on. It helps the author to relate and refresh the theoretical knowledge obtained in 4 years study.

1.5 Feasibility of Project

This project will involve laboratory work and software such as Microsoft Office. Equipments are readily available in the cementing lab in Block 15, Universiti Teknologi PETRONAS. The materials involved in experiment have been purchased, received and will not cause health issues provided rules are followed and proper personal protective equipment (PPE) are worn. Project can be completed on time as framed in the Gantt chart within the give time period.

Chapter 2

LITERATURE REVIEW

2.1 Literature Review

2.1.1 Geopolymer and Goepolymerization

Geopolymer is a type of amorphous alumina-silicate cementatious material that pose a high strength, with good volume durability, stability and resistance to acids (Nasvi MCM, 2011). This amorphous solid phase transforms into semi crystalline phase after a long curing period after undergoing the reaction with alkaline activator, which will be discussed in the next subtopic. The most commonly used alkaline activator is Sodium Hydroxide. The term "Geopolymer" was defined and patented by Davidovits first around 1978 which mean a material consisting polymeric Si-O-Al bonds. Davidovits (1991) highlighted that formation of geopolymer is due to reaction of base material such as aluminum and silicate with high pH alkali metals found in alkali medium. This is referred as polymerization process. The main difference between OPC and Geopolymer cement is the way of getting its strength. OPC forms calcium-silicate-hydrates (CSHs) to attain strength ,while geopolymer cement uses the advantage of polycondensation process of silica and alumina precursors and a high alkali content (Rangan, 2008). Rangan(2008) also supported that polymerization is a process that cause quick chemical reaction under alkaline solution on aluminasilicates resulting three dimensional structure.Unfortunately, geopolymer cement has some drawback to be applied in our current industry. Dam (2010) mentioned that the high alkalinity of activator solution and sensitivity of polymerization effect to temperature pose a safety risk in the transportation infrastructure. Kambic(1999) mentioned that goepolymerization is an exothermic process that releases out heat. Alkaline activators such as sodium hydroxide or potassium hydroxide combined with silicate reacts with aluminum and silicon ions to induce polymerization. The result of hardening mechanism provides a 3D structure framework and it's a result of hydration of aluminasilicates (Davidovits,1991).

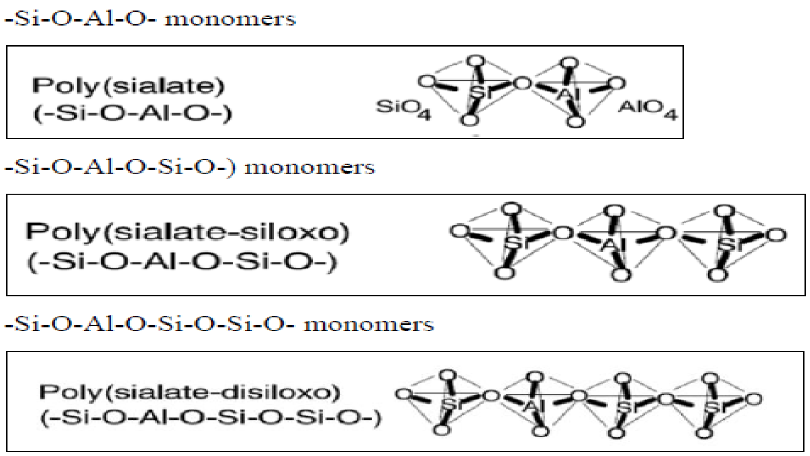


Figure 1: Goepolymerization chain process

2.1.2 Low Calcium Fly Ash

2.1.2.1 Introduction to Low Calcium Fly Ash

Coal burned in power plant produces byproduct called coal ash. It is residue left from burning coal, which is collected on an electrostatic precipitator or in a bag house (Wagih, 2006). In general, coal ash has two types which are bottom ash, collected at the bottom of coal furnace and fly ash, caught in the smokestacks. Fly ash is more used as it contains more mineral in its composition. During coal combustion at combustion chamber, the bottom ash sets down very quickly, while simultaneously the mineral impurities (clay, feldspar and quartz) undergo suspension and float out of the combustion chamber. As this material rise up and turns cool, they then solidify and crystallize are formed which is referred as fly ash. Fly ash is identified as materials that can vary significantly in composition. According to Ahmaruzzaman (2010), fly ash is considered as the 5th world’s highest raw material with India being the dominant producer. Fly ash is a byproduct not able to be recycled causing it to be landfilled. It takes around 113 million m^2 valuable agriculture land to landfill the fly ash (Ahmaruzzaman, 2010). This may cause severe environmental issue in near future. The world production of fly ash is currently greater than 400 million tones and is projected to increase significantly (Seabrook P., 2003). Fly ash also known as pulverized fuel ash produces cement when mixed with calcium hydroxide in state of calcium silica hydrate.

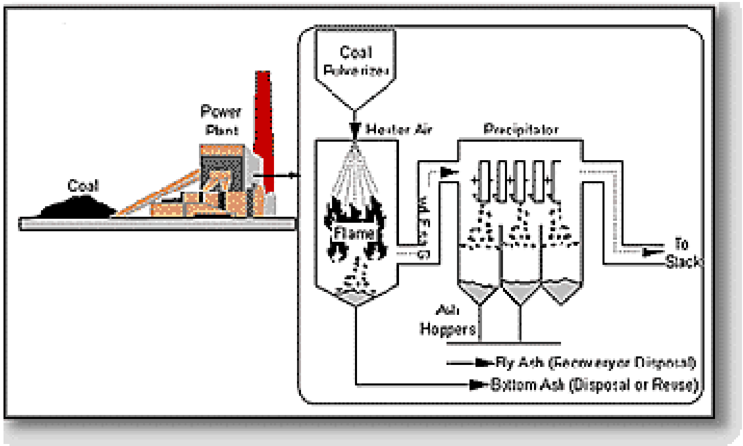


Figure 2 :Fly Ash Production

2.1.2.2 Classification of Fly Ash

Fly ash is defined as per its chemical composition and origin of coal which then concludes to Class C & F. Class C produced by burning low rank coals (sub-bituminous) and has cementatious property while class F produced by burning high ranked coal (anthracites) and has pozzolanic property in nature. (Wagih, 2006). According to American Society for Testing Material(ASTM C618), class F is defined as ash containing more than 70wt% SiO_2- +Al_2O_3+Fe_2O_3 and least lime content, while class C is defined as ash with high lime and 50-70wt% SiO_2- +Al_2O_3+Fe_2O_3.Class C fly ash has a higher amount of calcium, however, is less favorable as it was stated out that calcium was a contaminant producing different hydrate assemblages causing decrease in strength and rate of reaction (Xueying Li, 2013).The chief difference between Class F and C is the amount of calcium,silica,aluminium and iron(Ahmaruzzaman,2010). Blended fly ash with Portland cement can contribute to the cost saving as compared to disposal cost of fly ash when viewed in term of economy. The physical properties of fly ash, which is being far smaller than cement and spherical in shape made its durability where voids are filled. Application of fly ash can reduce the carbon dioxide emissions resulted from production of current OPC slurry system as well to reduce the dumpsite threats. (Malhotra, 2004).

Table 1:Composition of Fly Ash Class F & Class C, and Portland cement

Compounds	Fly Ash Class F	Fly Ash Class C	Portland Cement
Silicon Dioxide (SiO_2)	55%	40%	23%
Aluminum Oxide (Al_2O_3)	26%	17%	4%
Iron Oxide (Fe_2O_3)	7%	6%	2%
Calcium Oxide (CaO)	9%	24%	64%
Magnesium Oxide (MgO)	2%	5%	2%
Sulfur Trioxide (SO_3)	1%	3%	2%

Figure 3:Fly Ash Class F

Figure 4 :Fly Ash Class C

2.1.2.3 Benefits of Fly Ash

In term of cost saving, using geopolymer cement with fly ash as compared to Portland cement can help to save a lot of cost and enhance the economy. Application of fly ash in oil well cementing can avoid the materials to end up on a landfill sites, and reduce the carbon dioxide emissions resulted from production of current conventional cement system (Malhotra, 2004).). The use of fly ash as a partial replacement for Portland clinker in a blended cement can be seen as providing significant environmental benefits through a saving of the energy which would have been employed in producing and grinding the clinker submitted and a reduction in the amount of fly ash which must go to landfill(Barsom,2006).This new technology has posed various advantages, such as reasonable cost saving, enhancing the mechanical properties of the cement. The preparation of this cement slurry contributes very little amount of carbon dioxide due to no presence of Portland cement content. This reduces the emission of greenhouse gases emissions. Rangan (2008) mentioned the geopolymer cement requires less amount of water to prepare the slurry. Usage of fly means directs less amount of coal combustion products to be deposited on landfills and also to reduce the adverse air emission of fly ash as compared when it is disposed on landfill.

2.1.3 Cement Properties

2.1.3.1 Thickening Time

Thickening time is a measurement of time to identify the period where the slurry has the capable of being circulated when it is in the fluid state only. In other word, it is defined as time required for the cement slurry to reach maximum pumpable viscosity. Thickening time is assesses with cell aging equipment under simulated downhole conditions to have the real time data. The consistency of slurry to remain in fluid state at the expected downhole temperature and pressure is then recorded and compared with OPC. In most experimental and literature data, the acceptable thickening time is around 50-70Bc.HPHT Cement Consistometer is the device used as per API Testing for Cementing procedure to identify the thickening time of cement slurry. HPHT Curing Chamber is used to cure cement under the real wellbore condition, mostly at 150°F and 3000psi.Having high viscosity would reduce the thickening time. To increase thickening time, retards (sugar derivatives, cellulose derivatives and lignosulphonate) can be added while to reduce accelerators (calcium chloride and sodium chloride) can be added. Usually lower thickening time is preferred for an early compressive strength which are most applicable during surface casing string cementing and directional drilling plugs. Few common issues anticipated to have longer thickening time are delays in hardening, settling of slurry due to density, loss of hydrostatic head pressure and free-water pockets formation. Free formation water usually has high sulphate content which reacts and cause expansion and disintegration in the cement. It was highlighted that the cement slurry when pumped to certain depth downhole, it shall always remain in fluid state. (Fred L. Sabin, 1986).

2.1.3.2 Compressive Strength

The cement should be able to develop calculated compressive strength (cement strength) within estimated time when the cement is set at downhole. Compressive strength of a cement is defined as the maximum stress a material can withstand under crush pressure (McGraw-Hill, 2003). In nutshell it is the compression strength required to crush the cement by the cross sectional area of sample. Further study on tensile and compressive strength can also be tested if required.

In OPC, the major strength is most influenced by the presence of $3CaO.SiO_2$ (Tricalcium silicate) and $2CaO.SiO_2$ (Dicalcium silicate). Usually for most well applications, compressive strength of 500 psi (35 bar) is considered adequate. The strength is also affected by the water-to-cement ratio of slurry, curing time, curing temperature and curing time. Compressive strength can be calculated using strength testing machines available. The experimental data is then average as the final answer. In an extend, shear force can also be calculated when a proper bond is available between set of cement and cylinder (as casing).Using the formula, shear force can be calculated:

$$\underline{\mathbf{F_s(lb) = 0.969\sigma_c \ x \ d \ x \ h}};$$

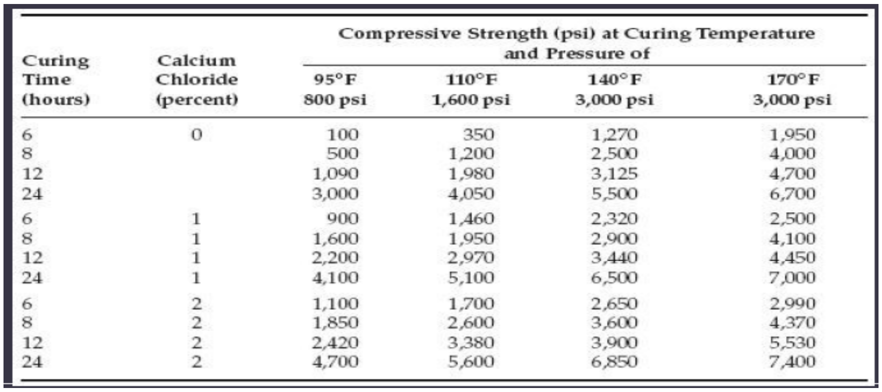
Where d = outside diameter of casing (inch)

h = height of the cement column (inch)

σ_c = compressive strength (psi)

Research and studies done has managed to prove that compressive strength increases with increase in temperature and slurry weight (Joel O. F., 2011). The presence of accelerator such as calcium chloride also enhances an early compressive strength of the cement downhole. Compressive strength tester equipment is used to calculate the compressive strength.

Table 2: Compressive Strength of cement at different curing time and temperature.



Curing Time (hours)	Calcium Chloride (percent)	Compressive Strength (psi) at Curing Temperature and Pressure of			
		95°F 800 psi	110°F 1,600 psi	140°F 3,000 psi	170°F 3,000 psi
6	0	100	350	1,270	1,950
8		500	1,200	2,500	4,000
12		1,090	1,980	3,125	4,700
24		3,000	4,050	5,500	6,700
6	1	900	1,460	2,320	2,500
8	1	1,600	1,950	2,900	4,100
12	1	2,200	2,970	3,440	4,450
24	1	4,100	5,100	6,500	7,000
6	2	1,100	1,700	2,650	2,990
8	2	1,850	2,600	3,600	4,370
12	2	2,420	3,380	3,900	5,530
24	2	4,700	5,600	6,850	7,400

2.1.3.3 Fluid Loss

Fluid loss is the rate at which cement slurry loses the water required for its fluidity through a permeable barrier, also called filtration rate. API Tests use Filter Press device for Fluid Loss Test, which the filtrate volume collected in

a 30-min time period is reported as the standard water loss (Nguyen, 2011). Uncontrolled fluid loss can resulted in formation fracture, resulting from increase in additional pump pressure needed to move the slurry as the slurry become more viscous as they lose water. To control, addictive such as latex and bentonite can be added to reduce fluid loss. HPHT Filter Press equipment was used to identify the amount of fluid loss from the best cement mould that gives the highest compressive strength.

2.1.3.4 Acid Resistance

This test is experimented to identify how much the cement durable against the aggressive environment such as acidic environment which is common in downhole condition. In most bottomhole, the minerals are usually abraised by carbonic acid. Study by Arjunan (2001) has shown that no universal or widely accepted standard procedures for acid resistance test exist, thus the testing can involve variable concentration of acid tested. Common acid used for testing is the sulfuric acid as the hydrogen sulfide presence basically generate problem to the cement. The cement will be immersed in solution of concentrated acid mostly from 2% to 10% hydrochloric acid, which can be left up to 24 weeks. The acid effect was then evaluated based on the change in the compressive strength and the change in mass after acid exposure(Wallah & Rangan, 2006). Protective measures must be taken care when handling the chemicals. Usually, sulfuric acid of 98% concentration is diluted by adding a volume of water using the formula:

$$m_1 V_1 = m_2 V_2$$

The dilution process must be done in the fume hood because the acid is strong and may affect the health when inhaled. Mixing of acid and water must not be in direct contact and high speed, so that any reaction between the two liquids can be handled effectively and safely.

2.1.4 Experimental Constant Variable

2.1.4.1 Curing Temperature and Pressure

After the geopolymer paste are prepared, the paste will be poured into mould for heat-curing or also termed as geopolymerization. Pressure and temperature greatly affect the mechanical development of geopolymer binders; however, a temperature threshold exists, beyond which strength gain rate is extremely low (Wallah & Rangan, 2006). Previous research has found that temperatures in the range of 50-80ºCare widely accepted values that are used for successful geopolymer hydration (Petermann & Saeed, 2010). Geopolymer gains strength with curing temperature as Silica and Aluminum readily dissolves from the source material with increasing temperature. However, at very high curing temperature (>100ºC), inter granular structure of geopolymer are possible to break up which could reduce its strength (Nasvi, Ranjith, & Sanjayan, 2012). Optimum curing pressure for higher strength of geopolymer cement is found to be lying between 2500-3000psi(Nasvi et al., 2012)**.**However, study found that increasing the curing temperature beyond 60ºC did not increase the compressive strength substantially (Hardjito, Wallah, Sumajouw, & Rangan, 2004).

2.1.4.2 Alkali Activator/Fly Ash Ratio

Preparation of fly ash-based geopolymer require the mixing of fly ash and a mixture of alkaline activators at specific alkaline activator/fly ash ratio(Bapat,2012). The most used alkaline liquid activator is a mixture of mixture of sodium or potassium hydroxide (NaOH, KOH) with sodium waterglass (nSiO2Na2O) or potassium waterglass (nSiO2K2O)(Palomo et al, 1999), where it found agreement by Xu’s work that the most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide (NaOH) and sodium silicate (Xu & Deventer, 2000). The ratio of alkaline activator to fly ash of 0.25, 0.30, 0.35, and 0.40 only are found to be workable. Previous study has discovered that the alkaline activator/fly ash ratio of 0.4 has the optimum amount of alkaline liquid, which could activate the fly ash in highest rate of geopolymerization comparing to other ratio (Al-Bakari et al., 2012). For the mass ratio of sodium silicate to sodium hydroxide, it is found that ratio of 2.50 is the best one (Rangan ,2008). This finding shows agreement with results from a journal where sodium silicate to sodium hydroxide ratio of 2.5 yielded highest compressive strength of the cement (Hardjito et al., 2004).

2.1.4.3 Water/Fly Ash Ratio

Water content in order to mix the geopolymer cement with fly ash is important to ensure the goepolymerization process takes place completely. In our experimental study ratio of 0.4 is considered. According to Malhotra (2004) the optimum compressive strength can be obtained with 0.33-0.4 ratio for water to fly ash value. 230g of fly ash was used in every sample preparation and 92g of water is used to prepare the sample in the mixer.

2.1.4.4 Molarity of Alkali Activator

Molarity of alkaline activator is basically known as the concentration of sodium hydroxide (NaOH). Various molarity of NaOH solution affect the strength of geopolymer paste fly ash. A study in 2011 revealed that a 12M NaOH solution produced the highest compressive strength for the geopolymer (Tiemeyer,2013). Study on the effect of NaOH molarity on geopolymer compressive strength also found that the compressive strength of geopolymer increases with increase in molar concentration of sodium hydroxide and best suited concentration is 12 with respect to safety in handling and the cost effectiveness as well(Vishie,2009)This shows agreement with a research finding which revealed that concentration of 12M produced the highest compressive strength for all days of testing. However, the research also discovered that as the strength of geopolymer cement was increased when the concentration of NaOH solution increased from 8M to 12M, but strength decreased when the concentration was increased from 12M to 14M (Panggunan, 2014)

2.1.5 Experimental Manipulative Variable

2.1.5.1 Silica Fume

Silica fume is an industrial waste product of smelting process of ferrosilicon alloy and silicon production. Silica fume are regarded as amorphous and non crystalline silicon dioxide formed by the silicon dioxide vapor. Khan (2011) mentioned that this vapor then condensates into tiny particle during reduction of quartz at 2000°C. Hisham (2013) summarized silica fume as byproduct of quartz reduction with coal in electric furnace. In physical, silica fumes are extremely fine and have very small grain size ranging from 10-100μm. Hisham(2013) supported that due to its small grain size and fineness, silica fume is a highly effective pozzolanic material . High content of silica in the fume enable silica fume to be effectively reactive material (Rangan, 2008). Khater (2013) mentioned in his research that compressive strength of geopolymer cement increases up to 10% ratio of silica fume. The maximum compressive strength with 10% ratio was 28MPa. The smaller the grain size, the higher the compressive strength can be achieved. Fatin (2013) mentioned that 10% of silica fume ratio enables the cement to achieve the highest compressive strength.

2.1.5.2 Curing Time

The best curing time was chose based on the time given and taken in real time operation on the rig. Curing time is referred as time taken for the hydration of goepolymerization process. In most cases, cementing job are given from 8- 24 hours to complete the process depending on the depth. For this experimental study, curing time of 8 and 24 hours were taken as curing time to cure the cement completely using the HPHT Curing Chamber. Panggunan (2014) mentioned that the longer the curing time, the better the compressive strength reading would be.

2.1.6 Previous study on Geopolymer cement

Many papers regarding Fly ash based geopolymer cement has been researched previously by students of UTP. Experiment done by Fatin (2013) was focused to identify the best parameters of variable in order to achieve the best compressive strength. The paper was more focused on identify the best water content ratio, best molarity of alkaline activator, best ratio of alkaline activator to fly ash and best curing temperature. Lastly, acid resistance test was also done by the student. Two types of alkali activator was proposed; sodium and potassium hydroxide. According to Rangan (2008) potassium has more K+ ion, leading to denser polycondensation reaction which produces a higher strength of compressive strength value. However Fatin(2013) concluded for low calcium fly ash, it is best to use sodium hydroxide. Sodium silicate is used together with sodium hydroxide for the goepolymerization process. Sodium silicate improves goepolymerization rate and enhances the mechanical properties of cement (Fatin,2013). In summary, according to Fatin (2013) research:

- Alkaline Activator : 12M of Sodium Hydroxide
- Sodium Silicate : Sodium Hydroxide ratio : 2.5
- Water Content Ratio : 0.4
- Curing Temperature : 60 °C.
- Alkaline Activator : Fly Ash ratio : 0.44

This data was used as base to design the experiment design and methodology. Permission to use this formula was obtained from Fatin.

Chapter 3

METHODOLOGY

3.1 Research Methodology

This project utilized both quantitative and qualitative data collection tools. Qualitative method is the way to gather required information from library, manuals, journals and other source to acquire adequate knowledge on geopolymer and current conventional cement technology. Quantitative method is study the effect of interdependent of dependant variable and manipulated variable. For this case, experimental tool is used. Methodology proposed is synced as per our required dependant variable result. Figure 5 portraits the methodology and the flow of the research for the whole project.

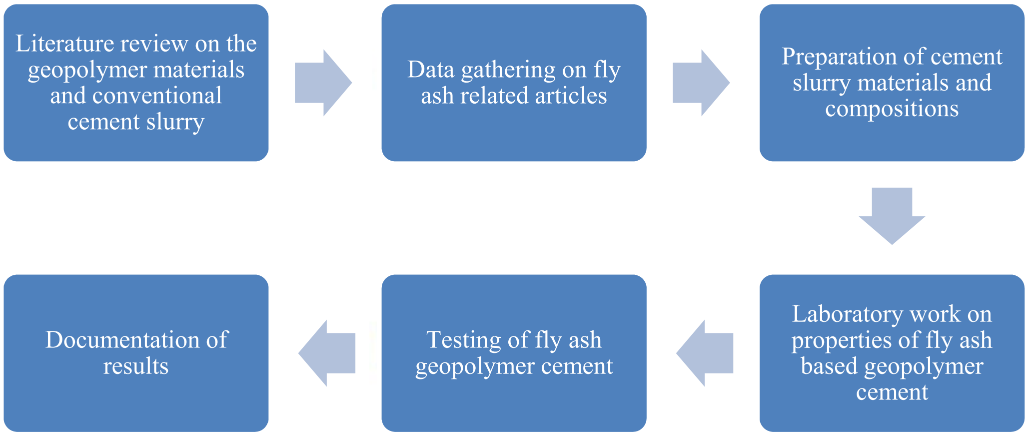


Figure 5: Research Methodology

Figure 5 : Research Methodology

3.1.1 Experimentation Design

First 5 different composition of geopolymer cement was mixed accordingly which varies by the content of silica fume value.

Composition 1 (with 0% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	0.0	230.0	92.0	26.4	65.7

Composition 2 (with 5% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	11.5	241.5	96.6	27.6	69.0

Composition 3 (with 10% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	23.0	253.0	101.2	28.9	72.28

Composition 4 (with 15% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	34.5	264.5	105.8	30.22	75.6

Composition 5 (with 20% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	46.0	276.0	110.4	31.54	78.85

All composition was made in two samples since in order to ensure that we meet two curing time which are 8 and 24 hours. This is to study the effect of curing time on compressive strength. All the moulds after being cured are tested for compressive strength and then the best cement slurry in term of highest compressive strength will be tested for fluid loss, thickening time and acid resistance.

3.1.2 Experimentation Procedure

To identify the properties of the geopolymer cement, it was planned to conduct few testing experiment which are compressive strength test, acid resistance test and lastly to identify the properties of the best cement mould which gives the highest compressive strength in term of density, fluid loss, thickening time and viscosity to be compared to Class G cement properties to ensure its compatibility for oil well cementing. Prior to that, cement mould was prepared and cured before the testing was taking place.

3.1.2.1 Preparation of Geopolymer Paste

Low calcium fly ash was dried and sieved in according to ASTM C136 standard to ensure the micron size of the particles are fine enough. The smaller the size of the grain, the better compressive strength can be obtained (Rangan, 2008). Prior to the preparation, SEM and XRD study was done to analyze the mechanical properties of the base material.50mm^{3}x50mm^{3}x50mm^3 cement mould cube will be produced, therefore ample amount of fly ash was prepared. The mould chamber can hold up to 8 blocks per time when it is to be cured with HPHT Curing Chamber. The needed material for this preparation is fly ash, sodium silicate, water, silica fume, and sodium hydroxide solution. The proportion of the amount of chemical used depends on the ratio referred to literature review as per below:

- Water to Fly Ash ratio = 0.4
- Sodium Hydroxide to Fly Ash ratio = 0.4 : 1
- Sodium Hydroxide Molarity = 12M
- Sodium Silicate to Sodium Hydroxide : 2.5

- Silica Fume : 5%, 10% ,15% and 20% of Fly Ash mass.

The amount of fly ash that was used in this experiment to prepare one cement mould is 230.0g. The amount of silica fume in mass was 5%,10%,15% and 20% mass of 230.0g of fly ash. The mass of alkali activator and water then depends on the total mass of fly ash and silica fume combined together.

Prior starting, sufficient volume of water and sodium silicate shall be prepared and mixed together for 5 minute in magnetic stirrer. This is to ensure the chemical and water has diluted and mixed well to ensure a complete process of goepolymerization. The solution is then mixed with constant speed mixer at 4000rpm. Fly ash is then added gradually and then followed by sodium hydroxide solution into the solution which is mixed in constant speed mixer. Let the mixture to mix for 10 minutes before adding silica fume. This is vital to keep the slurry at constant density. Face mask should be worn since fine silica fume may affect the respiratory process of human beings. Below is the composition of the formulation of the geopolymer cement without the addition of silica fume. Fatin (2013) mentioned that the composition was the best to give the highest compressive strength.

Fly Ash Mass,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230	92	26.3	65.7

The above composition was referred as base case to identify the compressive strength without the addition of silica fume. This is referred as 0% Silica Fume Fly Ash cement mould. Different composition was formulates for 5%, 10%, 15% and 20% of silica fume. The paste are then poured into mould and left in HPHT Curing Chamber for 200°F and 3000 psi. The curing time was differed into two; 8 hours and 24 hours to simulate real wellbore condition. The moulds will then be sent for compressive strength testing.

Separate mixing is used when mixing the fly ash with alkaline activator since it gives more adequate time for reaction to happen completely.(Duguid,2009). Mixing all the material at same time, will reduce the value of compressive strength.

3.1.2.2 Curing process

All cement cube produced is the submerged in brine water in HPHT Curing Chamber equipment at 3000 psi and 200 °F to simulate the real downhole environment for the cement slurry to cure. According to API-10A, the best curing time for the cement are 8 and 24 hours. Therefore, two curing time was used before proceeding to test the compressive strength.

3.1.2.3 Compressive Strength Testing

In this test, the prepared mould was tested with compressive strength tester to identify the maximum compressive strength the mould can withstand. The cement composition varied in terms of amount of silica fume added and as well as the curing time given for the cement to cure. This may affect the compressive strength of geopolymer cement. The procedure for the testing is as follow:

1. The cured cube sample is placed in the compressive strength digital testing machine. The adjustable surface above the sample is ensured to evenly touch and the nut is adjusted tightly.
2. The pump is switched on by pressing the ‘pump on’ button on the equipment software.
3. The load is applied uniformly until the mould fails by pressing the ‘start testing’ button o the software application. The mouse pressing must not be released until the cube fails.
4. The results are recorded automatically on the software.
5. Steps 1 until 4 are repeated for other samples.
6. The calculation of the compressive strength are as per the below formula.

Table 3 :Compressive Strength Calculation

$$\sigma_i = \frac{F_i}{A_i}$$

Where;

σ_i = the compressive strength, N/mm^2

F_i = the maximum load, N

A_i = the cross-section area at which load is applied, mm^2

3.1.2.4 Fluid Loss Testing

Once the best compressive strength has been obtained, the composition of the cement slurry is recorded and identified. The same composition slurry is mixed and tested for fluid loss test. This test was done using HPHT Fluid Loss Tester by preparing 500ml of cement slurry. This experiment is used to calculate the rate of water loss slurry through a permeable barrier and thus compared to Portland cement's fluid loss level. The equipment was set at 200 °F and 3000 psi

3.1.2.5 Thickening Time Testing

Once the best compressive strength has been obtained, the composition of the cement slurry is recorded and identified. The same composition slurry is mixed and tested for to record thickening time. HPHT Consistometer is used to run this experiment where the expected thickening time at 70 Bc is recorded. 500ml of slurry was prepared to run this experiment. This will help to justify if the given value is applicable to used for high depth well in terms of HPHT well.

3.1.2.6 Acid Resistance Testing

The best cement slurry is then tested on it's durability to withstand acidic downhole condition.Samples was used in 4 different concentration of hydrochloric acid and immersed completely for 72 hours. Using the formula , $m_1V_1= m_2V_2$, it is determined that 52.1 ml volume of 96% hydrochloric acid needed to be mixed with distilled water to obtain 500 ml of 10% hydrochloric acid, whilst 10.4 ml of 96% hydrochloric acid is required to obtain the one of 2% hydrochloric acid. All the works must be done in the fume hood. Firstly, a flask with capacity of 500 ml is filled with 250mldistilled water. Its purpose is to avoid direct contact of acid drops with the flask. 52.1 ml 96% hydrochloric acid is added into the conical flask slowly and carefully, then an amount of distilled water is added so that the total liquid volume in the conical flask is up to 500ml.The flask is moved gently to mix the two liquid, do not shake it roughly as the reaction are strong. The produced acid is 500 ml of 10% hydrochloric acid. The acid is poured into a beaker so that the cement specimen would fit to be immersed in that beaker for a period of 72 hours, which will be as the base case period (minimum period of supervision). The same procedure was repeated for 5 and 20 % hydrochloric acid concentration.

3.1.2.7 Sample Study

The best cement slurry sample was sent for XRD, FESEM, FTIR and EDX to study the composition and the reaction that enhances the compressive strength. Prior, silica fume and fly ash was sent for the latter study to study the chemical and mechanical properties.

3.2 Project Activities

The project activities must be directed towards the achieving the objectives of the project:

Table 4 :Objectives

OBJECTIVES	METHODOLOGY
To assess the effect of fly ash and silica fume in geopolymer cement properties	1) Preparation of NaOH solution, Na2SiO3 solution, and water 2) Mixing of solution with fly ash 3) Addition of silica fume 4) Goepolymerization
To investigate the advantages of fly ash based geopolymer cement	1) Compressive strength testing 2) Testing for resistance against acidic environment 3) Testing for thickening time and fluid loss

As planned, the research will be carried in 3 main phases which are Primary, Secondary and Final Phase. In the Primary phase, the activities are mainly focusing in background researches. Journals, papers and books are referred to have adequate knowledge on project. Detailed studies are executed to further enhance the technicality and relevancy of this project. Frequent meeting and discussion with Supervisor is done to clear doubts. A visit to industry player's lab is done prior beginning the experimental data to identify the current industry meets and demands. Required materials are purchased and prepared before stepping into the secondary phase. In the Secondary phase, planned experiments are set up and executed. The data are collected to identify the dependant and manipulated variable interdependent. The relationship between the data is plotted into a graph. Experiments are carried out until the ideal and expected result is achieved. Required corrections and adjustment is made to further fine the results accuracy.In the Final phase, range of data is collected and tabulated for proper presentation. Results are reviewed and sent to supervisor for improvement purpose. At the end, documentation preparation becomes the priority. A complete report is prepared and technical paper is produced for further publication. The subject is finalized and end after the documentation is evaluated and reviewed for viva purpose.

3.3 Key Milestone

Table 5: Milestone Activities

Milestone	Week
Primary Phase - **Project Proposal** - **Project Background** - **Objectives & Scope of Studies** - **Concept Research**	1 - 9
Secondary Phase - **Material Preparation** - **Data collection** - **Experimental Work**	10 - 21
Final Phase - **Finalization of Experimental Work** - **Preparation of report**	22 - 26

3.4 Gantt Chart

Below is the Gantt Chart proposed for the progress of my project. This ensures the continuity of my project to be on given fixed time frame.

Table 6: Gantt Chart FYP 1

Phase	FYP 1													
Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Project Title Selection Preliminary Study on Title Study on Factor affecting the required properties		■	■											
Background Study Purchasing of raw material Enhance Relevancy of the project			■	■	■	■								
Extended Proposal Visit to Cement Company Study on designing geopolymer cement slurry					■	■	■ ●							
Proposal Defense Receive purchased raw material Sample preparation						■	■	■ ●						
Planning of Experimental Work Submission of fly ash sample XRD study								■	■	■	■			
Interim Draft Report Receive XRD result. Analyze XRD results								■	■	■	■			
Submission of Interim Report										■	■	■ ●		

Table 7: Gantt Chart FYP 2

Phase	**FYP 2**													
Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Preparation of material Safety Briefing Lab Booking	🟩	🟩												
Preparation of composition Curing for 8 hours Compressive Strength Testing		🟩	🟩	🟩	🟩	🟩								
Progress Report 2nd phase of composition preparation Curing for 24 hours Compressive Strength Testing							🟩●	🟩						
Sample to be sent for XRD, FTIR, and FESEM Acid Test								🟩	🟩					
Pre Sedex Preparation for final draft report Receive sample study result Analyze the sample study report Comparison with Class G cement									🟩●	🟩	🟩	🟩		
Submission of Final Draft												🟩●		
Viva														🟩●

3.5 Tools and Equipment

Table 8 listed the required materials used in this project.

Table 8: Project Materials

No	Materials
1	Low Calcium Fly Ash
2	Sulphuric Acid
3	Silica Fume
4	Alkaline activator (NaOH)
5	Sodium Silicate
6	Water

Other main equipments required are shown below in Table 9

Table 9 :Equipments involved in the project

No	Equipments	Function
1	Compressive Strength Tester	Testing the compressive strength
2	HPHT Consistometer	Testing the thickening time
3	HPHT Fluid Loss Tester	Testing the fluid loss rate.
4	Constant Speed Mixer	Mixing the cement slurry
5	HPHT Curing Chamber	Curing of cement at 3000psi and 200 F

Chapter 4

RESULT AND DISCUSSION

4.1 Geopolymer Cement Slurry Production

Based on the stated formulation of geopolymer cement in methodology, all the cement slurry was prepared and cured for 8 and 24 hours for now. The cement was cured under HPHT Curing Chamber of 3000 psi and 200°F. 5 cement cubes was made, each one for each composition and was sent to testing in term of compressive strength.

All composition varied in term of the silica fume content which was added to enhance the compressive strength. The volume of alkali activator and water doesn't depend on fly ash mass instead the total solid mass after adding silica fume. Below is the list of composition used for the preparation of slurry.

Composition 1 (with 0% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	0.0	230.0	92.0	26.4	65.7

Composition 2 (with 5% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	11.5	241.5	96.6	27.6	69.0

Composition 3 (with 10% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	23.0	253.0	101.2	28.9	72.28

Composition 4 (with 15% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	34.5	264.5	105.8	30.22	75.6

Composition 5 (with 20% Silica Fume)

Fly Ash Mass,g	Silica Fume,g	Total Solid,g	Water,g	Sodium Hydroxide of 12M,g	Sodium Silicate,g
230.0	46.0	276.0	110.4	31.54	78.85

4.2 Results

4.2.1 X-Ray Diffraction (XRD) Analysis

4.2.1.1 Low Calcium Fly Ash

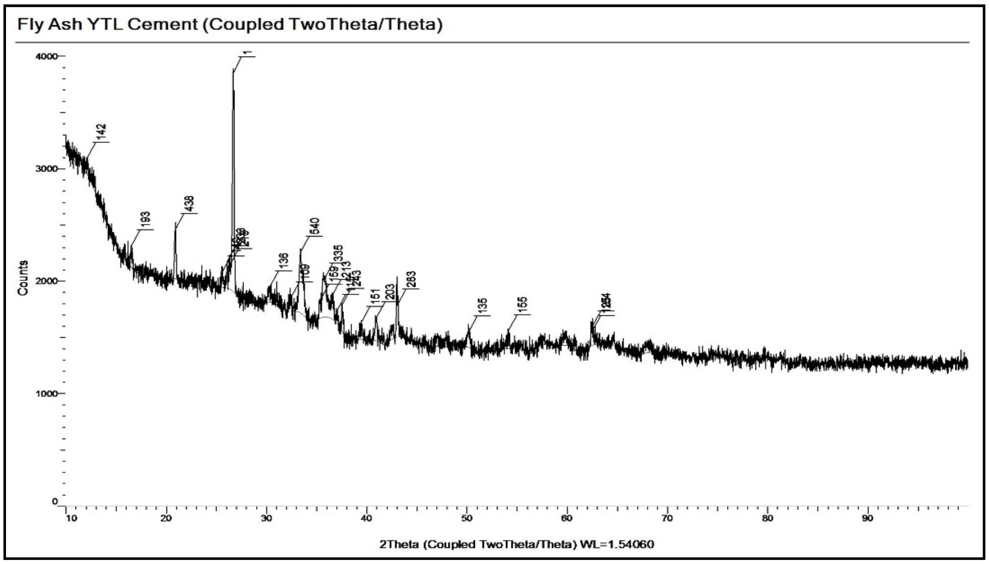


Figure 6 : XRD Analysis of Fly Ash

XRD analysis was done on low calcium fly ash that was sent to lab to study the chemical composition..XRD basically revolves between the Bragg's Law which is **$n\lambda=2d \sin\theta$** in which n is positive integer and;

D= distance between atomic layers in crystal

λ = *wavelength of the incident X-ray (1.54060)*

θ = *theta , the reflection angle of beam*

Based on the graph given, it was seen a high "spike" at about $2\theta = 28°$. This has proved the presence of cristobalite. Cristobalite is actually high temperature silica which has the same chemical formula of SiO_2. The advantage of this element is that it assist in binding effect of the cement and is only stable above 1470°C , in which its always reactive to the most full since most reservoir pressure is not above 1470°C and our curing temperature is relatively lower than latter. It was noted that cristobalite needs higher activation energy to form as compared to quartz which is more flexible. On the other, silica are an important component to induce goepolymerization and to enhance mechanical strength. The main component from XRD are cristobalite (SiO_2), sodium aluminum silicate ($Na(AlSi_2O_6)$), Tricalcium magnesium orthosilicate ($Ca_3Mg(SiO_4)_2$) and magnesium silicate (Mg_2SiO_4). XRD pattern has identified that the presence of Calcium-Silica-Hydrate (CSH) gel are the main product for occurring of hydration process together with some $Ca(OH)_2$. In normal cases, the cement strength development strongly depends on the amount of hydrates formed since it may cause reaction with calcium and aluminum causing an uneven proximity of reaction process. High amount of calcium available in network structure also helps to enhance mechanical strength.

4.2.1.2 Silica Fume

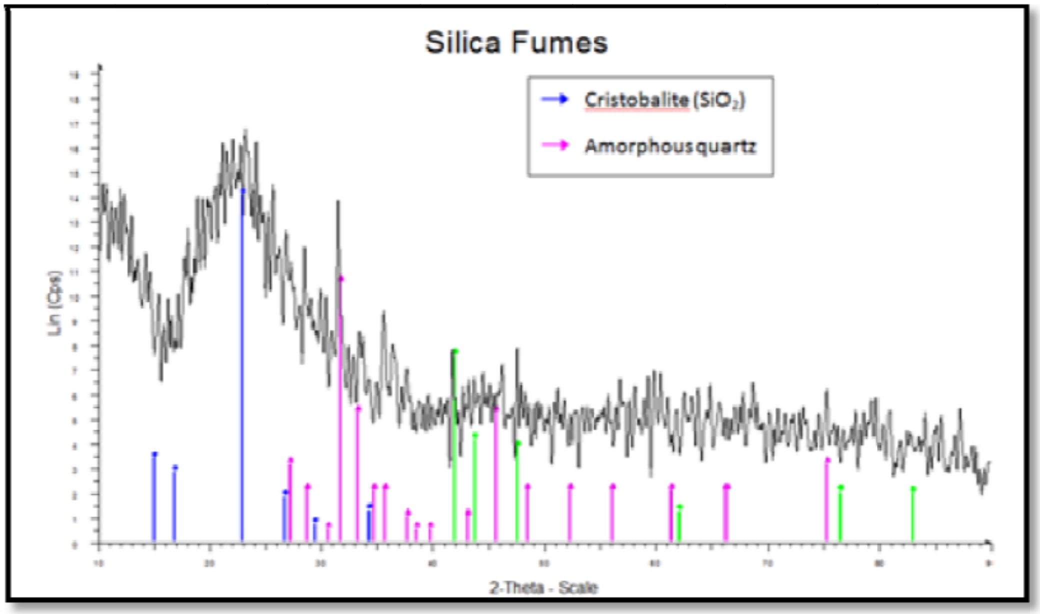


Figure 7 :XRD Analysis of Silica Fume

Figure 7 show that silica fume is mainly built with amorphous quartz and cristobalite. Presence of these two element helps to accelerate the geopolymer characterization in which the varying amount of it quantity can reflect the performance of the geopolymer cement. Mostly there are in the form of SiO2 however amorphous quartz is the non-crystalline allotropic form of silica and cristobalite is a type of crystalline structure. Amorphous silica is more flexible and easy to work on with, while cristobalite requires high amount of activation energy to form. . Cristobalite is formed due to the burning of rice husk at high temperature of 800°C. (M.M. Haslinawati, 2009). Cristobalite is only stable at temperature above 1470° C, below the said temperature, cristobalite will start to crystallize. Silica fume is known for its characteristics to reduce the viscosity of the slurry.

4.2.2 Compressive Strength Test

Once the cement moulds of 5 different composition was prepared and cured under 3000psi and 200F, it was sent to test the compressive strength of the cement mould. The cement moulds of 0%, 5%, 10%, 15%, and 20% was sent to test compressive strength. All the cement moulds was cured for 8 hours and 24 hours respectively to study on the effect of curing time.

Table 10 :Compressive Strength with different curing time

Composition (% of silica)	8 hours curing time strength (MPa)	24 hours curing time strength (MPa)
0	3.1	4
5	3.3	5.5
10	4.5	9.6
15	5.6	11.6
20	4.2	9.8

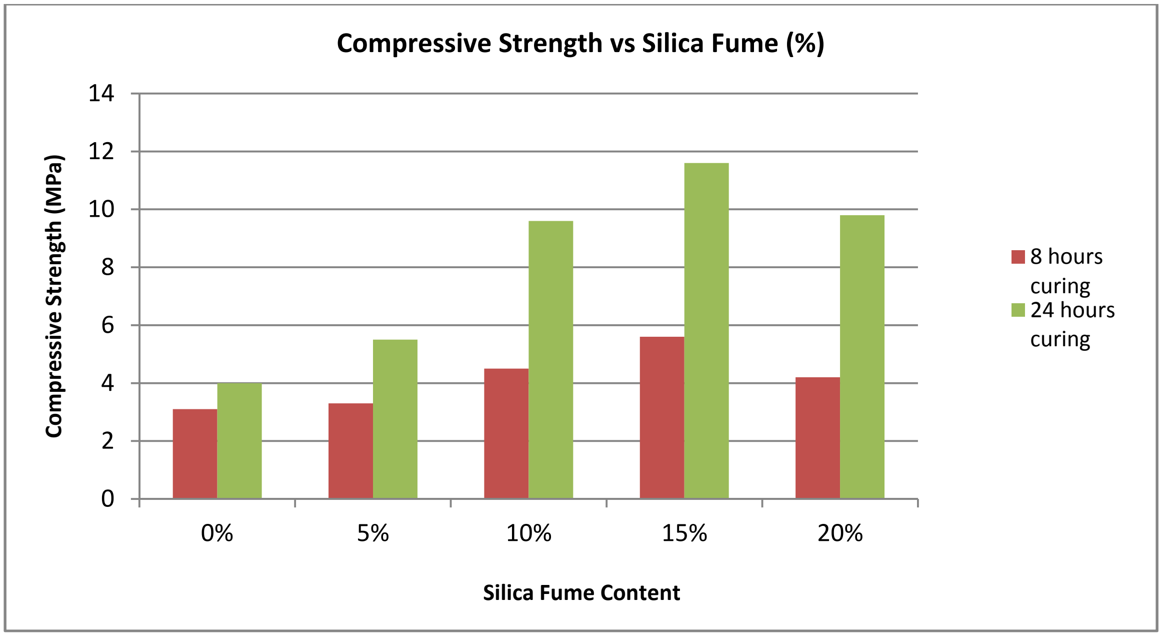


Figure 8 :Effect of Silica Fume on Compressive Strength

The above figure is the compressive strength for the cement mould which has been cured up to 8 hours and 24 hours under 200F and 3000psi.The above result has proved that the 15% Silica Fume addition; for both tested curing time has managed to increase and optimize the compressive strength to the highest compressive strength up to 5.6MPa and 11.6MPa respectively. The geopolymer without any silica added shown compressive strength of 3.1MPa and 4MPa respectively. Both geopolymer of different curing time, showed a decrease in compressive strength with addition of 20% silica fume. This has proved that 15% silica fume is the most optimized addition rate that can yield the highest compressive strength. With latter, compressive strength showed an increment of 65% (24 hours curing) and 45% (8 hours curing).

The presence of silica in the geopolymer mix helps to form crystalline structure that fills the void pores providing a denser and compact structure. This reflects a reason on the increment of compressive strength of the structure. Addition of optimized amount of silica (15%) helps to completely consume the hydrated lime, which helps to weaken the cement structure and provokes the CSH bonds. Malhotra (1996) stated that CSH bonds increases the additional strength of cement and helps to form extra nucleation process for the precipitation of crystalline structure to occur. Silica fume acts as reactant in total to increase the mechanical properties of the cement such as compressive strength and abrasion resistance.

Higher content of silica than the optimized value reduced the compressive strength of the cement. It was observed that the 20% silica fume composition experienced a crack on the surface when it was removed from the curing chamber. This is because the silica forms agglomerates in structure which inhibits the formation of geo-polymerization chain-process completely. This can be largely related to lesser water absorption by the silica material when present in large amount. The silica then acts as micro-filter due to its high specific surface area which reduces the water level to fill void spaces. Absence of water also reduces the wetting medium that is vital for goepolymerization process to occur. Addition of adequate water or other materials such as superplasticizer may help to reduce the formation of agglomerates. Davidovits (1999) mentioned that excessive silica forms two dimensional (2D) chains than three dimensional (3D) which pose a lower mechanical strength due to low compaction of the structure.

Higher curing time posed a higher mechanical strength due to the active and positive hydration process which poses a stronger and longer polycondensation chain. . Rangan (2008) supported that the longer the curing time, the higher the compressive strength. Author agreed that the size and finess of fly ash and silica fume also contributes to the compressive strength by accelerating a complete polycondensation process.

Once all samples have been tested, the cement mould with highest compressive strength was selected. The cement was re-prepared and tested for compressive strength after immersing in acid solution for 3days. Purpose is to observe if the acidic environment has some effect on the properties of the cement. Refer appendix for pictures of the crushed blocks.

4.2.3 Thickening Time Test

The thickening time for the best cement slurry which gives the highest compressive strength was tested using HPHT Consistometer. The cement slurry from composition of 15% Silica fume was chose for this test. The thickening time was measured for wellbore static and dynamic condition. Cement pH value was 10.3 while density was 13.8ppg

WELLBORE CONDITION	**THICKENING TIME (minutes)**
Static Gel Time	21
Dynamic (for 70Bc)	36

Figure 9: Thickening Time

4.2.4 Fluid Loss

Fluid loss test was performed on 15% silica fume slurry to identify the rate of water loss of the slurry The result was tabulated and graphed as per below:

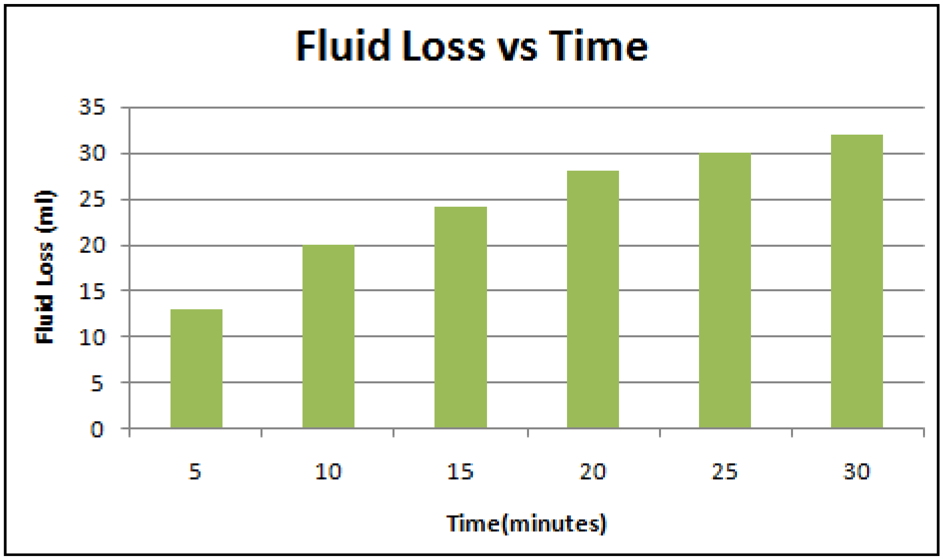


Figure 10 :Fluid Loss Rate vs. Time (minutes)

Based on the graph above, the maximum amount of fluid loss for every 500ml of slurry was recorded at 32ml. According to API-10A standards, the maximum acceptable standards of fluid loss vary by drilling depth and therefore it acceptable for medium to shallow well cementing.

4.2.5 Effect of Acid on Strength Retrogradation Test

The cement mould after being cured at 8 and 24 hours, the best mould which is with 15% Silica fumes was immersed in hydrochloric acid of different molarity solution for 72 hours before proceeding to test its compressive strength again.

Table 11: Compressive Strength after acid test

Type of Acid (%)	Compressive Strength for 8 hours (MPa)		Compressive Strength for 24 hours (MPa)	
	Without Acid	With Acid	Without Acid	With Acid
2% HCl	5.6	2.2	11.6	4.5
10% HCl		2.16		4.3
15% HCl		2.06		4.2
20% HCl		2		4.05

The acid test resistance has reduced the compressive strength of the cement block by approximately by 35% for both slurries. The durability of the cement is proved to be eligible for oil well cementing. However, it is proposed that geopolymer cement can be an alternative for the Class G cement at shallow depth which poses more acidic environment as compared to shallow depth where higher concentration of acid may occur. In term of acidizing operation, geopolymer cement can still be able to withstand since the operation uses about 12% of HCl only in which the compressive strength is still under a good reading. However, from physical observation of the cement after immersion in acid shows that large amount of fly ash maybe needed to withstand the acidic environment. Author believe well may experience invasion of gas into wellbore via annulus if less amount fly ash is used than the minimum recommended value. As per figure 10 and 11, the moulds remain solid and intact after 3 days of submersion and slight colour changes was observed. The acid has only penetrated the external section of cement while the inner composition remains intact and not affected by acid. This proved that the acid penetration level is small. Thokchom (2003) stated that the higher alkali content cement loses more weight than low alkali content cement . When compared for weight loss, geopolymer cement results seems to be better than the OPC cement weight loss indicating latter capability to withstand higher acidic environment(Panggunan, 2014).

The geopolymer cement actually deteriorates by fissures formation in the amorphous polymer or via the crystallization of zeolites. This reduces the stability of the aluminosilicate polycondensation chain that has been formed.

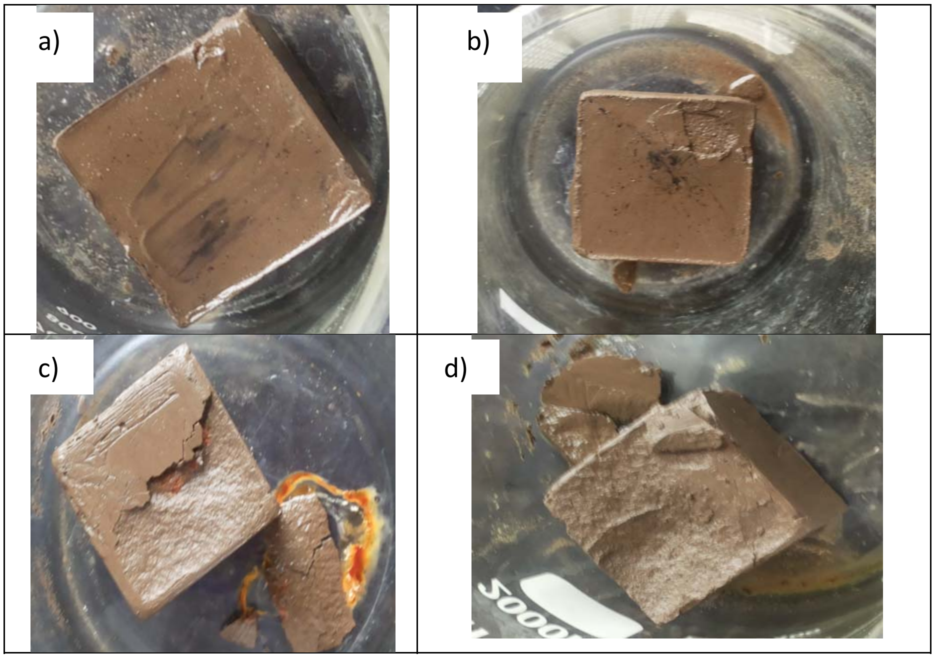


Figure 11 :Top View a) 2% , b) 10% , c) 15% , d) 20%

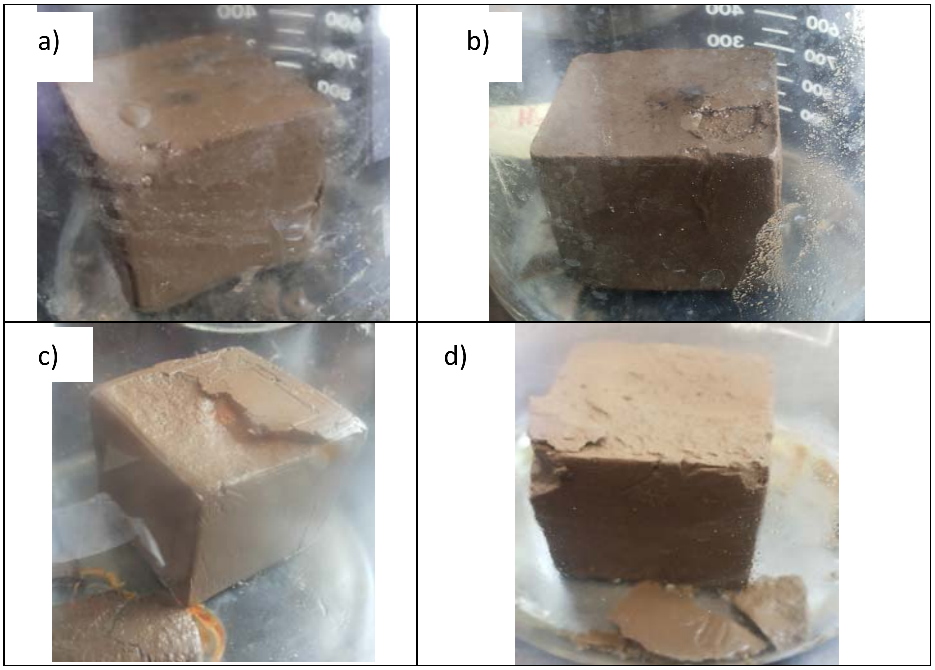


Figure 12:Side View a) 2% , b) 10% , c) 15% , d) 20%

4.2.6 Scanning Electron Micrograph (SEM)

SEM study was conducted to study the nature and morphology of fly ash and the composition with 0% and 15% silica fume. This was done to study the effect of silica fume on reaction mechanism and how does it alter the polymerization process.

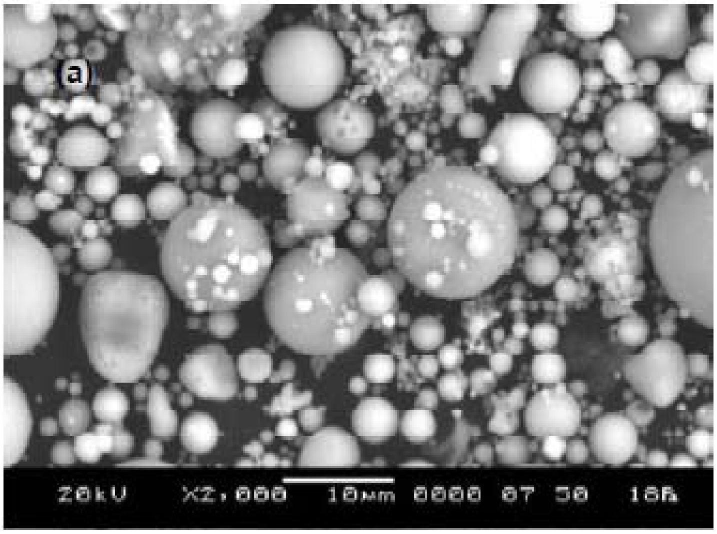


Figure 13:SEM Picture of Fly Ash only

The fly ash particle was found to be in spherical and round in size by origin. The diameter ranges from different sizes which are not even when tabulated to get the average diameter value. Possibility of having some other smaller particle inside the particle is possible since most of the particles are hollow in nature.

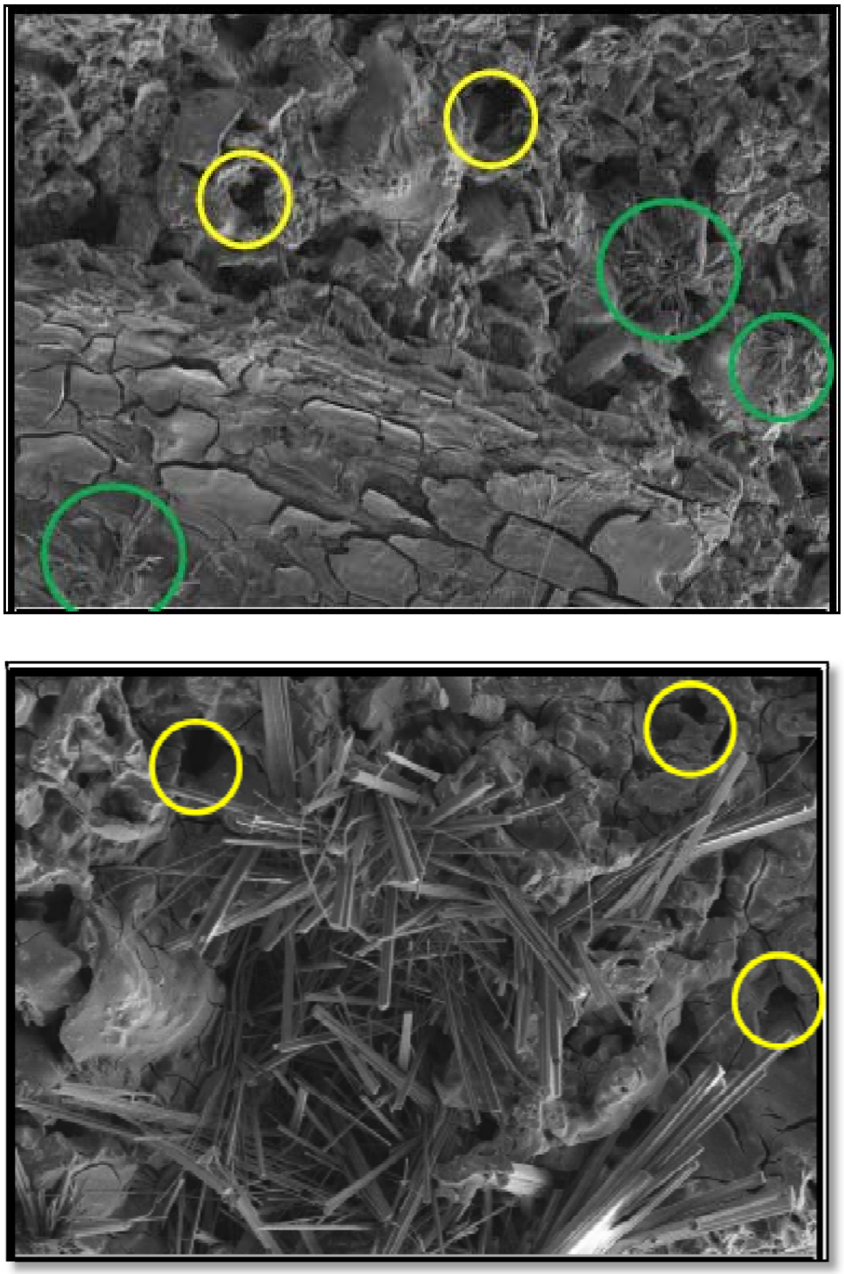


Figure 14 :SEM Picture of Fly Ash Geopolymer Cement of 0% Silica

Figure 14 shows the geopolymer that has undergone polycondensation and the precipitation without silica fume addition can be clearly seen in the image. The crystalline structure had filled the pore and formed a dense structure of geopolymer cement (green circle). Khater (2012) mentioned that the after certain days, the oligomer undergoes condensation and precipitation to form a crystalline structure Several void pores (yellow circle) have been identified too. This explains the need of silica fume in order to be able to fill up the pore space and making the structure denser. Presence of pores reduces the mechanical strength of the cement..The chief difference observed here is that the hollow sphere of fly ash particle has been filled with other elements making them intact. This is because the exterior layer of the hollow sphere was broke by sodium particle which allowed smaller particle to penetrate into the bigger particle. When the entire hollow sphere was completely broke, thus aluminosilicate formation takes place. This explains the hardening mechanism in goepolymerization process.

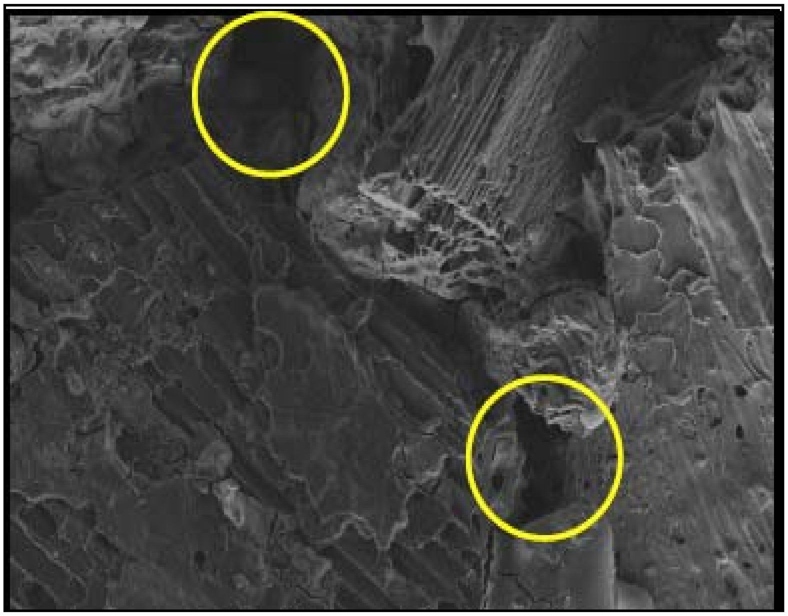


Figure 15:SEM Picture of Fly Ash Geopolymer Cement of 15% Silica

Figure 15 shows the structure of geopolymer cement cured for 24 hours with 15% silica fume added to the composition. Having a high amount of silica has managed to the reaction to completely take away present hydrated lime that weakens the aluminosilicate bonds. A denser and smoother layer of cement was observed indicating the reaction was complete and more compact structure has been formed. Silica has managed to fill the pores left void in the structure to make the structure denser and to pose higher compressive strength. However, some cracking (yellow circle) was found on the image although physically it did not show any cracking as what observed for 20% silica fume composition. Khater (2012) stated that the cracking inhibits the3-D crystalline formation which reduced the compressive strength. Davidovits (1999) supported that too high silica content accelerates 2-D crystalline structure instead of 3-D structure which weakens the cement strength. Therefore, adequate amount of water needs to be considered to ensure a complete reactivity of the polycondensation process. With this higher reading of compressive strength can be obtained.

4.2.7 Fourier Transform Infrared Spectroscopy (FTIR)

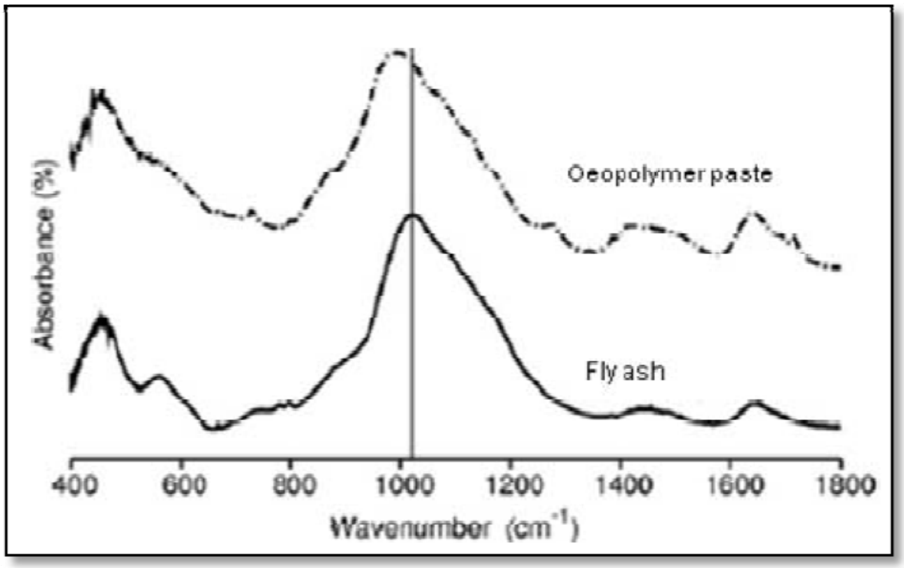


Figure 16 :FTIR of Fly Ash and Fly Ash Geopolymer Cement

Both the line shows a big difference in terms of the wave number. The geopolymer paste had a highest vibration at 900 cm^{-1} while the fly has at 1000cm^{-1}. According to Sathia (2008) the shift to the lower frequencies for fly ash geopolymer paste is primarily due to the Al^{4+} penetrating into the SiO_2 structure. Higher amount of Al^{4+} will enter the structure if we experience a larger shift in the vibration value, which may weaken the stability of the naturally occurring silica bonds. Therefore, the addition of alkali activator has managed to further secure the silica bond and enhance it strength to the highest level. The stretch vibration between 850 and 1000cm^{-1} quantifies the Si-O-Si bonds and the study of chemical changes at that peak can be identified.

4.2.8 Comparison EDX (Energy Dispersive X-ray) Study

This study was analyzed to study the element present in the composition and analyze how it affects our responding variable. The same sample of 0% and 15% silica fume was used to be studied under this test.

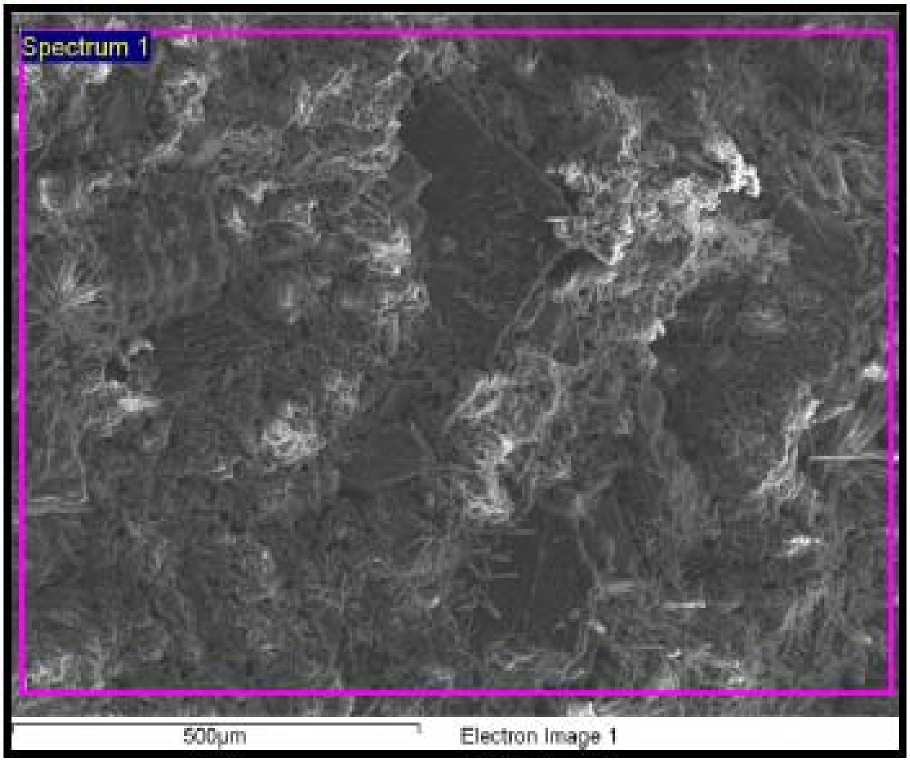


Figure 17: EDX – 0% Silica Fume

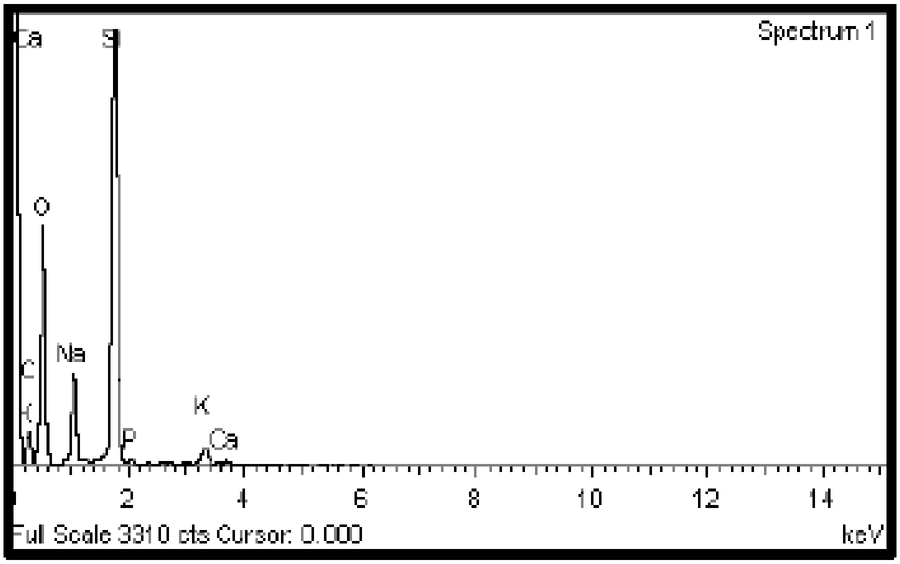


Figure 18: EDX Element Classification – 0% Silica Fume

Table 12: EDX Element Classification – 0% Silica Fume

Element	Weight (%)	Atomic (%)
C	9.13	13.80
O	54.32	61.66
Na	8.65	6.84
Si	25.76	16.66
P	0.47	0.28
K	1.33	0.62
Ca	0.33	0.15
TOTAL	**100.00**	

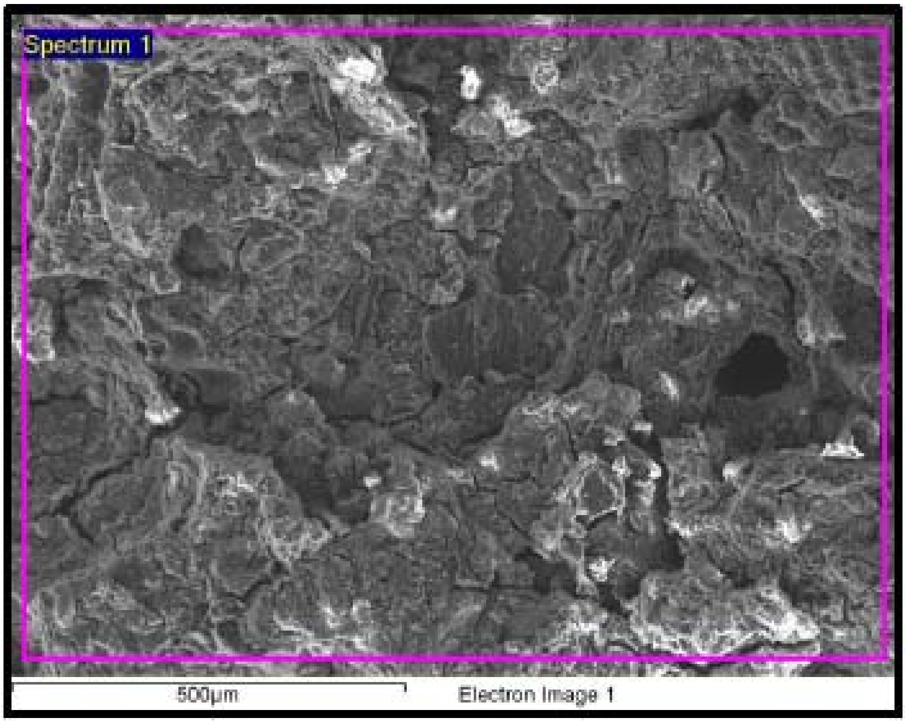


Figure 19: EDX – 15% Silica Fume

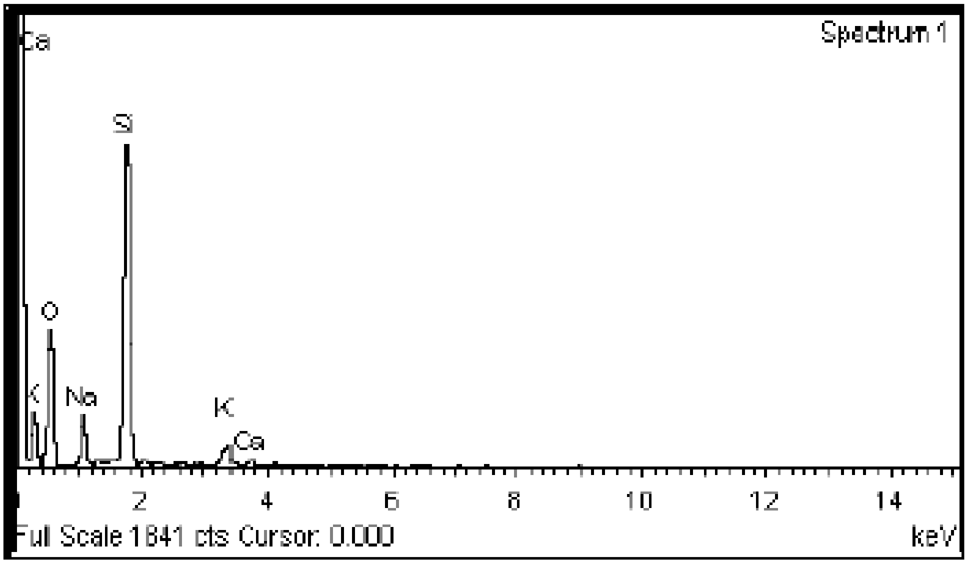


Figure 20 :EDX Element Classification – 15% Silica Fume

Table 13 :EDX Element Classification – 15% Silica Fume

Element	Weight (%)	Atomic (%)
O	54.29	67.28
Na	7.87	6.79
Si	33.96	23.98
K	2.68	1.36
Ca	1.19	0.59
TOTAL	**100.00**	

The result has shown the element and their quantity respectively.

For 0% SF cement, Oxygen and Silica showed a high percentage value which then reasons the formation of silica dioxide (80%). This bond helps in formation of aluminosilicate network structure which results in hardening mechanism of cement.

For 15% SF cement, Si value proved to be higher than latter by 31% due to the addition of silica fume while value of oxygen remained unchanged. Presence of silica has enhanced the compressive strength of the cement mould.

4.3 COMPARISON WITH OPC

As mentioned in objectives, the properties of the low calcium fly ash cement were compared to study on the feasibility of the cement for oil well cementing procedure. We would be comparing with properties tested such as compressive strength, thickening time and fluid loss.

Class G cement block was prepared in this experiment without the addition of addictives to test its compressive strength, thickening time and fluid loss. The Class G cement was cured for 24 hours under the same curing pressure and temperature of geopolymer cement.

Table 14 :Comparison Table

Properties	**Class G cement**		**Fly ash geopolymer cement**	
	8 hours	24 hours	8 hours	24 hours
Compressive Strength	4.6MPa	8.3MPa	5.6 MPa	11.6MPa
Dynamic Thickening Time	2 hours		36 minutes	
Fluid Loss	5.9ml		32ml	

In term of compressive strength, fly ash geopolymer cement pose higher compressive strength. However, with the addition of addictive to Class G cement, higher compressive strength can be obtained with Class G.

According to API-10A standards, most minimum acceptable thickening time is 30 minutes. With our test, we obtained 36 minutes. Addition of retarders such as sugar and lignosulphate may help to delay thickening time depending on the well operation for cementing process.

High fluid loss is seen with geopolymer cement which is not accepted in the industry. A more proper mitigation has to be studies to reduce fluid loss.

Chapter 5

CONCLUSION

5.1 Conclusion

The study on the effect of silica fume addition on low calcium fly ash to increase its compressive strength and to study it reliability for oil well cementing was done. 5 different compositions with 0, 5, 10, 15 and 20% silica fume was prepared and tested. Testing was done after curing the cement under wellbore condition for 3000 psi and 200 F for two different curing times; 8 and 24 hours. Compressive strength of the cement blocks of two different curing time was tested and recorded. Composition of 15% Silica Fume (SF) posed the highest compressive strength of 5.6MPa (8 hours curing) and 11.6MPa (24 hours curing). The same composition was tested for strength after being immersed in HCl of different molarity for 3 days. Reduction of 35% compressive strength was observed after being immersed in acid solutions. Next, slurry of the highest strength composition was tested for thickening time and fluid loss. Thickening time was recorded at 36 minutes (dynamic) and 21 minutes (static). This value has to be increased by the use of retarders to delay the thickening time depending on well operations. Fluid loss was 32 ml for every for 500ml. Fluid loss rate is too high for this geopolymer cement as compared to Class G cements that yields about 5.9ml only. In terms of effect of acid on strength retrogradation, geopolymer cement can resist up to 10% of HCl. This is applicable enough whenever the acidizing process takes place. Since the physical durability seems to be low, its suggested to add more fly ash to withstand the corrosion.

In nutshell, fly ash based geopolymer cement can be applicable as a replacement material for Class G cement from a shallow to medium depth cementing process. Addition of addictive may enhance the studied properties of the cement. It helps to reduce greenhouse gas emissions, reduces landfill dumping issues and saves cost. With available material and equipment, further study on this topic is recommended. Thus, the objectives of this project have been achieved. The reduction of chemical usage and reduction of carbon dioxide gas has been achieved. Issue on landfill dump of fly ash can also be reduced. However, geopolymer cement also posed the same problem statement that it requires high amount of water to enhance it workability thus reducing settling problem.

5.2 Recommendation

Suggested recommendations are to perform experimental work to compare carbon dioxide emission from cement. Besides, also to perform experimental work adding more water and superplasticizer to enhance the compressive strength and workability with increasing silica fume. Study on effect of fly ash and silica fume particle size on compressive strength shall be focused. Effect of alkaline activator molarity on the viscosity of the cement shall also be tested. Ways to reduce the fluid loss level shall also be focused and implemented. In regard of acid test, weight loss test after acid immersion test to identify the corrosion rate by the acid. Lastly, testing of fly ash performance with different compositions with added addictives to identify further application of geopolymer cement can be considered for further improvement.

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APPENDIX

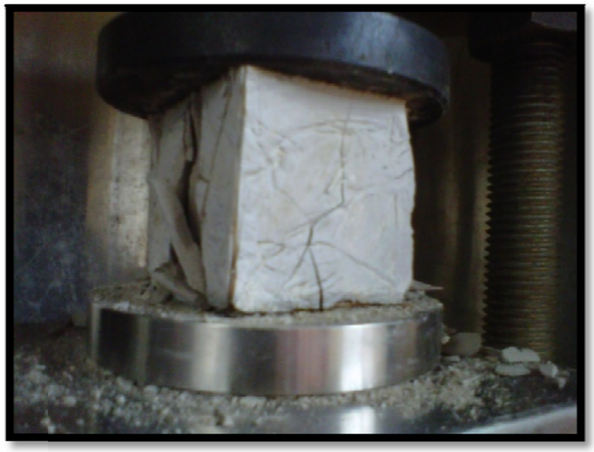


Figure 21: Compressive Strength Testing

Figure 22: Compressive Strength Tester designed to test the compressive strength

Figure 23: Constant Speed Mixer designed for mixing to produce pastes

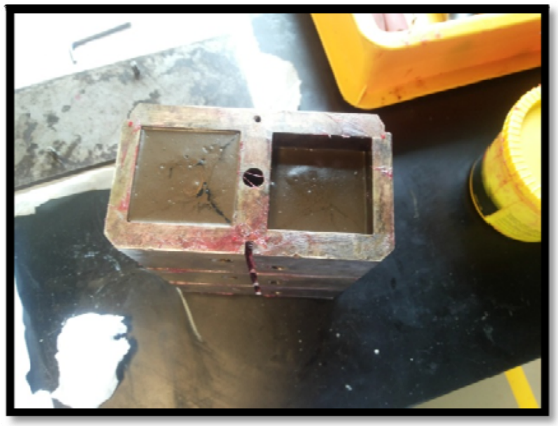


Figure 24 :Cement Mould before curing

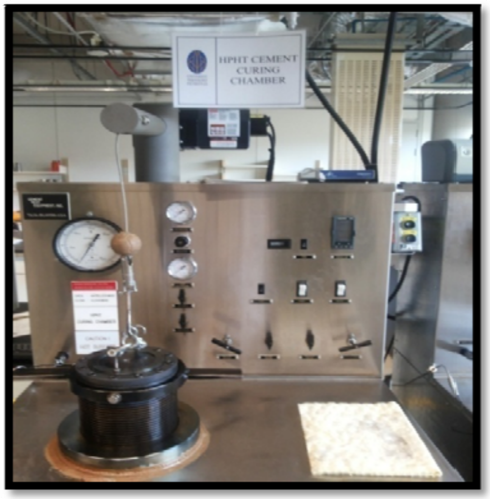


Figure 25 :HPHT Curing Chamber

Figure 26 :HPHT Fluid Loss Tester

Figure 27 :HPHT Consistometer

Figure 28 :Silica Fume

Figure 29 :Sodium Silicate solution

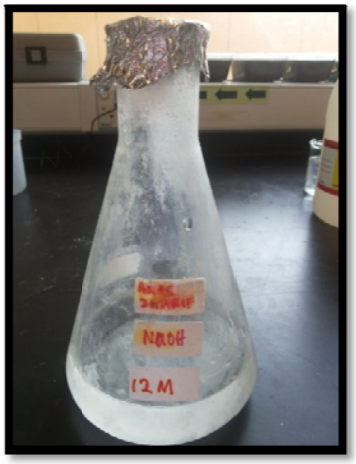


Figure 30:12M Sodium Hydroxide

Figure 31 :Cement Block after curing

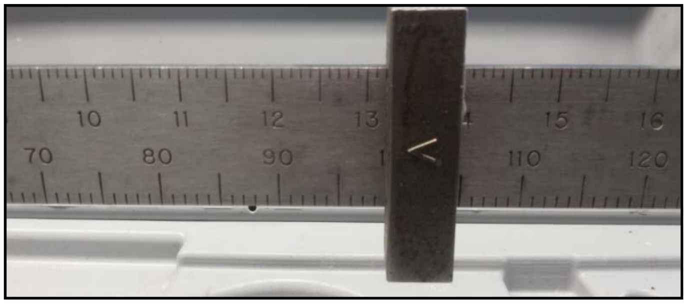
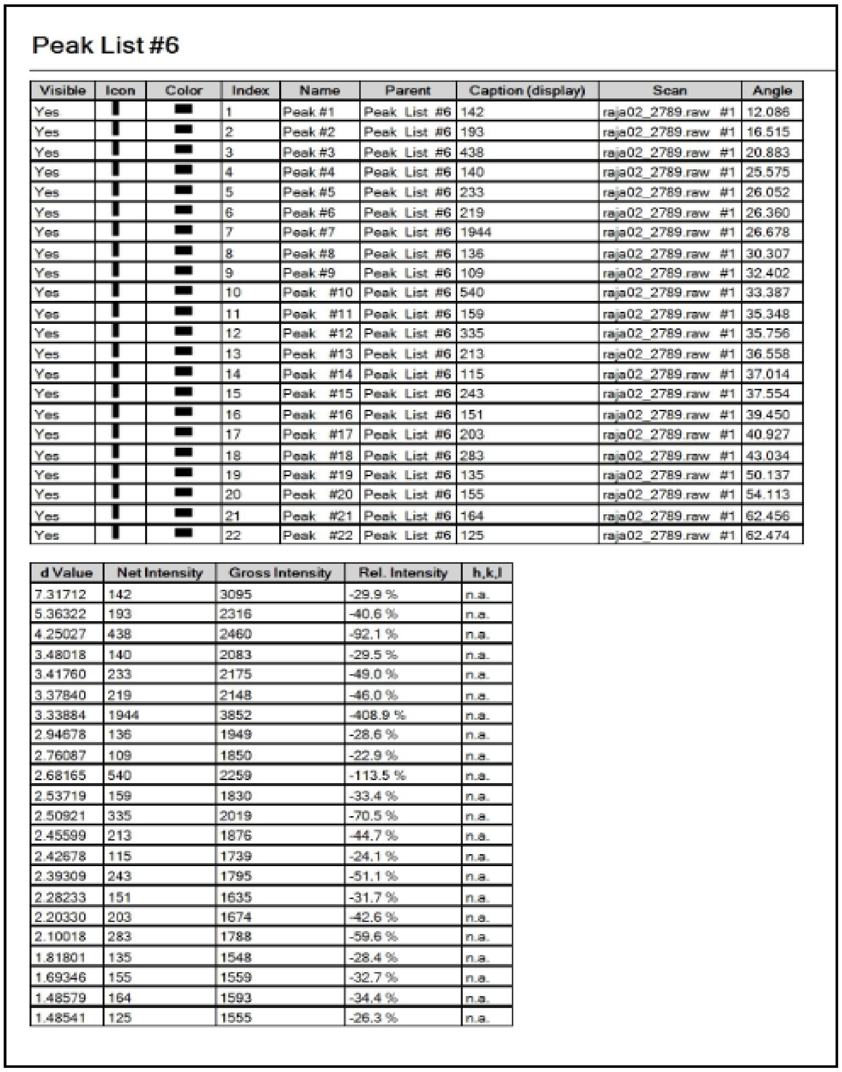


Figure 32: Cement Density (13.2ppg)

Figure 33: Crushed Blocks after Compressive Strength



Peak List #6

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Yes	▮	▬	3	Peak #3	Peak List #6	438	raja02_2789.raw #1	20.883
Yes	▮	▬	4	Peak #4	Peak List #6	140	raja02_2789.raw #1	25.575
Yes	▮	▬	5	Peak #5	Peak List #6	233	raja02_2789.raw #1	26.052
Yes	▮	▬	6	Peak #6	Peak List #6	219	raja02_2789.raw #1	26.360
Yes	▮	▬	7	Peak #7	Peak List #6	1944	raja02_2789.raw #1	26.678
Yes	▮	▬	8	Peak #8	Peak List #6	136	raja02_2789.raw #1	30.307
Yes	▮	▬	9	Peak #9	Peak List #6	109	raja02_2789.raw #1	32.402
Yes	▮	▬	10	Peak #10	Peak List #6	540	raja02_2789.raw #1	33.387
Yes	▮	▬	11	Peak #11	Peak List #6	159	raja02_2789.raw #1	35.348
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Yes	▮	▬	13	Peak #13	Peak List #6	213	raja02_2789.raw #1	36.558
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Yes	▮	▬	18	Peak #18	Peak List #6	283	raja02_2789.raw #1	43.034
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Yes	▮	▬	20	Peak #20	Peak List #6	155	raja02_2789.raw #1	54.113
Yes	▮	▬	21	Peak #21	Peak List #6	164	raja02_2789.raw #1	62.456
Yes	▮	▬	22	Peak #22	Peak List #6	125	raja02_2789.raw #1	62.474

d Value	Net Intensity	Gross Intensity	Rel. Intensity	h,k,l
7.31712	142	3095	-29.9 %	n.a.
5.36322	193	2316	-40.6 %	n.a.
4.25027	438	2460	-92.1 %	n.a.
3.48018	140	2083	-29.5 %	n.a.
3.41760	233	2175	-49.0 %	n.a.
3.37840	219	2148	-46.0 %	n.a.
3.33884	1944	3852	-408.9 %	n.a.
2.94678	136	1949	-28.6 %	n.a.
2.76087	109	1850	-22.9 %	n.a.
2.68165	540	2259	-113.5 %	n.a.
2.53719	159	1830	-33.4 %	n.a.
2.50921	335	2019	-70.5 %	n.a.
2.45599	213	1876	-44.7 %	n.a.
2.42678	115	1739	-24.1 %	n.a.
2.39309	243	1795	-51.1 %	n.a.
2.28233	151	1635	-31.7 %	n.a.
2.20330	203	1674	-42.6 %	n.a.
2.10018	283	1788	-59.6 %	n.a.
1.81801	135	1548	-28.4 %	n.a.
1.69346	155	1559	-32.7 %	n.a.
1.48579	164	1593	-34.4 %	n.a.
1.48541	125	1555	-26.3 %	n.a.

Figure 34 : XRD Analysis detailed report