THE SUITABILITY OF FLY ASH BASED GEOPOLYMER CEMENT FOR OIL WELL CEMENTING APPLICATIONS: A REVIEW

Dinesh Kanesan¹, Sonny Irawan¹, Syahrir Ridha¹, Davannendran Chandran² and Nuriman Amsha Bin Azhar¹
¹Universiti Teknologi Petronas, Seri Iskandar, Perak Darul Ridzuan, Malaysia
²Sunway University, Subang Jaya, Selangor, Malaysia
Email: dinesh.kanesan@utp.edu.my

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°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. 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.

Keywords: fly ash, geopolymer cement, compressive strength, thickening time.

1. INTRODUCTION
As the most common anthropogenic greenhouse gas, carbon dioxide (CO₂) is a major contributor to global warming. According to Worrell et al. [1] the cement industry contributes approximately 5% of the total CO₂ emitted due to activities carried out by mankind and it would be the appropriate industry to implement CO₂ emission mitigation strategies. Approximately one ton of CO₂ is released to the atmosphere for the production of one ton of Portland cement whereby the calcination of Calcium Carbonate (CaCO₃) releases 0.53 tons of CO₂ and another 0.45 tons of CO₂ 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 [4-7]. 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 [8]. 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.

2. WELL 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. The wellbore integrity can be damaged during the pre-production phase and also in the production phase of a well.
2.1 Pre-production phase
The wellbore integrity is said to be affected during the pre-production phase due to the following activities:

a) Damage to the formation during drilling activities.

b) Poor casing centralization leading to incomplete cementing due to eccentric cement setting and non-uniform thickness around wellbore.

c) Incomplete drilling mud removal which results in formation of mud pockets during cementing which will affect the wellbore integrity.

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

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

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

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

2.2 Production phase
During the production phase, the mechanical stress/strain and geochemical attack may affect the wellbore integrity. 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 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.

Besides that, 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.

3. OIL WELL 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 and the latter can be defined as remedial works to address flaws associated with primary cementing. 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 is to prevent fluid movement between subsequent formations and to support the casing. In addition, upon setting in between the casing and the borehole, the cement sheath between the casing and borehole, functions as follows:

a) To support the surface casing string.

b) To protect the casing from corrosive fluids arising from the formation.

c) To prevent blowouts by aptly forming a seal.

d) To protect the casing from shock loads especially when drilling in deep zones.

e) To establish sealing off zones during lost circulation.

3.1 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 [9]. In addition, the developed mechanical properties upon setting of the cement must also be considered during the cement designing stage.

3.1.1 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]. The compressive strength of the cement sheath would depend on the curing conditions (temperature and pressure); amount of mix-water 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.

3.1.2 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.

3.1.3 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 reduce 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.

3.1.4 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]. The corrosion would decrease the compressive strength and make the cement sheath more permeable.

3.1.5 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.

3.1.6 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.

3.1.7 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 the change in volume of products and reactants and the overall bulk volume change [10]. The process whereby the absolute volume after the cement sets is less than the volume occupied by the initial reactants is termed hydration shrinkage [10]. The commonly used Portland cement would continue to experience shrinkage even after during the hardening period and also after setting [6].

3.1.8 Crack propagation stress threshold

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.

3.2 Conventional oil well cement - Portland cement

Till date, well cementing has been done using OPC [4, 8]. 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_{3}S), dicalcium silicate (C_{2}S), tricalcium aluminate (C_{3}A) and tetracalcium aluminoferrite (C_{4}AF) [4]. 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]. Table-1 illustrates the API cement classes and their intended use.

<table>
<thead>
<tr>
<th>Class A</th>
<th>For use from surface to 6000 ft (1830 m) depth, when special properties are not required.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class B</td>
<td>For use from surface to 6000 ft (1830) depth, when conditions require moderate to high sulfate resistance.</td>
</tr>
<tr>
<td>Class C</td>
<td>For use from surface to 6000 ft (1830 m) depth, when conditions require high early strength.</td>
</tr>
<tr>
<td>Class D</td>
<td>For use from 6000 ft to 10,000 ft (1830 m to 3050 m), under conditions of high temperatures and pressures.</td>
</tr>
<tr>
<td>Class E</td>
<td>For use from 10,000 ft to 14,000 ft depth (3050 m to 4270 m), under conditions of high temperature and pressures.</td>
</tr>
<tr>
<td>Class F</td>
<td>For use from 10,000 ft to 16,000 ft depth (3050 m to 4880 m), under conditions of extremely high temperatures and pressures.</td>
</tr>
<tr>
<td>Class G</td>
<td>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.</td>
</tr>
<tr>
<td>Class H</td>
<td>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.</td>
</tr>
<tr>
<td>Class J</td>
<td>Intended for use as manufactured from 12,000 ft to 16,000 ft (3600 m to 4880 m) depth under conditions of extremely high temperatures and pressures. It can be used with accelerators and retarders to cover a range of well depths and temperatures.</td>
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3.2.1 Problems associated with the use of OPC 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 [6]. 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 [6].

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 [12]. 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 [12]. 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 leak through the surrounding. According to Nasvi et al. [8, 12], 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.

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 [13]. 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 [14]. These rapid reactions would result in a three dimensional polymeric chain and a ring structure which consists of Si-O-Al-O bonds [14].

The source of alkaline chemicals is usually Ca(OH)$_2$, NaOH, Na$_2$SiO$_3$, the combination of NaOH and Na$_2$SiO$_3$, the combination of KOH and NaOH, K$_2$SiO$_3$ 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 [15]:

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

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

c) 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 [15].

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.

4.1 Applications of geopolymer cement

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 [16]. 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 [17]. 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 shipmaking industry, automobile industry, construction in maritime settings and also for nuclear and toxic waste immobilisation [14, 17]. 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 [14, 18]. According to Kim [19], 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.

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.

4.2 Suitability of fly ash based geopolymer cement as oil well cement

Among the available raw materials, fly ash is the best option as it provides the most sustainable solution for waste management [8]. 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 [14]. 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 [14-18, 20]. In addition, FAGP exhibits higher workability and mechanical properties with one fourth of the water consumption required to produce metakaolin based geopolymers [17]. 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 [21].

5. PROPERTIES OF FLY ASH BASED GEOPOLYMER CEMENT

The results of studies conducted by various researchers on the prospects of using FAGP comparing to the conventional Class G cement for oil well cementing applications were analysed. The analysis was divided into the following sections:

a) Compressive Strength

b) Chemical Durability

c) Permeability

d) Cement Shrinkage
e) Crack propagation threshold

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.

5.1 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 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 are curing temperature, time and medium. In addition, the other factors which govern the compressive strength of FAGP cement such as mixture proportions, aging duration and water/geopolymer binder ratio was also studied to obtain the optimum parameters to achieve compressive strengths which are superior to Class G cement.

5.1.1 Curing 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 [8, 15, 22-27]. Studies have shown that the fly ash geopolymerization reaction at ambient temperatures is extremely slow and results in a very low compressive strength [8, 14, 23, 26]. 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°C.

In a recent study using geopolymer cement formulated using fly ash and slag, it was found that that the increase in curing temperature from 80°C to 90°C resulted in an increase in compressive strength [27]. The study also reported that the compressive strength attained by geopolymer cement was higher than the compressive strength reported by researchers using OPC [27]. The ratio of NaOH and Na₂SiO₃ was set at 1:1 while the molarity of NaOH was varied between 3,6,10 and 12ml. Although the optimum curing temperature was not identified, the findings suggest that increasing the temperature until the optimum temperature accelerates the dissolution and polymerization process of the geopolymerization reaction.

Figure-1 illustrates the experimental results obtained from the experiment conducted by Nasvi et al. [8] 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.

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-2 illustrates the experimental results obtained from the experiment conducted by Al Bakria et al. [28] 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.

In addition, the experiments conducted by Swanepoel et al. [24] 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 [9, 24, 28]
the highest compressive strength was achieved at an optimum curing temperature of 60 °C.

Figure-2. The compressive strength of FAGP cement at different curing temperatures [28].

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). Comparing the results from the experiments conducted by Nasvi et al. [8] and Mustafa et al. [28], 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. [26] 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 3 illustrates the results obtained for the three curing temperatures studied.

From Figure-3, 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. Firstly, at temperatures close to ambient temperature (23 °C), the rate of geopolymerization reaction is slow.

Figure-3. The effect of curing temperature on the compressive strength of FAGP cement cured at 7, 14 and 28 days.

However, as the slow rate of reaction occurs and as time elapses, the geopolymerization process takes place and a minimal compressive strength is attained. At the optimum temperature (50°C 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. At 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 [29]. 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.

5.1.2 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 [15, 22, 24, 25] 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. [22] 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 4 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°C which is close to the optimum curing temperature of 60°C as discussed in the curing temperature section.

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 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.

Both Figure 5 and 6 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).

Swanepoel et al. [24] 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 5 and 6 illustrates the compressive strength which was developed at different curing timing and temperature at 7th day and 28th day of testing [24].

Swanepoel et al. [24] 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 5 and 6 illustrate the compressive strength which was developed at different curing timing and temperature at 7th day and 28th day of testing [24].
suggests that the geopolymerization rate of reaction requires heat addition in the range of 60 °C -70 °C.

d) 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:

a) 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.

b) 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.

c) 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-7 illustrates the effect of curing time on compressive strength for two different mixture proportions [15].

5.1.3 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. [30] 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-8 illustrates the results obtained from the experiment conducted [30]. From Figure-8, 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.

Figure-8. The 28 day compressive strength for FAGP and API Class G cement under water, 8% saline water and 15% saline water curing [30].

Another study focusing on the effects of water/brine solution as the curing medium of FAGP cement was conducted by Nasvi et al. [8] and similar trend were observed (as illustrated in Figure-9) 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-9. The compressive strengths of FAGP under fresh water and 15% brine water conditions [8].](image)

### 5.1.4 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, 15, 20, 25, 26, 31-35]:

#### 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 [25]. 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 [25]. In most cases, researches preferred to use Sodium Hydroxide compared to Potassium Hydroxide since it is cheaper and widely available.

### Sodium hydroxide concentration

There have been several researchers conducted on the effects of NaOH Concentration on the compressive strength of geopolymer cement and concrete [26, 31-35]. 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 / Na2SiO3) and curing regime were the same.

For the geopolymer cement study, Park, S et al. [26] 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 10. 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-10. The compressive strength of different geopolymer cement prepared using different liquid/fly ash ratio and concentration of NaOH [26].](image)

Based on the research conducted by Chindapasirt et al. [33] 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. However, Alida et al. [34] found that the FAGP aggregates obtain the highest compressive strength at an optimum NaOH molarity of 12 M.

Based on all the studies reviewed, 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. [34]. 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 [36]. 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 Na2SiO3 which serves as a stimulating tool to improve the alkalinity of the solution, hence resulting in higher compressive strengths [21, 36, 37]. Kanesan et al. [37] found that the compressive strength of geopolymer cement increases as the concentration of Na2SiO3 was increased. In their experiment using slag based geopolymer, the samples were cured for 24 hours at pressure and temperature of 2000 psi and 80 °C mimicking oil well conditions. The dissolution of the calcium ions and the participation of the silica ions to form Si-O-Al-O bonds which leads to higher compressive strength would take place at a higher rate if there are more quantities of silica ions in the solution.

On the other hand, the experiments conducted by Chindaprasirt et al. [33] and Law [2] focuses on the effect of the Na2SiO3/NaOH ratio on the compressive strength of geopolymer concrete. According to the research done by Chindaprasirt et al. [33] the optimum Na2SiO3/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 (Na2SiO3/NaOH = 0.95) to Ms=1.00 (Na2SiO3/NaOH = 1.59) however, further increase to Ms=1.50 (Na2SiO3/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 Na2SiO3/NaOH ratio which has to be determined for the specific curing regime and aging duration. Until the optimum Na2SiO3/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 Na2SiO3/NaOH ratio above its optimum value would not result in a positive outcome on the reaction rate (compressive strength).

**Alkaline liquid/Fly ash ratio**

Researchers have performed several experimental studies on the effects of varying the alkaline liquid to fly ash ratio [15, 31, 38]. As illustrated in Figure 10, based on the experiments on FAGP cements conducted by Park, S et al.[26] 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 et al. [25] 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 et al. [31], 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 et al. [31] also showed similar behaviour whereby the optimum alkaline liquid/fly ash ratio was 0.4.

5.1.5 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. Based on the experiment conducted by Tempest et al. [39] on geopolymer concrete, as illustrated in Figure-11, 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.

Based on the experiment conducted by Chindaprasirt et al. [33] 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 12 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 [33].
In addition, in the study conducted by Lloyd and Rangan [40], 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-13.

### 5.1.6 Water/Geopolymer binder ratio

Jaarsveld et al. [41] 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 Table-2. Based on Table-2, 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 et al. [42] also found that the increase in water/geopolymer binder resulted in increase in 3rd day and 7th day Compressive Strength until an optimum value (0.3 for this experiment) was obtained and further increase in water/geopolymer binder ratio resulted in the decrease in compressive strength as illustrated in Table-3.
Table-2. The effect of water/fly ash ratio of the 14th day compressive strength of geopolymer cement for different alkali activating solutions (NaOH and KOH) [41].

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Hydroxide</th>
<th>Clay (Mass %)</th>
<th>Water (Mass %)</th>
<th>Water/fly ash ratio (mass)</th>
<th>Strength (MPa)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S11</td>
<td>K</td>
<td>7</td>
<td>20</td>
<td>0.33</td>
<td>11.0</td>
<td>0.8</td>
</tr>
<tr>
<td>S6</td>
<td>K</td>
<td>14</td>
<td>20</td>
<td>0.35</td>
<td>11.0</td>
<td>1.0</td>
</tr>
<tr>
<td>S8</td>
<td>K</td>
<td>21</td>
<td>20</td>
<td>0.43</td>
<td>11.4</td>
<td>0.7</td>
</tr>
<tr>
<td>S25</td>
<td>K</td>
<td>41</td>
<td>20</td>
<td>0.75</td>
<td>5.0</td>
<td>1.1</td>
</tr>
<tr>
<td>S12</td>
<td>Na</td>
<td>7</td>
<td>20</td>
<td>0.33</td>
<td>8.5</td>
<td>0.3</td>
</tr>
<tr>
<td>S7</td>
<td>Na</td>
<td>14</td>
<td>20</td>
<td>0.36</td>
<td>8.0</td>
<td>0.6</td>
</tr>
<tr>
<td>S9</td>
<td>Na</td>
<td>21</td>
<td>20</td>
<td>0.43</td>
<td>10.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table-3. The effect of water/geopolymer binder the 3rd day and 7th day compressive strength of FAGP cement [42].

<table>
<thead>
<tr>
<th>Composition of geopolymer mix (molar ratio)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix No.</td>
<td>Na₂O/Al₂O₃</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>S11</td>
<td>0.50</td>
</tr>
<tr>
<td>S12</td>
<td>0.50</td>
</tr>
<tr>
<td>S13</td>
<td>0.50</td>
</tr>
<tr>
<td>S14</td>
<td>0.50</td>
</tr>
<tr>
<td>S15</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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.

5.2 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 [43]. 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. Illustrated in Figure-14, a study conducted by Chanh et al. [15] 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-14. The percentage of weight of FAGP of different mix proportion when exposed to 5%HCl Solution.](image_url)
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 [15]:

a) Alkaline liquid concentration

Alida et al. [34] 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.

b) Water content

From the experiments conducted by Chanh et al. [15], it was found that as the water content is increased, the compressive strength of the cement decreases which is illustrated in Figure-14.

However, there is still a 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.

5.3 Permeability

According to Nasvi et al. [12] 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. They further added in their 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 less porous structure. Zhang et al. [44] 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[43]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, injection and confining pressures and addition of slag have been identified as contributing factors to its permeability [12, 20, 38, 45].

5.3.1 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. [12] studied the CO$_2$ permeability to FAGP cement and found that the permeability of geopolymer pastes ranged from $2 \times 10^{-21}$ to $2 \times 10^{-20}$ m$^2$ which was lower than the permeability of conventional oil well cement ($10^{-20}$ to $10^{-21}$ 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 Figures 16 and 17 [12]:
Figure-17. The effect of variable confining pressures on the CO\textsubscript{2} permeability of geopolymer [12].

From Figure-16, it can be seen that the permeability of CO\textsubscript{2} to geopolymer cement reduces as the injection pressure is increased for each case of the confining pressure [12]. 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 increase. 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-17, it can be seen that CO\textsubscript{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.

5.3.2 Addition of slag

Nasvi et al. [45] 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-4 and Figure-18.

Table-4. The Mercury intrusion porosimetry test on Geopolymer cement, Class G cement and geopolymer cement with slag additions (8% and 15%) [45].

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Geopolymer cement</th>
<th>Class G cement</th>
<th>Geopolymer cement with 8% slag</th>
<th>Geopolymer cement with 15% slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>30.60</td>
<td>28.90</td>
<td>27.80</td>
<td>25.80</td>
</tr>
<tr>
<td>Total pore area (m\textsuperscript{2}/g)</td>
<td>42.40</td>
<td>20.65</td>
<td>46.27</td>
<td>50.05</td>
</tr>
<tr>
<td>Average pore diameter (gm)</td>
<td>18.00</td>
<td>29.70</td>
<td>14.90</td>
<td>13.50</td>
</tr>
</tbody>
</table>

From Table-4 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-18, 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 [45]. 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 [45]) 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 [45]. 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.
5.4 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 Diaz et al. [46], the geopolymer concrete undergoes little shrinkage in comparison to the geopolymer concrete. In addition, Li et al. [16] 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[6]. Table 5 illustrates the comparison of shrinkage percentage between OPC cement and geopolymeric cement based on the research work conducted by Jaarsveld et al. [47]. 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 [47].

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 must be comparable with FAGP according to the ASTM C618 standards. The chemical composition of Norite used in the study by Kolberg [48] satisfied the requirements of ASTM C618 by having the total amount of silicon dioxide, aluminium oxide and iron oxide of 71 %. Kolberg [48] found that the Class G cement undergoes 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.
5.5 Crack propagation threshold

Nasvi, M et al. [23] studied the crack propagation stress thresholds of Class G cement (denoted GC) and FAGP cement (denoted GP) and the results are illustrated in Figure-19. 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 °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 °C (crack initiation of Class G Cement was lower than Geopolymer Cement at ambient temperature-23 °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.

Table-5. The comparison of shrinkage percentage of OPC and Geopolymeric cement over 7 and 28 days [47].

<table>
<thead>
<tr>
<th>Matrix</th>
<th>7th Day shrinkage percentage (%)</th>
<th>28th Day shrinkage percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement</td>
<td>1.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Type I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portland Cement</td>
<td>1.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Type II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geopolymer Cement</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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 FAGP cements compared to Class G cement at temperatures above 40 °C suggests it is more suitable to ensure wellbore integrity of oil wells.

Figure-19. The comparison between the crack propagation stress thresholds of Class G cement and FAGP cement at different curing temperatures [23].

6. CONCLUSIONS

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:

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

b) 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.
c) 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.

d) 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.

e) 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.

f) 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.

g) 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.

h) 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.

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:

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

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

c) 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


[33] P. Chindaprasirt, T. Charerat and V. Sirivivatnanon. 2007. Workability and strength of coarse high calcium


