OPTIMIZATION OF WELLBORE INTEGRITY USING GEOPOLYMER CEMENT

By

DINESH A/L KANESAN

Dissertation submitted in partial fulfilment of

the requirement for the

MSc. Petroleum Engineering

JULY 2014

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

OPTIMIZATION OF WELLBORE INTEGRITY USING GEOPOLYMER CEMENT

By

Dinesh Kanesan

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
MSc. PETROLEUM ENGINEERING

Approved by,

DR. SYAHRIR RIDHA

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JULY 2014

CERTIFICATION OF ORIGINALITY

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

DINESH A/L KANESAN

ABSTRACT

The increase in awareness towards global warming has prompted the research of alternatives to the conventional ordinary Portland Cement (OPC). In addition, studies have demonstrated that the use of geopolymer cement slurries resulted in lower carbon emission and superior cement properties compared to the ordinary Portland cement. In this study, the factors which affect the wellbore integrity in regards to cementing were identified and a comparison between Class G cement and Fly Ash Geopolymer (FAGP) cement pertaining to the identified factors were made. In addition, a thorough analysis on the factors affecting the properties of geopolymer in regards to its application in oil well cementing was performed. The results enable the finding of optimum parameters required to produce geopolymer cements for oil well applications. The FAGP cement achieved higher compressive strengths compared to Class G cement for all curing temperatures above 36^{o}C. At optimum curing temperatures, for all curing time FAGP cement achieved higher compressive strengths in comparison Class G cement. Moreover, FAGP cement was found to be more susceptible to marine environment whereby curing medium of brine water resulted in higher compressive strengths. In addition, FAGP cement has lesser carbon footprint, superior chemical durability, lower permeability and higher crack propagation threshold in comparison the Class G cement. In addition, key variables which influence the compressive strength of FAGP cement such as type of activating solution, concentration of activating solution alkaline liquid to fly ash ratio, aging duration and water to binder ratio were identified and the corresponding optimum values in achieving highest compressive strength were suggested. However, there are minimal economic benefits of FAGP cement whereby the optimum mix proportion results in only a slight reduction in cost compared to OPC. The conclusion supports the usage of geopolymer cement for oil well cementing whereby it has an edge over conventional Portland cement for better short term and long term performance to ensure wellbore integrity throughout the producing life span of the well, with less hazards imposed on the environment.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude firstly to God for having granted me the will to work on this dissertation and completing it successfully.

My sincere appreciation to my Individual Project Supervisor, Dr.Syahrir Ridha for giving me the opportunity to carry out this project. I am thankful for all his guidance and dedication in ensuring that I gain as much related knowledge as possible throughout this project. In times of doubt and dead end situations, he was always there to guide me and clarify my uncertainties.

I would also like to extend my sincere thankfulness to the MSc Petroleum Engineering Program Manager, Dr Masoud Rashidi for his whole hearted support and encouragement. My heartfelt gratitude also goes to the MSc Petroleum Engineering Individual Project Coordinator, Mr Saleem Qadir Tunio for his kind coordination and support to ensure the success of this dissertation.

I would also like to thank my family for their tremendous moral support and encouragement during the duration of this dissertation. Last but not least, my heartfelt gratitude goes to each and every person who directly or indirectly helped me in this dissertation.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

FAGP : Fly Ash Based Geopolymer
OPC : Ordinary Portland Cement
API : American Petroleum Institute
ASTM : American Society of Testing Materials
WOC : Waiting on Cement
CO_2 : Carbon Dioxide
M : Molarity
Ms : Activator Modulus
$CaCO_3$: Calcium Carbonate
C_3S : Tricalcium Silicate
C_2S : Dicalcium Silicate
C_3A : Tricalcium Aluminate
C_4AF : Tetracalcium Aluminoferrite
H_2O : Water
Si : Silica
Al : Alumina
O : Oxygen
NaOH : Sodium Hydroxide
KOH : Potassium Hydroxide
Na_2SiO_3 : Sodium Silicate
K_2SiO_3 : Potassium Metasilicate
$NaCO_3$: Sodium Carbonate
SiO_2 : Silicon Oxide
Al_2O_3 : Aluminium Oxide
Fe_2O_3 : Iron Oxide
HCl : Hydrochloric Acid
OH^- : Hydroxide Ion
^oC : Degree Celsius
ft : feet
g : gram
kg : kilogram
psi : pound square inch
cm : Centimetre
s : seconds
mD : mili Darcy
Mpa : Mega Pascal
BW : brine water

LIST OF APPENDICES

CHAPTER 1.

INTRODUCTION

1.1 Background Study

As the most common anthropogenic greenhouse gas, carbon dioxide (CO_2) is a major contributor to global warming. According to Ernst et al.[1] the cement industry contributes approximately 5% of the total CO_2 emitted due to activities carried out by mankind and it would be the appropriate industry to implement CO_2 emission mitigation strategies. Approximately one ton of CO_2 is released to the atmosphere for the production of one ton of Portland cement whereby the calcination of Calcium Carbonate ($CaCO_3$) releases 0.53 tons of CO_2 and another 0.45 tons of CO_2 is emitted if carbon based fuel is used as the energy source for the production of Portland cement [2]. Due to the increasing awareness to curb rapid global climate changes, viable replacement for the conventional Portland cement is currently being reviewed and studied in detail.

Comprising different chemical and physical standards depending on their application, the oil and gas industry generally adheres to the classifications in accordance with the American Petroleum Institute (API). To ensure consistency and reliability of the cement manufactured, API provides standardisation of eight classes of oil well cement namely Classes A to H depending on the specifications of downhole temperatures and pressures[3].However, the API Class G is the most common type of cement used in the oil and gas industry [4-8]. Recent studies show that there are several problems associated with the use of Portland cement such as degradation of well cement, susceptibility to chemical reactions, poor durability and leakage [9]. Therefore there is a dire need to develop a sustainable cement technology which possesses superior properties compared to the conventional Portland cement for oil well cementing. This research focuses on the potential of geopolymer cement for the optimization of wellbore integrity.

1.2 Problem Statement

The need to reduce carbon dioxide emissions due to anthropogenic activities has led to the research and development of a more environment friendly class of cement, namely geopolymer cement. More importantly, there are rising cases of loss of well integrity over the life of the well by utilising the conventional Portland cement which calls for remedial cementing work. This would result in loss of production and additional cost for workover operations. The utilisation of geopolymer cement would significantly reduce the overall carbon footprint ,however the properties of geopolymer cement at downhole conditions for the total life of a producing well has to be studied in detail for the application of geopolymer cement in well cementing. Besides, the possible causes of loss of wellbore integrity over the life of the well by utilising Portland cement is to be analysed and compared with the analytical results of geopolymer based cement material. In addition, the factors which affect the mechanical and geochemical properties of the geopolymer based cement has to be identified and optimum parameters be proposed for further studies before it can be utilised at well site. Lastly the economic feasibility of FAGP cement has to be evaluated to enable commercial usage in oil well cementing.

1.3 Objectives

The main objectives of this research are as follows:

- (i) To assess the factors which affect wellbore integrity with regard to cementing.
- (ii) To review the problems associated with the usage of the conventional oil well cement (API Class G cement) and to evaluate the reduction in carbon dioxide emission with the usage of FAGP cement in comparison to Class G cement.
- (iii) To review and analyse the factors which affect the properties of geopolymer cement.
- (iv) To compare the properties of API Class G cement and FAGP cement with respect to the optimization of the wellbore integrity.
- (v) To evaluate the economic feasibility of the usage of FAGP cement for commercial oil well cementing purposes.

1.4 Scope of Study

One of the aims of this research is to identify the possible causes of loss of wellbore integrity due to the usage of the conventional OPC. Besides that, the adaptability and economic benefits of geopolymer based cement at wellbore conditions is also to be analysed. In addition, the properties of API Class G cement and FAGP cement in the identified areas which contributes to wellbore integrity such as the compressive strength, chemical durability, permeability, shrinkage and crack propagation threshold are compared.

CHAPTER 2.

LITERATURE REVIEW AND THEORY

This chapter discusses the wellbore integrity, cementing operations, and factors to consider when designing oil well cement, the chemistry and application of OPC and Geopolymer cement, the applications of Geopolymer cement and also the problems associated with the usage of OPC and Geopolymer cement.

2.1 Wellbore Integrity and its Relation to Cementing Activity.

To safeguard the environment, to produce oil and gas without compromising the safety of workers and surrounding communities and to ensure that the well is able to provide effective barriers for containment of well fluids and pressures, it is important to properly design and construct wells. In relation to oil well cementing, wellbore integrity can be defined as the ability to provide a complete zonal isolation throughout the lifetime of the well to enable effective and economical production. In most cases, the well would be able to preserve its integrity in the short term, but may lose its integrity as hydrocarbons are produced for several years due to different materials degradation, change in type of stresses due to depletion and/or cyclic pressures and also thermal loads [10]. According to Carey, [11] the wellbore integrity can be damaged during the pre-production phase and also in the production phase of a well.

2.1.1 Pre Production Phase

The wellbore integrity is said to be affected during the pre-production phase due to the following activities [11]:

(i) Damage to the formation during drilling activities.
(ii) Poor casing centralization leading to incomplete cementing due to eccentric cement setting and non-uniform thickness around wellbore.
(iii) Incomplete drilling mud removal which results in formation of mud pockets during cementing which will affect the wellbore integrity.

(iv) Incomplete cement placement whereby empty pockets exist after cementing operation.

(v) Poor bonding between the cement and the formation or casing due to wrong selection of cement slurry composition.

(vi) Poor selection of cement which results in cement shrinkage during hydration process.

(vii) Contamination of cement slurry by drilling mud or formation fluid which may alter the properties of cement upon setting.

2.1.2 Production Phase

During the production phase, the following factors may affect the wellbore integrity: [11]

(i) Mechanical Stress/ Strain

Pressure and temperature changes often occur during production and workover operations. The pressure changes taking place inside the casing would normally induce forces to the cement which may result in the inability of the cement to provide isolation as designed. In addition, temperature changes may also result in the thermal expansion of the casing. The casing would be subjected to compressive forces but it is restricted by the adjacent cement structure. However, a certain amount of compressive force would be transferred to the adjacent cement structure. This would result in the formation of micro-annulus between the casing and cement interface, breakdown of the bond between the cement and the formation and also the formation of fractures within the cement structure.

(ii) Geochemical attack

During the production of oil and gas, the well is exposed to fluids from the formation which is of high temperatures and with corrosive properties. This in turn would corrode the casing and even cause degradation of the cement structure due to carbonation, sulphate attack and also acid attack.

On the whole, the wellbore integrity can be affected due to the above mentioned reasons which are related very much to the cementing activity and the properties of the cement used. Therefore it is evident that cementing is a critical element in well construction and its integrity.

2.2 Cementing

The cementing operations in the oil and gas industry can be divided into two categories namely primary cementing and secondary cementing. The former can be defined as a process of displacing cement into the annulus area located between the casing and the formation [5] and the latter can be defined as remedial works to address flaws associated with primary cementing [4].The oil well cementing procedure can be summarized as a process of mixing cement slurry and subsequently pumping the slurry down the casing to the open hole below the casing string or the annulus area around the casing. The primary functions of oil well cement are to prevent fluid movement between subsequent formations and to support the casing [3]. In addition, upon setting in between the casing and the borehole, the cement sheath between the casing and borehole, functions as follows[3,4]:

(i) To support the surface casing string
(ii) To protect the casing from corrosive fluids arising from the formation
(iii) To prevent blowouts by aptly forming a seal
(iv) To protect the casing from shock loads especially when drilling in deep zones
(v) To establish sealing off zones during lost circulation

2.2.1 Factors to Consider When Designing Oil Well Cement to Ensure Wellbore Integrity

Cement sheaths are designed to provide zonal isolation. However, to preserve the integrity of the cement sheaths, the placement of the fluid has to be optimized and the mud must be completely removed from the wellbore. The properties of the oil well cement such as mixability, stability, rheology, fluid loss and thickening time has to be considered during the cement design phase to ensure optimum wellbore integrity [12].In addition, the developed mechanical properties upon setting of the cement must also be considered during the cement designing stage.

Cement Strength

The compressive strength of the cement sheath plays a pivotal role in achieving wellbore integrity where inadequate compressive strengths can lead to failure to provide zonal isolation. The cement sheath in the oil wells is subjected to static and dynamic stresses. The former is mainly due to the dead weight of the casing and compressive stresses which is resulted from the action of fluids and formations and the latter is resulted from drilling operations especially from the vibration caused by the drill string. In general, a compressive strength of 500 psi is required after 24 hours of curing to withstand the stresses it is subjected whereby the developed compressive strength is considered to be sufficient to support the casing string and to enable drilling to be continued for the next section without disintegrating the cement sheath [3,4]. The compressive strength of the cement sheath would depend on the curing conditions (temperature and pressure), amount of mixwater added and also the time elapsed after mixing. It is important to understand the strength development characteristics of the cement to be used when deciding on the waiting on cement (WOC) time.

Curing Temperature and Pressure

The two critical elements which determine the downhole performance of cement slurries are temperature and pressure at which it is subjected to downhole conditions. However, the effect of temperature is more significant whereby the cement slurry hydrates and sets faster and consequently develops strength quicker as temperature increases [3].Alternatively, pressure is subjected on the cement slurry by hydrostatic load of the well fluids.

Slurry Density

The designed cement slurry should have the density similar to the mud to minimise the risk of blowouts or lost circulation. The density of the cement slurry is usually controlled via volume of mix-water and also chemical additives. Some of the chemicals added to cement slurry to reduces its density are bentonite, diatomaceous earth and pozzolan where else the chemicals added to increase the cement slurry density are barite, hematite and also sand [4].

Chemical Durability

At the reservoir level, the presence of formation water in the pores may cause deterioration of the cement sheath. The presence of corrosive liquids such as sodium sulphate, magnesium chloride and magnesium sulphate in the formation water may corrode the set cement [3,4].The corrosion would decrease the compressive strength and make the cement sheath more permeable.

Permeability

Once the cement slurry has set in place, it would ideally have very low permeability whereby it is very much lower than the permeability of the producing formation itself. The permeability of the cement sheath should be as low as possible to provide complete zonal isolation at designated locations in the wellbore. However, if the cement slurry is not allowed to set accordingly during the cement placing operations, permeability channels may be created as a result. In addition, high water/cement ratio may also lead to an increase in permeability. Besides that, permeability of the cement sheath would reduce if it is subjected to high pressure at wellbore conditions.

Thickening Time

The length of time in which the slurry would remain in a fluid state in the wellbore condition is termed as thickening time. The cement would fail to reach the required depth of cementing operation if the thickening time is too short and if the thickening time is too long, the cost of operating expenditure would increase. During the cement designing stage, the allowances of thickening time for cement slurry would mainly depend on the wellbore conditions and the volume of the cement being pumped. The thickening time for the cement slurry would be shorter if there is an increase in temperature, pressure of fluid loss. Therefore, the wellbore conditions have to be simulated whilst testing the cement slurry in laboratory before the cementing operations are carried out. The standard thickening time for cement slurries during the cementing of casing for depths ranging from 6000 ft to 18,000 ft is 3 to 3.5 hours of pumping time [3].However; precautionary measures have to be taken to ensure that there are minimal shutdowns during the pumping of cement as it will cause the cement slurry to develop gel strength.

Cement Shrinkage

After the placement of cement slurry in the annulus, the shrinkage of the cement sheath would be detrimental in achieving long term zonal isolation. The cement shrinkage in oil wells can be categorised in two components namely [13]:

(i) The volume changes of products and reactants
(ii) The bulk volume changes

The process whereby the absolute volume after the cement sets is less than the volume occupied by the initial reactants is termed hydration shrinkage [13].The commonly used Portland cement would continue to experience shrinkage even after during the hardening period and also after setting [8].

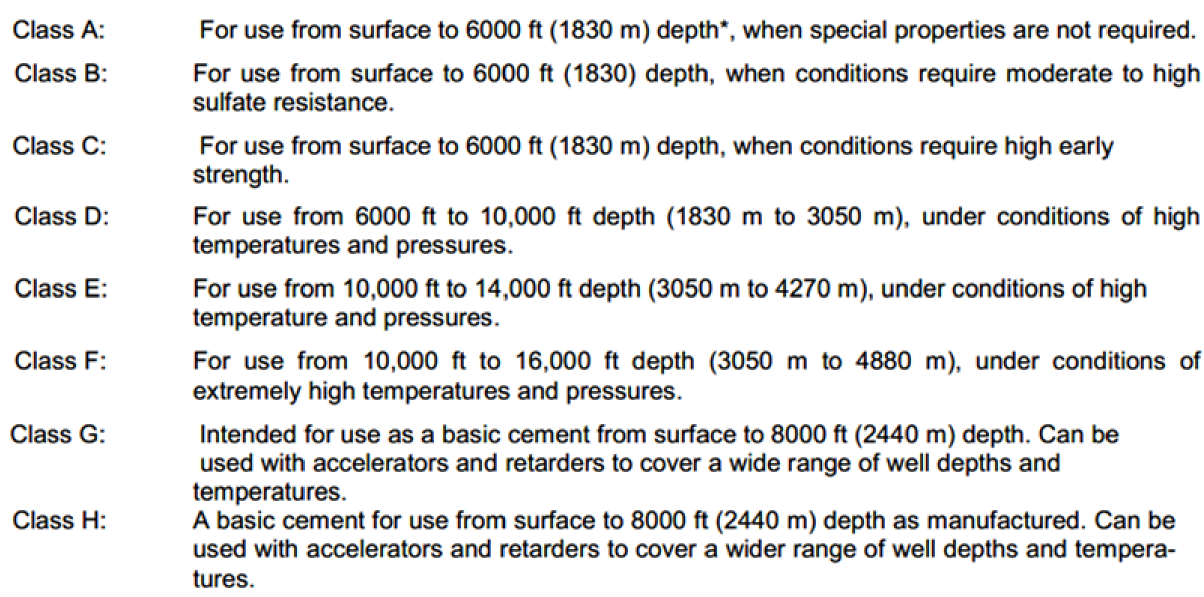
Crack Propagation Stress Threshold

In any brittle material which is exposed to uni-axial forces, three crack propagation stress threshold would occur. At any instance, the fracture phase starts with the crack closure. During this phase, the crack remains in a closed position despite the presence of external forces acting on the brittle material. Next an elastic region is encountered before the crack initiation phase begins. The crack initiation phase is followed by the crack growth (stable) phase. Lastly, after the crack growth phase, the crack damage phase takes place which is superseded by the unstable crack growth.

2.3 Conventional Oil Well Cement – Portland Cement

Till date, well cementing has been done using OPC [5,9].The basic raw material which is used in the manufacture of Portland cement is calcium carbonate and clay or shale whereby iron and alumina are added in the mix if these are not significantly present in the clay or shale product. Upon manufacturing, the four basic compounds which are present in Portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) [5].Water is then used as a carrier for placement of the reactive silicates which are present upon manufacturing. Upon pumping and placing of the cement slurry, the plastic lattice structure would develop gel strength and eventually result in a set solid mass. The manufacturing of Portland cement is done in requirement to meet the standards set for its application. For the oil and gas industry, the American Society of Testing Materials (ASTM) and American Institute of Petroleum (API) would decide on the specification of the cement to be used in oil wells. The ASTM provides five types of specification namely Types I, II, III, IV and V and API provides eight classes of specifications namely Classes A to H. Comparing both the governing bodies, the oil and gas industry generally adheres to the classifications in accordance to the API classifications [3].Table1 illustrates the API cement classes and their intended use [14]:

Table 1.The API cement classes and their intended use [14].



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

However, the API Class G is the most common type of cement used in the oil and gas industry [4-8].In addition, in the USA, the usage of API Class G and H contributes to 80% of the cement used in oil wells and for the rest of the world, API Class G cement accounts for 95% of the cement used in oil wells [15].

2.3.1 Problems Associated with the Use of Ordinary Portland Cement as Oil Well Cement

Firstly, the emission of carbon dioxide from the production of OPC is becoming a threat to the environment and also to the oil and gas industry. This is because approximately one ton of CO_2 is released to the environment for the production of one ton of OPC. The adverse effect of OPC production to the environment is the major problem associated with its usage.

In the North America, it was reported that there are tens of thousands of wells (abandoned, active or inactive) which are faced with gas leakage to the surface [8].This was attributed to the cement shrinkage as a result of using low density cement slurries whereby their properties would be affected at high temperature and pressures at downhole conditions [8].

Besides that, in terms of permeability, based on a research conducted in Canada, it was found that 4.6% of abandoned wells had leakage and 81% of the leaks was due to cementing whereby the commonly used type of well cement was the API class G and H type of cements [16].It was reported that the permeability of the API class G cement had increased in a range of 10-100 higher than the allowable range after curing for one month [16].This would jeopardise the goal of well cementing which is to provide complete zonal isolation whereby the permeability of the cement structure is said to be increasing over the lifetime of the well.

Lately, the carbon capture and storage has captured the limelight in providing a sustainable solution to reduce the contents of greenhouse gasses in the atmosphere. The carbon sequestration as an enhanced oil recovery mechanism would also aid in the increase in oil recovery from the formation. However, the well cement plays a pivotal role in the sequestration project to ensure that the CO_2 injected does not leach through the surrounding. According to Nasvi et al. [9,16].OPC which is used for well cementing would undergo cement carbonation followed by degradation of cement, reduction of strength, increase in permeability and shrinkage. In addition, the cement degradation increases the porosity and permeability of the cement which provides poor zonal isolation especially for carbon sequestration projects.

2.4 Geopolymer Cement

Geopolymer cement is an inorganic binder which can be polymerized from materials which are rich in silica and alumina. Joseph Davidovits (1970), a renowned French scientist and engineer, first introduced the term “geopolymer” by synthesising a reaction between alumina silicate powders with an alkaline solution. As compared to the conventional Portland cement, the geopolymer cement significantly reduces the emission of CO_2 without compromising the overall cement performance in an array of applications [17].The geopolymerization process can be described as the geosynthesis which incorporates naturally occurring silico-aluminates. Upon the synthesis, geopolymers should ideally consist of alumina and silica tetrahedral interlinked in an alternating manner whereby oxygen atoms are shared among the alumina and silica atoms. On the whole, the process of geopolymerization involves the rapid chemical reaction in an alkaline environment on Si-Al minerals. The geosynthesis of geopolymer would greatly depend on the ability aluminium ion to initiate chemical changes in the silica backbone [18]. These rapid reactions would result in a three dimensional polymeric chain and a ring structure which consists of Si-O-Al-O bonds which can be written as the following formula [18]:

$$\mathbf{Mn\ [-(SiO_2)\ z\text{-}AlO_2]\ n.\ wH_2O}$$

Where : M is the alkaline element (or cation)
n is the degree of polymerisation
z is the ratio of Al/Si which can be 1, 2, 3 or higher

The source of alkaline chemicals are usually $Ca(OH)_2$, NaOH, Na_2SiO_3, the combination of NaOH and Na_2SiO_3, the combination of KOH and NaOH, K_2SiO_3 and its combination, and $NaCO_3$. Different combinations of alkaline solutions will yield in different geopolymer strength and properties associated with it.

Despite continuous efforts in the development of geopolymer cement, the accurate mechanism governing the setting and hardening of geopolymer cement remains ambiguous. However, the chemical reaction pathway is comprised of three major steps as follows [19]:

(i) The dissolution of Si and Al atoms from the source material from the reaction of hydroxide ions.

(ii) The transportation or orientation or condensation of the precursor ions forming monomers.

(iii) The polymerisation of the formed monomers into polymeric structures

However, the three steps are complex whereby the different steps can overlap each other and it may take place simultaneously. Therefore, the study of the chemical reaction pathway is challenging mainly because it is difficult to distinguish and examine each step separately [19]. According to Van N.C the synthesised geopolymer can be classified in three basic forms as shows in Figure 1 [19].

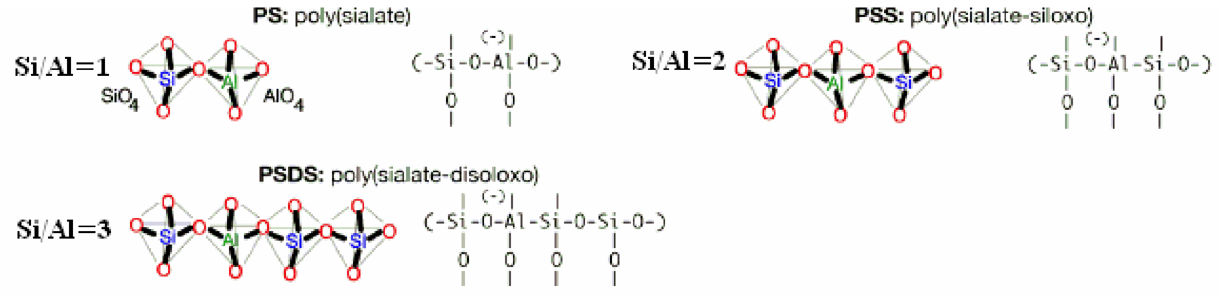


Figure 1.The three basic forms of the synthesised geopolymer.[19]

For the production of geopolymer, the raw materials which can be utilised include fly ash, metakaolin, recycled concrete slag and also silica fume and others. Despite having a range of raw materials from different sources, the activation of any of the mentioned raw material by alkaline solution will result in well compacted cement composites [20].However, based on the raw material selection and processing conditions, synthesized geopolymers can display a wide range of properties such as slow or fast setting, high compressive strength, low shrinkage, acid and fire resistance and also low thermal conductivity.

2.4.1 Applications of Geopolymer

The properties of geopolymers such as a sustainable option to reduce waste products, the availability of raw products, lower energy consumption, lower manufacturing cost, and its superior mechanical properties has prompted the research and development of geopolymers to be used commercially [21]. However, the research and development of geopolymer technology is focused mainly in the construction industry in efforts to develop reduced CO_2 construction materials to replace the conventional Portland cement (calcium silicate cements) [22]. Besides that, since geopolymers have a wide range of properties, there are also many other potential areas in which it can be used such as in the aviation industry, civil and military ship making industry, automobile industry, construction in maritime settings and also for nuclear and toxic waste immobilisation [18,22-24].However, the chemical structure in the polysialate in terms of the atomic ratio Si:Al can be used to classify the type of application in which the synthesised geopolymer can be utilised [18,25].According to Kim [26],the increase in Si/Al ratio resulted in the increase in Si-O-Si bonds and consequently the decrease in the Si-O-Al bonds which in turn results in geopolymers with higher compressive strength. Table2 illustrates applications of the geopolymeric materials in relation to the Si:Al atomic ratio [18]:

Table 2.The applications of geopolymeric materials in relation to Si:Al atomic ratio [18].

Si:Al Ratio	**Applications**
1	- Bricks - Ceramics - Fire Protection
2	- Low CO_2 cements and concretes - Radioactive and toxic waste encapsulation
3	- Fire protection fibre glass composite - Foundry equipment - Heat resistant composites, 200°C to 1000 °C. - Tooling for aeronautics titanium process
>3	- Sealants for industry, 200°C to 600°C - Tooling for aeronautics SPF Aluminium
20-35	- Fire resistant and heat resistant fibre composites

A new technology cannot be forced into an unwilling market, whereby the market itself must demand for new improved technology. The development of geopolymer technology for the use in oil well cementing is still in the research and development stage whereby many researchers are looking at the possibility of using geopolymer as oil well cement.

2.4.2 Type of Geopolymer as Well Cement

Among the available raw materials, fly ash is the best option as it provides the most sustainable solution for waste management [9].Besides that, fly ash is the preferred raw material in the manufacturing of geopolymer cement because the life cycle expectancy and durability of the structure was found to be superior in comparison to the other available raw materials [18].Moreover, its availability in abundance worldwide and low utilisation rate is also another factor why fly ash would be the preferred raw material for the synthesis of geopolymers [18-25].In addition, FAGP exhibits higher workability and mechanical properties with one fourth of the water consumption required to produce metakaolin based geopolymers [22].Besides that, the ASTM Class F Fly Ash is preferred compared to the low-calcium fly ash, ASTM Class C Fly Ash in the synthesis of geopolymers since the presence of the calcium element in substantial amount would affect the polymerization process adversely [27].

2.4.3 Problems in Association With the Use of Geopolymers as Oil Well Cement.

Many researchers have reported that geopolymer cements have properties which favour its potential use in oil well cementing such as acid resistivity, low shrinkage and high compressive strength development at variable curing periods, temperatures and environments [9, 16, 28-32].However, the wellbore conditions may display a more complex curing regime compared to the conventional high temperature curing regime which was experimented by researchers. Many experiments have been conducted to study the influence of curing temperature on the compressive strength of geopolymers and some of them in common have concluded that there is an optimum temperature at which the highest compressive strength is achieved [9,33].There maybe variations in the wellbore conditions in terms of temperature and the ability of geopolymers to yield sufficient compressive strength at that particular curing temperature has to be considered for the application of geopolymers as oil well cement.

In addition, most researchers have reported that the geopolymer cement achieves higher compressive strength quicker compared to ordinary Portland cement at elevated temperatures [9, 17, 21, 31]. This may be a critical problem in terms of pumpability of cement during the cementing operations especially if the thickening time is too short which would result in the setting of cement at different depth from the designed depth. However, some factors such as raw material selection, type of activator used, activator to fly ash ratio, curing temperature and pressure, alkali concentration (pH), liquid to solid ratio, and the relative humidity during the curing process can be manipulated to optimise the setting time of the geopolymer slurry. Therefore, the optimum properties of the geopolymer slurry in accordance to the wellbore conditions have to be studied in detail before it can be applied to the cementing operations.

Besides that, in most of the experiments conducted, the curing conditions did not reflect the saline water environment which is the case in most of the oil wellbore environment. According to Schlumberger Cementing Research, polymers do not perform well in high-salinity environments [34].Therefore, it is vital to study the concentration of salinity of wellbore conditions on the whole and to evaluate the properties of geopolymers according to various saline concentrations to identify potential saline concentration conditions in which geopolymers can be used.

One of the advantages of replacing ordinary Portland cement with geopolymer cement is that, the permeability of geopolymer cement is lower. Nasvi et al. [16] reported that the permeability of Portland cement is 10^{-10} cm/s whereas the permeability of geopolymer is 10^{-9} cm/s. In addition of being a better option, the permeability of geopolymers can still be reduced to ensure a more effective zonal isolation for a longer duration. However, the effect of pressure has not been covered thoroughly on the effect of geopolymer permeability whereby there is a 60% reduction in permeability at a confining pressure of 25MPa [16].Therefore, the effect of pressure on the geopolymer permeability and the optimum composition and manufacturing parameters of geopolymers should be identified for wells with a wide range of pressure variation.

2.5 Comparison between the Manufacturing of Portland cement and Geopolymer cement

Figure 2 illustrates the reaction mechanism and process conditions in the manufacturing of Portland cement and Geopolymer cement.

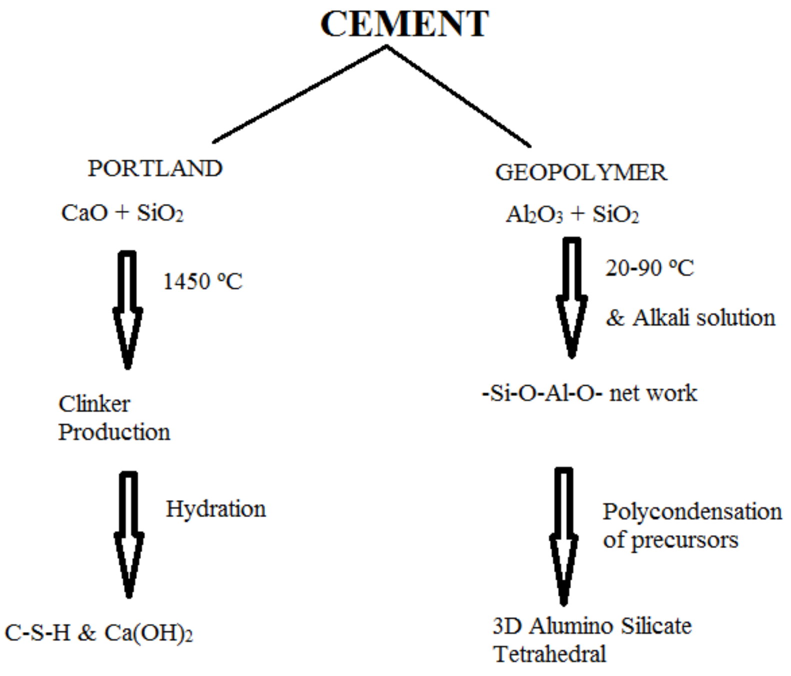


Figure 2. The comparison between the manufacturing of Portland cement and Geopolymer cement [9].

For the production of Portland cement, the clinker is first manufactured by sintering limestone and alumina-silicate rich materials such as clay. The clinker is then cooled and pulverized into fine powdered particles which are termed Portland cement. The Portland cement is then reacted with water and undergoes a series of reactions which is termed “hydration”. In each of the reaction, the Portland cement continues to set and harden. The developed Portland cement structure would normally be made up of calcium silicate hydrates (C-S-H). On the other hand, Geopolymer cement is manufactured by reacting alumina and silicate rich materials with alkali activating solutions at temperatures ranging from 20-90^{o}C. The geopolymerization reaction results in a three dimensional polymeric chain and a ring structure which consists of Si-O-Al-O bonds.

CHAPTER 3.

METHODOLOGY/PROJECT WORK

3.1 Research Methodology

The items which are covered in the research methodology can be divided into the following sections:

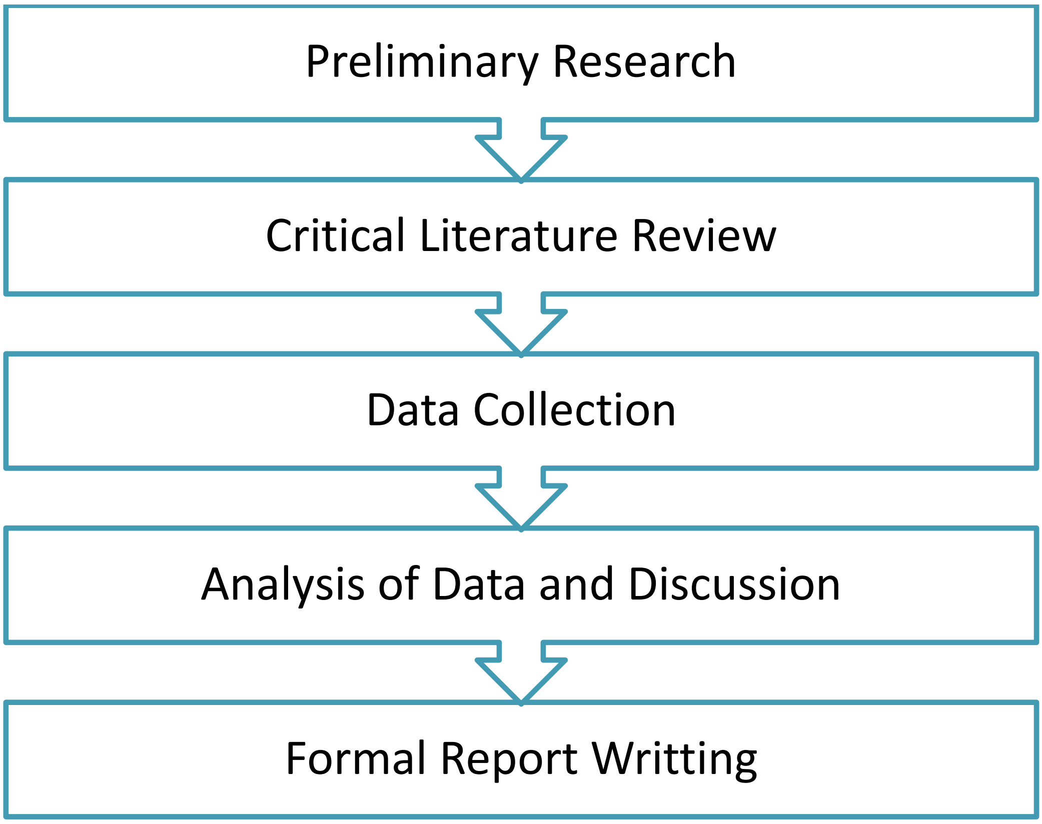


Figure 3. Project Flow Chart

3.2 Project Work Outline

The timeline given to complete this project was 12 weeks and the key scope of work has been identified in the Project Flow Chart (Figure 2).The scope of work performed can be divided into the following segments:

(i) Preliminary Research
(ii) Critical Literature Review
(iii) Data Collection
(iv) Analysis of Data and Discussion
(v) Formal Report Writing

3.2.1 Preliminary Research

Firstly, research on wellbore integrity and its relation to cementing activity was carried out. Besides that, the cementing operation was also studied whereby the factors which have to be taken into consideration when designing oil well cement which affects its integrity was evaluated. Next, the background study of conventional oil well cement (OPC) was carried out and their adverse effects particularly to the environment were assessed. Lastly, the chemistry and development of geopolymer technology were researched.

3.2.2 Critical Literature Review.

In the critical literature review, the research activities were focused mainly on factors affecting the wellbore integrity during cementing operations and also throughout the producing lifetime of the well. In addition, problems associated with the application of OPC as oil well cement were reviewed. A comparison between the properties of API Class G cement and FAGP cement which affect wellbore integrity were identified and analysed based on published research and experiments conducted by other researchers. The reaction mechanism and the factors which contribute to the rate of reaction were also researched to better understand the curing process. Besides, the factors which affect the final properties of the geopolymer cement to achieve its optimum mechanical strength and permeability were analysed based on the geopolymerization reaction chemistry.

3.2.3 Data Collection.

In this section, the work/experiments conducted by other researchers in the context of properties which affects the compressive strength, chemical durability, permeability, cement shrinkage crack propagation FAGP cement and API Class G cement were reviewed, compiled and summarized based on the following criteria:

(i) Type of test conducted
(ii) Parameters Varied

(iii) Source Material
(iv) Concentration of Alkali Activating Solution
(v) Materials Used
(vi) Curing Regime
(vii) Key Observations/Findings/Results

The compiled data are then tabulated in tables corresponding to the identified parameters which affects wellbore integrity such as Compressive Strength, Chemical Durability, Permeability, Cement Shrinkage and Crack Propagation Threshold. In addition, several tables which indicate the effects of varying mixture proportion on the compressive strength of geopolymer cement were also tabulated. Besides that, researches performed in the carbon dioxide emission and economic benefits of geopolymer cement in comparison to OPC were also obtained for evaluation.

3.2.4 Discussion of the analysis

In this section, the results from the compilation of data were analysed in terms of their consistency and reliability. The experimental results of various research work performed by the utilisation of API Class G cement and FAGP cement to enhance wellbore integrity were studied and the more superior type of cement was identified and discussed upon. The key parameters which are important for the application of geopolymers for oil well cementing was identified and their optimum parameters to provide superior wellbore integrity were highlighted and discussed.

3.2.5 Conclusion and Recommendation

Lastly, the findings based on the objectives of this project were highlighted and the key areas for further study were proposed.

CHAPTER4.
RESULTS AND DISCUSSION

The results of studies conducted by various researchers on the prospects of using FAGP comparing to the conventional Class G cement to optimize wellbore integrity were analysed and tabulated in Appendices A-H. The analysis was divided into the following sections:

(i) Compressive Strength
(ii) Chemical Durability
(iii) Permeability
(iv) Cement Shrinkage
(v) Crack Propagation Threshold
(vi) Carbon Dioxide Emission
(vii) Economic Evaluation

In each section, the comparison between FAGP cement and Class G cement were made and their advantages were discussed. The factors which contribute to the desired final property of the FAGP cement were also analysed to study its optimum requirements.

4.1 Compressive Strength

OPC based cement materials are made up of the formation of calcium silicate hydrates which provides strength to the structure. However, geopolymer cement would depend on the polycondensation of silica and alumina precursor to gain structural strength. The analysis of the comparison between the compressive strength of Class G cement and FAGP cement performed by various researches was done and is tabulated in Appendix A. The mutual factors which influence the compressive strengths of both the cement types are identified as the following, based on the availability of the research work performed:

(i) Curing Temperature
(ii) Curing Time

(iii) Curing Medium

In addition, the other factors which govern the compressive strength of FAGP cement such as the following was also studied to obtain the optimum parameters to achieve compressive strengths which are superior to Class G cement.

(i) Mixture Proportions
(ii) Aging Duration
(iii) Water/Geopolymer Binder Ratio

4.1.1Curing Temperature

The temperature at which the geopolymer cement is cured plays a pivotal role in achieving the final compressive strength. Many authors have reported that the rate of fly ash geopolymerization reaction increases as the curing temperature increases until the optimum curing temperature is reached [9,19,29,31,35-37]. Besides that, the synthesis of geopolymerization process would require a temperature ranging from 20^oC to 80^oC which was one of the basis whereby many experiments were conducted in that temperature range [38]. However, studies have shown that the fly ash geopolymerization reaction at ambient temperatures is extremely slow and results in a very low compressive strength [9,18,31,37]. Therefore, the temperature profile of the well has to be studied accordingly as it would not be practical to provide heat curing for the entire length of the wellbore in cases where the temperatures are below 23^oC.

Figure 4 illustrates the experimental results obtained from the study conducted by Nasvi et al. [9] which is the comparison of Uni-Axial Compressive Strength (UCS) (at 48 hours testing period) of FAGP cement and Class G cement at different curing temperatures.

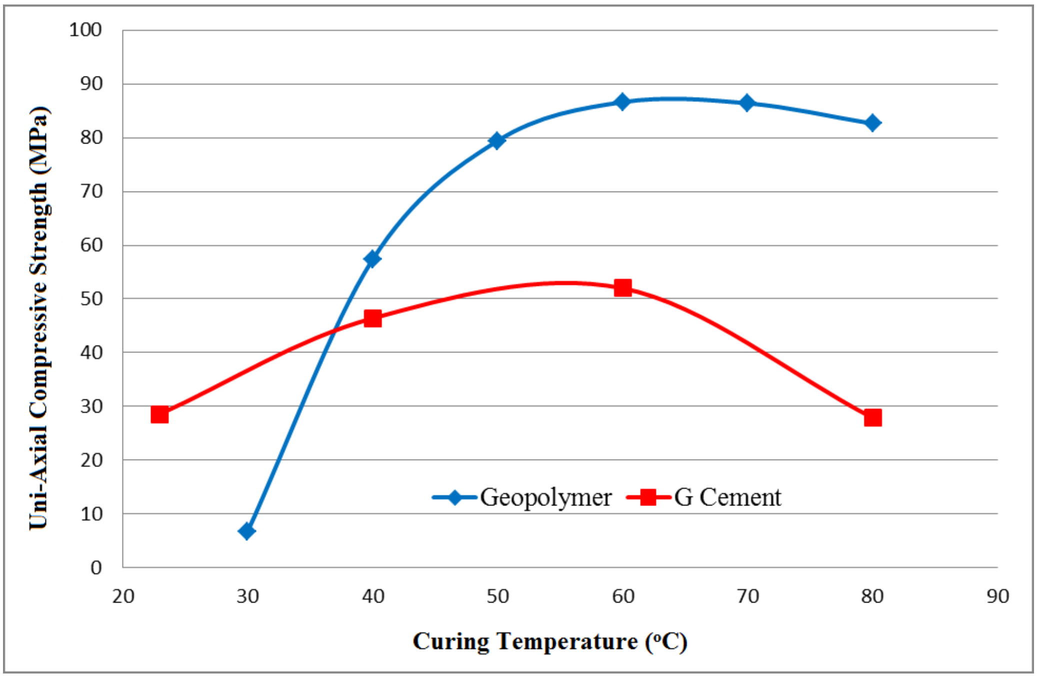


Figure 4.The effect of curing temperature on the compressive strength of FAGP and Class G cement [9].

In both cases, it can be observed that the compressive strength increases as the curing temperature is increased until the optimum temperature is reached before the compressive strength declines. For the FAGP cement, the highest strength achieved was 87.5 MPa at 60°C and the highest strength achieved for Class G cement was 53 MPa at approximately 56°C.The compressive strength achieved by FAGP cement is far more superior compared to the Class G cement for curing temperatures above 36°C. The effect of curing temperature is more pronounced in the FAGP cement compared to the Class G cement because of the higher strength increment as the curing temperature is increased. This is mainly due to the chemistry of geopolymerization whereby the Si and Al dissolve at a higher rate if the curing temperature is increased. Besides that, the strength reduction due to increase of temperature higher than the optimum temperature has a more pronounced effect on the Class G cement as it experiences 48% of strength reduction from the optimum condition compared to 6% reduction experienced by the geopolymer cement. This effect can be attributed to the nature of chemistry for the development of OPC cement whereby higher losses of silica occurs at elevated temperatures resulting in significant reduced compressive strength.

Figure 5 illustrates the experimental results obtained from the experiment conducted by Mustafa et al.[33] to study the effects of curing temperature on 7th day compressive strength. Similarly, the trend observed was that the compressive strength of FAGP cement increased until the highest compressive strength was achieved (at the optimum temperature) and decreased in strength when the temperature is further increased. The optimum temperature in this experiment was also found to be 60°C.

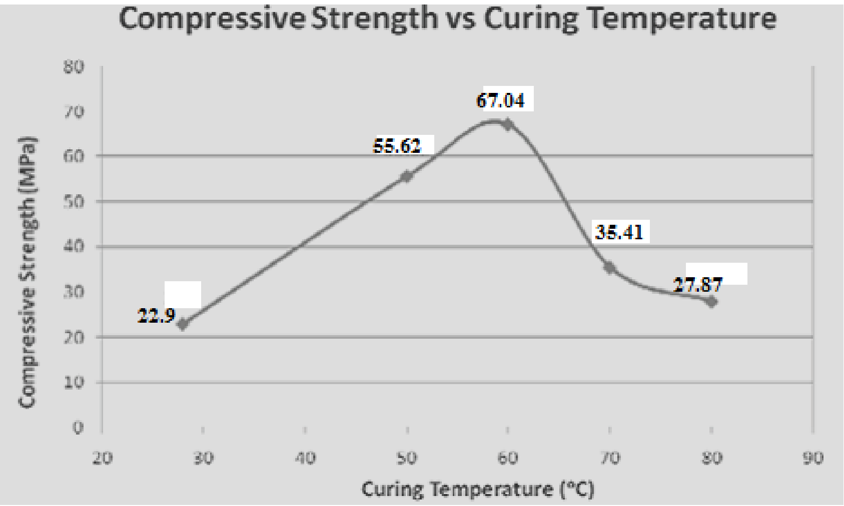


Figure 5.The compressive strength of FAGP cement at different curing temperatures [33].

In addition, the experiments conducted by Swanepoel et al.[35] also indicated that highest compressive strength (7th day and 28th day) for FAGP cement recorded was from curing at the optimum temperature of 60°C. The optimum temperature (60°C) for the geopolymerization reaction was similar for both the 7th day and 28th day of testing. In all three cases [12,33,35]the highest compressive strength was achieved at an optimum curing temperature of 60°C.

In most of the experiments conducted, the specimens are cured at a certain regime and the compressive strength test is performed immediately or after a certain time interval (usually 7th day or 28th day). From Table 13, comparing the results from the experiments conducted by Nasvi et al. and Mustafa et al.[9,33], it is evident that the timeline at which the compressive strength test was conducted does not affect the optimum curing temperature. This may be due to the inactivity of the geopolymer reaction at ambient temperature (below 36°C). Furthermore, it also implies that the rate of geopolymerization reaction heavily depends on higher than ambient condition (23°C) but below than the optimum curing temperature of 60°C.

Park et al.[37] studied the effect of curing temperature (only at selected temperatures of 20°C, 50°C and 80°C) on the compressive strength of fly ash geopolymer cement with curing time of 7,14 and 28 days. Figure 6 illustrates the results obtained for the three curing temperatures studied.

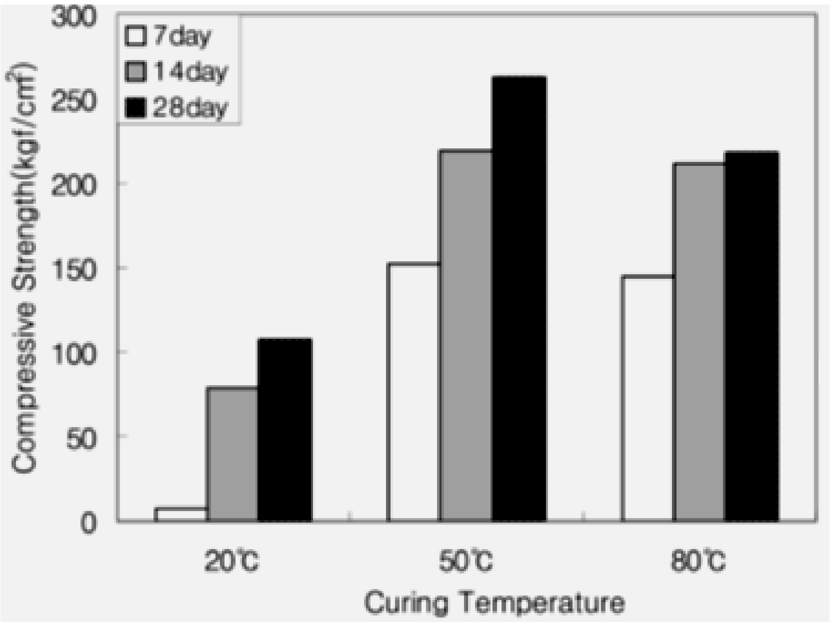


Figure 6. The effect of curing temperature on the compressive strength of FAGP cement cured at 7,14 and 28 days [37].

From Figure 6, the geopolymerization reaction rate at 20°C is very low which translates to low 7th day compressive strength. Similar to the other experiments conducted, the compressive strength increases until the optimum temperature is reached and declines as the temperature is further increased. However, several important hypotheses can be gained from this experiment.

(i) <u>For the 20°C Curing Temperature:</u>

At temperatures close to ambient temperature (23°C), the rate of geopolymerization reaction is slow. However, as the slow rate of reaction occurs and as time elapses, the geopolymerization process takes place and a minimal compressive strength is attained.

(ii) For the 50°C Curing Temperature:

At the optimum temperature (for this case) the compressive strength continues to increase as the curing duration is increased. This suggests that not all the raw materials have reacted and there is more room for improved compressive strength at longer curing duration.

(iii) For the 80°C Curing Temperature:

Due to the higher initial temperature, the geopolymerization reaction takes place however it is limited because the geopolymerization reaction requires the presence of water molecules in order to develop substantial compressive strength and most of the moisture is lost due to drying/heating at elevated temperatures. Besides that, at higher temperatures the intergranular structure of geopolymers may be broken which reduces the compressive strength. The increment of compressive strength from the 14th day till the 28th day is very minimal which translates to the above mentioned causes.

Hence the optimum curing temperature has to be identified to ensure the effectiveness of having a prolonged curing duration.

In conclusion, with comparison to Class G cements, the FAGP cement would be a better option for temperatures above 36°C. In relation to oil well cementing, the temperature profile at the oil well is a function of two independent variables, namely the geothermal gradient and also the bottom hole static temperature [39].Since the temperature profile varies according to the geographical location, the temperature profile has to be taken into consideration before deciding on the utilisation of the FGAP cement. In addition, at any temperatures above 40°C, the FAGP cement continues to gain compressive strength for a minimum of 28 days at least.

4.1.2 Curing Time

Apart from curing temperature, the curing time is an important factor for the development of compressive strength of FAGP cement. The curing duration is analogous to the thickening time whereby the thickening time of oil well cement is a function of mixing and pumping time, displacement time and plug release time.

The experimental results carried out by most researchers [19,29,35,36] shows that the curing time is dependent on curing temperature and similar trend was observed as in the curing temperature analysis whereby the compressive strength reduces after an optimum curing time.

Mahmoudkhani et al.[29] had performed experiments to study the effects of curing time on the compressive strength of an undisclosed geopolymer mixture (denoted GeoCem-XX) and compared its values with data of API Class G cement. The data from the experiment was extracted and Figure 7 was plotted to illustrate the effects of curing time on the compressive strength of the GeoCem-XX geopolymer cement and Class G cement. The experiment was conducted at 50^{o}C which is close to the optimum curing temperature of 60^{o}C as discussed in the curing temperature section.

Table 3. The effect of curing time on the compressive strength of geopolymer cement and API Class G Cement [29].

Curing Duration (hours)	8 hours	16 hours	24 hours	48 hours
Cement G Compressive Strength (MPa)	6.53	10.16	11.61	13.56
GeoCem Compressive Strength (MPa)	9.27	14.58	17.51	24.02

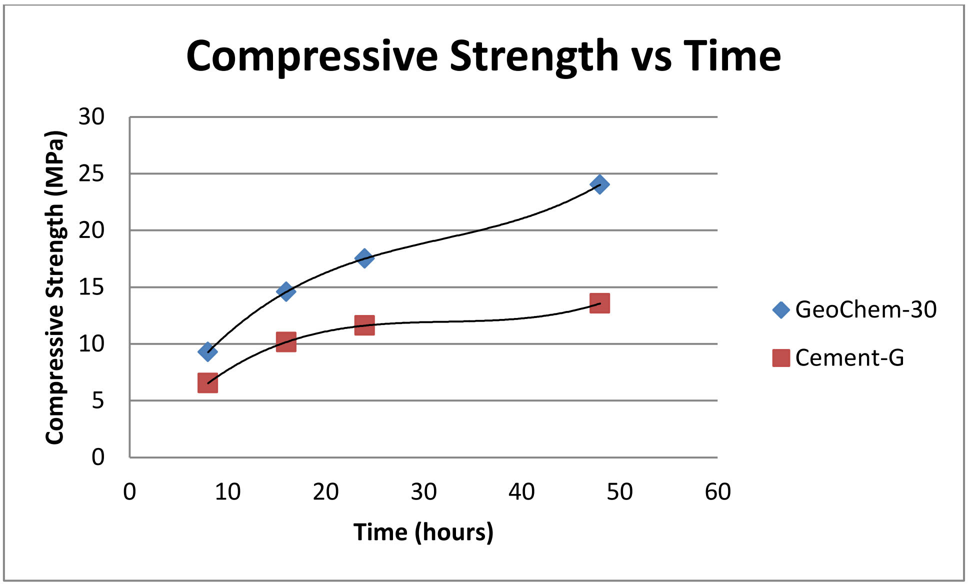


Figure 7 . The effect of curing time on the compressive strength of geopolymer cement and API Class G cement [29].

Firstly, the GeoChem-30 Geopolymer Cement possesses higher compressive strength compared to the API Class G Cement for all curing timing. Besides that, based on the shape of the graph profile of GeoChem-30, it can be seen that the there is more room for improvement in compressive strength compared to the API Class G Cement. In addition, the increase in compressive strength of GeoChem-30 from 24 hours to 48 hours is 37% compared to 17% increase observed in the API Class G Cement. The API Class G cement appears to be reaching a plateau on the compressive strength after 48 hours of curing time; however the GeoChem 30 Geopolymer Cement appears to have a continual improvement even beyond 48 hours.

Swanepoel et al.[35]had conducted a series of experiments to study effect of curing time (6,24,48 and 72 hours) on the developed compressive strength of FAGP cement with kaolinite additive. Figures 8 and 9 illustrate the compressive strength which was developed at different curing timing and temperature at 7th day and 28th day of testing [35].

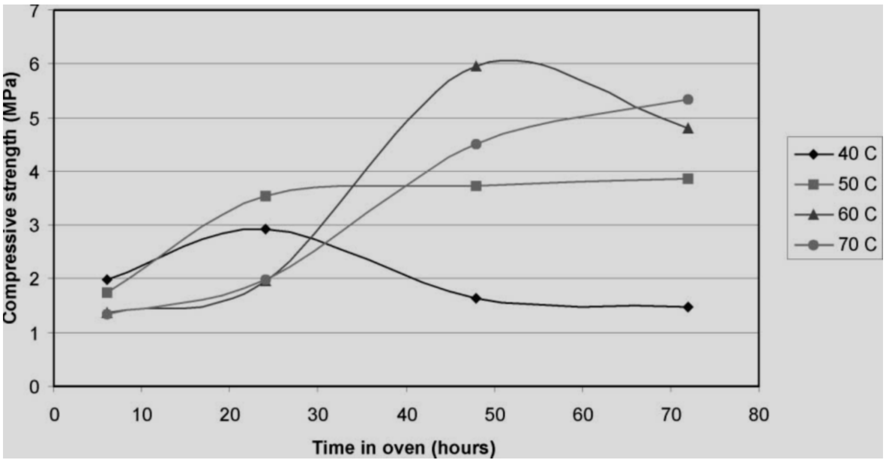


Figure 8.The resultant compressive strength on 7th day of testing [35].

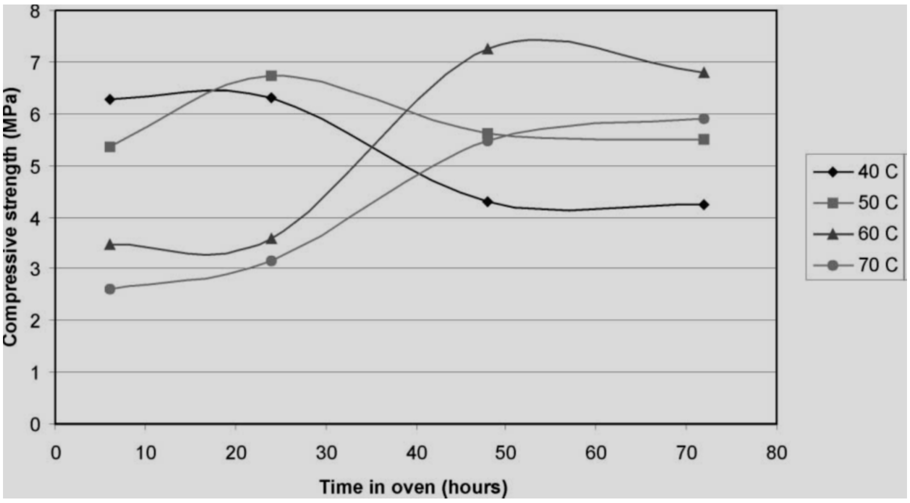


Figure 9.The resultant compressive strength on 28th day of testing [35].

Both Figure 8 and 9 exhibit different curves for different testing dates. This is mainly due to the continuous geopolymerization reaction taking place at room temperature from the 3rd day (after 72 hours of curing at respective temperatures) till the 7th day (the date at which the first compressive strength test was carried out) and until the 28th day (the date at which the final compressive strength was carried out).

For the 7th day compressive strength test the following are some of the key observations to be noted:

(i) The highest compressive strength recorded was at the optimum curing temperature of 60°c at 48 hours of curing time.

(ii) The 24 hour curing time showed positive response for all curing temperatures. However, specimens cured at 40°C showed a dip in compressive strength and specimens cured at 50°C showed a flattened response.

(iii) Up to 48 hours of curing time, all curing temperature regimes showed incremental geopolymerization reaction taking place (indicated by improved compressive strength) except for curing temperature of 40°C. In addition, a huge incremental increase in compressive strength was observed for the curing temperature of 60°C and 70°C. This evidently suggests that the geopolymerization rate of reaction requires heat addition in the range of 60°C -70°C.

(iv) After exceeding the curing time of 48 hours, the specimen cured at 60°C experiences a dip in compressive strength. Besides that, the specimens cured at 40°C and 50°C showed a flattened response.

On the other hand the following are some of the key observations observed from the 28th day compressive strength test:

(i) The 28th day compressive strength graph profile for the curing temperatures and its respective curing time is notably similar to the 7th day compressive strength graph profile. This correlation suggests that the frequency and test intervals need not be taken as a key consideration for experimental studies of curing regime of FAGP cement.

(ii) The compressive strength measured on the 28th day showed a small increase in compressive strength at similar curing regime (temperature and time) compared to test conducted on the 7th day. This suggests possibilities of low rate of geopolymerization occurring at room temperature after the curing regime until the date of test.

(iii) Similar to the 7th day compressive test, the optimum curing time corresponding to the highest compressive strength was observed to be 48 hours which also corresponds to the optimum curing temperature of 60°C.

Figure 10 illustrates the effect of curing time on compressive strength for two different mixes proportion of geopolymer concrete at curing temperature of 80°C which was experimented by Chanh et al. [19]. The two mix proportions namely CP3 and CP5 denote different alkaline liquid molarity used to manufacture the geopolymer concrete which is 18M and 14M respectively.

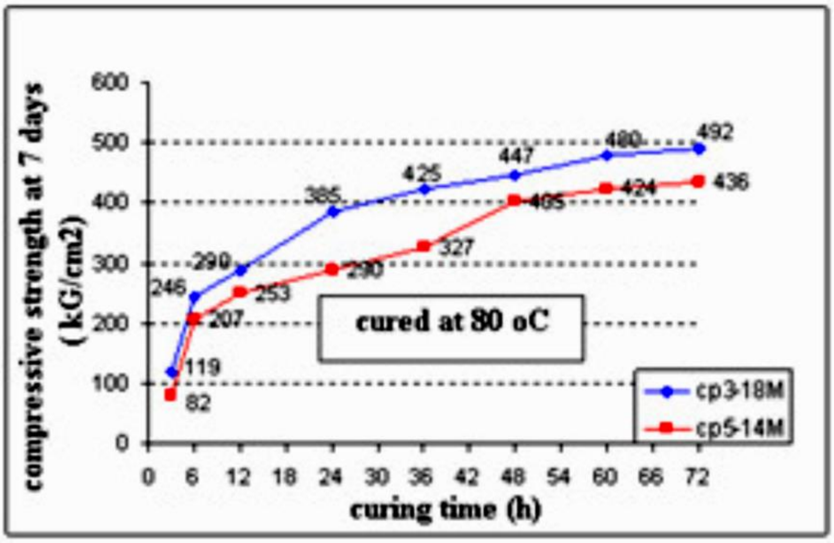


Figure 10. The study of effects of curing time on compressive strength for two different mixture proportions [19].

The data was extracted from the Figure 10 manually to further study the effects of curing time and was tabulated in Table 4.

Table 4. Data extracted from Figure 10 to study the effects of curing time on compressive strength for two mixture proportion.

	Compressive Strength at 7 days (kg/cm2)	
Curing Time (hours)	Mix 1	Mix 2
3	82	119
6	207	246
12	253	290
24	290	385
36	327	425
48	405	447
60	424	480
72	436	492

In both cases, it was found that the compressive strength of 90-92% was achieved at curing of 48 hours. This suggests that most of the geopolymerization reaction takes place within the first 48 hours of curing. In addition, the shape of the compressive strength profile appears to be reaching a plateau approaching 72 hours of curing also suggesting that additional research has to be carried out to study the feasibility of curing for more than 72 hours with minimum improvement in compressive strengths.

4.1.3 Curing Medium

To assess the suitability of geopolymer cement to be used for oil well cementing, the downhole conditions are to be simulated and studied. In order to simulate downhole conditions, Giasuddin et al. [32] studied the uniaxial compressive strength of FAGP cement and API Class G Cement under different medium namely water curing 8% saline water curing, 15% saline water curing, and heated water/saline water curing. Figure 11 illustrates the results obtained from the experiment conducted [32]:

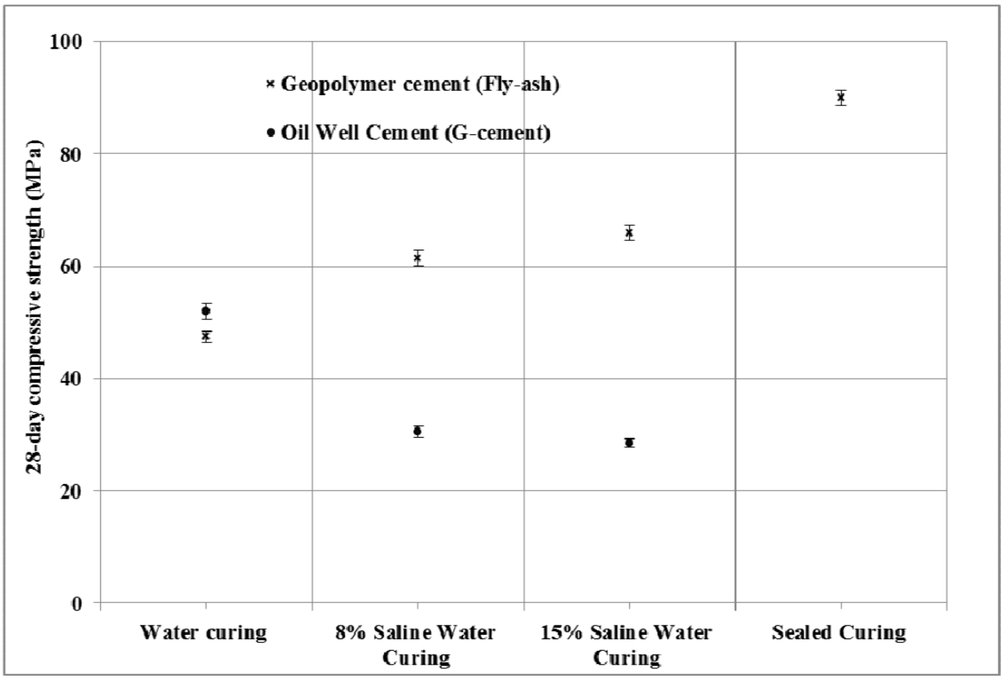


Figure 11.The 28 day compressive strength for FAGP and API Class G cement under water, 8% saline water and 15% saline water curing[32].

The data was extracted and tabulated in Table 5

Table 5. The 28th day compressive strength for FAGP and API Class G cement under water, 8% saline water and 15% saline water curing [32].

	28th Day Compressive Strength (MPa)	
Curing Medium	FAGP Cement	API Class G Cement
Water Curing	47.5	52.0
8 % Saline Water Curing	61.5	30.5
15 % Saline Water Curing	66.0	28.5

From Table 5, it can be seen that under the water curing medium, the FAGP cement developed lower compressive strength in comparison to API Class G Cement. However, it developed 50% higher compressive strength under 8 % Saline Water Curing and 57% higher compressive strength under 15 % Saline Water Curing in comparison to the API Class G Cement.

Another study focusing on the effects of water/brine solution as the curing medium of FAGP cement was conducted by Nasvi et al. [9]and similar trend were observed (as illustrated in Figure 12) whereby higher compressive strengths were attained when cured under brine (15%) compared to water. The scenario in which geopolymers attain higher compressive strengths can be described in its reaction. In normal water curing, the alkalis (K/Na) from the geopolymers would leach out into the water causing strength reduction. However, in the case of brine water, the chlorine ions present in the solution would not react with the –Si-O-Al- bonds which are the basic structure of geopolymers but would react with the alkali ions (K/Na) to produce NaCl or KCl. The higher content of NaCl or KCl in the solution will increase the geopolymerization rate and also provide resistance to the leaching of alkaline from the geopolymers.

Therefore, in a curing regime of saline condition, in particular offshore regions where some salinity of sea water can be observed, the curing conditions (medium) favours the FAGP cement whereby much higher compressive strengths are attained. The favourable conditions of sea water for the geopolymerization reaction would be an added advantage because it not only achieves higher compressive strength compared to Class G cement but also provides an option of directly using sea water for the curing regime. In addition, the cost of offshore water treatment or transportation of potable water for the use of cement mixing can be reduced with the application of geopolymer cement for oil well cementing.

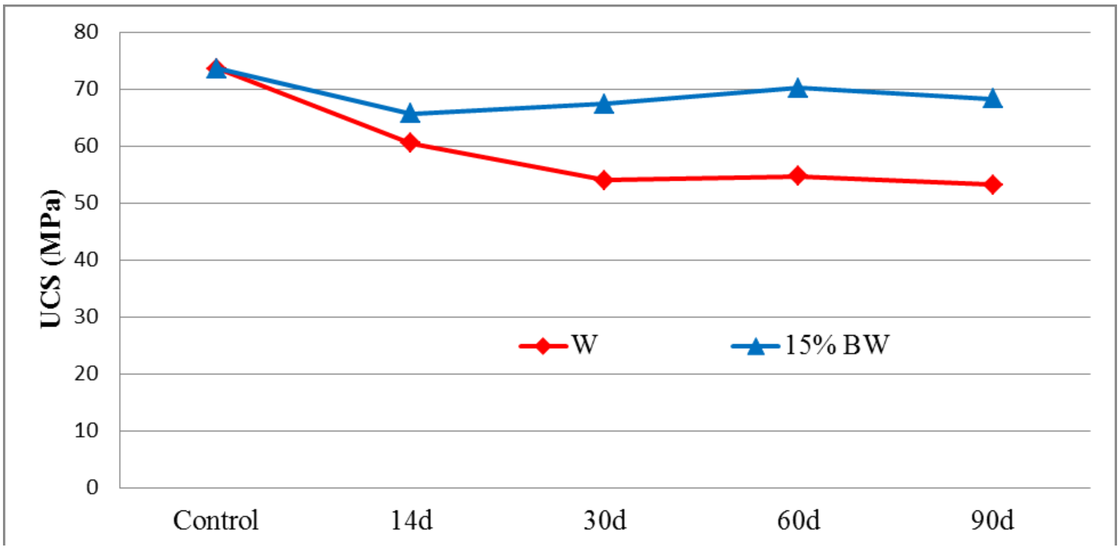


Figure 12.The compressive strengths of FAGP under fresh water and 15% brine water conditions [9].

4.1.4 Mixture Proportion

In this section, the variables which affect the compressive strength of FAGP cement and concrete would be discussed since very limited amount of experiments have been conducted using geopolymer cement alone. The following variables have been identified to affect the final compressive strength of the geopolymer cement/concrete [2,19,36,37,40-46]:

Activating Solution

The activation of fly ash would depend on the type of activation solution used. The activation solution which contains soluble silicates in them (such as sodium or potassium silicate) would result in quicker mechanical strength development due to higher reaction rates compared to the usage of hydroxides alone as the activator solution [36]. However, there are no clear experimental results which distinguish the better option between Sodium Hydroxide and Potassium Hydroxide on their effect on the reaction rates of Fly Ash [36].In most cases, researches preferred to use Sodium Hydroxide compared to Potassium Hydroxide since it is cheaper and widely available [47].

Sodium Hydroxide Concentration

Appendix B illustrates the work done by several authors on effects of NaOH Concentration on the compressive strength of geopolymer cement and concrete [37,40-45]. Due to the limitations in the area of geopolymer cement concerning the effect of NaOH on the compressive strength achieved, the research work on geopolymer concrete was also incorporated in this study. However, none of the experimental results could be comparable as other parameters such as alkaline liquid/fly ash ratio, type of alkaline liquid used (the ratio of NaOH / Na_2SiO_3) and curing regime were the same.

For the geopolymer cement study, Park, S et al. [37] found that the compressive strength increases when the concentration of the NaOH in the solution is increased irrespective of liquid/fly ash ratio as illustrated in Figure 13. However, the corresponding liquid to fly ash ratio of 0.4:1 produced the highest compressive strengths at the corresponding increments of solution concentration. Moreover, the increasing trend of compressive strength with the increase in NaOH concentration suggests that further increase in NaOH would also result in higher compressive strengths.

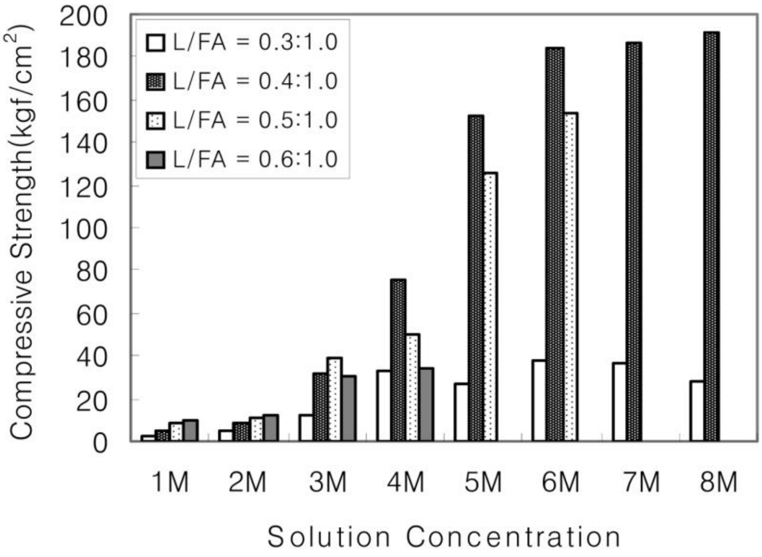


Figure 13. The compressive strength of different geopolymer cement prepared using different liquid/fly ash ratio and concentration of NaOH [37].

Based on the research conducted by Chindaprasirt et al. [43] the average compressive strengths of the geopolymer mortars at NaOH concentrations of 10,15 and 20 M were 48.4, 49.1 and 50.2 MPa respectively. The compressive strength did not show much variations in different NaOH concentrations which suggests that the NaOH doesn’t influence the compressive strengths of geopolymer concrete in the range of 10-20 M. In addition, Rachel,P et al. [41] also found that at room temperature curing, the 7th and 28th day compressive strengths were same for 10M and 12 M NaOH and at curing temperatures of $60^{o}C$, the 10M geopolymer mix had higher 7th day compressive strength but was lower than the 12 M mix in the 28th day test. However, Alida, A et al.[48]found that the FAGP aggregates obtain the highest compressive strength at an optimum NaOH molarity of 12 M.

Based on all the studies reviewed (illustrated in Appendix B), it was found that the NaOH molarity ranging from 8-20M had minimal impact on the final compressive strength of the geopolymer concrete whereby the optimum NaOH Molarity of 12M can be taken as the optimum molarity as reported by Alida et al.[48]. The role of the activating solution would be to activate the precipitation and crystallisation of siliceous and aluminous species which are available in the solution. In the solution, the OH^- would act as a catalyst to enhance reaction rates and the metal cation (Na^+ or K^+) would be the building blocks for the structural element. Initially, the high concentration of NaOH would yield higher strengths but excessive OH- in the solution would result in adverse morphology and non-uniformity resulting in lower strengths [49].Therefore, only optimum conditions would favour the highest reaction rate (corresponding to higher compressive strength) and the conditions varies for different fly ash compositions, curing regime and mix proportions.

Sodium Silicate Concentration

In most experiments conducted, alkali activating solution such as NaOH and KOH are added to Sodium Silicate which serves as a stimulating tool to improve the alkalinity of the solution, hence resulting in higher compressive strengths [27,49]. Appendix C illustrates the experiments conducted by Chindaprasirt et al.[43] and Law, D [2]which focuses on the effect of the Na_2SiO_3/NaOH ratio on the compressive strength of geopolymer concrete. According to the research done by Chindaprasirt et al.[43] the optimum Na_2SiO_3/NaOH ratio was found to be 0.67-1.00

and increasing the ratio will only further decrease the compressive strength of the geopolymer concrete. Besides that, Law, D [2] found that there was a substantial increase in compressive strength between Ms =0.75 (Na_2SiO_3/NaOH = 0.95) to Ms=1.00 (Na_2SiO_3/NaOH = 1.59) however, further increase to Ms=1.50 (Na_2SiO_3/NaOH = 2.63) resulted in only a small increase in compressive strength. Both the experiments cannot be compared directly as there were variations in curing regime and aging duration. However, the results show that there is an optimum value for Na_2SiO_3/NaOH ratio which has to be determined for the specific curing regime and aging duration. Until the optimum Na_2SiO_3/NaOH ratio is reached, the increase in soluble silicates increases the dissolution process of the fly ash particles. As this process takes place, the rate of reaction increases as there are large amounts of reaction products available. However, as the reaction takes place, the precipitation of the reaction products also occurs. This results in less contact between the fly ash particles and the alkaline solution resulting lower dissolution rates. Therefore, further increasing the Na_2SiO_3/NaOH ratio above its optimum value would not result in a positive outcome on the reaction rate (compressive strength).

Alkaline Liquid/Fly Ash Ratio

Appendix D illustrates the experimental studies performed by researchers which combines the experiments conducted on geopolymer cement and concrete (experiments on geopolymer concrete was also considered since limited experiments on geopolymer cement alone was conducted)[19,40,46,47]. As illustrated in Figure 13, based on the experiments on FAGP cements conducted by Park, S et al.[47]it was observed that the alkaline liquid / fly ash ratio of 0.4 gave the highest compressive strength for different NaOH concentrations ranging from 1M-10M. In addition, Palomo, A et al.[36] studied the influence of alkaline liquid/fly ash ratio (range from 0.30-0.40) and found that the increase in alkaline liquid/fly ash ratio results in the increase in compressive strength of the geopolymer cement. This phenomenon is attributed to the excess in OH^- ions present in the solution which decreases the strength of the geopolymer cement. According to a cited reference in the journal written by Hardjito, D et al.[40], the excess content of sodium in the solution would form sodium carbonate by carbonation process which leads to lower polymerization reaction taking place.

In addition, studies on the effect of alkaline liquid/fly ash ratio on geopolymer concrete conducted by Hardjito, D et al.[40] also showed similar behaviour whereby the optimum alkaline liquid/ fly ash ratio was 0.4.

4.1.5 Aging Duration

The experiment conducted on geopolymer concrete was used to study the effect of aging duration on its developed compressive strength due to limitations in work done on geopolymer cement for the aging duration scope and is tabulated in Appendix E. Based on the experiment conducted by Tempest, B et al.[48] on geopolymer concrete, as illustrated in Figure 14, it was found that for all cases, the compressive strength test performed on the 28th day improved with increase in aging time. Besides that, another key observation from the experiment is that the compressive strength may be further improved if the aging time is increased which would require more studies to be conducted.

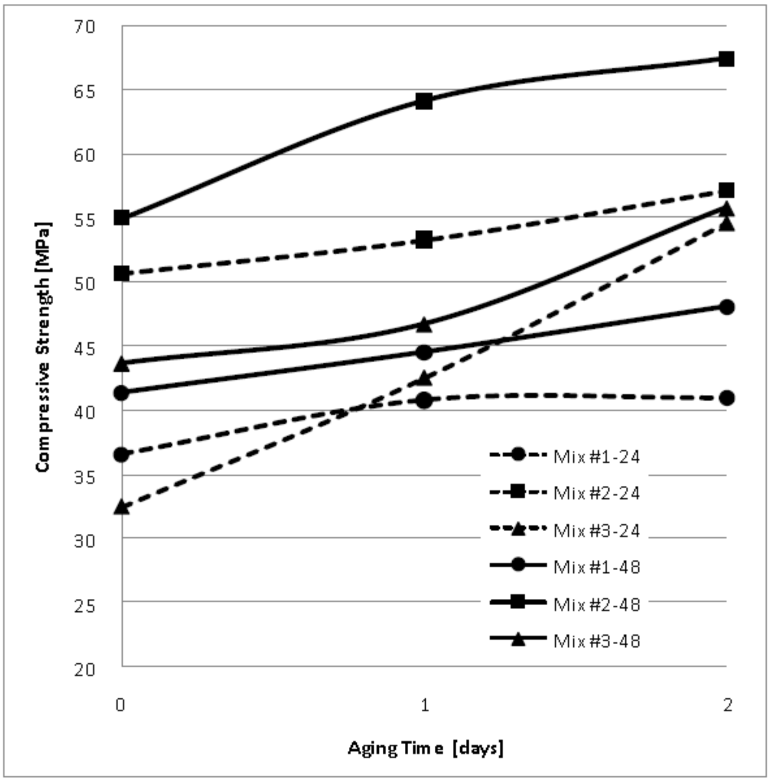


Figure 14. The effect of aging duration on the compressive strength of FAGP concrete [48].

Based on the experiment conducted by Chindaprasirt et al.[43]on geopolymer concrete, the optimum aging time was found to be 1 day which produced 43.5 MPa and further increase in aging time reduced the compressive strength. Figure 15 illustrates the effect of aging duration on the 7th day compressive strength test of geopolymer mortar when a curing regime of 60°C for 24 hours was applied in the experiment conducted by Chindaprasirt et al [46].

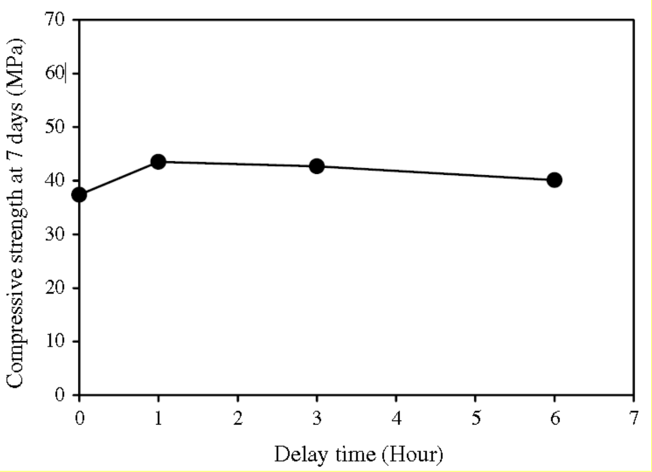


Figure 15. The effect of aging duration on the 7th day compressive strength of geopolymer mortar cured at 60°C for 24 hours [43].

In addition, in the study conducted by Lloyd, N and Rangan, B [50], it was found that the aging period of 24 hours resulted in an increase of compressive strength of 37.5 MPa to 46.4 MPa as illustrated in Figure 16.

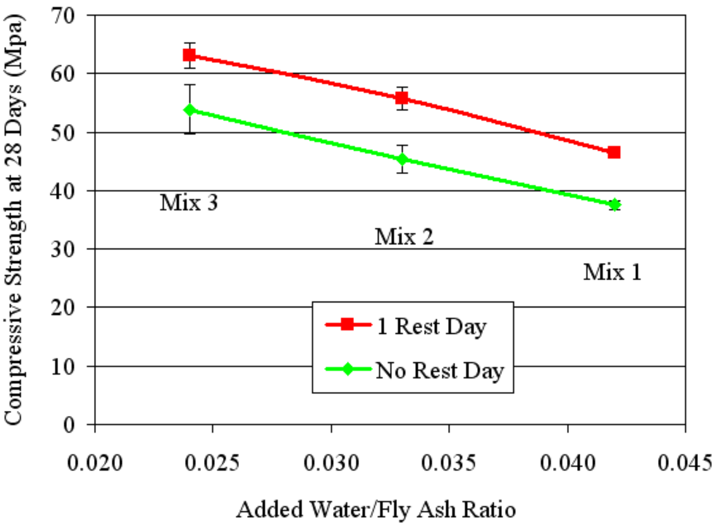


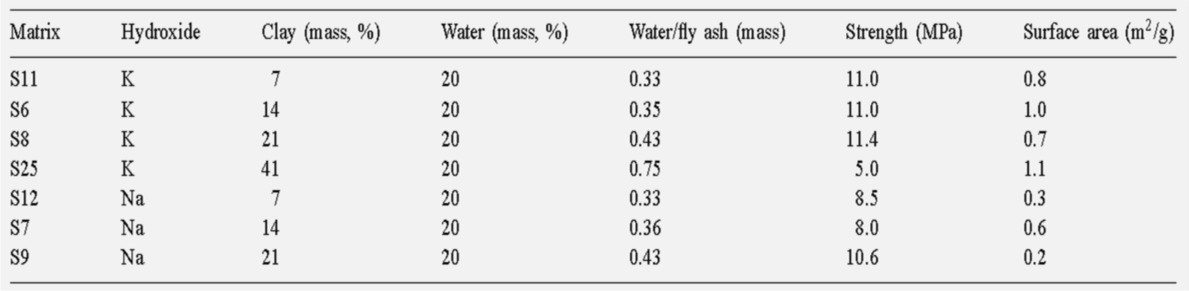
Figure 16. The effect of aging period of 24 hours on the compressive strength of FAGP concrete [50].

4.1.6 Water/Geopolymer Binder Ratio

The water content effect on the compressive strength of geopolymer cement was studied and is tabulated in Appendix F.

Jaarsveld et al.[51]studied the effect of water content on the 14th day compressive strength for geopolymer cement and found that the optimum water/fly ash ratio was 0.43 for both alkali activating solution of NaOH and KOH as illustrated in Table6.

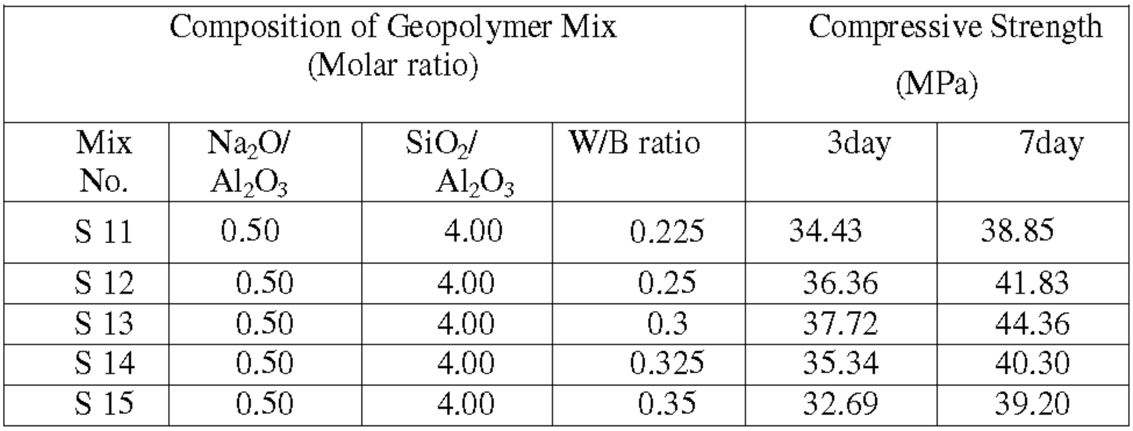
Table 6.The effect of water/fly ash ratio of the 14th day compressive strength of geopolymer cement for different alkali activating solutions (NaOH and KOH) [51].



Matrix	Hydroxide	Clay (mass, %)	Water (mass, %)	Water/fly ash (mass)	Strength (MPa)	Surface area (m^2/g)
S11	K	7	20	0.33	11.0	0.8
S6	K	14	20	0.35	11.0	1.0
S8	K	21	20	0.43	11.4	0.7
S25	K	41	20	0.75	5.0	1.1
S12	Na	7	20	0.33	8.5	0.3
S7	Na	14	20	0.36	8.0	0.6
S9	Na	21	20	0.43	10.6	0.2

Based on Table 6, it can be observed that for the alkaline activating solution of KOH, the 14th day compressive strength increases until an optimum water/fly ash ratio and decreases when the water/fly ash ratio is further increased. In addition, the similar observation was observed for the activating solution of NaOH but the optimum water/fly ash ratio cannot be ascertained as additional experiments on the impact of water/fly ash ratio beyond 0.45 for was not conducted. Besides that, Ghosh,K et al. [52]also found that the increase in water/geopolymer binder resulted in increase in 3rd day and 7th day Compressive Strength until an optimum value (0.3for this experiment) was obtained and further increase in water/geopolymer binder ratio resulted in the decrease in compressive strength as illustrated in Table 7.

Table 7. The effect of water/geopolymer binder the 3rd day and 7th day compressive strength of FAGP cement [52].



Composition of Geopolymer Mix (Molar ratio)				Compressive Strength (MPa)	
Mix No.	Na_2O/ Al_2O_3	SiO_2/ Al_2O_3	W/B ratio	3day	7day
S 11	0.50	4.00	0.225	34.43	38.85
S 12	0.50	4.00	0.25	36.36	41.83
S 13	0.50	4.00	0.3	37.72	44.36
S 14	0.50	4.00	0.325	35.34	40.30
S 15	0.50	4.00	0.35	32.69	39.20

The results from both the experiments cannot be compared directly as the curing regime and the date of testing conducted was different in both experiments. However, the similar trend observed suggests that the final compressive strength is dependent on the alkali concentration ultimately. This is because as the water content increases, the concentrations of alkali in the geopolymer mix decreases proportionally. The alkali concentration is the deciding parameters in the dissolution rates of alumina silicate oxide which results in the availability of raw materials for the geopolymerization process. Therefore, beyond the optimum water/fly ash ratio, additional water content would result in lower alkali concentration which reduces the dissolution of base material. The reduction of base materials would result in lower geopolymerization reaction which causes the reduction in the overall compressive strength. Therefore, the optimum water/fly ash ratio has to be determined for appropriate mixture proportion to achieve the desired final compressive strength.

4.2 Chemical Durability

One of the significant attributes of geopolymer cement is its superior chemical resistance to a wide range of acids and alkaline solution in comparison to OPC based cement [53,54].This is because, geopolymers are made up of alumina and silicate polymerization which are more resistant to acids and bases compared to Portland cement which are made up of calcium silicate hydrate bonds possessing poorer resistance qualities towards acid.

In a study conducted by Iveron Materials [53],it was found that the FAGP mortars lost only 5% of their mass when immersed in 10% concentration of sulphuric acid over a 30 days period but silica fume OPC based concrete (the chemical resistant variety for OPC Concrete) experienced a total failure. Illustrated in Figure 17, a study conducted by Chanh et al. [19] showed that the cured geopolymer cement experiences less than 1.2% of weight loss after 25 days of exposure to 5% HCl and does not further lose its weight from the 25th day till the 50th day (end of experiment).

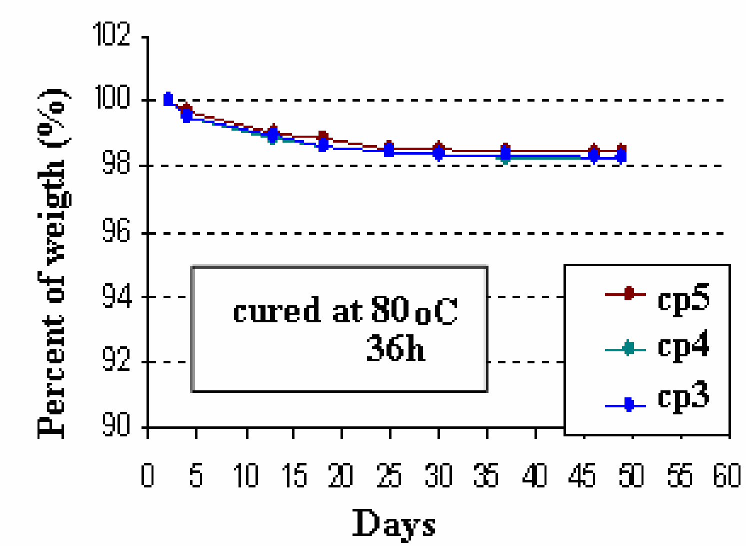


Figure 17. The percentage of weight of FAGP of different mix proportion when exposed to 5%HCl Solution [19].

In addition, the corresponding effects of the exposure to 5% HCl on the compressive strength was also studied and is illustrated in Figure 18 [19].It was found that at different mixture proportions, the geopolymer mixture which was cured at 80°C for 36 hours experienced 19.6-21.3% of decrease in compressive strength after 7 weeks of exposure.

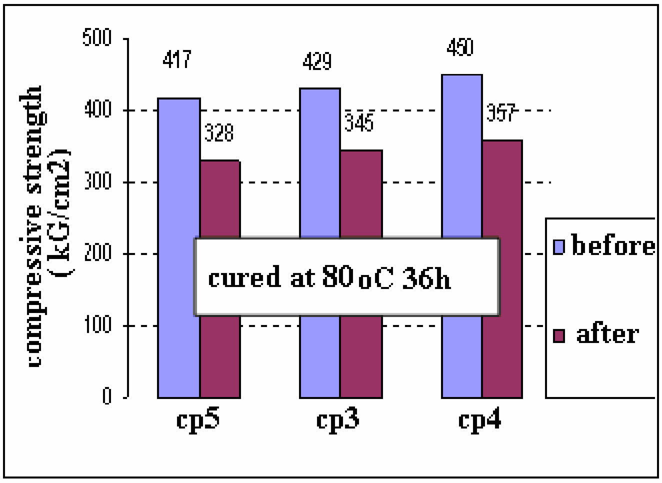


Figure 18. The effect of 5% HCl for 7 weeks on various mix proportion of FAGP cement cured at 80°C for 36 hours [19].

However, the amount of reduction in compressive strength due to exposure to corrosive environments (acids and salts) for FAGP cement is subjected to the following variables [19]:

(i) Alkaline Liquid Concentration

Alida et al.[44]performed a series of experiments to study the effect of the molarity alkaline liquid (10, 12 and 14 M) used on the acid resistance properties of FAGP cement and found that the 12 M molarity alkaline liquid was the optimum concentration to produce the highest compressive strength in the 28 week compressive tests conducted. Besides that, the microstructure figures also show that the 12M NaOH cured geopolymers had less cracks within its matrix [44].

(ii) Water Content

From the experiments conducted by Chanh et al.[19],it was found that as the water content is increased, the compressive strength of the cement decreases which is illustrated in Figure 17.

However, there is still need for further research to be conducted to obtain the optimum alkaline liquid concentration and water content which would increase the corrosion resistance capacity of FAGP cement.

4.3 Permeability

Appendix G illustrates the previous studies conducted by various researchers to evaluate the permeability of FAGP cement, Class G Cement, Geopolymer Concrete and Ordinary Portland Concrete. According to the cited reference of Nasvi et al. [16] in order to evaluate a successful cementing operation, the cement sheath should provide complete zonal isolation whereby the water permeability should be less than 0.1mD. Nasvi et al. [16] further added in his review on permeability citing several researchers that the typical values of API class cement ranges between 10^{-11} m^2 to 10^{-20} m^2 and within one month of curing, the water permeability of API Class G Cement in particular was 10-100 times higher than the allowable limit.

OPC based cement displays a coarse stacking of matter which results in the formation of more pores [53].On the other hand, geopolymer cement is made up of smooth and homogeneous structure which results in less porous structure [53].Zhang et al.[55] found that the permeability values (open pores/effective porosities) of geopolymers (synthesized with 90% metakaolin and 10% granulated blast furnace slag) were much lower than the OPC cement. However, Davidovits,J[57]found that the geopolymer cement permeability value was 10 times larger than Portland cement. This contrasting results obtained suggests that different mixture proportion and synthesising conditions would influence the permeability of geopolymer which needs to be addressed to be successful in replacing OPC based cement as oil well cement.

According to research work performed in assessing the permeability of geopolymers, the following parameters have been identified as contributing factors to its permeability [16,20,30,46]:

(i) Injection and Confining Pressures
(ii) Addition of Slag
(iii) Mixture Proportion (water/binder ratio and alkaline/fly ash ratio)
(iv) Curing Regime

4.3.1 Injection and Confining Pressures

In most cases, oil wells are subjected to gas injection during its production life as a method of enhanced oil recovery. Besides that, carbon sequestration which has become a popular subject of interest especially in the aid of reducing the global warming phenomena would require injection well of utmost wellbore integrity. Therefore, the well cement used should be of low permeability to avoid leakage of CO_2 to the formation which could be detrimental. Nasvi et al. [16]studied the CO_2 permeability to FAGP cement and found that the permeability of geopolymer pastes ranged from 2 x 10 $^{-21}$ to 2 x 10 $^{-20}$ m^2 which was lower than the permeability of conventional oil well cement (10^{-20} to 10^{-11} m^2) . It was also observed that flowrate produced a linear relationship with injection pressure, suggesting the suitability of the Darcy's Equation to obtain the CO_2 permeability of geopolymer. In addition, the CO_2 permeability was calculated assuming steady state flow rate and the variation of permeability to injection pressures and confining pressures are illustrated in Figure 19 and 20 [16]:

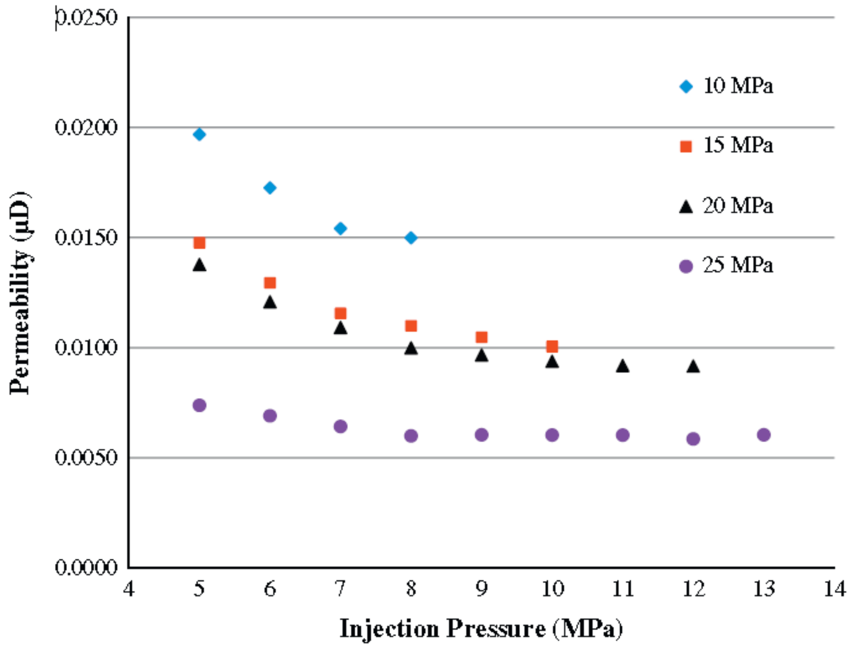


Figure 19. The effect of variable injection pressures on the CO_2 permeability of geopolymer [16].

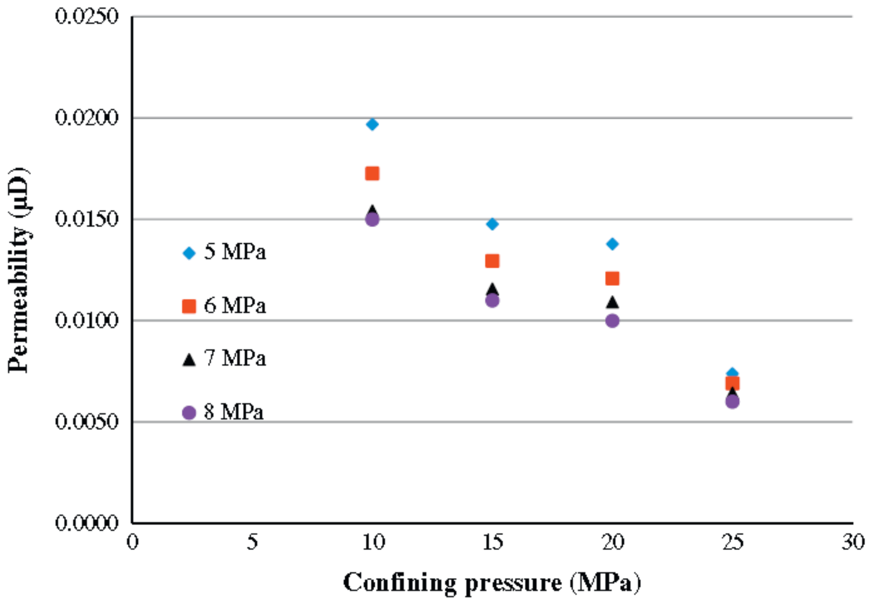


Figure 20. The effect of variable confining pressures on the CO_2 permeability of geopolymer [16].

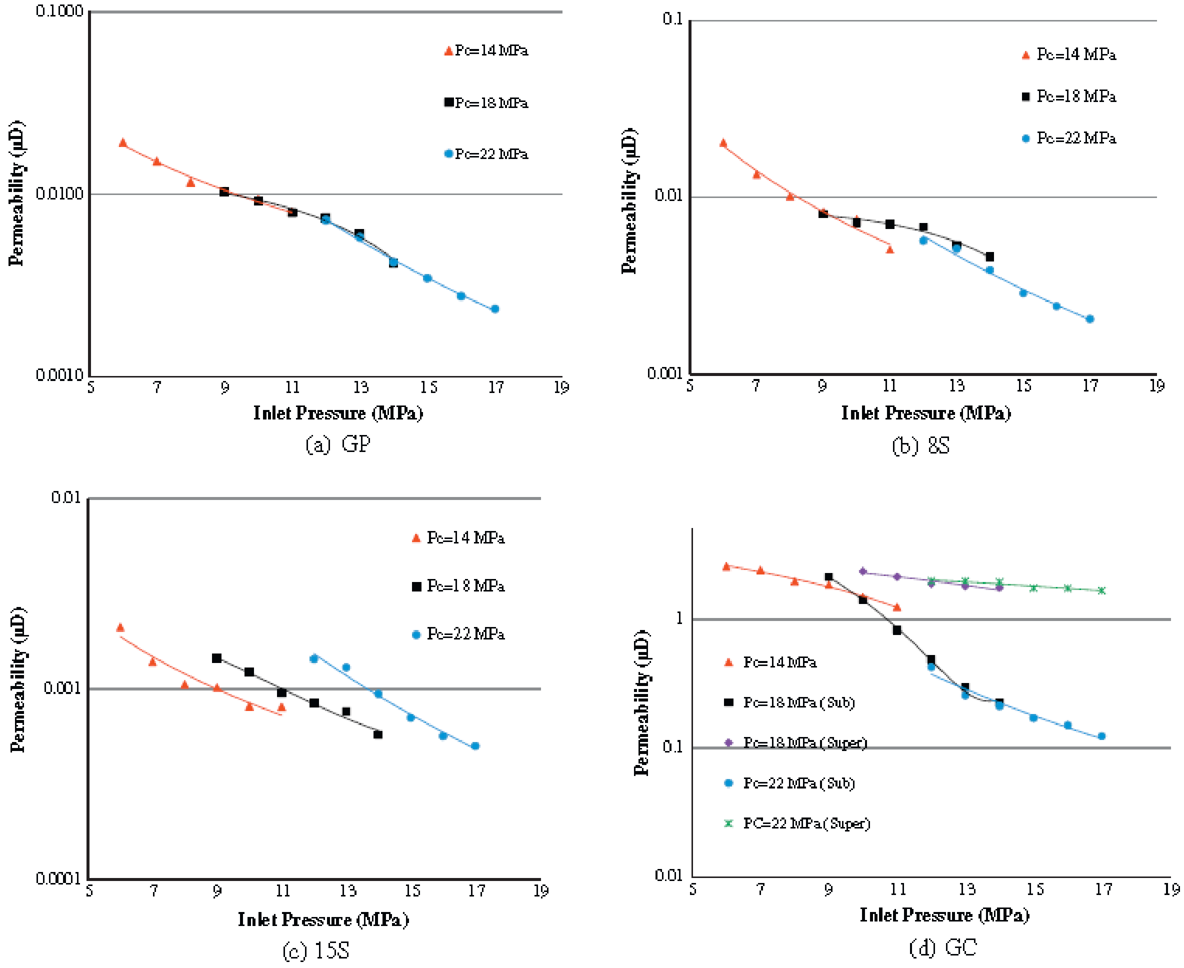
From Figure 19, it can be seen that the permeability of CO_2 to geopolymer cement reduces as the injection pressure is increased for each case of the confining pressure [16].This phenomenon is attributed to the Klinkenberg effect which is more pronounced in gas molecules whereby apparent permeability tends to decrease when the mean injection pressure of gas for a particular confining stress scenario increases. According to the “Klinkenberg Effect”, although the permeability of gas is relatively higher than the permeability of water in a porous medium, when the pore radius reaches the mean free path of gas molecules, “slip flow” takes place between the gas molecules and the pore walls of the porous medium. From Figure 20, it can be seen that CO_2 permeability reduces as the confining pressure is increased. In the downhole conditions, the confining pressure is regarded as the vertical stress imposed on the cement in the formation. This phenomenon can be explained from the additional vertical stress which results in a denser geopolymer matrix structure which causes permeability reduction. In conclusion, for the case of gas injection, apart from the matrix structure of geopolymers, the injection and confining pressures also affects the permeability values which prompts the combined evaluation of proposed production (or injection) plan with cementing design.

4.3.2 Addition of Slag

Nasvi et al.[30] performed a Mercury Intrusion Porosimetry Test and Tri-Axial Drained Testing on FAGP cement, Class G Cement and also geopolymers with slag addition (8% and 15%) and the results are shown in Table 8 and Figure 21.

Table 8. The Mercury Intrusion Porosimetry Test on Geopolymer cement, Class G cement and Geopolymer cement with Slag additions (8% and 15%)[30].

Cement Type	Geopolymer Cement	Class G Cement	Geopolymer Cement with 8 % Slag	Geopolymer Cement with 15 % Slag
Porosity (%)	30.6	28.9	27.8	25.8
Total pore area (m^2/g)	42.4	20.65	46.27	50.05
Average pore diameter (gm)	18	29.7	14.9	13.5



(a) GP

(b) 8S

(c) 15S

(d) GC

Figure 21. The apparent CO_2 permeability for different tested cement materials (Geopolymer, Class G cement, Geopolymer with 8% and 15% slag mixture) for varying inlet pressures [30].

From Table 8 it can be seen that porosity of geopolymer cement is the highest followed by Class G cement and Geopolymer cement with 8% and 15% respectively. However, the Geopolymer cement is made up of pores with lower average pore diameters (39% less) and higher total pore area (51% more) compared to Class G cement. Taking into consideration the permeability results as illustrated in Figure 21, whereby Geopolymer cement possesses lower permeability, it can be deduced that the Geopolymer cement is made up of a greater number of smaller pores which are not interconnected. Besides that, the addition of slag resulted in a denser cement structure with lower porosity and total average pore diameter.

Based on the experimental results, it was found that the permeability of FAGP cement was 100 times lower than the conventional Class G Oil Well Cement [30]. This attribute can be linked to the pore structure and connectivity of geopolymers and class G cement. The Class G cement possesses larger pores which are interconnected (appears to be interconnected by cross matching studies from Mercury Intrusion Porosimetry and the Permeability Study [30]) compared to the Geopolymer cement. Besides that, by incorporating 15% of slag in the geopolymer mixture, even lower permeability values were obtained which is approximately 1000 times lower than the conventional Class G cement [30]. Besides that, in comparison with geopolymers with the addition and without the addition of slag, the incorporation of 15% slag activated alkali reduces the permeability 10 times lesser than the geopolymer cement without addition of slag. On the whole, the reduced porosity and permeability can be attributed to the presence of slag in the geopolymer which improves the microstructure of the geopolymer.

4.3.3 Mixture Proportion

Due to the limitations in research work performed in comparison toFAGP cement and Class G cement, the research performed on the geopolymer concrete and OPC concrete are discussed in this section. Olivia et al.[20,46]conducted a series of experiments to study the effect of varying water, fly ash, NaOH and Na_2SiO_3 to geopolymer mix comparing with OPC concrete with equivalent strength of 35MPa on the apparent volume of permeable void ,sorptivity and water permeability. The following are the key observations from the experiments conducted by Olivia et al.[20,46]:

<u>Apparent Volume of Permeable Void</u>

As illustrated in Figure 22, the apparent volume of permeable void was higher in OPC concrete (mix C1 and C2) in comparison to geopolymer concrete (mix GP1 and GP5). Besides that, in the case of geopolymer concretes, the apparent volume of permeable void increases with an increase in water content and alkaline/fly ash ratio of the mixture which is illustrated in Figure 23. This is because additional water would create a more pervious matrix with higher capillary porosity. Besides that, high Na_2Sio_3 content would increase the amount of channels in the concrete.

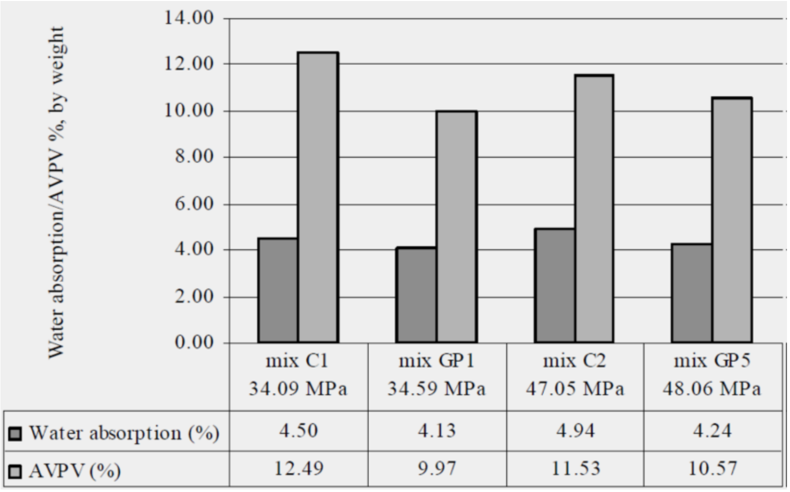


Figure 22. The apparent volume of permeable void of OPC concrete (C1 and C2) and Geopolymer concrete (GP1 and GP2)[20].

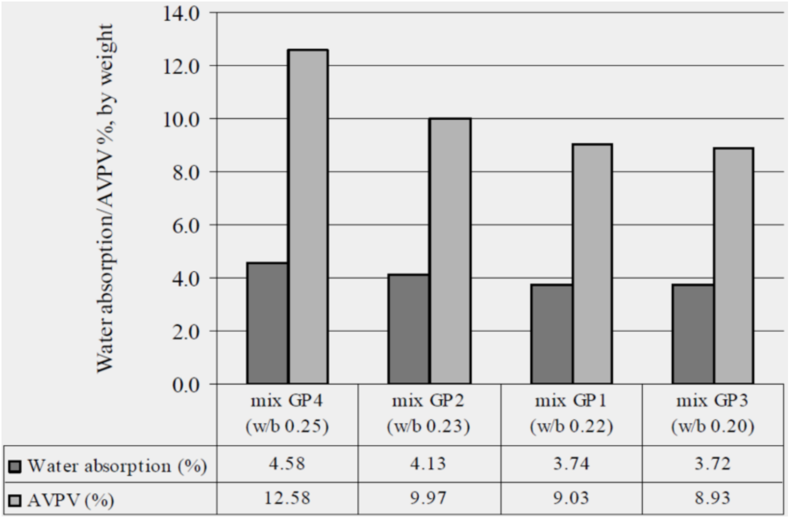


Figure 23. The apparent volume of permeable void of Geopolymer concrete with various water/binder (w/b) ratios[20].

Sorptivity

As shown in Table 9, the sorptivity of geopolymer concretes (GP1, GP2, GP4, GP5 and GP7) were found to be lower than the sorptivity of OPC concrete (C2). For the geopolymer mix proportion (GP1, GP2, GP4, GP5 and GP7), it was found that by increasing the water/binder ratio, the sorptivity increases. This is because, as the water/binder ratio is increased, the additional water present would result in more porous matrix structure which increases the capillary suction.

Table 9. The sorptivity and corresponding water/binder ratio of different mixture proportions [20].

Mixture no	Water/Binder Ratio	Sorptivity (mm/min$^{0.5}$)
C2	0.50	0.208
GP 1	0.23	0.1262
GP 2	0.22	0.1503
GP 4	0.25	0.2038
GP 5	0.22	0.1478
GP 7	0.23	0.1507

Water Permeability

Table 10 illustrates the water permeability coefficients and the void content of different geopolymer concrete mix proportions. The water permeability of the tested geopolymer mix proportions was similar to the OPC concrete which ranges from 10^{-11} to 10^{-12} m/s. However, for the geopolymer mix study, as the water/binder ratio increases, the water permeability coefficient of geopolymer also increases. This is because at higher water/binder ratios, the additional water present would result in more bigger and more porous matrix structure.

Table 10. The water permeability coefficients and void content of different Geopolymer concrete mix proportions[20].

Mixture no	Water/Binder Ratio	Aggregate/Binder Ratio	Water permeability coefficient (x10^{-11} m/s)	Void content
GP 1	0.23	3.9	4.67	10.5
GP 2	0.22	3.9	3.95	13
GP 3	0.2	3.9	2.46	10.8
GP 5	0.22	3.5	2.91	10
GP 7	0.23	3.9	2.61	8.2

In conclusion, from the experiments conducted, it was found that the water/solid ratio was the key parameter in controlling the apparent volume of permeable void, sorptivity and water permeability values. Besides that, the optimum alkali/fly ash ratio has to be determined from laboratory studies for that particular mixture to obtain the correct balance between the required compressive strength and its corresponding water permeability.

4.4 Cement Shrinkage

In order to achieve long term zonal isolation, the cement sheath upon placement of the cement slurry in the annulus should have minimal shrinkage. According to a reference cited in the study made by Diaz et al.[56], the geopolymer concrete undergoes little shrinkage in comparison to the geopolymer concrete. In addition, Li,Z et al.[21] observed that the geopolymer cements possesses 4/5 lower shrinkage values in comparison to OPC based cement. Moreover, OPC based cement is said to experience continuous shrinkage during the hardening phase and also after setting [8]. Table 11 illustrates the comparison of shrinkage percentage between OPC cement and Geopolymeric Cement which was cited in the research work conducted by Jaarsveld et al.[57].The geopolymer cement attains a minimum shrinkage percentage which is 5 times lesser in the 7 days period and 6.6 times lesser in the 28 days period test in comparison to the superior Portland cement type[57].

Table 11. The comparison of shrinkage percentage of OPC and Geopolymeric cement over 7 and 28 days[57].

Matrix	7th Day Shrinkage Percentage (%)	28th Day Shrinkage Percentage (%)
Portland Cement Type I	1	3.3
Portland Cement Type II	1.5	4.6
Geopolymer Cement	0.2	0.5

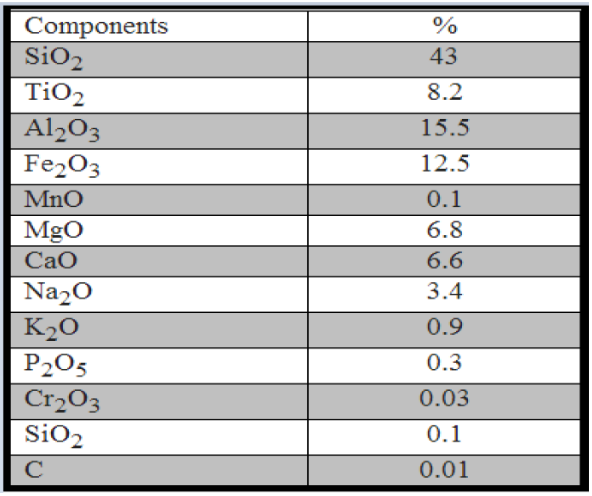
Due to lack of experiments conducted using FAGP to study its shrinkage, a study of Norite based Geopolymers were evaluated. The properties of Norite based geopolymers can be comparable with FAGP since, according to the ASTM C618 standards, the Class F Fly Ash based cement must have a minimum of the following chemical composition as illustrated in Table 12 [58]:

Table 12. The required chemical composition of Class F Fly Ash based Geopolymer cement [58].

Composition	Percentage (%)
Silicon Dioxide (SiO_2) + Aluminum Oxide (Al_2O_3) + Iron Oxide (Fe_2O_3), min, %	70
Sulfur trioxide (SO_3), max, %	4
Moisture content, max, %	3
Loss on ignition, max, %	10

The chemical composition of Norite used in the study by Kolberg [59] satisfied the requirements of ASTM C618 by having the total amount of Silicon dioxide, Aluminium Oxide and Iron Oxide of 71 % as illustrated in Table 13.

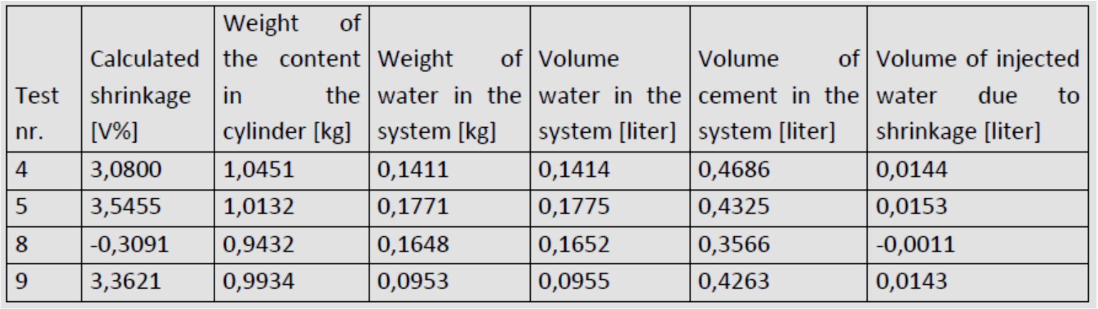
Table 13. The breakdown of the chemical composition of Norite [59].



Components	%
SiO_2	43
TiO_2	8.2
Al_2O_3	15.5
Fe_2O_3	12.5
MnO	0.1
MgO	6.8
CaO	6.6
Na_2O	3.4
K_2O	0.9
P_2O_5	0.3
Cr_2O_3	0.03
SiO_2	0.1
C	0.01

Kolberg[59] performed a study on the Norite based Geopolymer Cement comparing it with Class G cement to study the shrinkage properties (shown in Table 14) and found that the Class G cement has 3.1-3.55% shrinkage where else the Norite based Geopolymer cement seem to have zero shrinkage. The shrinkage of Class G cement was mainly attributed to the chemical/thermal shrinkage due to the hydration whereby water molecule would react with the molecules making up the cement. On the other hand, zero shrinkage was reported for the geopolymer cement suggesting that no water was lost from the structure of the cement matrix. Hence, geopolymer cement demonstrates a good potential in replacing OPC based cement for oil well cement due to its extremely low (or zero) shrinkage factor for the 28th day testing conducted.

Table 14. The shrinkage test performed on Class G cement and Norite based Geopolymer cement at curing regime of 5000psi and 87°C [59].



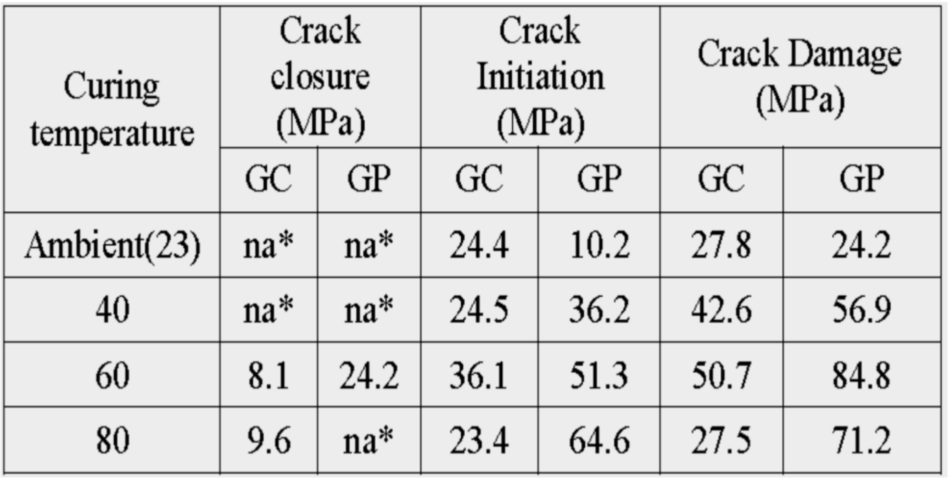
Test nr.	Calculated shrinkage [V%]	Weight of the content in the cylinder [kg]	Weight of water in the system [kg]	Volume water in the system [liter]	Volume of cement in the system [liter]	Volume of injected water due to shrinkage [liter]
4	3,0800	1,0451	0,1411	0,1414	0,4686	0,0144
5	3,5455	1,0132	0,1771	0,1775	0,4325	0,0153
8	-0,3091	0,9432	0,1648	0,1652	0,3566	-0,0011
9	3,3621	0,9934	0,0953	0,0955	0,4263	0,0143

* Test Number 4, 5 and 9 denotes Class G cement and Test Number 8 denotes Norite based Geopolymer cement.

4.5 Crack Propagation Stress Threshold

Appendix H illustrates the compilation of the experiments performed by researchers to study the crack propagation of FAGP cement in comparison to Class G cement. Nasvi, M et al.[31]studied the crack propagation stress thresholds of Class G cement (denoted GC) and FAGP cement (denoted GP) and the results are illustrated in Table 15 and Figure 24.

Table 15. The crack propagation stress thresholds of Class G cement and FAGP cement at different curing temperatures [31].



Curing temperature	Crack closure (MPa)		Crack Initiation (MPa)		Crack Damage (MPa)	
	GC	GP	GC	GP	GC	GP
Ambient(23)	na*	na*	24.4	10.2	27.8	24.2
40	na*	na*	24.5	36.2	42.6	56.9
60	8.1	24.2	36.1	51.3	50.7	84.8
80	9.6	na*	23.4	64.6	27.5	71.2

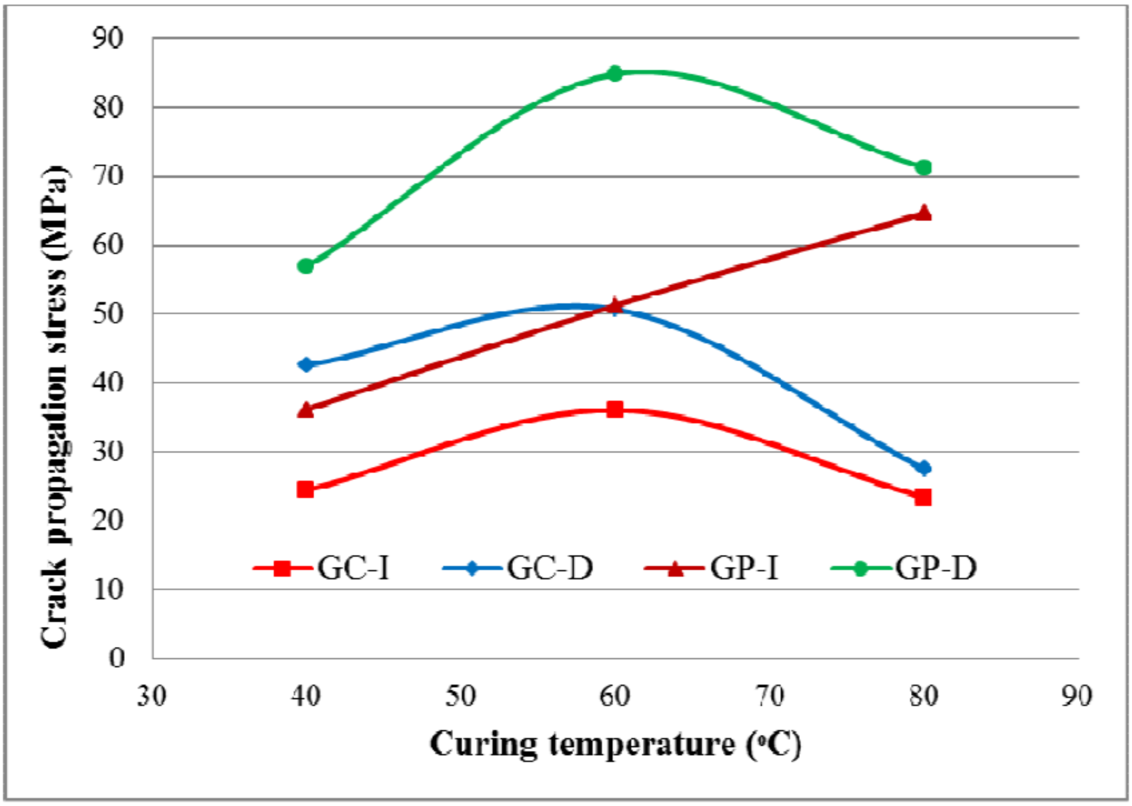


Figure 24. The comparison between the crack propagation stress thresholds of Class G cement and FAGP cement at different curing temperatures [31].

The analysis of the crack propagation threshold is as follows:

Crack Closure

Based on the measurable data, the crack closure of Geopolymer Cement was generally higher than the Class G Cement. Geopolymer Cement can withstand almost 3 times the amount of stress Class G Cement could withstand at 60^{o}C before the cracks present in the microstructure. This demonstrates the superiority of Geopolymer Cement in comparison to Class G Cement.

Crack Initiation

The crack initiation increases with an increase in time for cement type, however the crack initiation of Geopolymer Cement was higher than Class G Cement for temperatures above 40^{o}C (crack initiation of Class G Cement was lower than Geopolymer Cement at ambient temperature – 23^{o}C). The stress required to initiate a crack is low for geopolymer for ambient conditions compared to Class G Cement because at room temperature the rate of geopolymerization is relatively low and most of the reaction would not have been completed. However, as the curing temperature is increased, the geopolymerization reaction moves towards completion and the matrix gains compressive strength after which the crack initiation threshold is higher compared to the Class G Cement for temperatures above 40°C.

Crack Damage

It was found that the crack damage stress of Geopolymer Cement was higher than the Class G Cement for all curing temperatures above 40°C (crack damage of Class G Cement was lower than Geopolymer Cement at ambient temperature – 23°C). Similar to the trend observed for crack initiation, the crack damage trend can be attributed to the low rate of reaction at ambient temperature in which adequate compressive strength is not achieved. However, strength is gained as the geopolymerization process takes place rapidly as curing temperature is increased which results in a higher crack damage threshold.

The test conducted shows that the failure strain of geopolymer cement reduces when the curing temperature is increased. As the temperature is increased, the rate of dissolution of Silica and Alumina molecules is increased which results in an increased rate of reaction. The increased rate of reaction would result in a more brittle mix hence increasing the failure strain stress. In addition, at temperatures below ambient conditions, the geopolymer cement undergoes sheer failure. However, for Class G cement, there were no observable variation in failure strains corresponding to temperature variation and the type of failure is sheer failure irrespective of curing temperature. The relatively higher crack propagation threshold of FAGPcements compared to Class G cement at temperatures above 40°C suggests it is more suitable to ensure wellbore integrity of oil wells.

4.6 Carbon Dioxide Emission

Although the geopolymerization reaction itself does not release CO_2 to the environment, the reaction materials namely the manufacturing of Sodium Silicate Reagent releases CO_2. The reaction of which sodium silicate is manufactured is as the following:

$$\mathbf{Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2}$$

From the reaction balance, it can be seen one mole of sodium silicate solution produced results in the formation of one mole of CO_2 as the by product.

Habert,Get al. [60]studied the environmental impact of FAGP concrete in comparison with OPC concrete displaying similar mechanical strength and found that the global warming potential of Geopolymer concrete was 55% lesser than OPC concrete. Table 16 illustrates the extracted results from the environmental impact studies conducted by Habert,G et al. [60].

Table 16. The global warming potential of various components making up Geopolymer concrete and OPC concrete[60].

Component	Global Warming Potental (kg CO^2 eq)
Sand and Gravel	6.87
Fa	2.14
NaOH powder	3.71×10^{-1}
Na Silicate	117.8
Water	3.99×10^{-3}
Admixtrure	4.56
OPC	299.1
Geopolymer Concrete	168.5
OPC concrete	305.9

For the geopolymer concrete, the production of sodium silicate solution contributes to almost 70% of the total CO_2emitted.Besides that, Yang, K.H et al.[61] also performed several experiments to study the CO_2 footprint of various concretes namely OPC, Alkali Activated Ground Granulated Blast-Furnace Slag (GGBS), Fly Ash (FA), and Metakaoline(MK). Figure 25 illustrates the results obtained whereby each concrete type is compared with equivalent compressive strength of 24MPa, 40MPa and 70MPa [61].

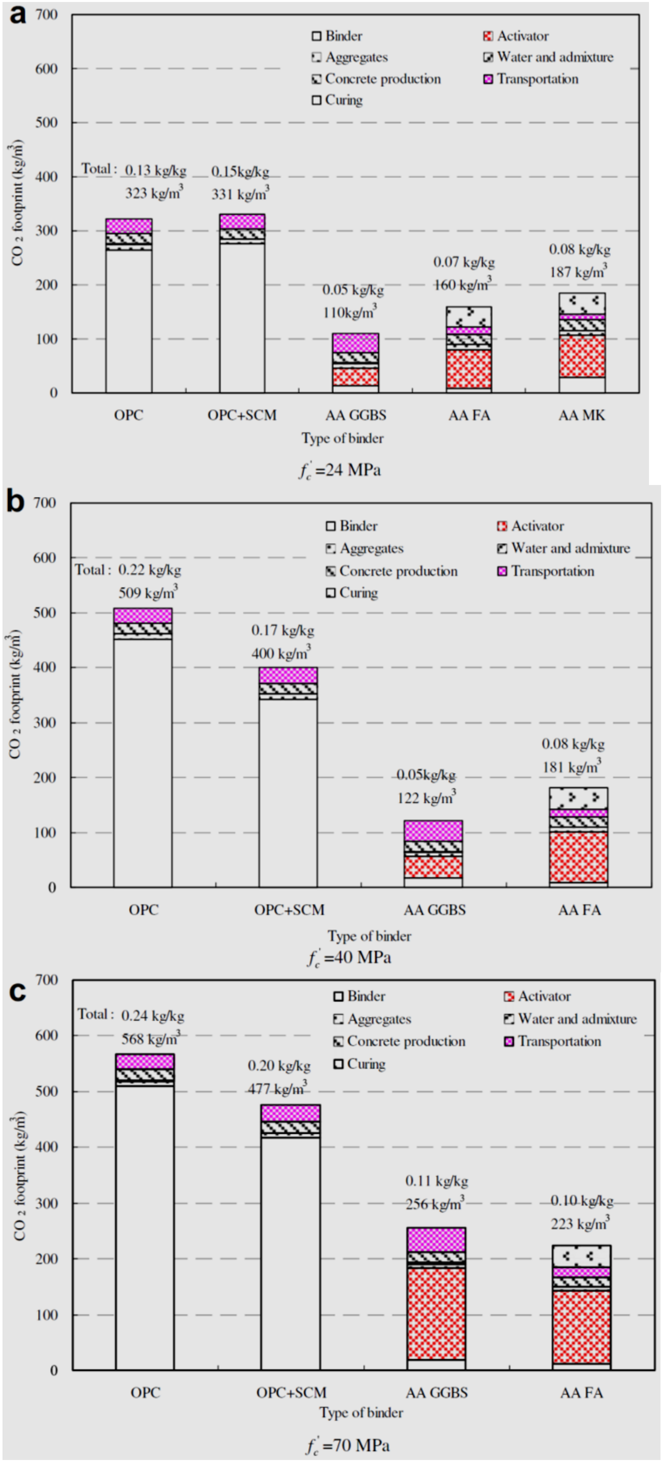


Figure 25. The CO_2 footprint for different types of binders [61].

Based on the experimental results it was found that the geopolymer concretes namely GGBS, FA and MK had lower carbon footprint in comparison to OPC concrete of equivalent compressive strength. For the highest compressive strength concrete type (70MPa), the carbon footprint of the alkali activated FA was 61 % less in comparison to the OPC concrete. For the alkali activated concretes, to achieve higher compressive strengths, more alkaline reagents (sodium silicate and sodium hyroxide) are required which translates to an increase in CO_2 emission due to the release of CO_2 for the manufacturing of the alkaline reagents. However, for the highest compressive strength concrete test, the alkali activated FA concrete CO_2 footprint was 13% lower than the Alkali Activated GGBS.

Turner K,L and Collins, F.G[62] performed an experiment to evaluate the CO_2 equivalent emissions which includes the collective emission of CO_2, CH_4, NO_2 and other synthetic gases which are potential global warming gases in the comparison study of CO_2 emission between Geopolymer Concrete and OPC Concrete. Based on Figure 26 which illustrates the results of the study conducted, it was found that the CO_2 equivalent emission of Geopolymer Concrete was 34 kg CO2/m3 (9.6%) lower than the OPC Concrete [62].

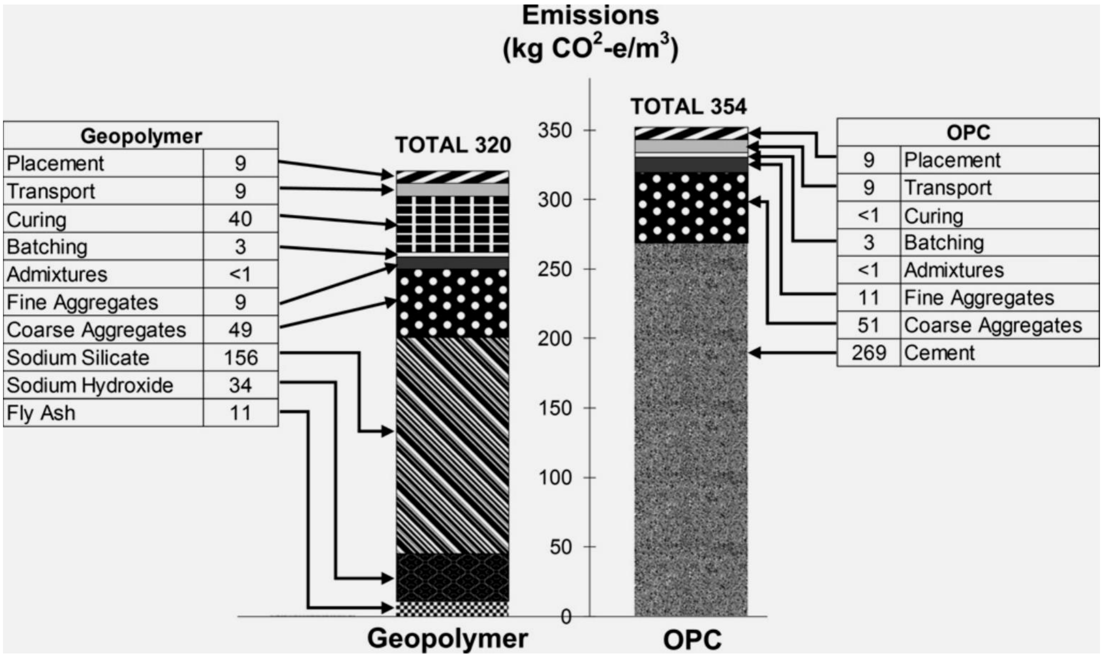


Figure 26. The comparison between the CO_2 equivalent emissions of Geopolymer concrete and OPC concrete [62].

However, the values obtained was indeed overestimated since the carbon footprint of the production of fly ash (a by product of coal power plants) was included in the calculations. Fly ash is a by product from the coal combustion which is available in abundance and the CO_2 emission from the coal combustion should be attributed to the main process which is the coal combustion itself.

Based on experiments performed by various researchers, [60-62]it is evident that the usage of FAGP concrete reduces the overall carbon footprint in comparison to the conventional OPC. Although the CO_2 emission is reduced when FAGP concrete is used, there are other problems associated with the usage of sodium silicate as the activating solution, such as human toxicity, freshwater eco-toxicity, marine eco-toxicity and terrestrial eco-toxicity [61]. Therefore, the potential environmental impact resultant from the usage of FAGP concrete has to be addressed and mitigation measures has to be implemented before commercial applications are manufactured.

4.7 Economic Evaluation

Dai, Y.S et al.[63] performed a study to the economic estimates of green cement (70% FA and 30 %GGBFS with different SiO_2/Na_2O molar ratio) and OPC cement and the results is shown in Table 17.

Table 17. The economic estimates of green cement and OPC [63].

<table>
<tr><td rowspan="3">Retail Price ($ / kg)</td><td colspan="2">Solid</td><td colspan="2">Alkaline solution</td></tr>
<tr><td>GGBFS</td><td>FA</td><td>Sodium Silicate</td><td>Sodium Hydroxide</td></tr>
<tr><td>1</td><td>-</td><td>11.5</td><td>6.5</td></tr>
<tr><td colspan="3">Green Cement and OPC</td><td colspan="2">Costs ($/ton)</td></tr>
<tr><td colspan="3">M-1.91</td><td colspan="2">2,989</td></tr>
<tr><td colspan="3">M-1.28</td><td colspan="2">2964</td></tr>
<tr><td colspan="3">M-0.96</td><td colspan="2">2938</td></tr>
<tr><td colspan="3">OPC</td><td colspan="2">2,500 - 3,500</td></tr>
</table>

The cost evaluation was performed in accordance to the price in the native country of the researcher which is Taiwan. For the green cement cost calculation, the cost of raw materials namely the GGBFS, Sodium Silicate and Sodium Hydroxide were taken into consideration but the cost of transportation were omitted in both the green cement and OPC scenario. It was found that the green cement cost were equivalent to the median value of the OPC cost.

Besides that, Mc Lellan, B.C[64] also performed a series of experiment to evaluate the cost of geopolymer paste (denoted Mix 1,2,3 and 4) in comparison to the ordinary Portland Cement. In their study, four geopolymer pastes with different mix proportions (Fly Ash, NaOH, Sodium Silicate, Silica Fume and Gibbsite) were compared with OPC and is tabulated in Table 18.

Table 18. The cost of various Geopolymer mixtures in comparison to OPC [64].

	Mix 1	Mix 2	Mix 3	Mix 4
Cost ($ / tonne binder)	152	118	140	176
OPC Cost ($ / tonne binder)	120			
Difference	-21%	7%	-11%	-39%

It was found that Geopolymer Mix-2 was 7% lower in cost compared to the OPC and the other mixes were higher in cost ranging from 11% to 39%. It was observed that mix 2 had the highest percentage of Fly Ash (91%) which corresponds to lower NaOH and Na_2SiO_3 percentages. Based on the available research in the economics of FAGP in comparison to OPC it can be concluded that the cost of both cement types are indifferent. However, the optimum mix proportion of FAGPcement can result in a slightly lesser cost in comparison to the OPC.

CHAPTER 5.
CONLCUSION AND RECOMMENDATION

In analysing the factors which contribute to the wellbore integrity, the properties of API Class G cement and FAGP cement were studied in detail from experiments conducted by various researchers. The results were analysed and reviewed and the following are the conclusion from the review made:

(i) FAGP cement is superior to Class G cement at temperatures above 36^{o}C. However, the optimum curing temperature lies in the range of 60^{o}C for most research work performed and curing above the optimum temperature causes a decrease in compressive strength.

(ii) In all curing duration at optimum temperatures, geopolymer cement gains higher compressive strength compared to Class G cement. The geopolymer cement achieves 90-92% of its total compressive strength within 48 hours of curing and further curing results in minimal increase in compressive strength.

(iii) The curing medium of brine/saline water favoured the strength development in FAGP cement whereby higher compressive strengths were attained compared to Class G cement.

(iv) The variables which were identified to influence the compressive strengths of FAGP cement were activating solution, sodium hydroxide concentration, sodium silicate concentration, alkaline liquid to fly ash ratio, aging duration and water to binder ratio. In all cases, the optimum parameters have to be identified according to the mix proportion used to attain maximum compressive strength.

(v) In terms of chemical durability, due to different materials and processes which both the cement types undergo, the FAGP cement is more superior in chemical resistance against a wide range of aggressive chemicals compared to the Class G cement.

(vi) The gas permeability of FAGP cement was found to be much lower than Class G cement. In addition, the review results also suggested that geopolymer concrete paste has lower water permeability compared to the OPC based concrete.

(vii) The review study also suggests that geopolymer cement undergoes very little shrinkage and in the order of 4-6.6 times lesser than OPC based cement.

(viii) Similar to the trend observed in the compressive strength analysis, Class G cement has higher crack propagation threshold for temperatures below 40°C compared to FAGP cement. However, for temperatures ranging above 40°C, the FAGP cement exhibits a much more superior Crack Propagation Threshold.

(ix) Based on the available research in the economics of FAGP cement in comparison to OPC it can be concluded that the cost of both cement types are indifferent. However, the optimum mix proportion of FAGP cement can result in a slightly lesser cost in comparison to the OPC.

Based on the review done, it was found that FAGP cement offers a substantial greater wellbore integrity in comparison to the conventional Class G cement at a very much lesser impact on the global carbon footprint. However, the following key areas have been identified through this review which requires further investigations to enable the application of FAGP cement as oil well cement:

(i) To study the effect of high pressure (corresponding to wellbore conditions) on the geopolymerization reaction.

(ii) To study the effect of using FAGP cement which has higher compressive strength on the perforating operations.

(iii) To conduct studies on the usage of additives for FAGP cement to enhance properties related to its usage as wellbore cement such as compressive strength, permeability, chemical durability and shrinkage.

REFERENCES

1) Worrell, E, Price, L, Martin, N, Hendriks, C and Meida, L.O. (2001). Carbon Dioxide Emissions from the Global Cement Industry. *Annual Rev Energy Environment*. 26 (N/A), 303-329
2) Law, D.W, Adam, A.A, Molyneaux, T.K, Patnaikuni,I and Wardhono,A. (2014). Long term durability properties of class F fly ash geopolymer concrete. *Materials and Structures*. N/A (N/A), 1-11
3) Smith, D.K (1989). *Cementing*. Texas: Society of Petroleum Engineers. 7-17,42-58.
4) Heriot Watt University (HWU), 2005, "Drilling Engineering", Manual of Heriot Watt Institute of Petroleum Engineering, Edinburgh, UK
5) Nelson, E.B (1990). *Well Cementing* . Texas: Elsevier Science. 1-30.
6) Teodoriu,C, Yuan,Z, Schubert,J and Amani,M. (2012). Experimental Measurements of Mechanical Parameters of Class G Cement. *SPE/EAGE European Unconventional Resources Conference & Exhibition - From Potential to Production*. Unknown (N/A), 1-7.
7) Teodoriu,C, Amani,M, Yuan,Z, Schubert,J and Kosinowski,C. (2012). Investigation of the mechanical properties of class g cement and their effect on well intergrity. *International Journal of Engineering and Applied Sciences*. 3 (2), 1-7
8) Dusseault, M.B, Gray,M.N and Nawrocki, P.A. (2000). Why Oilwells Leak: Cement Behavior and Long-Term Consequences.*SPE International Oil and Gas Conference and Exhibition in China held in Beijing, China*. N/A, 1-8.
9) Nasvi,C.M , Ranjith,P.G. and Sanjayan,J.. (2011). Geopolymer as Well Cement and Variation of its Mechanical Properties Under Different Curing Temperature and Curing Mediums. *Greenhouse Gases: Science and Technology*. 2 (1), 46-58.
10) Salehi,S. (Unknown). *ModelingNear Wellbore Leakage Pathways in Shale Gas Wells: Investigating Short and Long Terms Wellbore Integrity.* Available: http://www2.epa.gov/sites/production/files/documents/salehi.pdf. Last accessed 25th May 2014)

11) B. Carey. (2010). *Wellbore Integrity and CO_2 Sequestration.* Available: http://www.ieaghg.org/docs/General_Docs/Summer_School/CAREY%20Wellbore%20Integrity_Tues_secured.pdf. Last accessed 25th May 2014.

12) Garnier,A, Fraboulet,B, Marc, J.S and Bois,A.. (2007). Characterization of Cement Systems to Ensure Cement Sheath Integrity. *Offshore Technology Conference*. N/A (N/A), 1-11

13) Reddy, B. R., Xu, Y., Ravi, K., Gray, D. W., &Pattillo, P. (2009). Cement Shrinkage Measurement in Oilwell Cementing--A Comparative Study of Laboratory Methods and Procedures. Society of Petroleum Engineers.

14) Unknown.(N/A). *Chapter3:Cementing.* Available: http://gekengineering.com/Downloads/Free_Downloads/Cementing_Chapter_3.pdf. Last accessed 25th May 2014.

15) Piot, B. (2009). *Cement and Cementing: An Old Technique With a Future?*. Available: http://www.spe.org/dl/docs/2009/Piot.pdf. Last accessed 25th May 2014.

16) Nasvi,C.M , Ranjith,P.G. and Sanjayan,J.. (2013). The permeability of geopolymer at down-hole stress conditions: Application for carbon dioxide sequestration wells. *Applied Energy*. 102 (Unknown), 1391–1398.

17) Duxson,P,Jimenez,A.F, Provis,J.L, Lukey, G.C, Palomo,A and Deventer, J.S.J.. (2007). Geopolymer technology: the current state of the art. *Journal of Materials Science*. 42 (N/A), 2917-2933

18) Abdullah,M. M. A, Hussin,K, Bnhussain,M, .Ismail, K. N.andIbrahim,W. M. W. . (2011). Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement- A Review. *International Journal of Pure and Applied Sciences and Technology*. 6 (1), 35-44

19) Chanh, N.V, Trung, B.D and Tuan, D.V.. (2008). Recent Research Geopolymer Concrete. *The 3rd ACF International Conference-ACF/VCA 2008*. Unknown, 235-241

20) Olivia M, Sarker P, Nikraz H. Water penetrability of low calcium fly ash geopolymer concrete. IntConfConstr Build Technol (ICCBT) 2008;46:517–530.

21) Li,Z, Ding,Z and Zhang,Y. (Unknown). Development of Sustainable Cementitious Materials. *International Workshop on Sustainable Development and Concrete Technolog*. Unknown, 55-76.

22) Provis, J.L and Deventer, S.J (2009). *Geopolymers: Structures, Processing, Properties and Industrial Applications (Woodhead Publishing Series in Civil and Structural Engineering*. Cambridge: Woodhead Publishing Limited. 1-10.

23) Unknown.(2008). *Potential utilization for geopolymer composites materials.* Available: http://www.geopolymer.org/applications/potential-utilization-for-geopolymer-composites-materials. Last accessed 25th May 2014.

24) Kambic,M and Hammaker,J. (2012). Geopolymer Concrete: The Future of Green Building Materials. *Unknown*. N/A, 1-7

25) Bhikshma,V, Reddy, M.K, Rao, T.S. (2012). An Experimental Investigation on Properties of Geopolymer Concrete (No Cement Concrete). *Asian Journalof Civil Engineering (Building and Housing)*. 13 (Unknown), 841-853.

26) Kim,E.H. (2012). Understanding Effects of Silicon/Aluminium Ratio and Calcium Hydroxide on Chemical Composition, Nanostructure and Compressive Strength for Metakaolin Geopolymers. *Thesis-University of Illinois* . N/A (N/A), 1-100.

27) Srinivasam, K and Sivakumar, A. (2013). Geopolymer Binders: A Need for Future Concrete Construction. *ISRN Polymer Science*. 2013 (N/A), 1-9.

28) Nasvi,C.M , Ranjith,P.G. and Sanjayan,J.. (2012). Mechanical Properties of Geopolymer Cement in Brine: Its Suitability as Well Cement for Geological Sequestration of Carbon Dioxide (CO2). *7th Asian Rock Mechanics Symposium*. Unknown , 1034-1040.

29) Amir, H.M, Diana,N.T.H, Sylvestre,C.J and Schneider,J. (2008). New Environment-Friendly Cement Slurries With Enhanced Mechanical Properties. *CIPC/SPE Gas Technology Symposium 2008 Joint Conference, 16-19 June, Calgary, Alberta, Canada*. Unknown, 1-11.

30) Nasvi,C.M , Ranjith,P.G. and Sanjayan,J.. (2014). Effect of different mix compositions on apparent carbon dioxide (CO2) permeability of geopolymer: Suitability as well cement for CO2 sequestration wells. *Applied Energy*. 114 (Unknown), 939–948.

31) Nasvi,C.M , Ranjith,P.G. and Sanjayan,J.. (2012). Comparison of mechanical behaviors of geopolymer and class G cement as well cement at different

curing temperatures for geological sequestration of carbon dioxide. *46th US rock mechanics/geomechanics symposium*. Unknown , 1-8.

32) Haider M.G, Sanjayan,J. G and Ranjith,P. G. . (2013). Stress versus Strain Behavior of Geopolymer Cement under Triaxial Stress Conditions in Saline and Normal Water. *World Academy of Science, Engineering and Technology International Journal of Civil, Architectural Science and Engineering*. 7 (7), 80-83.
33) Mustafa, A.M, Kamarudina,H, BinHussain,M,KhairulNizar,I, Zarina, Y and Rafizaa, A.R. (2011). The Effect of Curing Temperature on Physical and Chemical Properties of Geopolymers. *Physics Procedia*. 22 (Unknown), 286–291.
34) Schlumberger.(Unknown). *Schlumberger-Materials.* Available: http://www.slb.com/~/media/Files/cementing/catalogs/05_cementing_materials.pdf. Last accessed 25th May 2014
35) Swanepoel,J.C and Strydom,C.A. (2002). Utilisation of fly ash in a geopolymeric material. *Applied Geochemistry*. 17 (8), 1143–1148.
36) Palomoa, A, Grutzeckb,M.W and Blancoa,M.T. . (1999). Alkali-activated fly ashes: A cement for the future. *Cement and Concrete Research*. 29 (8), 1323–1329.
37) Park,S.S and Kang,H.Y. (2006). Strength and microscopic characteristics of alkali-activated fly ash-cement. *Korean Journal of Chemical Engineering*. 23 (3), 367-373.
38) Mineral Strategies Pty Limited. (N/A). Geopolymers – Aiding the Pursuit of Sustainability in the Minerals Sector (and Beyond). *N/A*. N/A (N/A), 1-5.
39) Kutasov, M.I and Eppelbaum, L.V. (2014). Temperature Regime of Boreholes: Cementing of Production Liners. *Proceedings, Thirty-Ninth Workshop on Geothermal Reservoir Engineering* . Unknown, 1-5.
40) Hardjito,D, Cheak,C.C and Ing,H.L. (2008). Strength and Setting Times of Low Calcium Fly Ash-based Geopolymer Mortar. *Modern Applied Science*. 2 (4), 3-11.
41) Rachel, P.P and Partheeban,P. (2013). Durability Study of Low Calcium Flyash Based Geopolymer Concrete. *Indian Journal Of Applied Research*. 3 (N/A), 180-182.

42) Mishra,A, Choudhary,D, Jain,N , Kumar,M. (2008). Effect of Concentration of Alkaline Liquid and Curing Time on Strength and Water Absorption of Geopolymer Concrete. *ARPN Journal of Engineering and Applied Sciences*. 3 (N/A), 14-18.

43) Chindaprasirt,P, Chareerat,T and Sirivivatnanon,V. (2007). Workability and strength of coarse high calcium fly ash geopolymer. *Cement and Concrete Composites*. 29 (Unknown), 224–229.

44) Alida, A, Bakri A.M, Kamarudin,H, Ruzaidi,C.M, Salleh M.A.A and Chin,K.H. (2013). The Effect of Acidic to the Fly Ash Based Geopolymer Artificial Aggregate. *Australian Journal of Basic and Applied Sciences*. 7 (5), 303-307.

45) Djwantoro,H. (2005). Studies on fly ash-based geopolymer concrete. *Geopolymer: green chemistry and sustainable development solutions*. N/A (N/A), 133-138.

46) Olivia, M and Hamid R.N. (2011). Strength and Water Penetrability of Fly Ash Geopolymer Concrete.. *Journal of Engineering and Applied Sciences*. 6 (7), 70-78.

47) Unknown. (2008). *Sodium Hydroxide vs Potassium Hydroxide: A comparison too caustic?*. Available: http://sodium-hydroxide.com/sodium-hydroxide-vs-potassium-hydroxide-a-comparison-too-caustic/. Last accessed 26th May 2014.

48) Tempest, B, Sanusi, O, Gergely, J ,Ogunro,V, Weggel,D. (2009). Compressive Strength and Embodied Energy Optimization of Fly Ash Based Geopolymer Concrete.*Compressive Strength and Embodied Energy Optimization of Fly Ash Based Geopolymer Concrete*. N/A (N/A), 1-17.

49) Jeffrey, C.P, Athar,S and Michael, H.I. (2012). Alkali-Activated Geopolymers: A Literature Review. *Air Force Research LaboratoryMaterials and Manufacturing Directorate*. N/A , 1-92.

50) Lloyd, N.A and Rangan, B.V. (2010). Geopolymer Concrete: A Review of Development and Opportunities. *35th Conference on Our World in Concrete and Structures:* N/A (N/A), 1-9.

51) Jaarsveld,J.G.S,Deventer,J.S.J and Lukey,G.C . (2002). The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. *Chemical Engineering Journal*. 89 (1-3), 63–73.

52) Ghosh,K and Dr.Ghosh,P. (2012). Effect of Synthesizing Parameters on Compressive Strength of Fly Ash based Geopolymer Paste. *International Journal of Structural and Civil Engineering*. 1 (Unknown), 1-11.

53) Iveron Materials, Inc. (Unknown). *Geopolymer Concrete for the Oil and Gas Industry*. Available: http://www.ecgiveron.com/3g-concrete-technology.html. Last accessed 25th May 2014.

54) Davidovits,J. (1994). Properties of Geopolymer Cement.*Alkalines Cements and Concretes, KIEV Ukraine*. N/A, 131-149.

55) Zhang,Z, Yao,X and Zhu,H. (2010). Potential application of geopolymers as protection coatings for marine concrete: II. Microstructure and anticorrosion mechanism. *Applied Clay Science*. 49 (Unknown), 7-12.

56) Diaz,E.I. and Allouche,E.N.. (2010). Recycling of Fly Ash into Geopolymer Concrete: Creation of a Database. *Green Technologies Conference, 2010 IEEE*. Unknown (N/A), 1-7

57) Jaarsveld,J.G.S and Deventer, J.S.J. (1996). The Potential use of Geopolymeric Materials to Immobilize Toxic Materials. *Minerals Engineering*. 10 (7), 659-669.

58) ASTM International. (1996). *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*. Available: http://www.astm.org/Standards/C618.htm. Last accessed 25th May 2014.

59) Kolberg, L.E. (2013). Geopolymerization of Norite. *Masters Thesis*. N/A (N/A), 1-48.

60) Habert,G, Espinose de Lacaillerie,J.B, Roussel,N. (2011). An environmental evaluation of geopolymer based concrete production: reviewing current research trends. *Journal of Cleaner Production*. 19 (Unknown), 1229-1238.

61) Yang,K.H, Song, J.K, Song, K,I. (2013). Assessment of CO2 reduction of alkali-activated concrete. *Journal of Cleaner Production*. 39 (Unknown), 265-272.

62) Turner,L.K and Collins, F.G. (2013). Carbon dioxide equivalent (CO2-e) emissions: A comparison between geopolymer and OPC cement concrete. *Construction and Building Materials*. 43 (Unknown), 125-130.

63) Dai,Y.S, Yang, L.C, Ding, Y.C, Jhong, C.W, Cheng, T.W and Lin,K.L.. (Unknown). A Study on Application of Geopolymeric Green Cement.*Unknown*. Unknown (Unknown), 27-24.

64) McLellan,B.C, Williams,R.P, Lay,J, Riessen, A and Corder,G.D. (2011). Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. *Journal of Cleaner Production*. 19 (Unknown), 1080-1090.

APPENDICES

Appendix A.Compilation of research performed on the compressive strength of FAGP cement and API Class G cement

No	Ref	Type of Test	Variable	Test Performed On	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[6]	Compressive Strength	Low Brine (5%NaCl) and High Brine (15%NaCl)	14th, 30th, 60th and 90th Day	ASTM Class F Fly Ash (Low Calcium)	0.45	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2)	N/A	50^oC Oven for 24 hours	Compressive strength decreases under brine. However, the reduction rate is less in 15% NaCl compared to 5% NaCl.
2	[12]	Compressive Strength	Curing Temperature and Time	N/A	Fly Ash	0.3-0.45	NaOH and Na_2SiO_3	N/A	60^oC-90^oC for 24-72 hours	As the curing time and temperature increases, the compressive strength increases. As the curing temperature increases, the setting time decreases.
3	[39]	Compressive Strength	Curing Time and Curing Temperature	7th and 28th day	Fly Ash and Kaolinite	N/A	NaOH and Na_2SiO_3	N/A	40, 50, 60 ,70 ^oC for 6,24,48 ,72 hours	There are possibilities that geopolymerization reaction occurred with a larger reaction rate at the higher temperature. The optimum condition for this type of geopolymer is at 60^oC for 48 hours.

Appendix A. Compilation of research performed on the compressive strength of FAGP cement and API Class G cement [Continuation]

4	[22]	Compressive Strength	Curing Temperature (Room temperature & 60^{o}C) and Curing medium(air,water, 15%,8% saline water)	28th day	Class G Cement and Fly ash and slag (9:1) based Geopolymer Cement	N/A	NaOH and Na_2SiO_3	8M	Room temperature & 60^{o}C for 12 hours	Geopolymer showed higher compressive strength for saline water curing and lowest strength for water strength; class G cement showed higher strength for water curing and lower strength for saline water curing. To examine temperature effect, compressive strength for samples cured in air, normal water and saline water gained almost same compressive strength.
5	[9]	Compressive Strength	Comparison between geopolymer and Class A&G Cement	8-48 hours	Geopolymer Cement and Class G Cement	N/A	N/A	N/A	50^{o}C	Geopolymer cement gained a compressive strength 5 times higher thanthe neat cement and continues to gain strength even after 7 days whereby the neat cement blend reaches "plateau" much earlier.
6	[10]	Compressive Strength	Curing Temperature (23-80^{o}C) and Curing Medium (brine, water and C02 saturated brine)	2nd day	ASTM Class F Fly Ash (Low Calcium) and Class G Cement	0.4	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2)	10M	23, 30,40,50,60,70 and 80^{o}C for 24 hours	The optimum curing temperature of geopolymer is 60oC and it posseses higher strength compared to class G cement above ambient temperatures. Crack propagation stress thresholds such as crack closure, crack initiation and damage increases with curing temperature. The strength reduction rate is higher in fresh water compared to brine water.

Appendix A. Compilation of research performed on the compressive strength of FAGP cement and API Class G cement [Continuation]

7	[41]	Compressive Strength	Activator Solution, Curing Temperature, Curing Time and Liquid Solid Ratio	2h,5h and 24h	ASTM Class F Fly Ash (Low Calcium)	0.25-0.3	NaOH, Na_2SiO_3 ,K_2SiO_3	Various NaOH and KOH solution	65-85 ^{o}C for 2,5 and 24 hours	An increase in temperature results in an acceleration of the fly ash activation. The effect of activator/fly ash ratio is not significant. Alkali solution with soluble silicates produce higher rates which corresponds to higher compressive strength compared to hydroxides as activators. An increase in temperature would result in increase in mechanical strength. Temperature is especially important for 2-5 hours of curing, whereby the rise in strength is much smaller when curing time is 24 hours. Besides that, the type of activator also affects the mechanical strength.
8	[21]	Compressive Strength	Curing Temperature	2nd day	ASTM Class F Fly Ash (Low Calcium) and Class G Cement	0.4	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2	10M	23, 30-80^{o}C for 24 hours	The geopolymer and Class G cement gains strength as the curing temperature increases until the optimum temperature. In both cases, the optimum curing temperature is 55-60^{o}C. (geopolymer would not be a good option for temperatures below 30^{o}C). Recommended the use of geopolymer for depths more than 1 km (assuming thermal gradient of 30^{o}C/km)

Appendix A. Compilation of research performed on the compressive strength of FAGP cement and API Class G cement [Continuation]

9	[50]	Compressive Strength	Curing Temperature, NaOHConcetration,Liquid/FA Ratio and Curing Time	7th,14th and 28th day	ASTM Class F Fly Ash (Low Calcium)	0.3-0.6	NaOH	1-8M	50^{o}C for 7days	Irrespective of different liquid/fly ash ratio, the compressive strength increases as the concentration of sodium hydroxide increases. Highconcentration alkaline solution is required to activate the aluminosilicate solid dissolution. (Concentration of 5-6M is adequate for alkali activation). The optimum 7th day compressive strength at 50^{o}C was obtained with NaOH concentrations of 5&6M with liquid/fly ash ratio of 0.4. The optimum curing temperature was found to be 50^{o}C for 5/6 M of NaOH concentration.
10	[52]	Compressive Strength	Curing Temperature	7th	ASTM Class F Fly Ash (Low Calcium)		NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2.5)	12M	Room temperature,50, 60,70 and 80^{o}C for 24 hours	The maximum compressive strength was at curing temperature of 60^{o}C - 67.04MPa

Appendix B. Compilation of research performed on the effect of varying the Sodium Hydroxide concentration on the compressive strength of FAGP cement.

No	Ref	Type of Test	Test Performed On	Aging Duration	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[46]	Compressive Strength	N/A	0,1,3 and 6 hours	Lignite Fly Ash	N/A	NaOH and Na2SiO3 ratio of 0.67,1.00,1.50 and 3.00	10,15 and 20M	60^{o}C for 24 hours	No major differences was observed in the compressive strength for the concentration of NaOH between 10 to 20 M.
2	[38]	Compressive Strength	7th and 28th day	N/A	Fly Ash	0.5	NaOH and Na_2SiO_3 (Ratio NaOH/ Na_2SiO_3 =0.6)	8M, 12 M and 16M	Kept in 100^{o}C oven for 1 hour before curing at 60^{o}C for 24,48 and 72 hours	7 day compressive strength increased with the increase in concentration of NaOH from 8M to 16M for the same curing time, similarly for an increase in curing time from 24 to 48 hours. However, no significant increase in compressive strength when curing time was increased from 48 to 72 hours. The compressive strength increases with increase in air curing time from 7 days to 28 days.

Appendix B. Compilation of research performed on the effect of varying the Sodium Hydroxide concentration on the compressive strength of FAGP cement. [Continuation]

3	[48]	Compressive Strength	N/A	N/A	ASTM Class F Fly Ash	N/A	NaOH and Na_2SiO_3	8M, 10 M and 14M	60^{o}C - 90^{o}C	Higher NaOH mixtures have higher water content which resulted in lower compressive strength.
4	[35]	Compressive Strength	7th,14th and 28th Day	N/A	ASTM Class F Fly Ash	N/A	NaOH and Na2SiO3 (Ratio Na2SiO3/NaOH =2.5)	N/A	65,70 and 80 ^{o}C Oven for 24 hours	Alkaline concentration is proportionate to the compressive strength
5	[36]	Compressive Strength	7th and 28th day	N/A	ASTM Class F Fly Ash	0.45	NaOH and Na2SiO3 (Ratio Na2SiO3/NaOH =2.5)	10 M and 12 M	60^{o}C Oven for 24 hours	At room temperature curing, the 7th and 28th day compressive strengths were same for 10M and 12 M NaOH. At curing temperatures of 60oC, the 10M geopolymer mix had higher 7th day compressive strength but was lower than the 12 M mix in the 28th day test.
6	[47]	Compressive Strength	N/A	Few Hours	Fly Ash	1.5	NaOH and Na_2SiO_3	10M, 12M and 14M	70^{o}C for 24 hours	The optimum molarity if NaOH is 12M to produce geopolymer with maximum compressive strength. The optimum activator to fly ash ratio is 1.5.
7	[50]	Compressive Strength	7th,14th and 28th day	1 day at 20^{o}C	ASTM Class F Fly Ash (Low Calcium)	0.3-0.6	NaOH	1-8M	50^{o}C for 7days	High concentration alkaline solution is required to activate the aluminosilicate solid dissolution. (concentration of 5-6M is adequate for alkali activation)

Appendix C. Compilation of research performed on the effect of the concentration sodium silicate on the compressive strength of FAGP cement.

No	Ref	Type of Test	Variable	Test Performed On	Aging Duration	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Si/Al Molar Ratio	SiO2/Na2O ratio	Concentration of NaOH	Curing Regime	Observation
1	[8]	Compressive Strength	Activator Modulus(Ms) - Varying the mass ratio of SiO_2/Na_2O	28th Day	N/A	ASTM Class F Fly Ash (Low Calcium)	N/A	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH = 0.95, 1.6, 2.6)	N/A	0.75-1.25	10M	90^oC for 24 hours	Significant increase in strength when Ms is increase from 0.75 to 1 however, only a minor increase when increased from 1 to 1.25.
2	[46]	Compressive Strength	Different Concentrations of NaOH (and the corresponding $NaOH/Na_2SiO_3$ ratio), temperature ranging from 30-90 ^oC.	N/A	0,1,3 and 6 hours	Lignite Fly Ash	N/A	NaOH and Na_2SiO_3 ratio of 0.67,1.00 ,1.50 and 3.00	N/A	N/A	10,15 and 20M	60^oC for 24 hours	Na_2SiO_3/NaOH ratio of 0.67 and 1.00 produced a significantly higher compressive strength than the other mixtures.

Appendix D. Compilation of research performed on the effect of alkaline liquid to fly ash ratio on the compressive strength of FAGP cement.

No	Ref	Type of Test	Variable	Test Performed On	Aging Duration	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[50]	Compressive Strength	Alkaline Liquid / Fly Ash ratio	7th,14th and 28th day	1 day at 20°C	ASTM Class F Fly Ash (Low Calcium)	0.3-0.6	NaOH	1-8M	50°C for 7days	Irrespective of different liquid/fly ash ratio, the compressive strength increases as the concentration of sodium hydroxide increases.
2	[12]	Compressive Strength	Alkaline Liquid / Fly Ash ratio	N/A	N/A	Fly Ash	0.3-0.45	NaOH and Na_2SiO_3	18M	60°C-90°C for 24-72 hours	Alkaline Liquid to Fly Ash Ratio of 0.4 results in higher compressive strengths in comparison to Alkaline Liquid to Fly Ash Ratio of 0.3.
3	[35]	Compressive Strength	Alkaline Liquid / Fly Ash ratio	7th,14th and 28th Day	N/A	ASTM Class F Fly Ash (Low Calcium)	N/A	NaOH and Na_2SiO_3 (Ratio $Na_2SiO_3/NaOH$ =2.5)	N/A	65,70 and 80 °C Oven for 24 hours	The highest compressive strength was produced by the activator to fly ash ratio of 0.4
4	[49]	Compressive Strength	Alkaline Liquid / Fly Ash ratio	7th,28th,91st Day	N/A	ASTM Class F Fly Ash (Low Calcium)	0.35-0.45	NaOH and Na_2SiO_3	14M	N/A	The compressive strength of geopolymers increases by decreasing water/solid ratio, aggregate/solids ratio and alkaline/fly ash ratio.

Appendix E. Compilation of research performed on the effect of aging duration on the compressive strength of FAGP cement.

No	Ref	Type of Test	Test Performed On	Aging Duration	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[46]	Compressive Strength	N/A	0,1,3 and 6 hours	Lignite Fly Ash	N/A	NaOH and Na_2SiO_3 ratio of 0.67,1.00,1.50 and 3.00	10,15 and 20M	60^oC for 24 hours	The optimum aging time was found to be 1 day which produced 43.5 MPa and further increase in aging time reduced the compressive strength.
2	[37]	Compressive Strength	28th Day	0, 24 and 48 hours	Fly Ash	N/A	NaOH	N/A	$75\ ^oC$ Oven for 24 and 48 hours	Increasing aging time from 0 to 2 days improved the 28 day compressive strength in all cases.
3	[43]	Compressive Strength	1st,3rd,7th, 14th and 28th Day	0/24 hours	Low Calcium Class F Fly Ash	0.35	NaOH and Na_2SiO_3	14M	60^oC for 24 hours	By having an aging duration of 24 hours, the compressive strength for all mixtures increases.

Appendix F. Compilation of research performed on the effect on the effect of water content on the compressive strength of FAGP cement

No	Ref	Type of Test	Variable	Test Performed On	Aging Duration	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of Hydroxide Solution (NaOH/KOH)	Curing Regime	Observation
1	[23]	Compressive Strength	Water/Geopolymer Binder Ratio varied from 0.225-0.35	3rd and 7th day	2hours	ASTM Class F Fly Ash (Low Calcium)	N/A	NaOH and Na_2SiO_3	NaOH concentration not stated	85^{o}C for 48 hours	The optimum water/binder ration was found to be 0.3 which resulted in 44.36 MPa 7th day Compressive strength
2	[34]	Compressive Strength & BET Surface Area	Water/Fly Ash Ratio varied from 0.33-0.75	14th Day	None	Fly Ash	N/A	KOH and Na_2SiO_3	KOH/NaOH concentration not stated	30^{o}C for 24 hours	The optimum water/fly ash mass was 0.43 for KOH and NaOH

Appendix G. Compilation of research performed on the Permeability of FAGP cement and API Class G cement

No	Ref	Type of Test	Variable	Test Performed On	Source Material	Alkaline Liquid to Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[17]	Mercury intrusion porosimetry test and Triaxial Drainage Testing	Addition of alkali activated slag	N/A	ASTM Class F Fly Ash (Low Calcium) and Class G Cement	0.4	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2.5)	8M	50^oC for 24 hours	By adding/increasing the amount of slag, the porosity is reduced, the total pore area is increased and the average diameter is reduced. The microstructure created is much denser. The addition of 15% of slag reduces the permeability of geopolymers by almost 10 times compared to without adding slag. The apparent CO_2 permeability to geopolymers are 100-1000 times lower than the values obtained for class G cement.
2	[30]	Triaxial Drainage Testing	Confining and injection pressures	N/A	ASTM Class F Fly Ash (Low Calcium)	0.4	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2.5)	8M	50^oC for 24 hours	The CO2 permeability to FAGP and found that the permeability of geopolymer pastes ranged from 2 x 10^{21} to 2 x 10^{20} m^2 which was lower than the permeability of conventional oil well cement (10^{-20} to 10^{-11} m^2). The permeability of CO^2 to geopolymer cement reduces as the injection pressure is increased for each cases of the confining pressure
3	[49]	Water Penetrability, Water Absorption and AVPV	Water/binder ratio, aggregate/binder ratio, aggregate grading, alkaline/fly ash ratio	7th,28th ,91st Day	ASTM Class F Fly Ash (Low Calcium)	0.35-0.45	NaOH and Na_2SiO_3	Included	14M	N/A

Appendix G. Compilation of research performed on the Permeability of FAGP cement and API Class G cement. [Continuation]

4	[13]	Water Permeability, Water Absorption, Sorptivity and Apparent Volume of Permeable Voids	Water /binder ratio and Aggregate Composition	7th and 28th Day	Fly Ash	N/A	NaOH and Na_2SiO_3 (Ratio Na_2SiO_3/ NaOH =2	None	14M	60°C for 24 hours

Appendix H. Compilation of research performed on the Crack Propagation of FAGP and API Class G cement

No	Ref	Type of Test	Variable	Test Performed On	Aging Duration	Source Material	Alkaline Liquid / Fly Ash Ratio	Alkaline Liquid	Concentration of NaOH	Curing Regime	Observation
1	[10]	Crack Propagation Threshold	(i) Curing Temperature (23-80^{o}C) (ii)Curing Medium (brine, water and $C0_2$ saturated brine)	2nd day	N/A	ASTM Class F Fly Ash	0.4	NaOH and Na2SiO3 (Ratio Na2SiO3 /NaOH =2)	10M	23, 30-80^{o}C for 24 hours & another 48 hours at room temperature	The optimum curing temperature of geopolymer is 60^{o}C and it possesses higher strength compared to class G cement above ambient temperatures. Crack propagation stress thresholds such as crack closure, crack initiation and damage increases with curing temperature. The strength reduction rate is higher in fresh water compared to brine water.
2	[21]	Crack Propagation Threshold	Curing Temperature	2nd day	N/A	ASTM Class F Fly Ash (Low Calcium)	0.4	NaOH and Na2SiO3 (Ratio Na2SiO3 /NaOH =2	10M	23, 30-80oC for 24 hours	The geopolymer and Class G cement gains strength as the curing temperature increases until the optimum temperature of 55-60^{o}C. It was found that the at lower curing temperatures, the Young's Modulus (E) was higher in Class G Cement and in higher temperatures, E was higher in Geopolymer. At 40^{o}C, geopolymers possesses the highest crack initiation values and crack damage thresholds, the crack propagation threshold increases with an increase in curing temperature. The geopolymer failure strain reduces as the curing temperature is increased