Geopolymer based Oil Well Cementing Systems using Silica Fume

by

Tan Hui Xian

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Geopolymer based Oil Well Cementing Systems using Silica Fume

by

Tan Hui Xian

A project dissertation submitted to the

Petroleum Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(PETROLEUM ENGINEERING)

Approved by,

____

Associated Professor Dr. Nasir Shafiq

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

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.

____

TAN HUI XIAN

ABSTRACT

Nowadays, ordinary Portland cement is used extensively in the well cementing operations, due to its low cost and widespread availability of limestone, clay and shale. However, there are two big challenges presented with the usage of Portland cement for oil well cementing purpose, one is the occurrence of cement failure while the other one is the vast emission of carbon dioxide. The objective of this project is to develop geopolymer based oil well cementing systems by utilizing silica fume, as a better substitute for the current conventional Portland cement. Throughout the project, five types of cement slurries are prepared and laboratory tests are carried out to test their rheology properties, filtration loss and compressive strength. All these tests were carried out at a pressure ranging from 1000 psi to 3000 psi with varied temperatures (100°F, 150°F and 200°F), representing different oil well conditions. The test results show that the developed geopolymer cements appear to be in ideal plastic viscosity range while geopolymer cements with 20% and 30% of silica fume perform well in term of yield point. As for filtration loss, geopolymer cements with 10%, 20% and 30% of silica fume exhibit desired readings at temperature of 150 °F. Silica fume is proved to have a significant effect in improving compressive strength and the geopolymer cement with 30% of silica fume is the cement slurry with optimum performance. It is also found out that the developed geoplymer cements with silica fume are suitable to be used at low and medium temperature oil wells. Overall, geopolymer based oil well cementing systems using silica fume have better physical and mechanical properties compared to conventional Portland cement.

ACKNOWLEDGEMENT

I would like to thanks many people who contributed to the success of this final year project.

First and foremost, I would like to extend my utmost gratitude to Associated Professor Dr. Nasir Shafiq, my project supervisor for his valuable guidance and advice. I would also like to express my appreciation to Dr. Sonny Irawan who is my co-supervisor, for providing me with useful insights in completing the project. Other than that, I would like to acknowledge Universiti Teknologi PETRONAS, Malaysia for providing the financial support and research facilities.

Last but not least, to all I have sought help from and not stingy in sharing me their knowledge, I would like to thanks them from the bottom of my heart.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND NONMENCLATURES

API	American Petroleum Institute
$CaCO_3$	Calcium Carbonate
SiO_2	Silicon dioxide
CaO	Calcium Oxide
CO_2	Carbon dioxide
NaOH	Sodium hydroxide
Na_2SiO_3	Sodium silicate
rpm/ RPM	revolutions per minute
HPHT	High Pressure High Temperature

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the most general sense, cement is defined as a binder or a substance that sets and hardens independently and can bind other materials together. In the oil and gas industry, cement is used widely for the cementing jobs either in oil wells or gas wells. Cementing is one of the most crucial steps in well completion. Cementing a well is the procedure of circulating cement slurry through the inside of the casing and out into the annulus through the casing shoe at the bottom of the casing string. It serves three general purposes:

- Zone isolation and segregation
- Corrosion control
- Formation stability and pipe strength improvement

Cementing plays a vital role in ensuring complete zonal isolation and aquifer protection. Without it, the well may never reach its full production potential and liquids from one zone could interfere with another. This consequently results in uneconomical petroleum production. Moreover, cementing is important as it keeps the well safe for drilling oil and gas zones and protects the casing from corrosion, besides sealing off problematic zones.

Cementing is performed when the cement slurry is deployed into the well via pumps. The cement slurry then displaces the drilling fluid which is still located within the well and replaces the drilling fluid with cement. The cement slurry flows to the bottom of the wellbore through the casing, which will eventually be the pipe through which the hydrocarbons flow to the surface. From there, it fills in the space between the casing and the actual wellbore and hardens. This creates a seal to ensure that outside materials cannot enter the well flow, as well as permanently positions the casing in place [1].

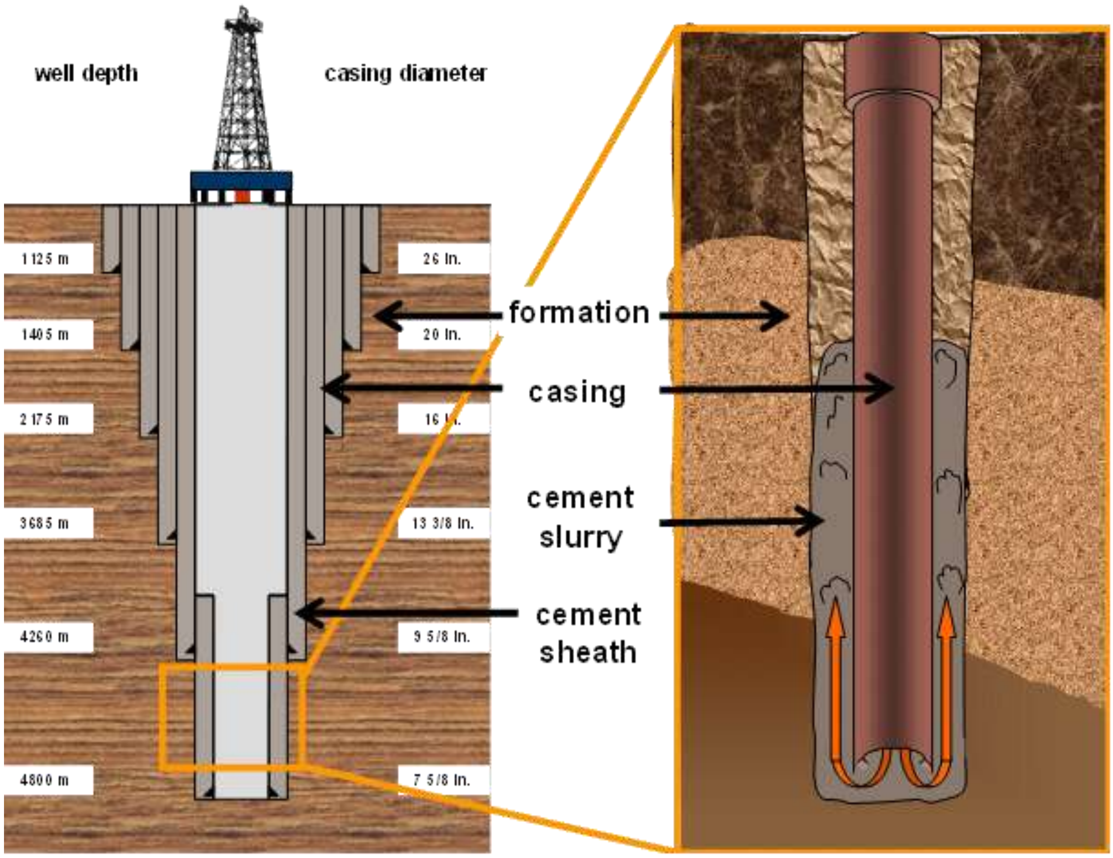


FIGURE 1-1: Cementing a Well [2]

The success of a cementing job lies especially on the design of the cement slurry. The properties of the cement slurry and its behaviour depend on the components and the additives in the cement slurry. Most cement used in the oil and gas industry is common type of Portland cement. Portland cement is produced from limestone and either clay or shale by roasting at 2600°F to 3000°F. The high temperature fuses the mixture into a material called clinker cement. After the roasting step, the rough clinker product is ground to a size specified by the grade of the cement. The final size of the cement particles has a direct relationship with how much water is required to make a slurry without producing an excess of water at the top of the cement or in pockets as the cement hardens [3].

Cement is mixed by jet mixers that combine cement and water in a single pass operation or the more precision batch mixers that mix by circulating in a large tank but only mix a limited volume at a time. Although acceptable slurry can be achieved in the jet mixer by an experienced operator, the batch mixer allows closer control in critical, small jobs. The jet mixers are used for almost all large jobs that require a constant supply of cement slurry at a high rate. The density of slurries mixed by these methods must be checked periodically with a pressurized mud balance to obtain consistent density. Density is important to control the reservoir pressure and prevent formation fracture breakdown.

After mixing, Portland cement is then calibrated with additives (as shown in TABLE 1-1) to form one of the nine different API classes of cement. The requirements for well cement are more rigorous than construction cement. Well cement must perform over a wide range of temperatures and pressures and is exposed to subterranean conditions that construction cement does not encounter. Each API class of cement is employed for various situations, as shown in TABLE 1-2 [4]. Portland cement that is commonly used in oil well cementing operations is Class G cement.

TABLE 1-1: Types of Additives and Their Purposes [4]

Type of Additives	Purposes
Accelerator	Shorten the setting time required for the cement
Retarder	Extend the setting time required for the cement
Lightweight additive	Decrease the density of the cement
Heavyweight additive	Increase the density of the cement
Extender	Expand the cement in order to reduce the cost of cementing
Antifoam additive	Prevent foaming within the well
Bridging material	Plug lost circulation zones

TABLE 1-2: API Cement Classes [4]

Class	Descriptions
A	For use from surface to 6000 ft (1830 m) depth, when special properties are not required
B	For use from surface to 6000 ft (1830) depth, when conditions require moderate to high sulfate resistance
C	For use from surface to 6000 ft (1830 m) depth, when conditions require high early strength
D	For use from 6000 ft to 10,000 ft depth (1830 m to 3050 m), under conditions of high temperatures and pressures
E	For use from 10,000 ft to 14,000 ft depth (3050 m to 4270 m), under conditions of high temperature and pressures

F	For use from 10,000 ft to 16,000 ft depth (3050 m to 4880 m), under conditions of extremely high temperatures and pressures
G	Intended for use as a basic cement from surface to 8000 ft (2440 m) depth. Can be used with accelerators and retarders to cover a wide range of well depths and temperatures
H	A basic cement for use from surface to 8000 ft (2440 m) depth as manufactured. Can be used with accelerators and retarders to cover a wider range of well depths and temperatures
J	Intended for use as manufactured from 12,000 ft to 16,000 ft (3600 m to 4880 m) depth under conditions of extremely high temperatures and pressures. It can be used with accelerators and retarders to cover a range of well depths and temperatures

The strength requirements of oil well cement are dependent on several factors. The cement must be strong enough to secure the pipe in the hole, to isolate the zone and to withstand the nominal shock of drilling, perforating and fracturing. For drilling ahead, the minimum Waiting On Cement (WOC) times are usually based on the time required for the cement to develop 50 psi tensile strength. The issue of the strength of cement has always been of interest since strength develops over a long period of time and rig time can be lost waiting on cement to set. This WOC time can be shortened by the use of accelerators. Cement requires very little strength to physically support the casing. More strength is required in withstanding loading from drill bits and pressure. In designing the cementing operation, it is imperative that high strength cements be used around the casing shoe (the bottom end of the pipe) and across potential pay, thief zones (areas of fluid loss) and water producing zones. Filling the annulus behind pipe and zone separation requires very little strength and more economical cements or cement extenders may be used [4].

1.2 Problem Statement

1.2.1 Problem Identification

Due to the low cost and widespread availability of limestone, clay and shale, Portland cement is used extensively in well cementing operations. However, problems exist. Basically, there are two big challenges presented with the usage of Portland cement for oil well cementing purposes, one is the occurrence of cement failure due to the mechanical properties of Portland cement while the other one is the emission of carbon dioxide caused by manufacture process of the Portland cement.

Cement Failure

Cement failure such as cracking which consequently leads to weakening of the well structure is the major cementing problem. The main factor that contributes to this problem is because of the well exposure to extreme temperatures and pressures cycle. As a result, the entire cement sheath cracks due to the shrinkage of the cement.

Cement failure can occur either in compression, traction or microannulus as shown in FIGURE 1-2. Compressional failure of the cement occurs if the rupture compressive strength of the cement is exceeded. This type of failure is typical particularly when there is major wellbore temperature increase and the formation bounding the cement sheath has relatively high young modulus. Rupture compressive strength can be defined as the maximum amount of compressive stress cement can withstand under confinement. Confinement occurs when it is not possible for the cement to expand laterally or away from the well. Therefore, the rupture compressive strength of cement is higher than the uniaxial compressive strength. Consequently, pockets or channels behind the casing and sufficient hydraulic isolation between the various permeable zones, which is the aim of the primary cementing job, is not achieved.

Changes in wellbore temperature during production also cause expansion and contraction of the casing. As a result, the bond between the casing and cement is not very strong, causing the casing to be pulled away from the cement, leaving a gap referred to as microannulus. Oil and other wellbore fluids may migrate through the microannulus up to the surface, causing degradation in the well integrity.

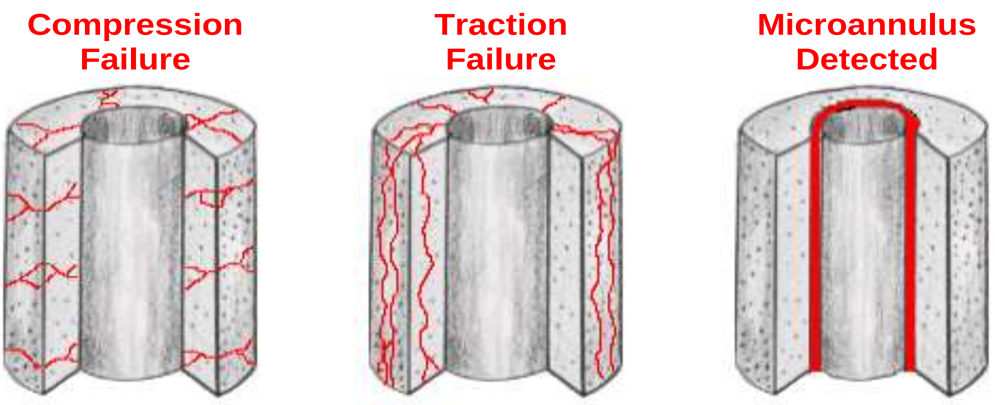


FIGURE 1-2: Defective Cement Bond due to Severe Change of Temperature and Pressure [5]

Emission of Carbon Dioxide

FIGURE 1-3: Portland Cement Chemistry [6]

It is reported that the worldwide cement industry contributes around 1.65 billion tons of the greenhouse gas emissions annually [7]-[9]. Due to the production of Portland cement, it is estimated that by the year 2020, the carbon dioxide emissions will rise by about 50% from the current levels [10], [11].

FIGURE 1-3 shows the Portland cement chemistry. The manufacture of Portland cement involves hardening of Portland cement through simple hydration of calcium silicate into calcium di-silicate hydrate and lime.

The manufacture of Portland cement clinker involves the calcination of calcium carbonate according to the reaction:

$$5CaCO_3 + 2SiO_2 \rightarrow (3CaO,SiO_2)(2CaO,SiO_2) + 5CO_2$$

The production of 1 tonne of Portland clinker directly generates 0.55 tonnes of chemical-CO_2 and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of carbon dioxide.

To simplify: 1 tonne of Portland cement = 0.95 Tonne of carbon dioxide

This clearly indicates that the production of Portland cement releases large amounts of carbon dioxide into the atmosphere, making a major contribution to the greenhouse effect and the global warming of the planet. Portland cement production is estimated to contribute around 7% of global carbon dioxide emissions [12].

1.2.2 Significance of the Project

To date various research studies have been conducted by many researchers on the behaviour of silica fume on geopolymer concrete or on Portland cement. However, to the author's knowledge, no published work or research study has been conducted so far around the world on geopolymer based oil well cementing systems using silica fume. Therefore, this research is dedicated to develop geopolymer cement by utilizing silica fume that would enhance the physical and mechanical properties of the cement. The worth of this project lies in its attempt to provide some performance data of silica fume on geopolymer oil well cement, so as to draw attention to its possible use in the oil well cementing operations.

1.3 Objectives and Scope of Study

This project besides developing geopolymer based oil well cementing systems using silica fume, the ultimate goals of this study are as follows:

1. To evaluate the viability of the developed geopolymer cements by examining their basic physical and mechanical properties
2. To compare the performance of the developed geopolymer cements which are varied by different amount of silica fume with the conventional Portland cement
3. To investigate the type of oil well condition in which the developed geopolymer cements are suitable to be used and recommend the cement with the optimal performance

The scope of study includes:

1. Development of the geopolymer based oil well cementing systems using silica fume
    - Research on the chemical compositions and their respective amount required to develop the geopolymer based oil well cementing systems
    - Alternate the amount of silica fume to look into the effect of silica fume on the cement physical and mechanical properties
2. Examination of the cement physical and mechanical properties, which include:
    - Rheological properties
    - Filtration loss
    - Compressive strength
3. Comparison of the performance between the developed geopolymer cements which are varied by different amount of silica fume and the conventional Portland cement
4. Investigation of the type of oil well condition in which the developed geopolymer cements are suitable to be used and recommendation of the cement with the optimal performance

1.4 The Relevancy of the Project

This project is mainly about oil well cementing systems. Therefore, in order to accomplish this project, thorough understanding about the cementing operations and the oil well cementing systems are necessary. Other than that, detailed study on geopolymer cement is required to develop the novel cementing systems using silica fume as a better substitute for the current conventional cementing system.

By working through this project, I am able to understand the major cementing problems and come out with solution to solve these problems by developing geopolymer based oil well cementing systems using silica fume. Hence, my knowledge in cementing is deepened. These are all relevant to my field of study as a petroleum engineering student.

1.5 Feasibility of the Project within the Scope and Time Frame

This project is feasible within the scope and time frame as shown at below:

Scope of Study	**Date**	**Duration**
Development of the geopolymer based oil well cementing systems using silica fume ➢ Research on the chemical compositions and their respective amount required to create the geopolymer based oil well cementing systems ➢ Alternate the amount of silica fume to look into the effect of silica fume on the cement physical and mechanical properties	4.2.2013-30.6.2013	21 weeks
Examination of the cement physical and mechanical properties, which include: ➢ Rheological properties ➢ Filtration loss ➢ Compressive strength	18.3.2013-30.6.2013	15 weeks
Comparison of the performance between the developed geopolymer cements which are varied by different amount of silica fume and the conventional cementing systems	1.7.2013-14.7.2013	2 weeks
Investigation of the type of well condition in which the developed geopolymer cements are suitable to be used and recommendation of the cement with the best performance	15.7.2013-21.7.2013	1 week

CHAPTER 2

LITERATURE REVIEW & THEORY

2.1 Literature Review

Portland cement is widely applied for the oil well cementing jobs. However, geopolymer materials have been extensively studied due to their good thermal and mechanical properties, which are relevant in cementing systems. Mechanical performance of Portland cement is limited in environments with high temperature and pressure due to its ceramic character. These work conditions are better tolerated by geopolymeric materials due to their high thermal stability and plastic behavior.

Earlier, most of the research studies were focused on geopolymer synthesised from metakaolin [13], [14], [15]. However, recently, many researches have been done on fly ash to investigate its possibilities to be used as an alumina-silicate source material. Fly ash, which is rich in silica and alumina, has full potential to be used as one of the source material for geopolymer binder [16]. Many research studies [17]-[20] have manifested the potential use of fly ash based geopolymer cement. Due to this reason, low-calcium fly ash has been chosen as a base material to synthesize geopolymer in order to better utilise this industrial waste.

In 2002, B.W. Langan, K. Weng and M.A. Ward from the Department of Civil Engineering, The University of Calgary initiated the research program to investigate the influence of silica fume and fly ash on the hydration of cement based mixtures at early ages. Fly ash has been widely utilized in concrete since it reduces cost of the concrete materials, conserves energy and resources and reduces environmental problems. However, problems are also associated with using this material, as fly ash has a relatively low surface area and accompanying pozzolanic activity. At normal temperatures, the pozzolanic reaction is slow to start and it does not progress to any significant degree until several weeks after the start of hydration. This results in slow strength development and inadequate strength at the normal age of loading, even though the concrete may have higher strength and durability in the longer term. To achieve the desired concrete properties, some special curing regimes such as prolonged moist curing may have to be used to ensure adequate early strength development. Overcoming the effects of fly ash on the early age properties of fly ash–cement mixtures is still a challenge. Silica fume appears to be a potential solution to this problem due to its highly reactive nature. Silica fume may provide significant amounts of calcium silicate hydrates (CSH) at an early age which would be expected to increase the early age strength. Based on the results obtained in this study, it has been shown that:

1. Silica fume accelerates cement hydration at high *water*/cement ratios. At low water/cement ratios, silica fume retards cement hydration and prolongs the dormant period, followed by enhanced hydration of the cement. Initial hydration of the cement is usually accelerated by the presence of silica fume. The higher the water/cement ratio, the higher the accelerating effect of the silica fume.
2. Fly ash also increases the initial hydration of cement. However, it retards hydration in the dormant and acceleration periods. It also accelerates hydration after the acceleration period. The higher the water/cement ratio, the greater the retardation effect.
3. When silica fume and fly ash are incorporated together in cement, the hydration of the cement is significantly retarded. The heat of hydration is decreased and the early reactivity of the silica fume is hampered. The accelerating effect of the silica fume is delayed [21].

In 2005, T. Bakharev from Monash University, Australia conducted a detailed study on geopolymeric materials prepared using Class F fly ash and elevated temperature curing. It was found out that long precuring at room temperature is beneficial for strength development of geopolymeric materials utilising fly ash and cured at elevated temperature as it allows shortening the time of heat treatment for achievement of high strength. For materials utilising fly ash activated by sodium silicate, 6 hours heat curing is more beneficial for the strength development than 24 hours heat treatment. Fly ash samples formed with sodium hydroxide activator had more stable strength properties than fly ash samples formed with sodium silicate [22].

In 2008, Amir H. Mahmoudkhani from Society of Petroleum Engineers (SPE) and Diana N.T. Huynh, Chuck Sylvestre and Jason Schneider from Sanjel Corporation presented a paper on new environment-friendly cement slurries with enhanced mechanical properties for gas well cementing. New cement slurries had been developed with significantly reduced greenhouse gas footprints when compared to conventional cement slurries used for oil and gas well cementing operations. The slurries which consist of geopolymeric materials exhibit superior chemical and mechanical properties at a competitive cost saving, which include:

- Variable densities from1200 to 1900 kg/m3
- Thickening times from several minutes to several hours
- Superior early and late strength development
- Fast gel strength development
- Controlled fluid loss
- Enhanced flexibility and elasticity
- Zonal isolation through strong bonding to formation and casing
- Ease of operation and handling
- Compatibility with most comment cements admixtures and additives
- Significantly reduced CO2 and water footprints
- Cost saving

A key attribute of the geopolymer technology is its robustness and versatility which enables products to have specific properties for slurries at densities as low as 1200 kg/m^3. In these slurries, cement has been replaced by up to 60% of its weight with aluminosilicate materials. This includes lightweight slurries with high compressive and flexural strengths and desirable elasticity. The new slurry has been successfully placed as a lightweight lead cement in intermediate casing operations [23].

In 2012, Lohani T.K, Jena S, Dash K.P and Padhy M conducted an experimental approach on geopolymeric recycled concrete using partial replacement of industrial byproduct. Geopolymer concrete is an advance technology in concrete technology by partial replacement of bonding material (cement) with fly ash after geopolymerization. A comparative study through detailed technical parameters between cement concrete and geopolymerised concrete resulted with a conclusion that the geopolymer concrete has better resistance to corrosion and fire (up to 2400°F), high compressive and tensile strengths, a rapid strength gain and lower shrinkage. As per recent researches conducted, geopolymer concrete reduces the cost of biding material as compared to standard cement. [24]

In 2012, Nasvi, M.C.M., Ranjith, P.G. and Sanjayan, J. did research on mechanical behaviours of geopolymer and class G cement as well cement at different curing temperatures for geological sequestration of carbon dioxide. A comprehensive experimental study had been undertaken to investigate the suitability of geopolymer as well cement and the mechanical behaviour of geopolymer and class G cement was compared under different down-hole temperatures. Geopolymer neat samples (without aggregate) were prepared using Class F fly ash (low calcium), sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) based on the mix design. When the Uniaxial Compressive Strength (UCS) of geopolymer and G cement was compared, it was found that geopolymer possess higher UCS values at elevated temperatures (above 50˚C) and G cement possesses the highest values at ambient conditions. The peak strength of both geopolymer and class G cement was observed at curing temperatures of 50-60˚C. In addition, Acoustic Emission (AE) test data revealed that the crack propagation stress thresholds of class G cement are higher at ambient conditions, whereas geopolymer possesses highest values at elevated temperatures. It is concluded that geopolymer is suitable to be the replacement for Portland cement as it possesses advantages, including being environmentally feasible, having higher strength compared to Portland cement and its excellence acid resistance [25].

2.2 Theory

2.2.1 Geopolymer Cement

Geopolymer cement is an innovative material and a real alternative to conventional Portland cement for use in offshore applications. It relies on minimally processed natural materials or industrial by-products to significantly reduce its carbon footprint, while also being very resistant to many of the durability issues that can plague conventional cements.

Creating geopolymer cement requires an alumina silicate material, a user-friendly alkaline reagent (sodium or potassium soluble silicates) and water. The most readily available raw material containing aluminium and silicon is fly ash. Room temperature hardening relies on the addition of calcium cations, essentially iron blast furnace slag [5].

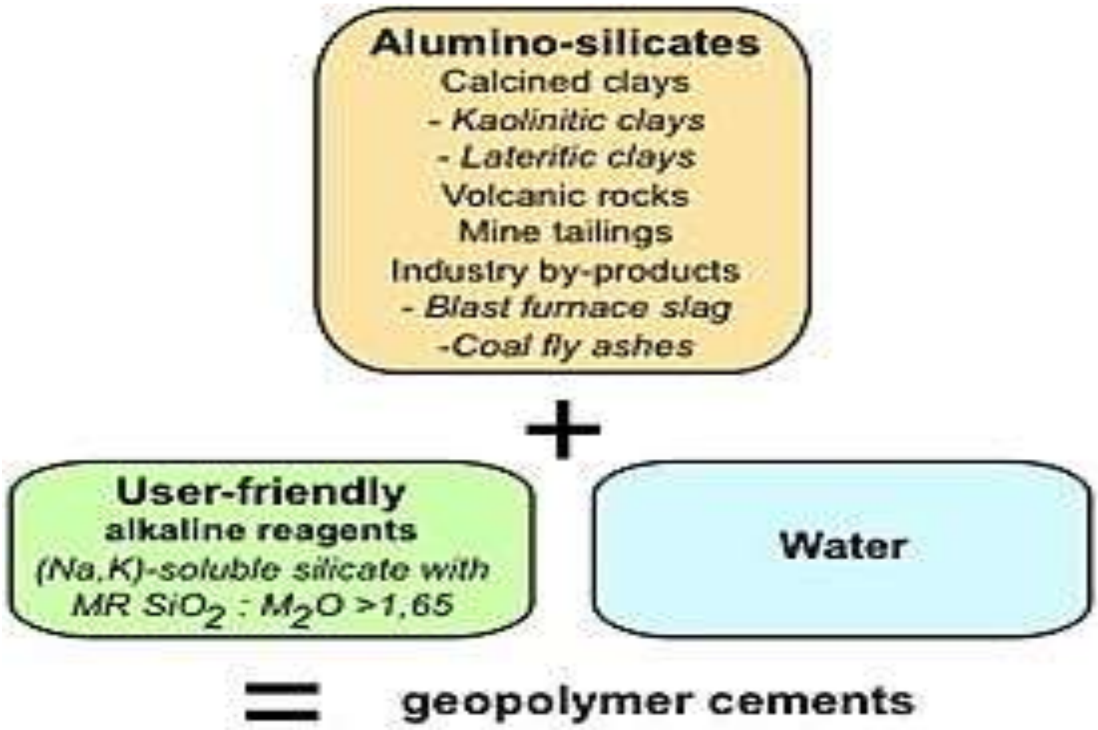


FIGURE 2-1: List of Minerals and Chemicals used for Making Geopolymer Cements [6]

Geopolymer based cements cure more rapidly than Portland based cements. They gain most of their strength within 24 hours. However, they set slowly enough that they can be mixed at a batch plant and delivered in a concrete mixer. Geopolymer cement also has the ability to form a strong chemical bond with all kind of rock-based aggregates.

Besides, the addition of silica fume in concrete has been investigated to have the following benefits:

- Substantial increase in compressive strength of concrete while maintaining the same mix design parameters
- Reduction in the required cement content for a specific target strength
- Increased durability of hardened concrete when added in optimum amounts [12]

Silica fume is a by-product of the smelting process in the silicon and ferrosilicon industry. It appears to be ultrafine power. Addition of silica fume helps to improve cement properties, in particular its compressive strength, bond strength and abrasion resistance. These improvements stem from both the mechanical improvements resulting from addition of a very fine powder to pozzolanic reactions between the silica fume and free calcium hydroxide in the cement paste mix as well as from the the paste [26].

2.2.2 Geopolymerization

Geopolymerization is a general term used to describe all the chemical processes that are involved in reacting alumina silicates with aqueous alkaline solutions to produce a new class of inorganic cement called geopolymer cement. The geopolymeric reaction occurs as a result of reacting alumina silicates with alkali and soluble alkali polysilicates. This reaction results in the formation of silica oxide and aluminium oxide tetrahedral linked by shared oxygen atoms [23].

A mild exothermic reaction in the alkali activated mixture is accompanied by hardening and polycondensation. Thus, a geopolymer can be described as a low calcium, alkali activated aluminosilicate cement. One of the primary advantages of geopolymers over conventional cements from an environmental perspective is the much lower carbon dioxide emission rate from geopolymer manufacture compared to Portland cement production. This is mainly due to the absence of a high-temperature calcination step in geopolymer synthesis from ashes and/or slags, whereas the calcination of cement clinker not only consumes a large amount of fossil fuel-derived energy, but also releases carbon dioxide as a reaction product. While the use of an alkaline hydroxide or silicate activating solution rather than water for cement hydration does reintroduce some greenhouse cost, the overall carbon dioxide saving due to widespread geopolymer utilization is expected to be highly significant [27].

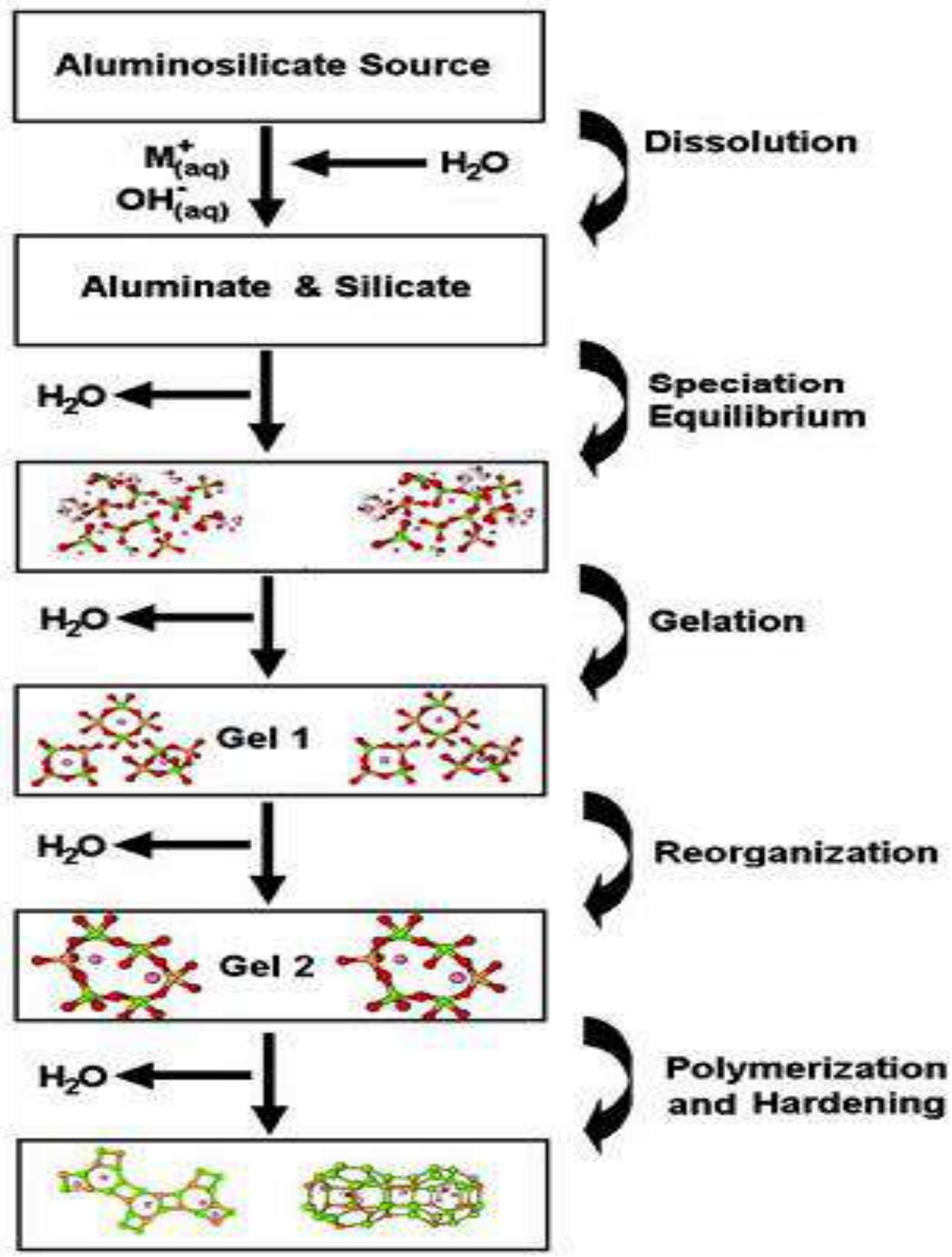


FIGURE 2-2: Conceptual Model for Geopolymerization [28]

Though presented linearly, these processes are largely coupled and occur concurrently. Dissolution of the solid alumina silicate source by alkaline hydrolysis (consuming water) produces aluminate and silicate species. It is important to note that the dissolution of solid particles at the surface resulting in the liberation of aluminate and silicate (most likely in monomeric form) into solution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerization. Once in solution the species released by dissolution are incorporated into the aqueous phase, which may already contain silicate present in the activating solution. A complex mixture of silicate, aluminate and alumina silicate species is thereby formed [28].

Dissolution of amorphous alumina silicates is rapid at high pH, and this quickly creates a supersaturated alumina silicate solution. In concentrated solutions this results in the formation of a gel, as the oligomers in the aqueous phase form large networks by condensation. This process releases the water that was nominally consumed during dissolution [28].

CHAPTER 3

METHODOLOGY/ PROJECT WORK

3.1 Research Methodology

Basically, three main stages of work are involved in accomplishing this project, as shown at below:

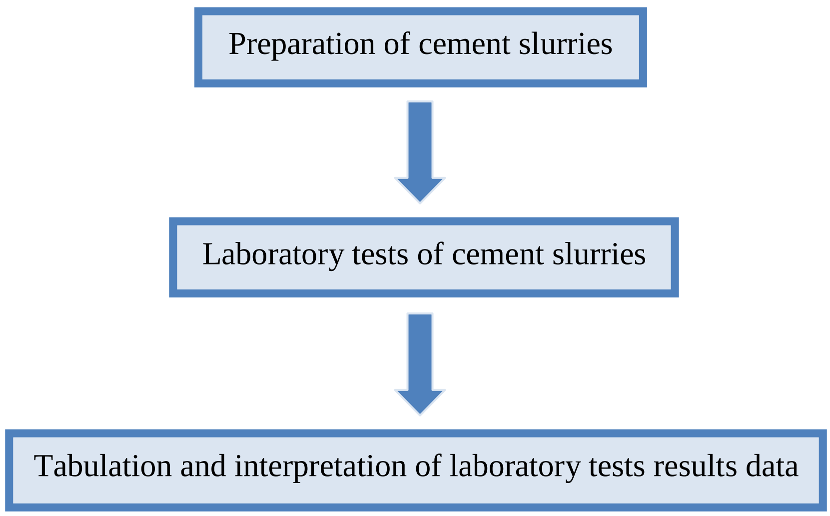


FIGURE 3-1: Research Methodology

3.2 Project Activities

3.2.1 Preparation of Cement Slurries

Five types of cement slurries were prepared, as shown in TABLE 3-1.

TABLE 3-1: Types of Cement Slurries

Cement Slurry	Chemical Composition
Conventional Portland	100% Class G cement + distilled water
Geopolymer A	100% fly ash + NaOH + Na_2SiO_3 + distilled water
Geopolymer B	90% fly ash + 10% silica fume + NaOH + Na_2SiO_3 + distilled water
Geopolymer C	80% fly ash + 20% silica fume + NaOH + Na_2SiO_3 + distilled water
Geopolymer D	70% fly ash + 30% silica fume + NaOH + Na_2SiO_3 + distilled water

Conventional Portland cement slurry was prepared by using high sulphate-resistant API Class G cement with a specific gravity of 3.20. Geopolymer cement slurries were prepared using ASTM Class F fly ash (low calcium) based on the mix design. The ratio of alkaline liquid/ fly ash selected was 0.50, as this would give optimum strength according to the research conducted by Mr. Fareed Ahmed Memon [29]. A combination of 40M NaOH and Na_2SiO_3 were used as the alkaline activator. NaOH was obtained in pellet form having 44% of pellet and 56% of water [29].In addition, Na_2SiO_3/ NaOH=2.5 was selected and extra water which was of 35% by weight of powder was added to the geopolymer mixes. Based on the mix design, the required amounts of fly ash, silica fume, NaOH pellets and Na_2SiO_3 solution were calculated. The density of both the conventional Portland and geopolymer cement slurries were 14 lb/ gal or 1678 kg/ m^3. Deionized distilled water was used for the mixing. Other than that, the amount of additives added for every sample was made constant, added fluid loss additive (FL-66L) and retarder additive (R-21LS) were 5% and 0.5% respectively.

Cement slurries preparation procedure:

1. The amount of materials required for the preparation of each type of cement slurries was calculated and measured using electronic balance scale.
2. All the materials were mixed using constant speed mixer model 3060 from Chandler Engineering with API mixing procedure.
3. The cement slurry mixing procedure was explained as below:
   i. Distilled water was placed in the mixer at 4000 rpm and agitated for 15 seconds.
   ii. Na_2SiO_3 and additives were added into the mixer.
   iii. Materials in powder and pellet forms (Class G cement, fly ash, silica fume and NaOH) were added into the mixer.
   iv. The mixer speed was increased to 12000 rpm and run for 35 seconds.

After the cement slurry was prepared, its density was measured by using Baroid mud balance to ensure that all the cement slurries were of same densities.

Density test procedure:

1. The lid was removed from the cup and the cup was completely filled with the cement slurry to be tested.

2. The lid was replaced and rotated until firmly seated, making sure that some cement slurry was expelled through the hole in the cup.
3. The balance arm was placed on the base, with the knife-edge resting on the fulcrum.
4. The rider was moved until the graduated arm was level, 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.

3.2.2 Laboratory Tests of Cement Slurries

After the cement slurry had been prepared, laboratory tests were conducted to test the physical and mechanical properties of the respective cement slurry, as shown in TABLE 3-2.

TABLE 3-2: Laboratory Tests Conducted

No.	Test	Purpose
1.	Rheology test	To test the rheological properties (plastic viscosity and yield point) of the cement slurries
2.	Filtration loss test	To measure the volume of liquid lost from a cement slurry due to filtration
3.	Compressive strength test	To test the compressive strength of the cement slurries

All these tests were carried out at a pressure ranging from 1000 psi to 3000 psi with varied temperatures (100°F, 150°F and 200°F), representing different oil well conditions.

The procedure for each test is explained as below:

Rheology Test

1. The cement slurry was placed in the cup, the upper housing of the viscometer was tilted back, the cup was located under the sleeve (the pins on the bottom of the cup fitted into the holes in the base plate) and the upper housing was lowered to its normal position.
2. The knurled knob between the rear support posts was turned to raise or lower the rotor sleeve until it was immersed in the cement slurry to the scribed line.

3. The cement slurry was stirred for about 5 seconds at 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm and 3 rpm.
4. The dial readings were recorded.

Filtration Loss Test

1. The cement slurry to be tested was poured into the cup assembly and the screw clamp was tightened.
2. With the air pressure valve closed, the mud cup assembly was clamped to the frame while holding the filtrate outlet end finger tight.
3. A graduated cylinder was placed underneath to collect filtrate.
4. The air pressure valve was opened and timing was started at the same time.
5. The volume of filtrate collected for 30 minutes was recorded.

Compressive Strength Test

1. The inside of the cell and bottom lid were greased with the low temperature grease in the container with a paintbrush.
2. The threads on the cells lids and small bottom plug were greased with high temperature grease.
3. The top lid on the cell was assembled in the following order: Metal ring (flat side down), rubber seal (Viton for temperatures over 300 F), metal plate (lid) small side up and threaded insert to hold the lid in place.
4. Lugs in the bottom of the cell stand were used to tighten the lid by inserting the cell upside down and turning the cell until the lid was tight.
5. The paddle stirrer was inserted in the cell while it was in the holder.
6. After mixing, the cement slurry was poured into the upside down cell until it completely covered the stirrer.
7. The bottom lid was screwed and tighten to the cell. Once the cell was filled with the rest of the slurry through the bottom plug hole, the bottom plug was screwed and tighten to the bottom lid with the 9/16" wrench.
8. The shaft drive was slided for the potentiometer on the paddle stirrer shaft, the potentiometer was lowered on the top of the shaft, the shaft drive was adjusted to where the shaft barely sticked out of the top of the potentiometer and the shaft drive was tightened on the shaft with it was set screw.

9. The potentiometer was removed from the shaft and the cell carrying device was used to lower the cell into the consistometer.
10. The two studs were lined up on the bottom of the cell with the two holes on top of the cell stirrer at the bottom of the chamber, the cell carrying device was removed and the motor switch on the bottom left side of the control panel was turned on. The cell should start to rotate if it had been aligned properly. The motor was turned off and adjusted if necessary.
11. The potentiometer carrying handle was used to lower the potentiometer on top of the cell and align it so that the shaft drive was in the notch on the bottom of the potentiometer and the cell stirring shaft was barely protruding from the top of the potentiometer.
12. The motor was turned on and the potentiometer was adjusted if the shaft drive had not been engaged.
13. The potentiometer carrying handle was used to tighten it in the consistometer by rotating it to the left or right. Then the carrying handle was removed.
14. The consistometer lid was lowered into its chamber and tighten. The two notches on the front of lid and chamber must align.
15. The temperature probe was lowered into the hole on the top of the consistometer lid and tighten to within ¼” of tight.
16. The front right door of the consistometer was opened and the fluid level in the reservoir was checked. If it was not 75% full then white oil 90 will need to be added.
17. The valves were closed: air to cylinder, cylinder cooling, pressure release valve, reservoir cooling, air exhaust and the air supply was opened.
18. When oil began to leak from the temperature fitting on top of the lid, the fitting was closed with a 5/8th open end wrench.
19. The temperature and pressure controllers were programmed using the same method used to program the UCA controllers.
20. The motor, heater switches and the potentiometer probe switch on the front of the panel were turned off. The direct current voltmeter was checked to see if the probe had engaged the potentiometer.
21. The auto/manual pump switch was switched from off to manual. The pump would begin to pressurize the chamber. After applying several hundred pounds of pressure, the pump was turned to off.

22. The pressure switch bypass was turned off, then the auto shutdown switch was turned off and the reset button next to it was pressed on each time. The consistometer should be reseted.
23. At the same time, the start buttons were pushed for the temperature and pressure controllers. The pump switch at the top right of the panel was turned to auto.
24. The cylinder cooling switch should always be in the off position, unless the chamber was being cooled. The main pressure control knob above the air supply should not be touched unless the air pressure controls were calibrated.
25. The timer on the left of the panel was reset by pushing the little red button then its switch was used to turn it on.
26. The consistometer was activated and the test data for the run was filled in.
27. After the run was finished, the cell was cooled to less than 180 F before removing it from the chamber.
28. When the cell is cool, the air supply valve was closed. The air exhaust, pressure release valve and the air to cylinder valve were opened to blow the oil back into the reservoir.
29. When air blowing out was heard, then the chamber was empty. The air was closed to cylinder valve, the temperature probe was carefully removed in case there was any pressure left in the chamber and the red plastic hammer was to loosen. The chamber lid was then unscrewed.
30. The cell was disassembled and cleaned using the hydraulic press to remove the cured cement core and the air impact wrench was used to remove the core from the paddle stirrer

3.2.3 Tabulation and Interpretation of Laboratory Tests Results Data

The results data from the laboratory tests was tabulated and interpreted to compare the performance between the developed geopolymer cements which are varied by different amount of silica fume and the conventional Portland cement, to investigate the type of well condition in which the developed geopolymer cements are suitable to be used and last but not least, to recommend the cement with the optimal performance. All the tabulation and interpretation of laboratory tests results data were documented in the next chapter.

3.3 Key Milestone

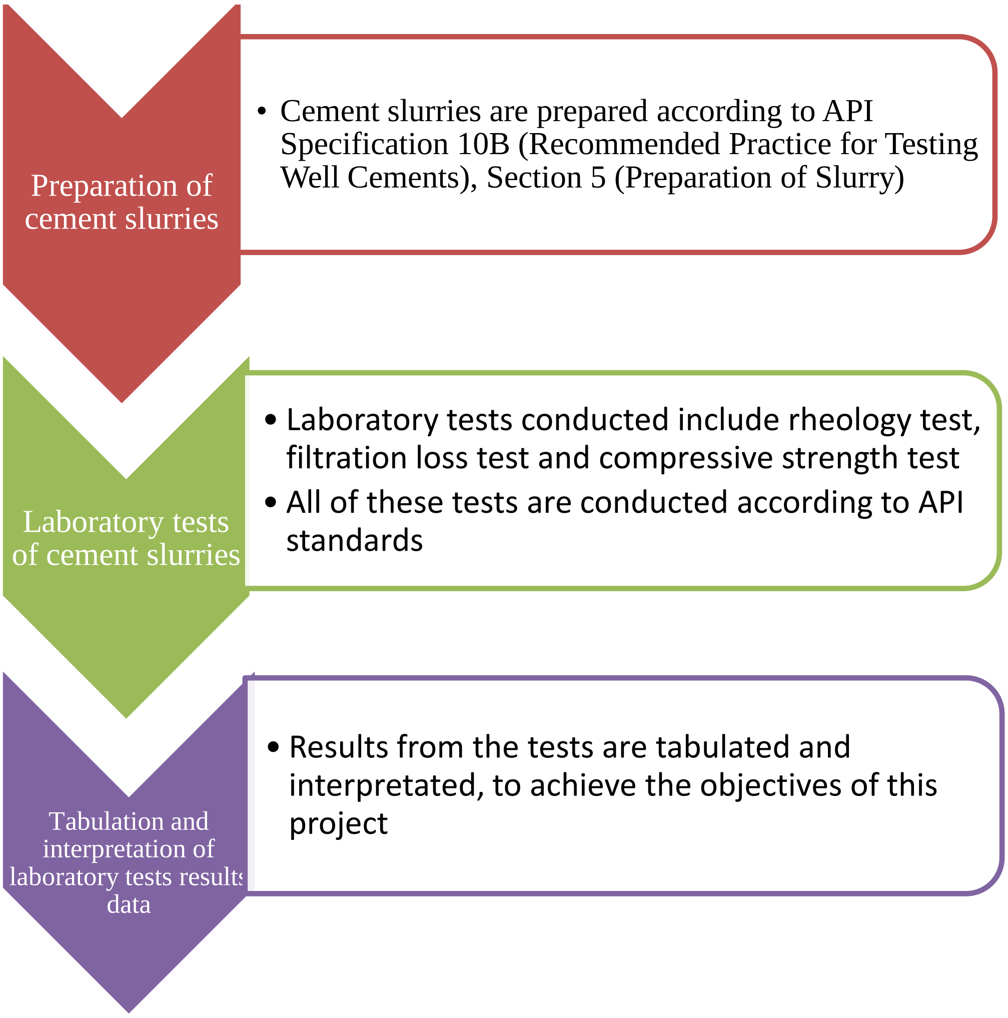


FIGURE 3-1: Key Milestone of the Project

3.4 Gantt Chart

Gantt Chart for the First Semester of Two Semesters Final Year Project

TABLE 3-3: Gantt Chart for First Semester

Detail/ Weeks	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
Selection of Project Topic															
Preliminary Research Work ➢ Background study ➢ Literature review ➢ Identify chemical components and equipments required ➢ Plan and find out research methodology								**Mid Semester Break**							
Submission of Extended Proposal															
Proposal Defence															
Project Work Continues ➢ Preparation of different cement slurries ➢ Laboratory tests of cement slurries ➢ Collection of laboratory tests results data															
Submission of Interim Draft Report															
Submission of Interim Report															

Gantt Chart for the Second Semester of Two Semesters Final Year Project

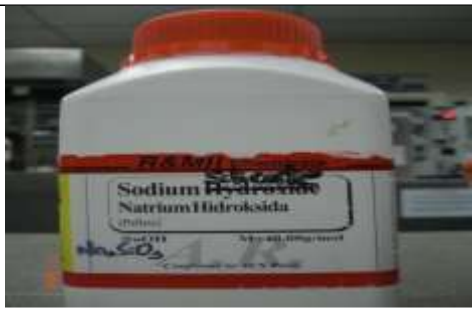
TABLE 3-4: Gantt Chart for Second Semester

Detail/ Weeks	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Mid Semester Break**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Project Work Continues ➢ Preparation of different cement systems ➢ Laboratory tests of cement systems ➢ Tabulation and interpretation of laboratory tests results data															
Submission of Progress Report															
Project Work Continues ➢ Preparation of different cement slurries ➢ Laboratory tests of cement slurries ➢ Tabulation and interpretation of laboratory tests results data															
Submission of Draft Report															
Submission of Dissertation (soft bound) and Technical Paper															
Preparation of Poster															
Pre- Sedex															
Oral Presentation															
Submission of Dissertation (hard bound)															

3.5 Tools

The materials and equipments required in accomplishing this project are listed,

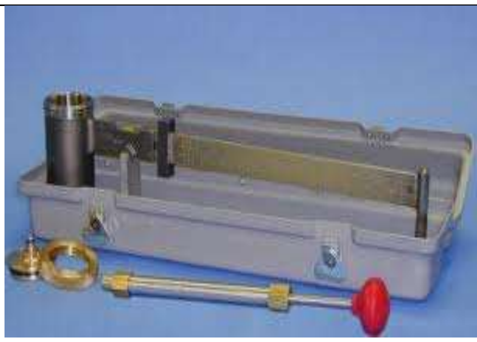
TABLE 3-5: Materials Required

No.	Material	
1.	Class G cement	
2.	Fly ash	
3.	Silica fume	
4.	Na_2SiO_3	
5.	NaOH	

6.	Fluid loss additive	
7.	Retarder additive	

TABLE 3-6: Equipments Required

No.	**Equipment**	
1.	Weighing scale	
2.	Constant speed mixer	

3.	Baroid mud balance	
4.	Viscometer	
5.	Fluid loss tester	
6.	Ultrasonic Cement Analyzer	
7.	Ultrasonic Cement Analyzer Cell	

CHAPTER 4
RESULT & DISCUSSION

4.1 Data Gathering and Analysis

Rheology test, filtration loss test and compressive strength test had been conducted on five types of cement slurry, namely conventional Portland, geopolymer A, geopolymer B, geopolymer C and geopolymer D. Results are exhibited and discussed as shown at the following section.

4.1.2 Rheology Test

TABLE 4-1: Rheology Test Results at Ambient Temperature (80 °F)

Cement Slurry	RPM @ ambient temperature (80 °F)					
	300	**200**	**100**	**6**	**3**	**600**
Conventional Portland	130	92	49	3	1	240
Geopolymer A	45	40	22	5	4	130
Geopolymer B	35	25	15	3	1	70
Geopolymer C	80	47	25	3	1	135
Geopolymer D	80	47	25	3	1	135

TABLE 4-2: Plastic Viscosity & Yield Point at Ambient Temperature (80 °F)

Cement Slurry	Plastic Viscosity, cp	Yield Point, lb/100 ft^2
Conventional Portland	110	20
Geopolymer A	85	-40
Geopolymer B	35	0
Geopolymer C	55	25
Geopolymer D	55	25

TABLE 4-3: Rheology Test Results at 100°F

Cement Slurry	RPM @ 100°F					
	300	**200**	**100**	**6**	**3**	**600**
Conventional Portland	135	98	53	6	2	244
Geopolymer A	50	45	27	10	9	135
Geopolymer B	38	29	20	6	2	76
Geopolymer C	85	52	29	6	2	140
Geopolymer D	85	52	29	6	2	140

TABLE 4-4: Plastic Viscosity & Yield Point at 100°F

Cement Slurry	Plastic Viscosity, cp	Yield Point, lb/100 ft^2
Conventional Portland	109	26
Geopolymer A	85	-35
Geopolymer B	38	0
Geopolymer C	55	30
Geopolymer D	55	30

TABLE 4-5: Rheology Test Results at 150°F

Cement Slurry	RPM @ 150°F					
	300	**200**	**100**	**6**	**3**	**600**
Conventional Portland	140	105	60	9	5	251
Geopolymer A	55	48	30	14	12	138
Geopolymer B	43	33	25	8	3	81
Geopolymer C	90	59	34	8	3	145
Geopolymer D	91	60	35	8	3	145

TABLE 4-6: Plastic Viscosity & Yield Point at 150°F

Cement Slurry	Plastic Viscosity, cp	Yield Point, lb/100 ft^2
Conventional Portland	111	29
Geopolymer A	83	-28
Geopolymer B	38	5
Geopolymer C	55	35

Geopolymer D	54	37

TABLE 4-7: Rheology Test Results at 200°F

Cement Slurry	**RPM @ 200°F**					
	300	**200**	**100**	**6**	**3**	**600**
Conventional Portland	145	111	64	12	7	254
Geopolymer A	59	53	36	20	14	141
Geopolymer B	48	38	30	10	5	86
Geopolymer C	96	63	38	10	5	150
Geopolymer D	96	63	39	10	5	152

TABLE 4-8: Plastic Viscosity & Yield Point at 200°F

Cement Slurry	**Plastic Viscosity, cp**	**Yield Point, lb/100 ft^2**
Conventional Portland	109	36
Geopolymer A	82	-23
Geopolymer B	38	10
Geopolymer C	54	42
Geopolymer D	56	40

Plastic viscosity, cp = 600 RPM reading – 300 RPM reading

Yield point, lb/100 ft^2 = 300 RPM reading – Plastic viscosity

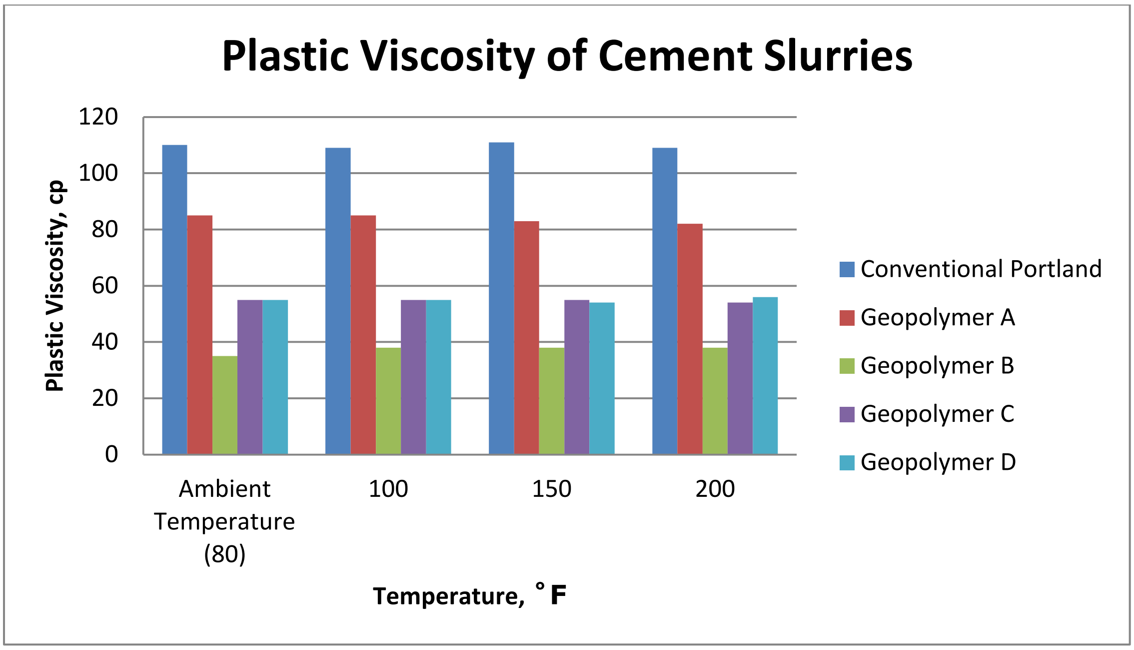


FIGURE 4-1: Plastic Viscosity of Cement Slurries

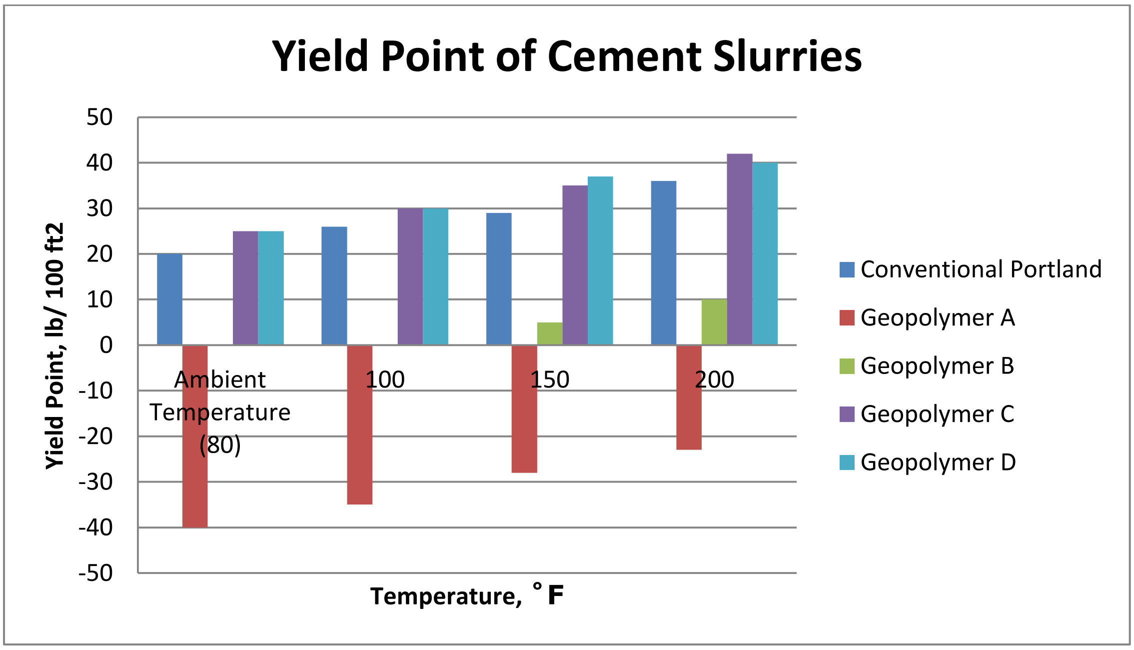


FIGURE 4-2: Yield Point of Cement Slurries

Rheology refers to the deformation and flow behavior of all forms of matter. Certain rheological measurements made on fluids, such as viscosity and yield point help to determine how this fluid will flow under a variety of different conditions. TABLE 4-1, 4-3, 4-5 & 4-7 show the readings obtained under different RPM at ambient temperature (80°F), 100°F, 150°F & 200°F and TABLE 4-2, 4-4, 4-6 & 4-8 exhibit the plastic viscosity and yield point for each cement slurry. From the tables, it can be seen that as the temperature increase, the readings obtained under different RPM increase, so do their plastic viscosity values.

Plastic viscosity is a parameter of the Bingham plastic model. It is the resistance of fluid to flow. A low plastic viscosity indicates that the cement slurry is capable of being pumped rapidly and smoothly into the well because of the low viscosity of cement slurry exiting at the bit. From TABLE 4-2, 4-4, 4-6 & 4-8, it can be clearly observed that conventional Portland cement slurry has the highest plastic viscosity which is of 110 cp, 109 cp, 111 cp and 109 cp at 80°F, 100°F, 150°F and 200°F respectively. There is no direct relationship noticed between the amount of silica fume and the values of plastic viscosity. However, all the geopolymer cement slurries either with or without silica fume added have plastic viscosity less than 100 cp under varied temperatures. A cement slurry is considered as a good one if its plastic viscosity is less than 100 cp.

Yield point is another parameter of the Bingham plastic model. Yield point is used to evaluate the ability of a cement slurry to lift cuttings out of the annulus. A high yield point implies a non-Newtonian fluid (plastic fluids where the viscosity is not constant, for examples cement slurry and drilling mud), one that carries cuttings better than a fluid of similar density but lower yield point. Generally, based on TABLE 4-2, 4-4, 4-6 and 4-7, geopolymer C and D have an excellent value of yield point, regardless of temperatures while geopolymer A shows undesired yield point values, indicating that pure geopolymer cement slurry without silica fume is not ideal in lifting cuttings out of the annulus.

Plastic viscosity and yield point of the cement slurries are summarized in FIGURE 4-1 and 4-2 respectively. In short, in term of plastic viscosity, all the geopolymer cements exhibit good performances. As for yield point, geopolymer cement slurry with 20% and 30% of silica fume have shown desired capability to lift cuttings out of the annulus.

4.1.2 Filtration Loss Test

	Conventional Portland	Geopolymer A	Geopolymer B	Geopolymer C	Geopolymer D
Fluid loss @ 100°F (ml/30 mins)	28	Blow Out	5	1	2
Fluid loss @ 150°F (ml/30 mins)	10	Blow Out	28	25	10
Fluid loss @ 200°F (ml/30 mins)	5	Blow Out	Blow Out	Blow Out	Blow Out
The API fluid loss of cement slurries must be within 70 ml in 30 minutes [30].					

TABLE 4-9: Filtration Loss Test Results

Filtration loss can be defined as the leakage of the liquid phase of cement slurry containing solid particles into the formation matrix. Excessive fluid loss may cause reservoir damage. Therefore, it is said that the less the fluid loss, the better the performance of the cement slurry. Based on TABLE 4-3, geopolymer A which contains no silica fume blows out in all three fluid loss tests conducted at 100°F, 150°F and 200°F. In this case, blowout refers to the release of gas after all the fluid in the cement slurry has been squeezed out.

Each individual particle of silica fume is spherical with an average diameter 0.15-0.3 μm (100 times finer than cement particle) and therefore its specific surface area is high. Silica fume reduces bleeding significantly because the free water is consumed in wetting of the large surface area of the silica fume and hence the free water left in the mix for bleeding also decreases. Moreover, silica fume particles are water wet and absorb excess water in cement slurry when cement slurry is extended by water [30]. All these properties explain the reason why geopolymer A blow out in all fluid loss tests as silica fume particles act as ideal particulate materials to reduce the fluid loss of slurry into the permeable formation.

On the other hand, cement slurries with added silica fume show desired fluid loss performance at 100°F and 150°F while they all blow out in fluid loss tests at 200°F. This indicates that geopolymer cement with silica fume is suitable to be used at low and medium temperature oil wells. Further approaches such as increase the dosage of fluid loss additive or introduction of new chemical into the cement should be made to improve its performance at high temperature.

Compared with conventional Portland cement slurry, geopolymer cements with added silica fume show better fluid loss properties at 100°F. At 150°F, although geopolymer B and C lose more water than conventional cement slurry in 30 minutes, the values are still within the desired range. Geopolymer D has the same amount of fluid loss as conventional Portland cement slurry at 150°F.

4.1.3 Compressive Strength Test

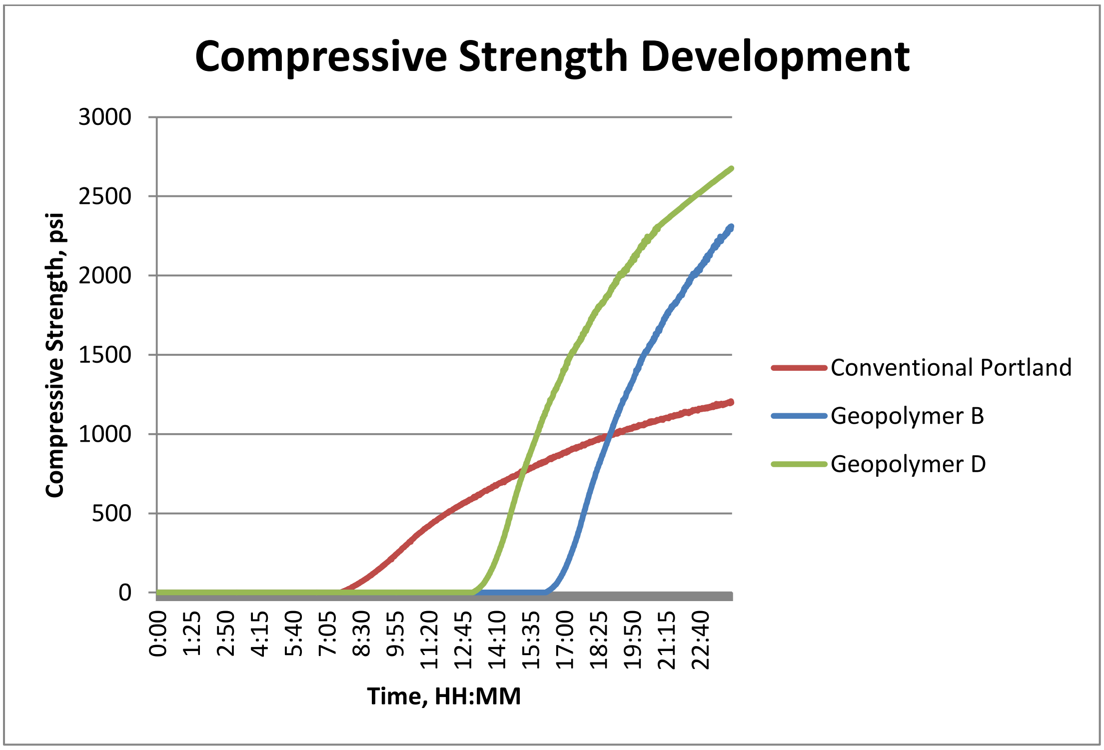


FIGURE 4-3: Compressive Strength Development of Cement Slurries

Compressive strength is the maximum stress a material can sustain under load crushing. Compressive strength plays an important role in cementing as it represents how well the cement slurry holds up to the compressive pressure around it. Compressive strength has a significant effect on well integrity. In some cases, the poor compressive strength can lead to structure failure, which may result in serious safety issues.

As shown in the filtration loss test, since all the geopolymer cemet slurries had blown out at a temperature of 200°F, which indicates that they are not suitable to be used in high temperature well, the compressive strength test is conducted at a temperature of 150 °F. Three types of cement slurries, which include conventional Portland, geopolymer B and geopolymer D are involved in the test. Geopolymer A is not considered for the compressive strength test as it has shown undesired result in the filtration loss test conducted at the same temperature while for geopolymer C, the effect of silica fume amount on compressive strength can be well evaluated just by using geopolymer B and geopolymer D.

FIGURE 4-3 shows the compressive strength development of conventional Portland, geopolymer B and geopolymer D cement slurries. Based on the figure, it can be clearly noted that geopolymer D has the highest compressive strength which is 2676 psi, compared to geopolymer B and conventional Portland cement slurries which are of 2311 psi and 1196 psi respectively. This indicates that silica fume has a considerable effect in improving compressive strength.

In term of WOC time, conventional Portland cement slurry exhibit better performance than geopolymer B and geopolymer D. Conventional Portland cement reaches strength 1 which is 50 psi in 8.21 hours, while for geopolymer B and geopolymer D, it is 16.40 and 13.37 hours. However, WOC time of geopolymer B and geopolymer D can be improved by accelerator additive, which its purpose is to shorten the setting time required for the cement.

CHAPTER 5
CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

The outcomes of this project are achieved. From the obtained data, it can be concluded that:

- All the developed geopolymer cements (geopolymer A, geopolymer B, geopolymer C and geopolymer D) appear to be in ideal plastic viscosity range, indicating that they are capable of being pumped rapidly and smoothly into the well
- Geopolymer cements with 20% and 30% of silica fume (geopolymer C and geopolymer D) perform well in term of yield point, showing that they are good at lifting cuttings out of the annulus
- As for filtration loss, geopolymer cements with 10%, 20% and 30% of silica fume exhibit desired readings at temperature of 150 °F
- Silica fume is proved to have a significant effect in improving compressive strength
- The geopolymer cement with 30% of silica fume is the cement slurry with optimum performance
- The developed geoplymer cements with silica fume are suitable to be used at low and medium temperature oil wells
- Overall, geopolymer based oil well cementing systems using silica fume have better physical and mechanical properties compared to conventional Portland cement

5.2 Recommendations

Suggested further works for expansion and continuation:

- Vary more different oil well conditions to be tested
- Extend the research by adjusting the ratio of fly ash and silica fume
- Develop novel geopolymer cement slurry by using new material

REFERENCES

[1] Rigzone. How does cementing work [Online]. Available: http://www.rigzone.com/training/insight.asp?insight_id=317&c_id=1

[2] Prof. Dr. Plank. Oil Well Cementing [Online]. Available: http://www.bauchemie-tum.de/master-framework/?p=Tief&i=13&m=1&lang=en

[3] Middle East Technical University. Chapter 5: Cementing [Online]. Available: http://www.metu.edu.tr/~kok/pete322/322CHAPTER-5.pdf

[4] George E King Consulting Inc. Chapter 3: Cementing [Online]. Available: http://gekengineering.com/Downloads/Free_Downloads/Cementing_Chapter_3.pdf

[5] Mitchell, A. L., & Casman, E. A. (2011). Economic Incentives and Regulatory Framework for Shale Gas Well Site Reclamation in Pennsylvania.*Environmental science & technology*, *45*(22), 9506-9514.

[6] Wikimedia Foundation, Inc. (2013,February 19).Geopolymer cement [Online]. Available: http://en.wikipedia.org/wiki/Geopolymer_cement

[7] V.M. Malhotra, "Introduction: Sustainable Development & Concrete Technology", *ACI Concrete International*, 24(7), pp. 22, 2002.

[8] R. McCaffrey, "Climate Change and the Cement Industry", *Global Cement and Lime Magazine*, (Environmental Special Issue), pp. 15-19, 2002.

[9] D. Hardjito, S. E. Wallah, D. M. J. Sumajouw, and B. V. Rangan, "Factors Influencing the Compressive Strength of Fly ash-Based Geopolymer Concrete", *Civil Engineering Dimension*, Vol. 6, No. 2, pp. 88–93, September 2004.

[10] T. R. Naik, "Sustainability of cement and concrete industries", *Proceedings of the International Conference Global Construction: Ultimate Concrete Opportunities*, Dundee, Scotland, pp. 141-150, July 2005.

[11] Tarek Salloum, "Effect of Fly ash Replacement on Alkali and Sulphate Resistance of Mortars", *MS Thesis*, Department of Building, Civil and Environmental Engineering, Concordia University Montreal, Quebec, Canada, July 2007.

[12] D. Bondar, C. J. Lynsdale, N. B. Milestone, N. Hassani, and A. A. Ramezanianpour, "Engineering Properties of Alkali Activated Natural

Pozzolan Concrete," in *Second International Conference on Sustainable Materials and Technologies*, 2010.

[13] J. Davidovits, "Geopolymers: inorganic polymeric new materials", *Journal of Thermal Analysis*, 37(8), pp. 1633–1656, 1991.

[14] Pavel Rovnanik, "Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer", *Construction and Building Materials*, 24 (2010), pp. 1176–1183.

[15] Franck Cassagnabère, Michel Mouret, Gilles Escadeillas, Philippe Broilliard, Alexandre Bertrand, "Metakaolin, a solution for the precast industry to limit the clinker content in concrete: Mechanical aspects", *Construction and Building Materials*, 24 (2010), pp. 1109–1118.

[16] Ubolluk Rattanasak, Prinya Chindaprasirt, "Influence of NaOH solution on the synthesis of fly ash geopolymer", *Minerals Engineering*, 22 (2009), pp. 1073–1078.

[17] A. Palomo, M. W. Grutzeck, M. T. Blanco, "Alkali-activated fly ashes: A cement for the future", *Cement and Concrete Research*, 29 (8), pp. 1323-1329, 1999.

[18] D. Hardjito, and B. V. Rangan, "Development and Properties of Low-Calcium Fly ash based Geopolymer Concrete", *Research report GC-1*, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2005.

[19] B. V. Rangan, "Fly Ash-Based Geopolymer Concrete", Research Report GC-4, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2008.

[20] Jae Eun Oh, Paulo J.M. Monteiro, Ssang Sun Jun, Sejin Choi, Simon M. Clark, "The evolution of strength and crystalline phases for alkaliactivated ground blast furnace slag and fly ash-based geopolymers", *Cement and Concrete Research*, 40 (2010), pp. 189–196.

[21] B.W. Langan, K. Weng and M.A. Ward, "Effect of silica fume and fly ash on heat of hydration of Portland cement," *Cement and Concrete Research*, vol. 32, (7), pp. 1045-1051, 2002.

[22] T. Bakharev, "Geopolymeric materials prepared using Class F fly ash and elevated temperature curing," *Cement and Concrete Research*, vol. 35, (6), pp. 1224-1232, 2005.

[23] Amir H. Mahmoudkhani, Diana N.T. Huynh, Chuck Sylvestre and Jason Schneider, "New Environment-Friendly Cement Slurries With Enhanced Mechanical Properties for Gas Well Cementing," in *CIPC/SPE Gas Technology Symposium 2008 Joint Conference*, 2008.

[24] T.K. Lohani, S. Jena, K.P. Dash, M. Padhy, "An Experimental Approach on Geopolymeric Recycled Concrete using Partial Replacement of Industrial Byproduct," *International Journal of Civil and Structural Engineering,* vol. 3, (1), pp. 141-149, 2012

[25] Nasvi, M.C.M., Ranjith, P.G. and Sanjayan, J., "Comparison of Mechanical Behaviors of Geopolymer And Class G Cement As Well Cement At Different Curing Temperatures For Geological Sequestration of Carbon Dioxide," in *46th U.S. Rock Mechanics/Geomechanics Symposium,* 2012.

[26] Wikimedia Foundation, Inc. (2013,February 26).Silica Fume. Available: http://en.wikipedia.org/wiki/Silica_fume

[27] Peter Duxson, John L. Provis, Grant C. Lukey and Jannie S.J. van Deventer, "The role of inorganic polymer technology in the development of 'green concrete'," *Cement and Concrete Research,* vol. 37, (12), pp. 1590-1597, 2001.

[28] P. Duxson, A. Fernandez Jimenez, J. L. Provis G. C. Lukey, A. Palomo and J. S. J. van Deventer "Geopolymer technology: the current state of the art," *J Mater Sci*, vol. 42, pp. 2917-2933, 2007.

[29] Fareed Ahmed Memon, " Development of Fly ash-based Self-compacting Geopolymer Concrete," PHD dissertation, Dept. Civil Engineering, Universiti Teknologi PETRONAS, Perak, Malaysia, 2013

[30] S. R. Shadizadeh, M. Kholghi and M. H. Salehi Kassaei, "Experimental Investigation of Silica Fume as a Cement Extender for Liner Cementing in Iranian Oil/Gas Wells," *Iranian Journal of Chemical Engineering*, Vol. 7, No. 1 (Winter), 2010