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The development of a new formulation of fly ash class C based geopolymer and assessing its performance in presence of drilling fluid contamination

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THE DEVELOPMENT OF A NEW FORMULATION OF FLY ASH CLASS C BASED GEOPOLYMER AND ASSESSING ITS PERFORMANCE IN PRESENCE OF DRILLING FLUID CONTAMINATION

by

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ABSTRACT

Cementing is one of the most critical steps in the drilling and completion of oil wells. Traditionally, Portland cement is used for oil cementing operations; however, geopolymer materials have recently attracted much attention because they are more cost-effective and have less environmental impacts.

An intensive laboratory work was conducted to obtain a new formulation of fly ash class C based geopolymer cement to be used as a potential alternative cementing material to Portland cement in oil and gas cementing. Twenty-four variations of fly ash class C based geopolymers were prepared, and by comparing several of their properties using API standard tests, the optimum geopolymer formulation was determined. The selection of the optimum formulation was based on five different tests, including rheology, density, compressive strength, and fluid loss. Further tests were performed for optimized geopolymer, including stability tests. Then, a comparison between the optimum mix design and Portland cement was done using the same tests.

One of the main issues regarding oil well cementing is drilling fluids' contamination. This research also investigates the effect of drilling fluid contamination with geopolymer cement to understand its impact on geopolymer rheological and mechanical performance. After geopolymer optimum design was selected, the slurries were mixed with 0, 5, and 10 weight percent drilling fluid ratio to determine the effects of drilling fluids on geopolymer properties using rheology, density, fluid-loss, and compressive strength tests. Results showed that geopolymer had better performance compared to Portland cement in the presence of drilling fluid contaminations, where geopolymer exhibited higher compressive strength compared to Portland cement.

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1. INTRODUCTION

1.1. STATEMENT AND SIGNIFICANCE OF THE PROBLEM

Well integrity is defined as “application of technical, operational, and organizational solutions, to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well” (Norsok D-010., 2013). The main goal of cementing is to provide full zonal isolation. Preventing fluid migration from the formation into wellbores is one of the most important purposes of the cementing operation. If zonal isolation is lost, it could result in severe operational difficulties and huge environmental issues as well as high remedy costs. Figure 1.1 shows an illustration of Portland cement drawbacks. As an example, the Gulf of Mexico experienced one of the worst blowouts in oil industry in 2010, Mocondo, which caused a major oil spill. One of the major reasons of this accident is primary cement failure (Santos & Ribeiro, 2017). Portland cement has been used for many years in cementing operations in oil and gas wells, but it has many drawbacks, including high cost, environmental impacts, and failure problems. Portland cement failures include radial cracks within the cement sheath, micro-annuli at the interfaces of the cement, and channels through the cement matrix (Bois et al., 2012).

Portland cement productions release an enormous amount of carbon dioxide (CO_2), which is a significant contributor to global warming. Manufacturing Portland cement requires a huge amount of heat achieved by burning a massive volume of fuel and decomposition of limestone, thus causing an enormous quantity of CO_2 emissions (Kong & Sanjayan, 2008). Almost one ton of CO_2 is released upon producing one ton of Portland cement (United Nations Environment Programme).

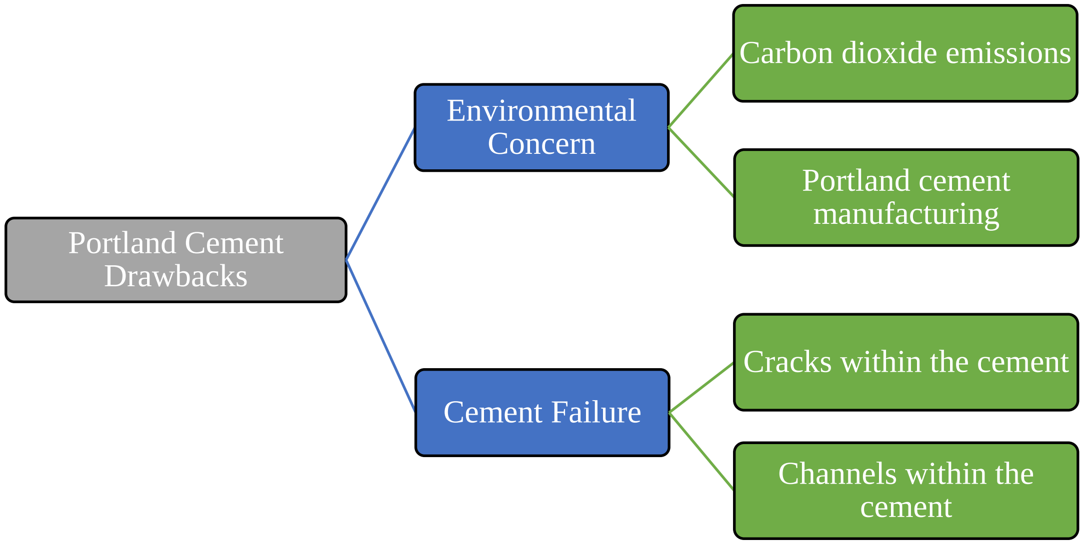

Figure 1.1. An illustration of Portland cement issues

Another prominent problem that faces cementing operations is drilling fluid contaminations. When injecting cement slurries into the casing and back through the annulus, cement slurry may contact the drilling fluids remaining after drilling operations. This could change the cement slurry properties, which could impact the cementing operations negatively. When drilling fluid contacts Portland cement, the compressive strength of Portland cement is impacted significantly (El Sayed, 1995; Aughenbaugh et al., 2014). Furthermore, drilling fluids have negative effects on Portland cement rheological properties; they increase Portland cement slurries' viscosity, which affects its pumpability (Liu, et al., 2016).

The main objective of this research is to provide an alternative material to replace Portland cement in the oil and gas industry, and to investigate the effects of drilling fluids contaminations on geopolymer properties.

1.2. EXPECTED IMPACTS AND CONTRIBUTION

The new formulation of fly ash class C based geopolymer was studied in this work and compared to Portland cement. A summary of the benefits of using the geopolymer is listed below:

- Geopolymer is an environmentally friendly material that can be used in oil and gas wells as an alternative to Portland cement.
- Since fly ash, which is the main material used to manufacture geopolymer, is a by-product of coal combustion, it is extremely cheap to acquire.
- Geopolymer could overcome failures of Portland cement to provide full zonal isolations.
- Geopolymer has the potential to have higher early compressive strength compared to Portland cement which could result in a reduced wait on cement time. This could result in a reduction in operational costs.
- Geopolymer could have ability to retain its water which would also increase the potential of reaching the desired height of cement in the annulus.

One of the problems associated with oil cementing operations is the drilling fluid contaminations because they can affect rheological and mechanical properties of geopolymer and Portland cement, which makes studying these properties essential. Expected results are as follows:

- Drilling fluids could improve the geopolymer viscosity. This improvement could increase the flowability of geopolymer.
- Geopolymer could perform better compared to Portland cement in presence of drilling fluids contaminations.

1.3. OBJECTIVES

The main objective of this research was to provide an environmentally friendly and cost-effective material to be a replacement to Portland cement in oil and gas well cementing. The following objectives will be achieved from this research:

- A study of the effect of changing the sodium silicate to sodium hydroxide ratios on the fly ash class C based geopolymer properties
- An investigation of the impact of increasing the sodium hydroxide molarity on the fly ash class C based geopolymer
- An examination of the influence of increasing the amount of fly ash to alkaline activator on the fly ash class C based geopolymer
- Development of a new formulation of geopolymer using fly ash class C to be used as a cost-effective and environmentally friendly alternative to Portland cement
- An investigation of the effect of drilling fluid contaminations on rheological and mechanical performance of fly ash class C based geopolymer
- A comparison of the results of drilling fluids contamination on geopolymer to Portland cement

1.4. SCOPE OF WORK

This research includes two main experimental tasks. Figure 1.2 shows the scope of work for this research. The first task is to develop a new formulation of fly ash class C based geopolymer by using different sodium hydroxide concentrations (NaOH molarity), sodium silicate to sodium hydroxide ratios (SS/SH), and alkaline activator to fly ash ratios

(AA/FA). The second task is to study the effect of drilling fluid contamination on the rheological and mechanical properties of geopolymer and Portland cement.

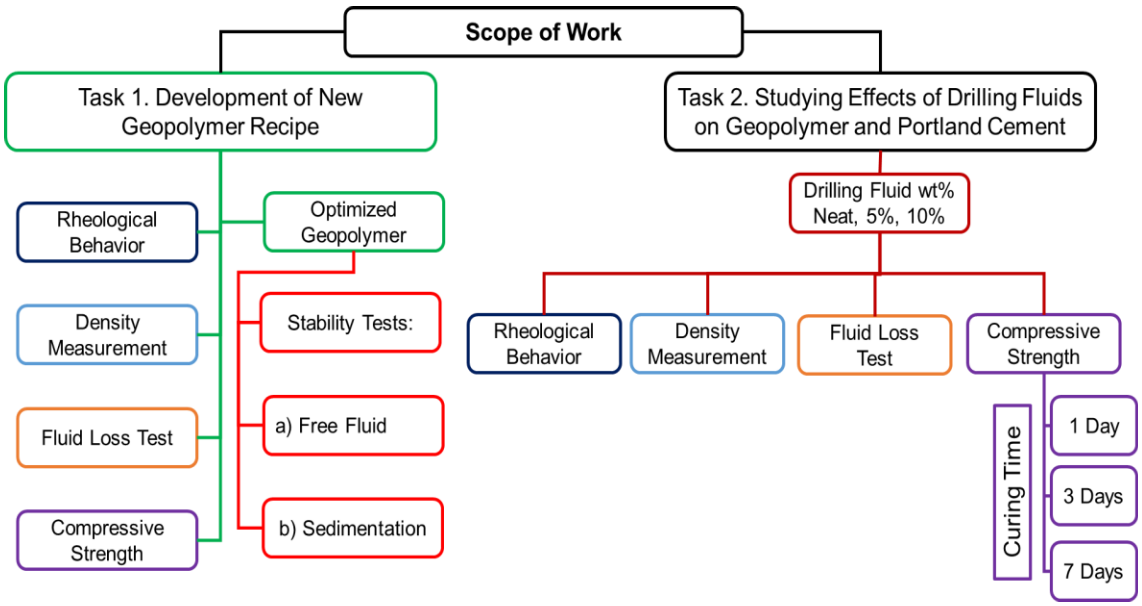

Figure 1.2. Scope of work

2. BACKGROUND AND EXISTING TECHNOLOGIES

2.1. FIELD LIFE CYCLE

The field goes through many stages throughout the duration of its life. Figure 2.1 shows the stages of field life cycle. These stages include

- Field Exploration: exploring the field for potential hydrocarbon accumulation
- Reservoir Evaluation: evaluating the volume of hydrocarbon accumulation and feasibility of extraction
- Reservoir Development: preparing the reservoir for production by drilling and completing several wells
- Oil and Gas Production: extracting of hydrocarbon
- Well Abandonment: abandoning the well when production is no longer feasible

When a seismic study has been done and it indicates a probable presence of hydrocarbons in this area, exploration wells will be drilled in order to discover the reservoir properties.

After the exploration is completed, an evaluation of this field will start. In this stage, the well will be evaluated from many aspects to make sure that the field has sufficient hydrocarbon in place and it will be economically produced.

The development of the field will take place after the evaluation is complete. In this stage, the field will be prepared for production. A production plan can take several months in order to take advantage of all the possibilities to get high production with minimum expenses. In this stage, the application of secondary and tertiary recoveries will be investigated.

After the development is completed, the field will be ready for production. In this stage, most wells will be used as production wells in order to produce at very high rates, especially if the oil prices are too high.

The last stage of the field life cycle is the abandonment. The abandonment stage is the final stage at which time the field will be left and isolated. In this stage, the field reaches the end of its life due to low production rate that cannot cover the field expenses. In this situation, the field has to be abandoned. All wells have to be plugged to avoid any contamination in the reservoir.

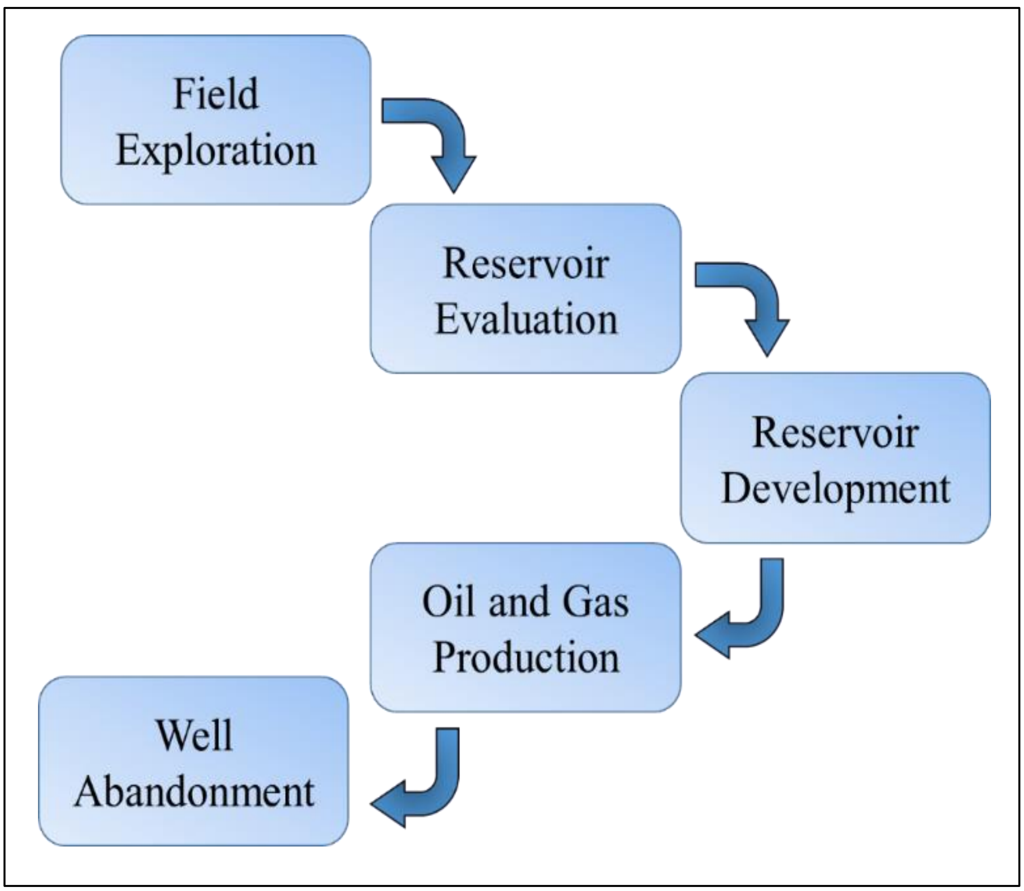

Figure 2.1. Field life cycle

2.2. CLASSIFICATION OF CEMENT

Cement is a fine mineral powder that is mixed with water to create a paste. The paste manufacturing is a very precise process. Before the use of cement, clay was the primary construction material. A cementitious material created by hydrating the ordinary lime used to connect the stones was then used (Cementing Technology, 1984). Cement is used in the oil and gas industry to isolate the formations, and it works as a backup for the casing. After preparing the cement slurry, it will be pumped through the well to fill the annuals and isolate the formation. In general, cement could be classified to four types (Atashnezhad et al., 2017):

- Natural cement
- Pozzolanic cement
- Slag cement
- Portland cement

2.2.1. Natural Cement. Natural cement is a mixture of limestone and clay. Natural cement is produced by crushing rock and then calcining the limestone. After that, the mixture is ground into a fine powder.

2.2.2. Pozzolanic Cement. Pozzolanic cement is rich of siliceous and aluminous materials (Atashnezhad et al., 2017). When mixing this material with lime, it shows high cementitious properties (Cementing Technology, 1984).

2.2.3. Slag Cement. Slag cement is a mixture of calcium silicate, aluminum silicate, and hydrated lime (Atashnezhad et al., 2017). During the hydration processes of this material, a small amount of heat will be released. This material can work in harsh conditions because it contains low grade sulfates (Vicat, 2017).

2.2.4. Portland Cement. Portland cement is a mixture of silica, iron, alumina, and lime. Portland cement is the type most used for the cementing operations in the oil industry due to its properties. Although Portland cement is inexpensive and has beneficial properties such as durability, it has some limitations. These limitations include shrinkage, possibility of gas influx, instability, low ductility, and long-term durability concerns (Khalifeh et al., 2015).

2.3. PORTLAND CEMENT

For many years, the most common material used in cementing operations is ordinary Portland cement (OPC). Portland cement has been used due to worldwide availability, making it cheap and durable. However, using Portland cement has negative impacts on the earth's temperature. According to Sugumran, (2015), the Canadian government mentioned that the biggest cause of carbon dioxide emissions is using Portland cement, and to reduce these emissions, an alternative to Portland cement should be developed and used.

Calcium oxide (CaO) mixed with silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) is the main component of Portland cement. Figure 2.2 shows the cement-making process, from crushing and grinding of raw materials, through roasting of the ground and mixed ingredients, to final cooling and storing of the finished product (Encyclopedia Britannica, Inc.; Rahman F., 2018). The process of manufacturing Portland cement includes the raw materials, the preparation of raw blends, the burning operation, the cooling process, and the final grinding (Alkhamis, M., 2018).

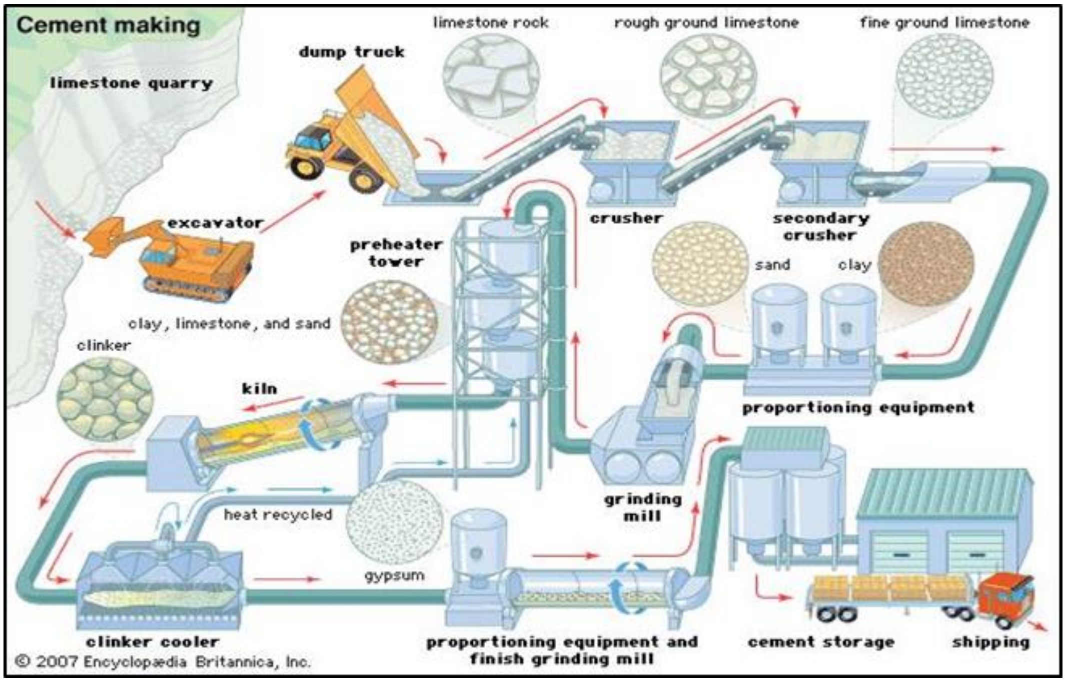

Figure 2.2. The cement making processes (Rahman, 2018)

2.3.1. Portland Cement Composition. The main composition of Portland cement is shown in Table 2.1 and Figure 2.3.

Table 2.1. Main constituents in typical Portland cement (Mindess & Young, 1981)

Chemical Name	Chemical Formula	Shorthand Notation	Percent by Weight
Tricalcium Silicate	$3CaO \times SiO_2$	C_3S	50
Dicalcium Silicate	$2CaO \times SiO_2$	C_2S	25
Tricalcium Aluminate	$3CaO \times Al_2O_3$	C_3A	12
Tetracalcium Aluminoferrite	$4CaO \times Al_2O_3 \times Fe_2O_3$	C_4AF	8
Gypsum	$CaSO_4 \times H_2O$	CSH_2	3.5

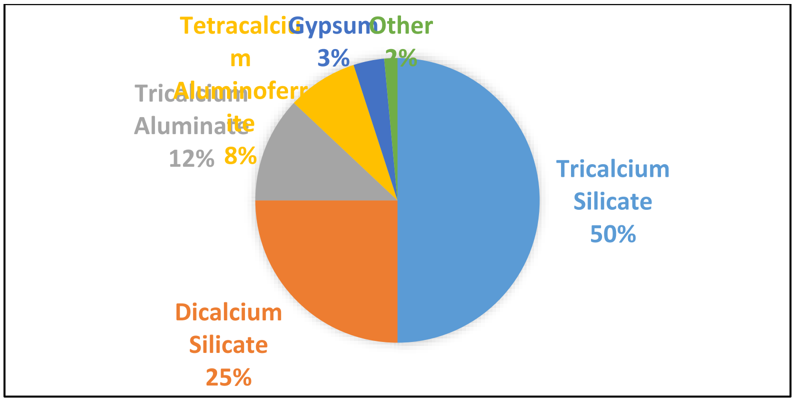

Figure 2.3. Typical oxide composition of a general-purpose Portland cement (Mindess & Young, 1981)

2.3.2. Portland Cement Activation. Although there are specific weights for Portland cement design, it is relatively easy to mix. Figure 2.4 gives an idea about Portland cement activation. Portland cement slurry mainly consists of Portland cement powder and water. To make Portland cement ready for use, water is added to the cement powder.

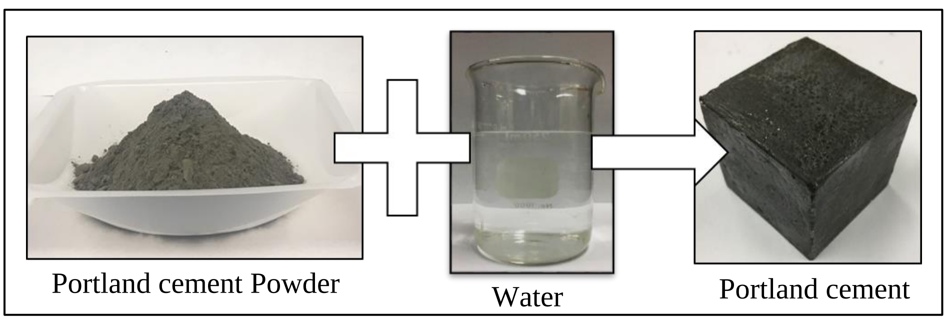

Figure 2.4. Portland cement activation

Production of Portland cement, in most cases, should follow specific standards that depend on the cement's application. In order to produce the optimum mixture, some additives have to be added, which include sand, siliceous loams, pozzolans, iron pyrites, and alumina.

According to Morga (1958), Portland cement is classified into seven types:

- Class A: Used when the depth is less than 6,000 ft.
- Class B: Also used for shallow depths of less than 6,000 ft. However, its main application is when sulfate resistance is required.
- Class C: Similar to class A and B, but is mainly applied when high early strength is needed.
- Class N: Used for higher depths than the previous types, ranging from 6000 to 9000 ft. It is applicable at moderate temperature and pressure.
- Class D: Similar to class N, but it is used at larger depth of 6,000 to 12,000 ft.
- Class E: Used for depths of 6,000 to 14,000 ft and for high pressure and temperature wells.
- Class F: Used for higher depths of 10,000 to 16,000 ft and for higher pressure and higher temperature.
- Class G: Where calcium sulfate and water are added during the production of class G cement, which requires a more thorough mixing.

2.4. GEOPOLYMER

In the last few years, researchers have studied geopolymer properties to be used as an alternative to Portland cement. A few papers were published in this area showing good results to consider geopolymer as a replacement to Portland cement. As was mentioned before, Portland cement is used mostly for cementing operations. However, Portland cement has a huge effect on the environment because of the way it is manufactured, which requires burning a huge amount of fuel and decomposition of limestone. This results in an enormous volume of carbon dioxide being released into the atmosphere (Kong & Sanjayan, 2008). Furthermore, there are other advantageous properties that characterize the geopolymer, which includes thermal stability, low surface roughness, and durability. (Khalifeh, 2014).

2.4.1. Geopolymer Definition. The thermal reactions between fly ash and alkaline activator make the geopolymer binders. In other words, the geopolymer can be defined as a reaction between fly ash and an alkaline activator, which could be sodium hydroxide (NaOH) or potassium hydroxide (KOH) added to sodium silicate (Na2SiO3). This result of this reaction is the geopolymer.

2.4.2. Benefits of Geopolymer. Geopolymer has many advantages over Portland cement including its low cost, and more environmentally friendly.

- Geopolymer is More Cost Effective: Although Portland cement is cheap, geopolymer is cheaper. As was mentioned before, the main component of the geopolymer is fly ash, the source of which is power plants. Since fly ash is a by-product of coal combustion, it is extremely cheap to acquire. Most countries depend on power plants to produce electricity. These power plants burn coal and produce an enormous amount of fly ash. Because of the availability of the fly ash, it is extremely cheap.

- Geopolymer is More Environmentally Friendly: Regarding environmental impacts, Portland cement has huge environmental effects due to its manufacturing process, which requires burning a vast amount of fuel and decomposition of limestone, thus causing enormous volumes of carbon dioxide (CO_2) emissions (Kong & Sanjayan., 2008). Manufacturing Portland cement releases carbon dioxide, and these emissions have negative effects on the climate. However, the main component of the geopolymer is fly ash, which comes from power plants and has fewer environmental impacts.

2.4.3. Fly Ash Activation. Figure 2.5 shows the basic components of geopolymer. Geopolymer can be defined as the reaction between fly ash and alkaline activator, which could be sodium hydroxide (NaOH) or potassium hydroxide (KOH) in the presence of a source of silicate other than the fly ash, such as include sodium silicate (Na2SiO3) or potassium silicate (K2O3Si). An image of geopolymer mix is shown in Figure 2.6.

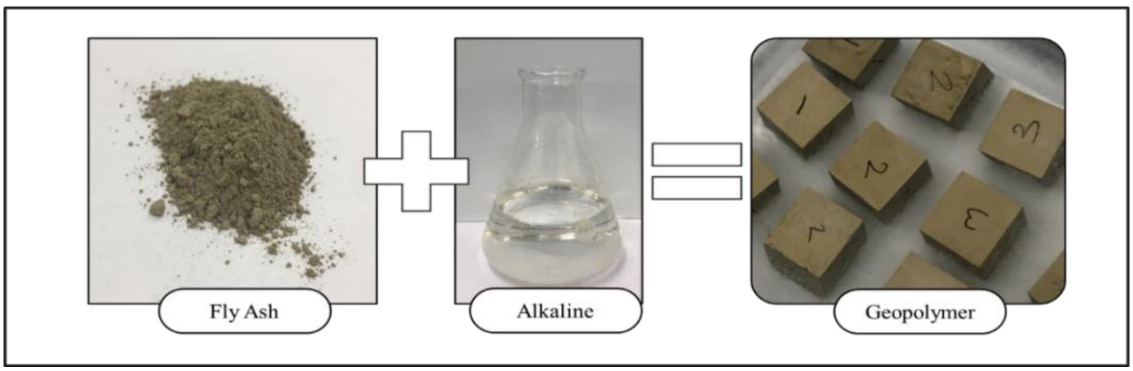

Figure 2.5. Geopolymer composition

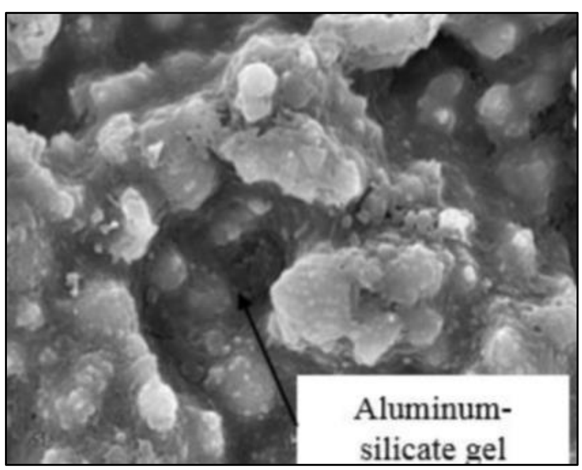

Figure 2.6. Image of geopolymer mix (Salehi et al., 2017)

2.4.4. Geopolymer as an Alternative to Portland Cement. Portland cement has been used as a common material in cementing operations in oil and gas wells for many years due to its properties and worldwide availability. However, according to Berry, et al. (2009), emissions of the greenhouse gases due to the manufacturing of the cement were 7% in 2004. Furthermore, according to Sugumaran, (2015), the Canadian government stated that the biggest cause of carbon dioxide emissions is the production of Portland cement and to reduce this emission, an alternative to Portland cement should be used. Geopolymer can be used as alternative material because geopolymer is cost effective and environmentally friendly.

The thermal reactions between fly ash and alkaline activator make geopolymer binders. Fly ash is considered a pozzolanic material, which consists of siliceous and aluminous components (Salehi et al., 2017). Figure 2.7 shows a simple comparison between Portland cement slurry and geopolymer slurry. As shown in this Figure, Portland cement consists of calcium hydroxide and calcium silicate, while geopolymer consists of alumino-silicate gel (Salehi et al., 2016)

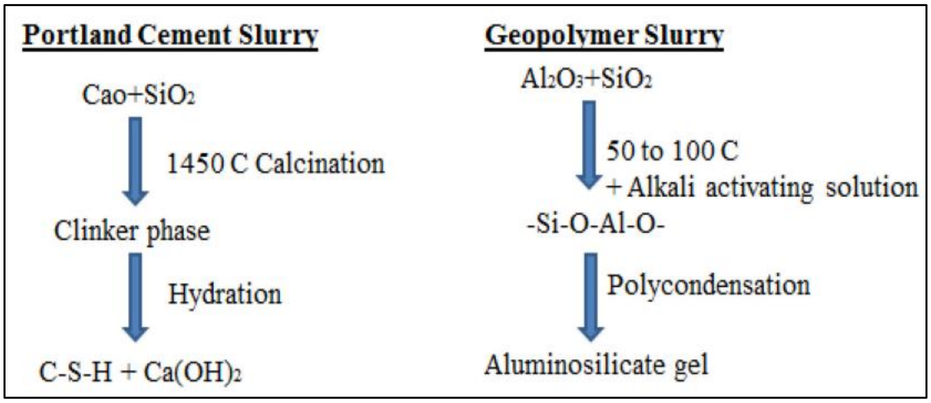

Figure 2.7. Comparison of Portland slurry vs. geopolymer slurry (Salehi et al., 2016)

2.4.5. Geopolymer Constituents. Geopolymer cement is formed from the reaction between the fly ash and alkaline activator.

2.4.5.1. Fly ash. Fly ash is a material that is formed at power plants after coal is combusted. After incineration, fly ash is collected from the flue and bottom ash is collected from the bottom of the boiler. Figure 2.8 shows this process. Fly ash components vary because it strongly depends on the properties of the coal that is burned. In general, fly ash contains large amounts of silicon dioxide (SiO_2) and calcium oxide (CaO).

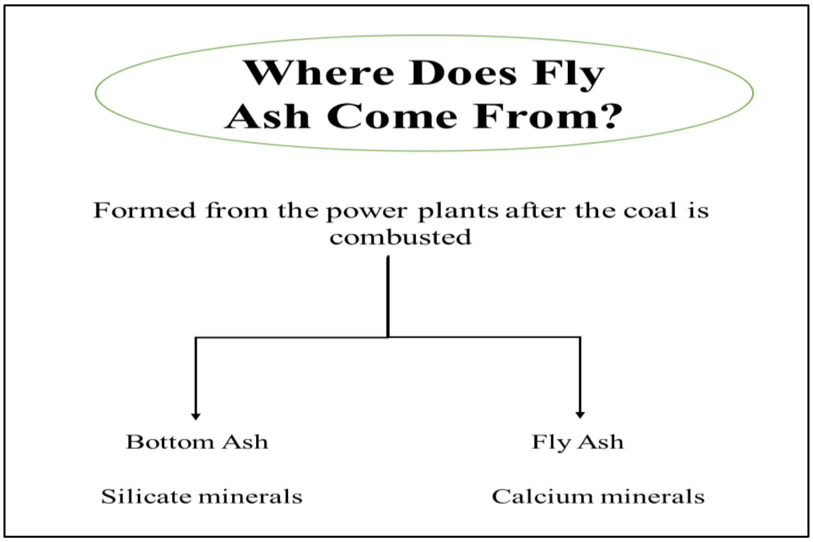

Figure 2.8. Source of fly ash

The difference between bottom ash and fly ash is the chemical compositions. Figure 2.9 shows the source of the ashes. During the combustion processes, lighter components such as calcium minerals are suspended in the air, thus representing the fly ash. However, heavier components such as silicate minerals stand in the bottom of the boiler, which is called the bottom ash.

The two most common types of fly ash are class C and class F. According to the American Society for Testing and Materials (ASTM C 618), the differences between these two types is that class C has a higher content of calcium oxide than class F, so class C is also known as high calcium fly ash. Table 2.2 shows the Chemical Requirements for Fly Ash Classification.

Table 2.2. The chemical requirements for fly ash classification (Boxley et al., 2012)

Properties	Fly Ash Classes	
	Class F	Class C
Minimum percentage of silicon dioxide, aluminum oxide, and iron oxide	70.0	50.0
Maximum percentage of sulfur trioxide	5.0	5.0
Maximum percentage of moisture content,	3.0	3.0
Maximum percentage of material loss on ignition (LOI)	6.0	6.0

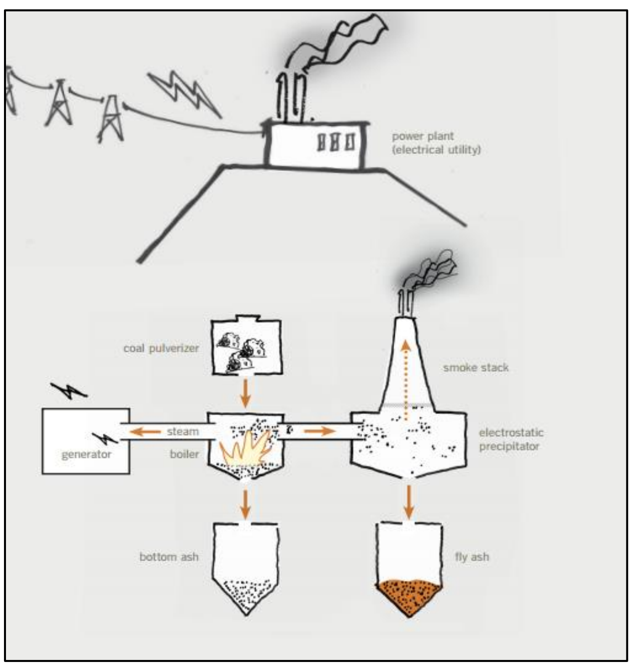

Figure 2.9. Coal fueled power plant process (Perkins & Will, 2011)

There is a huge amount of fly ash created around the world. The amount of fly ash will be increased in the next few years because of the huge increase of power demand. Because of the vast amount of fly ash, it is an extremely inexpensive material.

2.4.5.2. Alkaline liquids. Alkaline liquids are rich in silicate, which could be sodium silicate or potassium silicate, in addition to sodium hydroxide or potassium hydroxide, which is important for polymerization operation. Alkaline liquids are needed to activate fly ash in order to get a geopolymer.

To prepare the different concentrations of sodium hydroxide, specific weight of sodium hydroxide should be added to the water to make the volume 1 liter. This specific weight comes from the equivalent weight, which is equal to the molecular weight divided by 1. The molecular weight for NaOH is 40, so equivalent weight = 40/1 = 40. For instance, to prepare 1 N of sodium hydroxide solution (NaOH), 40.00 gm of NaOH should be added to the water to make 1 liter. So, if we need 10 M of sodium hydroxide solution, 400.00 gm of NaOH should be added to water to make 1 liter. Table 2.3 shows molecular and equivalent weights of some common compounds.

Table 2.3. Molecular and equivalent weights of some compounds (Dharmadhikari & Harris, 2017)

Chemical name	Formula	Molecular weight (g/mol)	Equivalent weight (g/equiv)
Hydrochloric acid	HCL	36.46	36.46
Nitric acid	HNO_3	63.01	63.01
Water	H_2O	18.02	18.02
Sodium hydroxide	NaOH	40.00	40.00
Potassium hydroxide	KOH	56.11	56.11

2.4.6. Geopolymer Properties. The mechanical and chemical properties of the geopolymer could be affected by the following factors:

- Curing temperature
- Curing time
- Type of alkaline
- Concentration of alkaline
- Fly ash to alkaline ratio
- Water ratio
- Alkali to silicate ratio

The curing time has a huge effect on the compressive strength according to several studies. Many studies indicate that as the concentration of alkaline increases, the compressive strength increases. However, at some point when the concentration reaches some level, it does not have a significant effect on the compressive strength.

2.4.7. Geopolymer Evaluation Methods. To ensure that geopolymer can be used as an alternative to Portland cement, some experiments need to be completed. These experiments aim to test the following properties of the geopolymer:

- Rheological property of cement slurry
- Cement slurry density
- Compressive strength
- Thickening time of cement slurry
- Cement slurry filter loss
- Permeability of the cement
- Bond strength and bulk shrinkage

2.4.7.1. Rheological property of cement slurry. Investigating the rheological behavior of geopolymer slurry is important to understand geopolymer performance. These properties help the people who work in the field to predict the behavior of the slurry in wellbore conditions. Due to some factors, the slurry rheological behavior is difficult to achieve. Rheology could be defined as the flow and deformation of materials as a result of some stress or force applied on that material.

The most common method to measure the viscosity is using a device that has a spinning wheel that rotates in the sample, as shown in Figure 2.10. By applying a certain amount of force and measuring the resulting forces, the fluids' rheological properties can be determined.

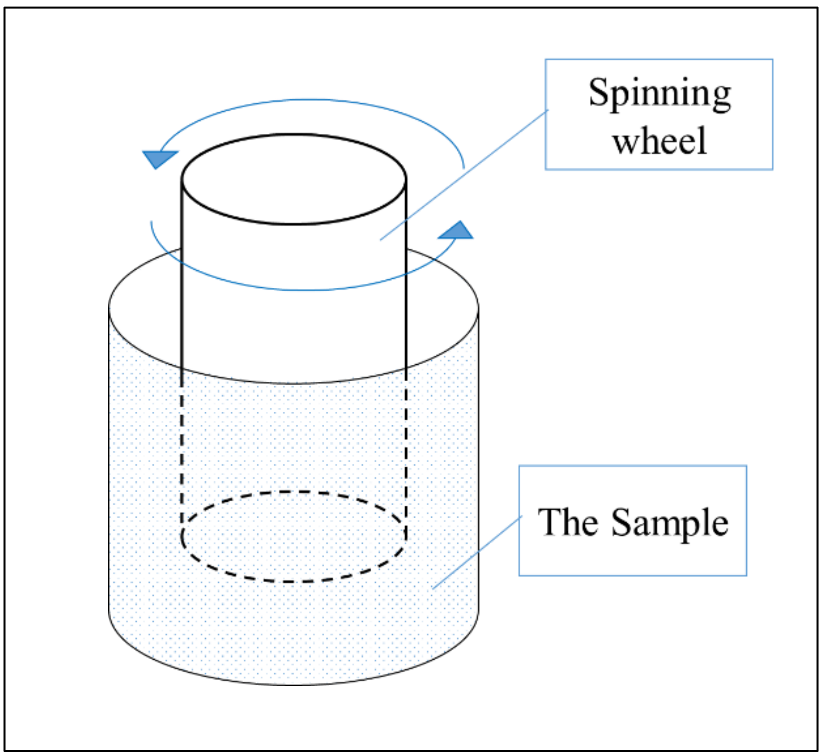

Figure 2.10. Mechanism to measure the fluid rheology

❖ Newtonian fluids:

In general, Newtonian fluids are fluids that have a constant relationship between shear stress and shear rate. Figure 2.11 shows the relationship between the shear stress and shear rate for the Newtonian fluid. The viscosity of the non-Newtonian fluids is constant and does not change with the shear rate change.

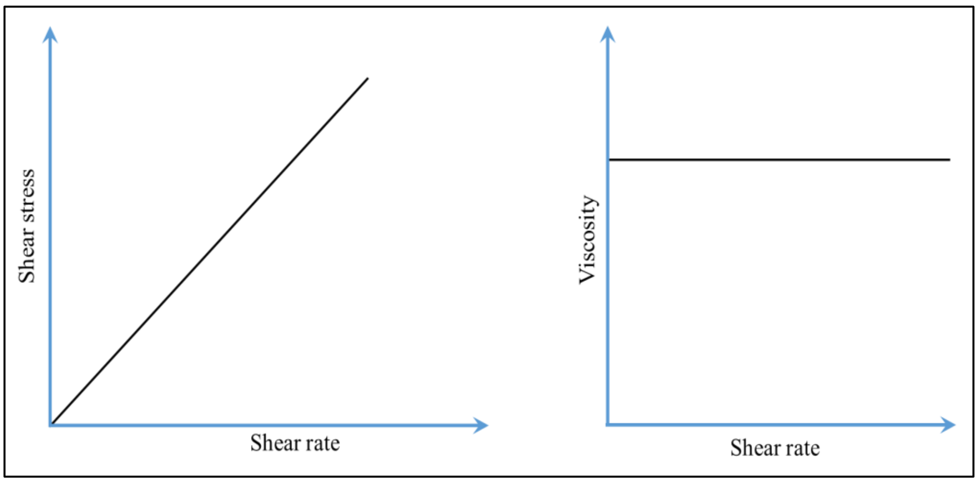

Figure 2.11. Newtonian fluid behavior

❖ Non-Newtonian fluids:

In general, non-Newtonian fluids are fluids that have a non-constant relationship between shear stress and shear rate. Figure 2.12 shows all types for the fluid flow behavior. The viscosity of the non-Newtonian fluids varies with the change in shear rate. Non-Newtonian fluids can be classified based on the fluid's viscosity changes into three types:

- Pseudo-plastic fluids:

  The viscosity of this fluid decreases as the shear rate increases; this is called shear thinning (e.g., emulsions).

- Dilatant fluids:

  The viscosity of this fluid increases as the shear rate increases (e.g., clay slurries).

- Bingham fluids:

  To induce this fluid to flow, some force should be applied; this is referred to as yield stress because these fluids act as a solid in static conditions.

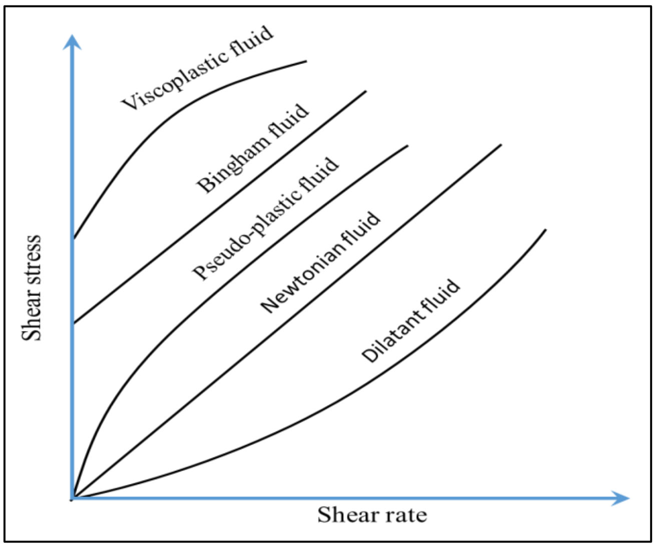

Figure 2.12. Fluid behavior

- Viscosity:

Viscosity is defined as the internal resistance of a fluid to flow. Plastic viscosity can be defined as fluid resistance to flow due to surface conditions that involve mechanical friction. Figure 2.13 shows an OFITE "rotational" viscometer. Plastic viscosity depends on several factors such as the number and size of particles in the cement slurry, and their distribution. To measure the rheology properties, the rotational viscometer is used.

Figure 2.13. OFITE "rotational" viscometer

- Test procedure:

1. Place the cement sample into the sample cup and place it on the base. Use the manual rotation sleeve to set it at 600 rpm and take the first reading.
2. Set the rotation sleeve at 300 rpm to take the second reading. The second reading at 300 rpm is the apparent viscosity. The difference between the two readings is the plastic viscosity. The difference between the plastic viscosity and the reading at 300 rpm is the yield point.
3. Set the sleeve at 600 rpm and then leave the sample for 10 seconds. Then, set the sleeve at 3 rpm and take the maximum result that appears. This reading is the 10 second gel strength.
4. Repeat step 3 but increase the setting time to 10 minutes to read the 10-minute gel strength.

2.4.7.2. Density of cement slurry. The density is defined as the mass per unit volume. Since the density controls the strength of the material, it affects the flow ability. The density of cement slurry should be higher than the drilling fluid density in the well because if the density of the cement slurry is lower than the drilling mud density, the cement will go through the drilling mud and the cementing operations will fail. Nevertheless, the density of cement should not be very high or it will break the formation and cause a kick. Furthermore, if cement slurry density is too high, it will be hard to pump it to the downhole and it will need a stronger pump.

- Density calculation:

The material density is equal to the material mass divided by the volume of this material as is shown in the following equation:

$$\rho = \frac{m}{v}$$

where ρ is the material density, lb/gal; m is the material mass, lb; and v is the volume, gal.

- Lab measurement of the density:

Fluid density scale balance is used to estimate the cement density in the lab. Figure 2.14 shows the structure of the fluid density balance, and Figure 2.15 shows the fluid density balance device.

- Test Procedure:

1- Set the base on the flat surface.

2- Use fresh water as a reference to make sure that your reading is accurate.

3- Fill the cup with fresh water and put the lid on. Make sure that some water goes out of the hole in the lid to verify that all the trapped air has been released. Move the rider until it becomes balanced by checking the bubble. (The fresh water should give a result of 8.33 lb/gal or 62.4 lb/cft at 70 ˚F).

4- Dry the cup and fill it with the cement that needs to be tested. Put the lid on and make sure that some cement goes out of the hole in the lid to verify that all the trapped air has been released.

5- Wash and clean the cement from the outside of the cup and wipe the outside.

6- Set the base on the flat surface and move the rider until the bubble stays in the center which makes the device balanced. Read the density toward the knife edge and then add the correction factor if the device needs further calibration.

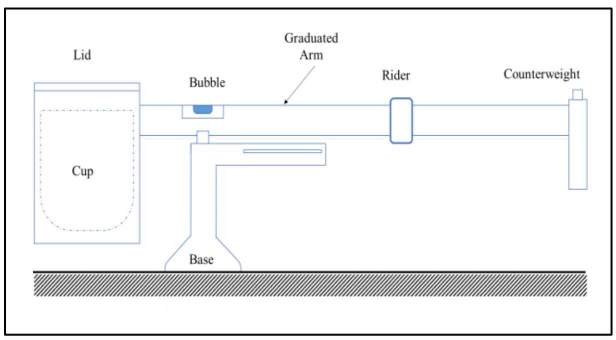

Figure 2.14. Fluid density balance

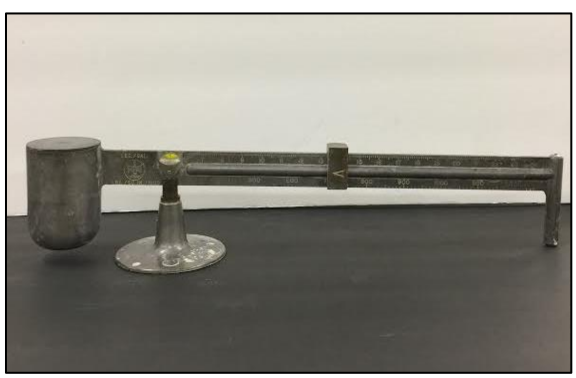

Figure 2.15. Fluid density balance device

2.4.7.3. Strength. There are three types of strengths as shown in Figure 2.16:

- Compressive strength
- Tensile strength
- Shear strength

Compressive strength is the ability of material to resist the forces that are applied on it. These forces could affect the volume of the material, which will make it smaller due to the compression force. However, tensile strength is the opposite of the compressive strength. Tensile strength is the ability of the material to withstand the opposite pulled forces applied on two sides of the material and each force tries to pull the material to it. This could impact the shape of the material by increasing the length.

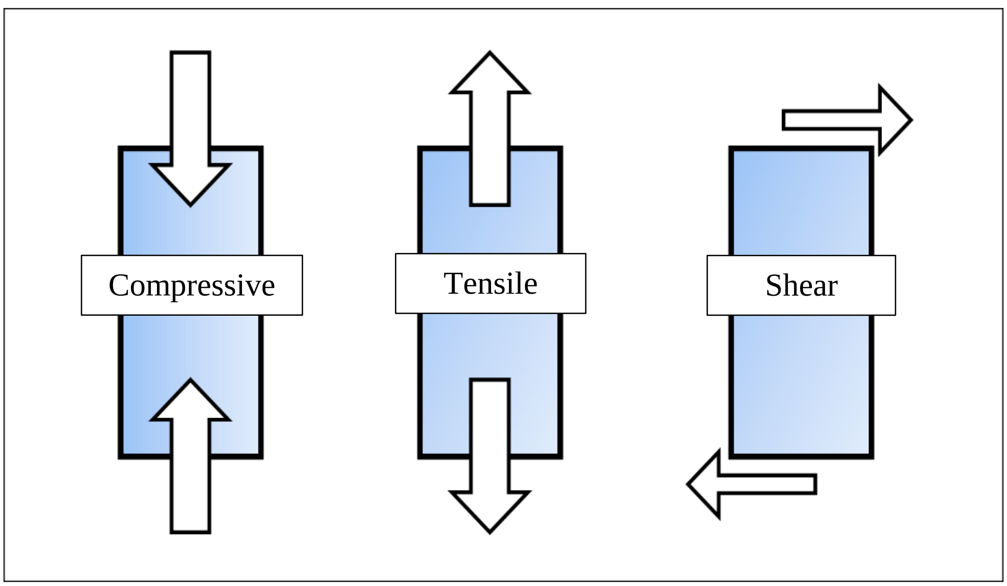

Figure 2.16. Types of strengths

The most important feature in the cement is the compressive strength. Compressive strength is the ability of the cement to withstand the pressure in downhole conditions.

- The measurement of compressive strength:

To measure the compressive strength, a triaxial compressive strength test has to be done using a device that applies the required force on the sample to calculate the compressive strength. Figure 2.17 shows the hydraulic pressure unit. The main concept of the compressive strength test is to estimate the maximum load that the sample can handle. The test can be done by placing the sample on its location and applying the load from above. The loading piston forces the sample down until the sample breaks. The pressure that the sample breaks at is called the compressive strength, which is the maximum pressure or load that the sample can withstand.

Figure 2.17. Hydraulic press unit

2.4.7.4. Setting time. The setting time can be defined as the time that cement needs to develop sufficient strength. Generally, this strength is equal to force required for a needle to penetrate the cement. It starts when the cement slurry is mixed and ends when all cement becomes solid and cannot flow. The setting time is important for cementing to avoid cement dehydration during cementing operations.

The measurement of the setting time is taken manually by using Vicat. Figure 2.18 shows the Vicat apparatus. The time recording should commence when mixing begins. The cement sample should be set it in a cylinder and checked with a needle. When the needle cannot break through the sample, the time recording should be stopped. This time is the setting time.

Figure 2.18. Vicat apparatus (Indiamart)

2.4.7.5. Thickening time. The thickening time is an important test to simulate the slurry pumping. Figure 2.19 shows cement consistometer. The slurry consistency, B_c, is obtained by using an appropriate consistometer depending on the temperature and pressure.

The consistometer consists of a chamber that withstands high conditions such as high pressure and high temperature. Inside this chamber, a rotating cylindrical slurry container is equipped with a stationery paddle assembly. The speed rate of the cylindrical slurry chamber is 150 rpm (Applied Drilling Engineering, 1991). The slurry consistency is defined in terms of the torque, *T*, that is exerted on the paddle by the cement slurry:

$$B_c = \frac{T - 78.2}{20.02}$$

where B_c is the slurry consistency in API units and *T* is the torque in gm-cm. The thickening time is the time required to reach the upper limit of pumpability, which is 100 B_c.

Figure 2.19. Cement consistometer (Cement Test Equipment)

2.4.7.6. Cement slurry filter loss. The filter loss is when the cement slurry loses the content of free water. The fluid loss occurs when the water goes from the cement slurry into the formation through the formation permeability paths in the wellbore and all the solids and sediments remain at the formation wall. The water loss is a big problem in all cementing processes because as the water content decreases, all cement properties will change. Furthermore, the decrease in the water content will lead to a reduction in the setting time and cement flowability. This loss of water will also cause a reduction in cement pumpability. When cement loses water, its properties change and the possibility increases of having channels and cracks within the cement formation.

- Measure the filter loss:

API filter pressure devices are used to measure the filter loss. Figure 2.20 shows the filter pressure apparatus.

1- Make sure that you have the filter paper, then install the cup and fill it with cement slurry. Cover the cup with the top cap and place the cup at its location.
2- Use the T screw to make sure that the cup is closed securely.
3- Set a graduated tube under the cup to measure the filter loss.
4- Plug the pressure pump into the pressure inlet but keep the valve closed.
5- Set the pressure at 100 psi and open the valve.
6- Record the filtrate volume for 1, 2, 3, 5, 7.5, 15, and 30 minutes.

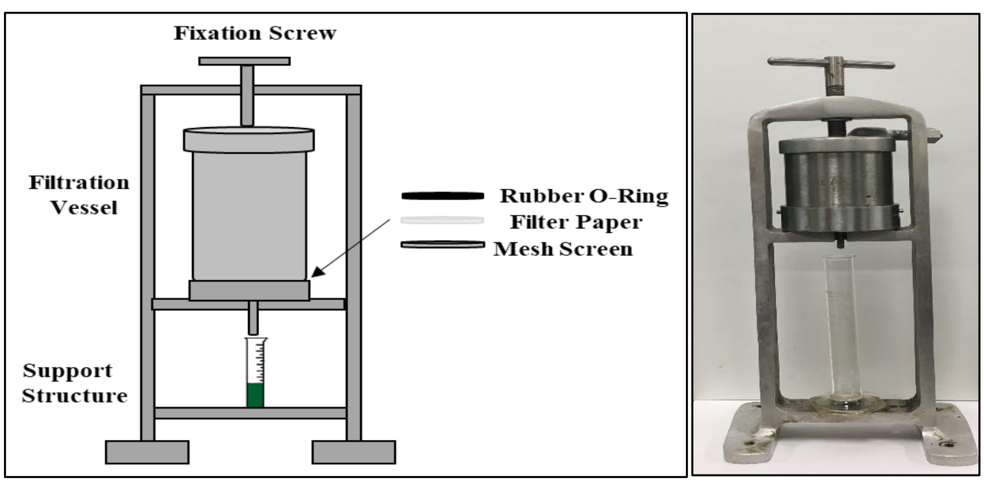

Figure 2.20. Filter pressure apparatus

2.4.7.7. Permeability. The permeability is another important property for the material that is used for cementing in oil and gas wells in order to obtain fully zonal isolations. As was mentioned before, the main objective of cementing is to prevent fluid migrations between the well and the formation. The material that is used should be impermeable to provide full isolation and avoid any contact between the well and the formation.

2.4.7.8. Bond strength. Bond strength is the ability of the material to interconnect with other materials. In other words, bond strength is defined as the strength that keeps two different materials connected to each other. Furthermore, it is a property of the material that indicates whether it can stick with another type of material or not. The cement should have a high bond strength in order to give a full isolation. As the bond strength increases, the cement will give better performance. If the cement fails to give a very good bond strength measurement, it could fail cementing operations because the cement will break from the casing or the formations, which will cause paths between them. These paths will leak fluids from the formation to the wellbore or to other formation and will not keep the well isolated.

- Measurement of bond strength:

In order to measure the bond strength, a sample (as is shown in Figure 2.21) has to be prepared. This sample is filled with cement and there is a steel pipe inside it. Tensile strength is used to pull the pipe steel from the cement sample. The force where the steel pipe is broken apart from the cement is used to calculate the bond strength of the tested sample.

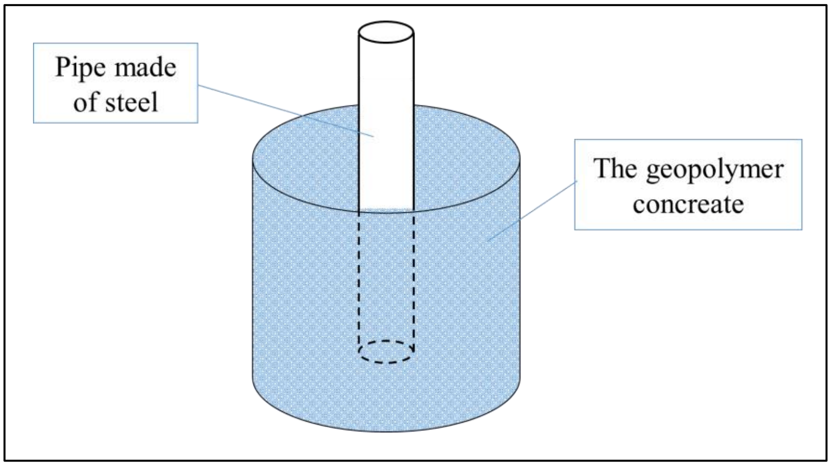

Figure 2.21. Sample design for the bond strength test

2.4.7.9. Bulk shrinkage. The decreasing volume of the cement due to the forces applied to it is known as bulk shrinkage. In other words, bulk shrinkage can be defined as the decreasing in the external volume. The length change shrinkage and expansion are shown in Figure 2.22.

Figure 2.22. Length change shrinkage (length change)

2.5. DRILLING FLUIDS

Drilling fluid, also called drilling mud, is a fluid that is used during drilling operations.

2.5.1. Drilling Fluid Functions. Drilling fluids have many functions during drilling operations. The main functions of the drilling fluids include

1. To carry the cutting that formed while drilling the well to the surface.
2. To lubricate the drilling bit and drill string.
3. To cool down the temperature of the drilling bit as the friction between the bit and the formation heat up the bit.
4. To apply hydrostatic pressure to prevent the formation fluids from entering the wellbore.
5. To maintain wellbore stability.

2.5.2. Drilling Fluid Types. Selection of the drilling fluid is based on many factors, including formation properties and the cost. Drilling fluids are classified into different types (ASME Shale Shaker Committee, 2005):

- Water based mud (WBM):

Water based mud is most common drilling fluid and mainly used due to its low cost. However, there are some limitations of using it including shale swelling. Since water based mud is mainly composed of water, it is considered environmentally friendly (Amani, et al., 2012).

- Oil based mud (OBM):

Oil based mud is mainly used in shale formations. OBM is a good choice in high-pressure and high-temperature conditions (Amani, et al., 2012).

- Synthetic based mud (SBM):

Synthetic based mud is considered more expensive than the other drilling fluids. SBM is considered a nontoxic material, unlike OBM which contains aromatics (Hart, et al., 2007). In the Gulf of Mexico, SBM drilling fluids have been commonly used in recent years (Neff, et al., 2000; Hart, et al., 2007).

3. LITERATURE REVIEW

3.1. GEOPOLYMER FORMALATION OPTIMIZATION

There are few studies have been published about using geopolymer in oil and gas wells. In these papers, the effects of changing of the chemical ratios on geopolymer properties were studied. These properties include:

- Rheology measurement
- Density measurement
- Compressive strength test
- Bond strength test
- Bulk shrinkage test
- Thickening time test
- Durability test
- Acid resistance

3.1.1. Rheology Behavior. The rheology has been studied due to the importance of understanding the behavior of the slurry. By studying these properties, better prediction of the behavior of the cement slurry in the wellbore condition can be achieved. Due to some factors, the slurry rheological behavior is difficult to obtain. Rheology could be defined as the flow and deformations of materials as a result of some stress or forces that are applied on that material.

In 2015, study has been done by Suppiah, et al., (2016). In this study, they investigated the effects of sodium hydroxide concentration and different ratios of silicate to hydroxide on the rheology of geopolymer. They produced different geopolymer slurries by mixing different ratios of class F fly ash with different ratios of sodium silicate to sodium hydroxide.

Figure 3.1 shows the effects of different ratios of fly ash to alkaline activator on viscosity of geopolymer cement slurry for different concentration of sodium hydroxide. As the concentration of sodium hydroxide increases, the viscosity of geopolymer increases. The increasing of viscosity leads to poor pumpability. Also, increasing in fly ash to alkaline activator ratio leads to increase in geopolymer viscosity.

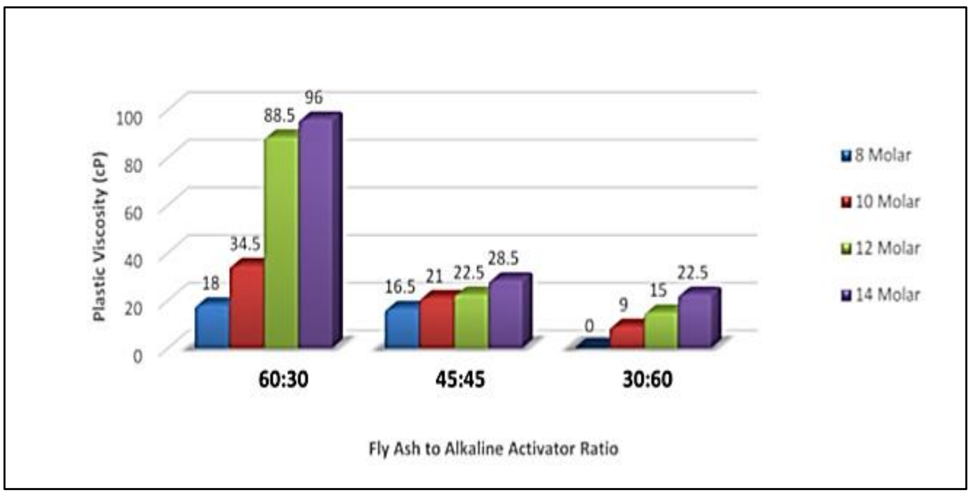

Figure 3.1. Effect of different ratios of fly ash to alkaline activator on viscosity of geopolymer cement slurry for different concentration of sodium hydroxide (Suppiah, et al., 2016)

3.1.2. Density Measurement Test. The density of the cement has big impacts on the formation. It affects the flowability and the pumpability. The cement density should be higher than that of the drilling fluid but should not reach the formation breakdown. Because if the density of cement is lower than that of the drilling fluid, it will fall down and the plugging will not be reached. And if the density of cement is too high and reaches the formation breakdown, it will cause a break and paths in the formation which will result in cement failure.

In 2016, the density of the geopolymer has been studied by Suppiah, et al., (2016) to investigate the effects sodium hydroxide concentration and different ratio of silicate to hydroxide. They produced different geopolymer slurries by mixing different ratio of class F fly ash with different ratios of sodium silicate to sodium hydroxide. As is shown in Figure 3.2, the highest density, which is 15.2 lb/gal, is in the cement slurry that was made with 14 Molar of sodium hydroxide and highest fly ash to alkaline ratio. In general, the results showed that the density of the geopolymer increases as the amount of fly ash to alkaline ratio increases.

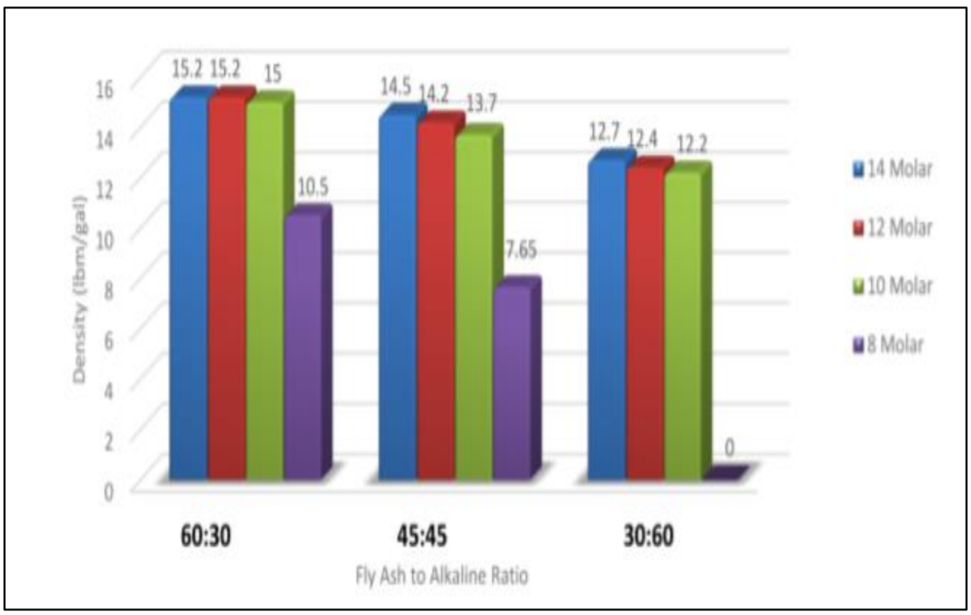

Figure 3.2. Effect of different ratios of fly ash to alkaline activator on density of geopolymer cement slurry for different concentration of sodium hydroxide (Suppiah, et al., 2016)

3.1.3. Compressive Strength. Compressive strength is the ability of the material to withstand the pressure or forces applied on it. Because of the downhole conditions (high pressure and high temperature), the compressive strength is significantly important.

Several studies have been done to evaluate the compressive strength for geopolymer. In 2012, Abdullah, et al., (2012). They studied the effect of the alkaline activator to fly ash ratios on the compressive strength. Three samples with three different alkaline activator to fly ash ratios were prepared. They found that as the alkaline activator to fly ash ratio increased, the compressive strength increased. Figure 3.3, shows that when the ratio increased from 0.3 to 0.35, the compressive strength increased rapidly from 3.695 MPa to 8.325 MPa. When the ratio increased from 0.35 to 0.4, the compressive strength increased as well, however, the increase was not very significant.

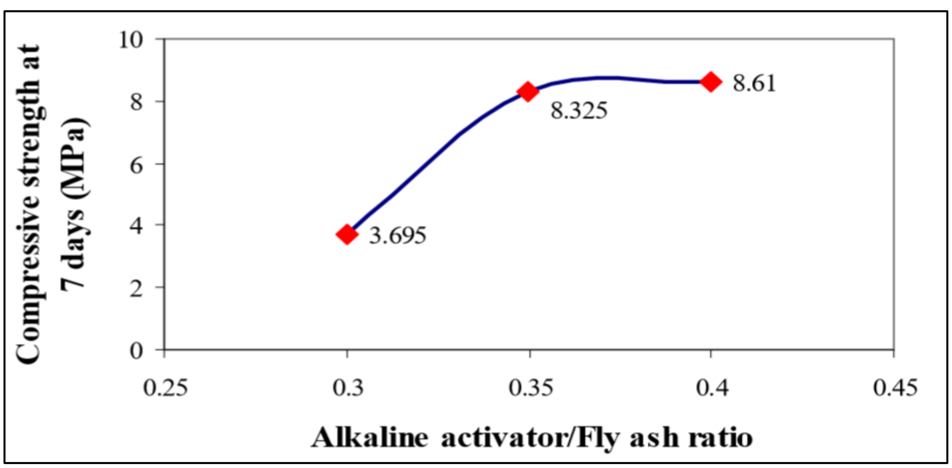

Figure 3.3. The effect of alkaline activator to fly ash ratio on the compressive strength (Abdullah, et al., 2012)

Nasvi et al., (2012) used geopolymer and class G cement to compare their mechanical behavior at different temperatures. Figure 3.4 shows the variation of uni-axial compressive strength (UCS) of geopolymer and class G cement using different curing temperature. They came up with a conclusion that the range of temperature 50 – 60 ºC is the optimum curing temperature for high strength of geopolymer and class G cement.

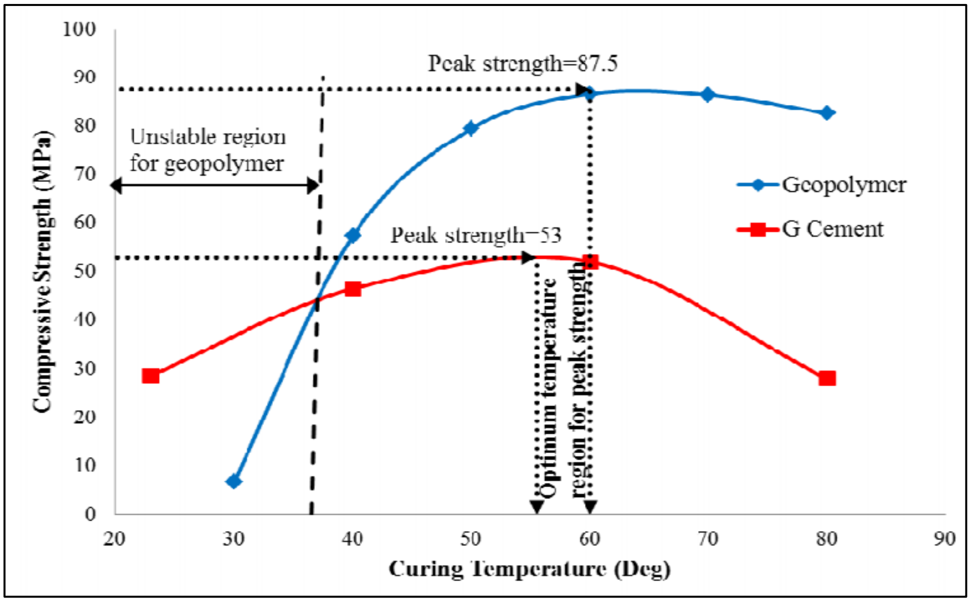

Figure 3.4. Compressive strength results of geopolymer and class G cement at different curing temperature (Nasvi et al., 2012)

Sugumaran, M. (2015) investigated the impacts of low calcium fly ash on geopolymer cement. He tested the water ratio, type and molarity of alkaline activator and alkaline activator ratio. He found that the ratio of water 0.3 in 12 M of sodium hydroxide, and 0.4 for alkaline activator ratio increased the compressive strength by 31%. Four experiments were conducted to find out the appropriate composition of fly ash. Figure 3.5 shows the temperature effect on compressive strength. As we can see, after 21 days, although the compressive strength at 100 ˚C after 12 days was higher than 60 ˚C, the sample was cracked. He found that the water ratio of 40 gm gives a higher compressive strength compared to 60 gm and 80 gm as is shown in Figure 3.6. Figure 3.7 shows the result of the effect of sodium hydroxide molarity. The 12 M showed a higher compressive strength compared to the 10 M and 15 M.

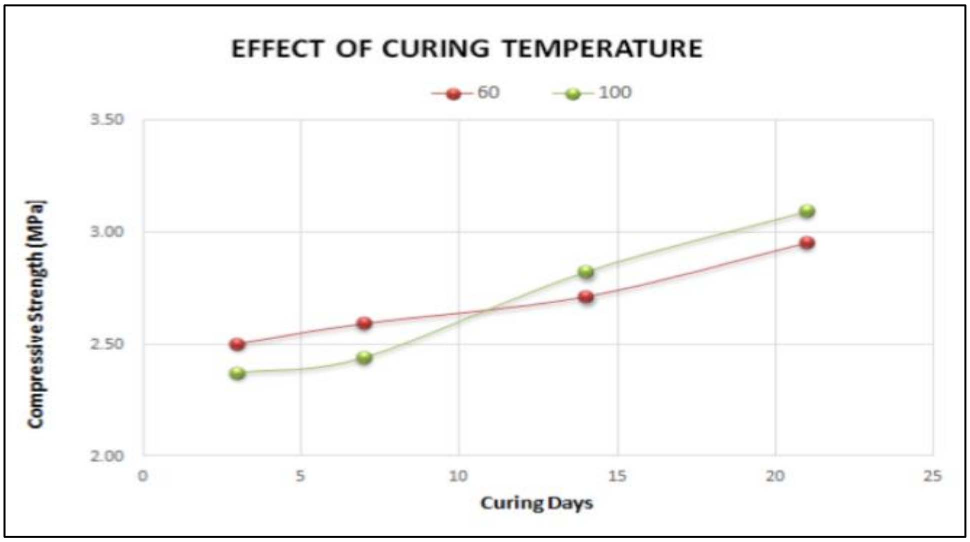

Figure 3.5. Effect of temperatures on compressive strength (Sugumaran, 2015)

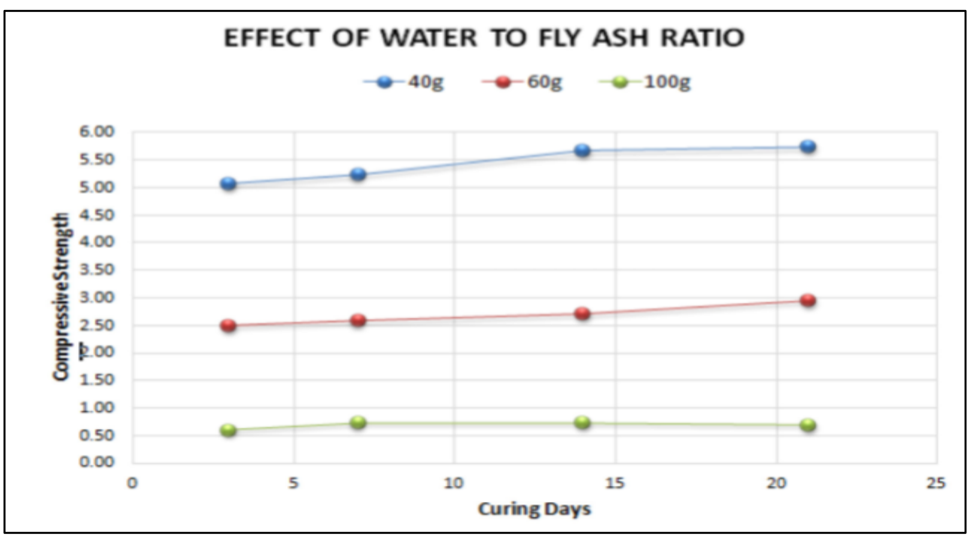

Figure 3.6. Effect of water to fly ash ratio on compressive strength at different curing days (Sugumaran, M. 2015)

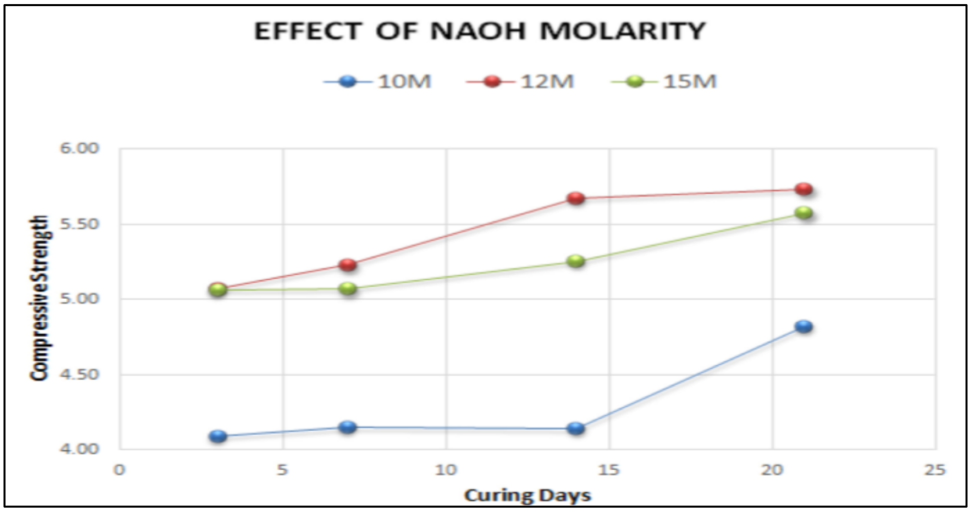

Figure 3.7. Effect of sodium hydroxide molarity on compressive strength at different curing days (Sugumaran, M. 2015)

Salehi et al. (2016) investigated the effects of sodium hydroxide concentration on the geopolymer properties. They did four experiments in order to develop the compressive strength, thickening time, durability and shear bond strength. They used the class F fly ash geopolymer with different design and class H Portland cement. Table 3.1 shows the elements ratios of fly ash geopolymer.

Table 3.1. Elemental ratios of fly ash geopolymer (Salehi et al., 2016)

Oxide	Ratio
SiO_2/Al_2O_3	1.7 - 9.2
Al_2O_3/CaO	1.2 - 5.4
Fe_2O_3/ SiO_2	0.1 – 0.9

Three samples were prepared with different sodium hydroxide concentration, 8 M, 10 M, and 12 M solutions. As is shown in Figure 3.8, as the concentration increased, the compressive strength increased until the concentration reached 10 M. Above the concentration of 10 M no significant change happened (Salehi et al., 2016). Both Salehi and Sugumaran results were close to each other since both of them reported that 12 M of sodium hydroxide gives a high compressive strength.

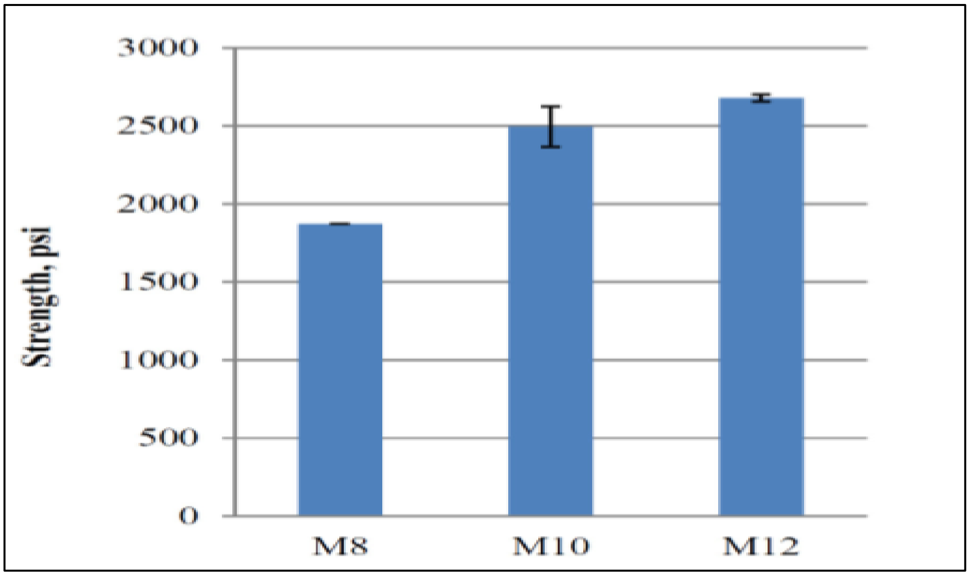

Figure 3.8. Effect of molarity of sodium hydroxide on geopolymer compressive strength (Salehi et al., 2016)

Salehi et al. (2016) also prepared another three samples to see the effect of curing time on compressive strength. Figure 3.9 shows the result of curing time effect. As time increased the compressive strength increased. Also, high improvement in strength for the first 14 days is shown. Moreover, they prepared 2 mixtures of geopolymer and Portland cement to examine the temperature impacts. Figure 3.10 shows compressive strength comparison at different curing temperatures. Their result showed that as temperature increased the compressive strength for the geopolymers increased. However, the compressive strength for the Portland cement decreased as temperature increased.

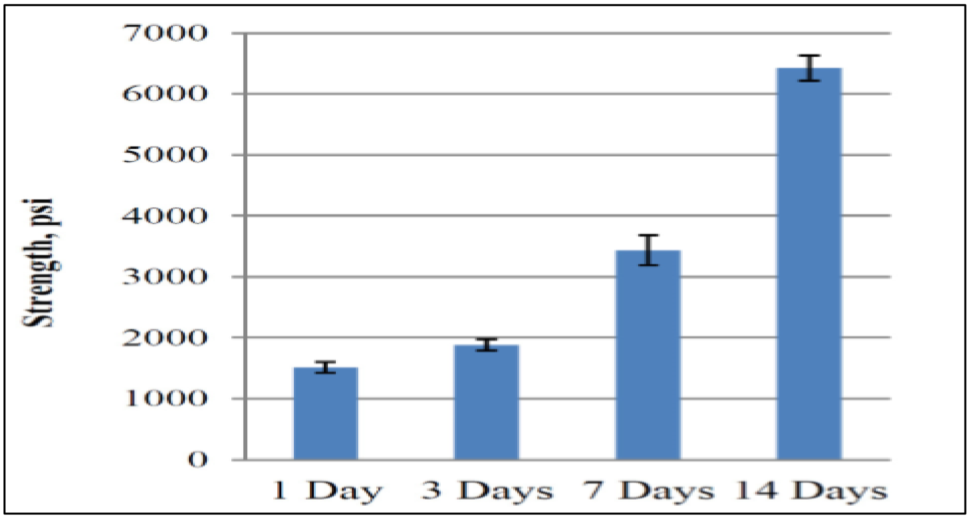

Figure 3.9. Compressive strength comparison at different curing times (Salehi et al., 2016)

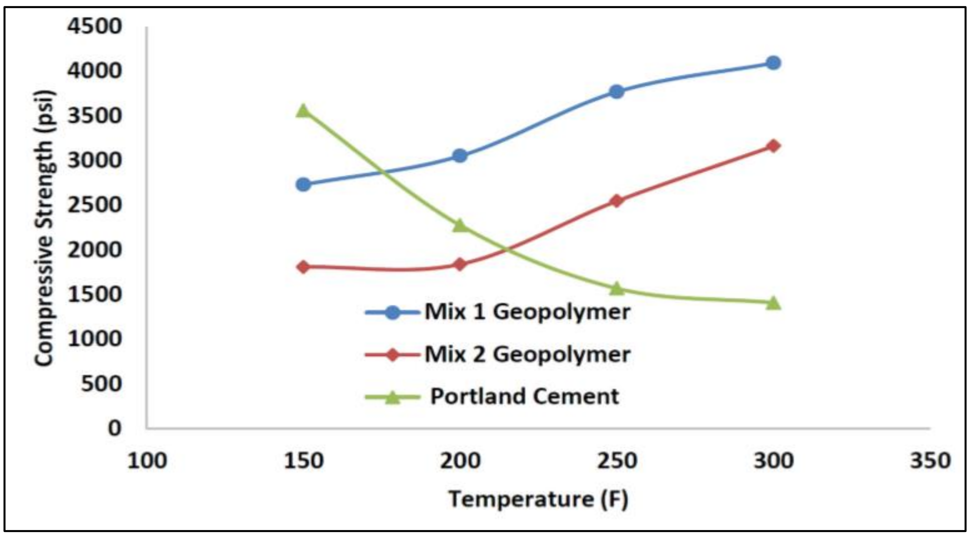

Figure 3.10. Compressive strength at different temperatures (Salehi et al., 2016)

Furthermore, another study has been done by Salehi (2016) to compare the compressive strength of fly ash geopolymer with class H Portland cement at different curing time. Their results showed that the compressive strength increased with curing time. As we can see in Figure 3.11, the compressive strength of fly ash reaches about 3,500 psi after 7 days, which is close to the compressive strength of Portland cement after 14 days. Also, this Figure shows that the compressive strength of fly ash has high improvement after 7 days.

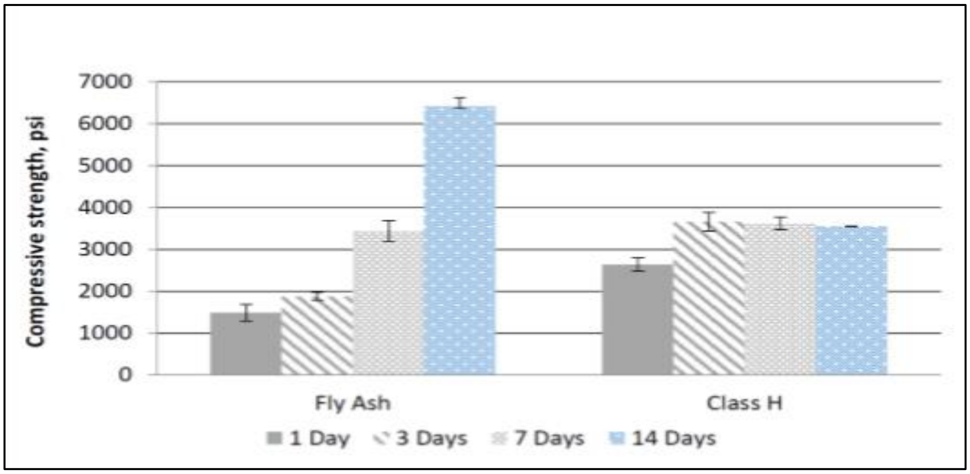

Figure 3.11 Results of compressive strength (Salehi et al., 2016)

Suppiah, et al., (2016) studied the compressive strength of geopolymer cement to investigate the sodium hydroxide concentration and different ratios of silicate to hydroxide. They produced different geopolymer slurries by mixing different ratios of class F fly ash with different ratios of sodium silicate to sodium hydroxide. Table 3.2 shows the different mixtures that they used.

Table 3.2. Details of mix proportions (Suppiah, et al., 2016)

Mix	Ratio Fly Ash / Alkaline Activator	Sodium Silicate / Sodium Hydroxide	Concentrations of Sodium Hydroxide
Mix 1	60:30	0.25, 0.5, 1, 2.5	8 M, 10 M, 12 M, 14 M
Mix 2	45:45	0.25, 0.5, 1, 2.5	8 M, 10 M, 12 M, 14 M
Mix 3	30:60	0.25, 0.5, 1, 2.5	8 M, 10 M, 12 M, 14 M

Figure 3.12 shows the effect of the concentration of sodium hydroxide on the compressive strength. As we can see in Figure 3.12, as the concentration of sodium hydroxide increased, the compressive strength increased until a specific point. When the sodium hydroxide concentration reaches 14 molarity, the compressive strength decreased due to the rate of polymerization being low at high concentrations of sodium hydroxide solution (Suppiah, et al., 2016). Suppiah, et al., (2016) results is similar to Salehi et al. (2016) and Sugumaran, (2015) results, where all of them agreed that the highest compressive strength comes from the concentration of 12 M sodium hydroxide.

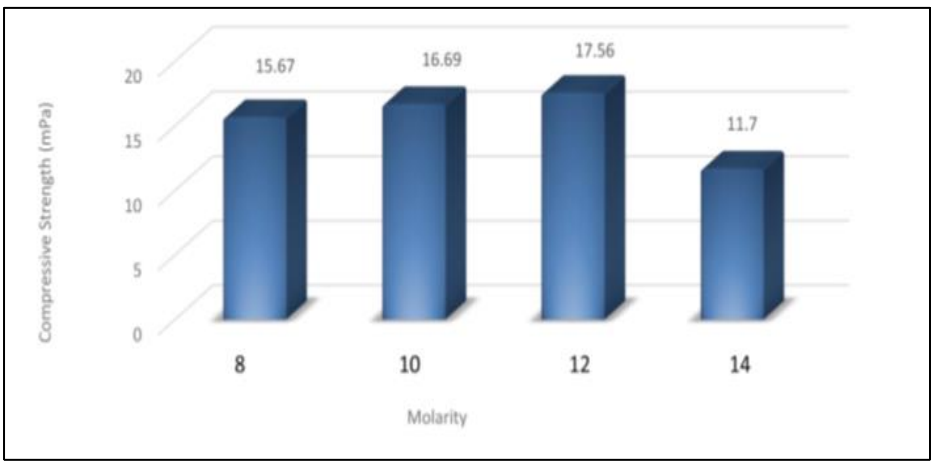

Figure 3.12. Effect of NaOH concentration on compressive strength (Suppiah, et al., 2016)

Liu et al. (2017) compared some properties including compressive strength between geopolymers, geopolymer hybrid and Portland cement. They used alkaline solution, which was 8 M sodium hydroxide, to activate the alumini-silicate precursor. Class F fly ash was used in all experiment. Table 3.3 shows the fly ash composition. The geopolymer slurries were mixed by using a spatula and then a paddle stirrer at 480 rpm for 30 seconds.

Table 3.3. Composition of fly ash (Liu et al., 2017)

Component	Weight %
SiO_2	49.9
Al_2O_3	25.3
Fe_2O_3	15.1
($SiO_2 + Al_2O_3 + Fe_2O_3$)	(90.3)
CaO	3.0
MgO	0.91
Alkalis ($Na_2O + 0.658\ K_2O$)	0.73
SO_3	0.44

Liu et al. (2017) investigated geopolymer slurries and geopolymer hybrid, which consists of 80% of geopolymer and 20% of SBM, which is commonly used in Gulf of Mexico. On other hand, the Portland slurries were composed of class H Portland cement and water using 38.5% "by weight of cement". They used a water bath at 170 ˚F for 7 days to prepare the samples, which were 2 inches length and with a dimeter of 1 inch (Liu et al., 2017). As can be seen in Table 3.4, the as confining pressure increases, the confined compressive strength increases. Even though the compressive strength for geopolymer hybrid is about 2,870 psi at 500 psi confining stress, it is enough for most types of cementation operations.

Table 3.4. Compressive strength results at 7 days (Liu et al., 2017)

	P_c = 100 Psi	P_c = 500 Psi
Geopolymer	3,330 Psi	5,000 Psi
Geopolymer Hybrid	2,000 Psi	2,870 Psi
Portland Cement	5,600 Psi	7,850 Psi

3.1.4. Bond Strength. Bond strength is defined as the strength that keeps two different materials connected to each other. In other words, it is a property of the material that define weather a material can stick with another type of material or not. The cement should have a high bond strength in order to produce full isolation. As the bond strength increases, the cement will provide a better performance. If the cement fails to give a very good bond strength value, operational problems may occur. The cement may break from the casing or the formations which will cause paths between them. These paths may result in fluid leakage from the formation to the wellbore and will not keep the well isolated.

Salehi et al., (2016) investigated the effects of sodium hydroxide concentration on the shear bond strength, by using class F fly ash geopolymer with different designs and class H Portland cement. The bond strength tests were prepared using two different pipes. The result showed that the geopolymer has higher bond strength than Portland cement. Table 3.5 shows the result of their tests. The bond strength for geopolymer is a slightly higher than the bond strength of Portland cement.

Table 3.5. Average shear bond strength (Salehi et al., 2016)

	Fly Ash Geopolymer		Portland Cement Class H	
	Pipe 1	Pipe 2	Pipe 1	Pipe 2
Bond Strength (psi)	170.7	99.4	139.6	81.3

Liu et al. (2017) compared the bond strength between fly ash class F based geopolymer, geopolymer hybrid, which is a mixture between geopolymer and synthetic based mud (SBM), and Portland cement. They used a plastic pipe with 3 inch diameter and placed a 1 inch steel bar, which was polished with a cloth, inside of it. Figure 3.13 shows their experimental setup. The sample was left at 170 ˚F for 7 days after they poured the cement in the plastic pipe. Following that, they removed the bottom cover placed the sample on a hollow base, and pushed the steel bar out. Figure 3.14 shows the cement to pipe shear bond strength of Portland cement and geopolymer with clean steel pipe at 170 F on day-7. The results showed that geopolymer had a higher bond strength than Portland cement for both clean steel and steel covered with SBM.

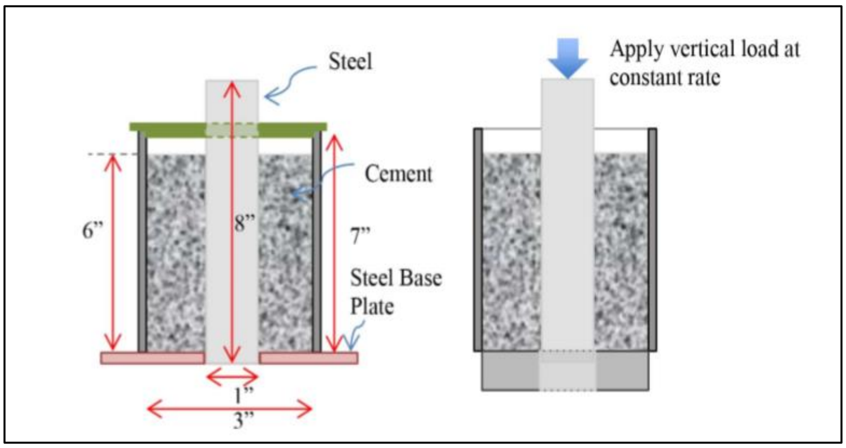

Figure 3.13. Bond strength setup (Liu et al., 2017)

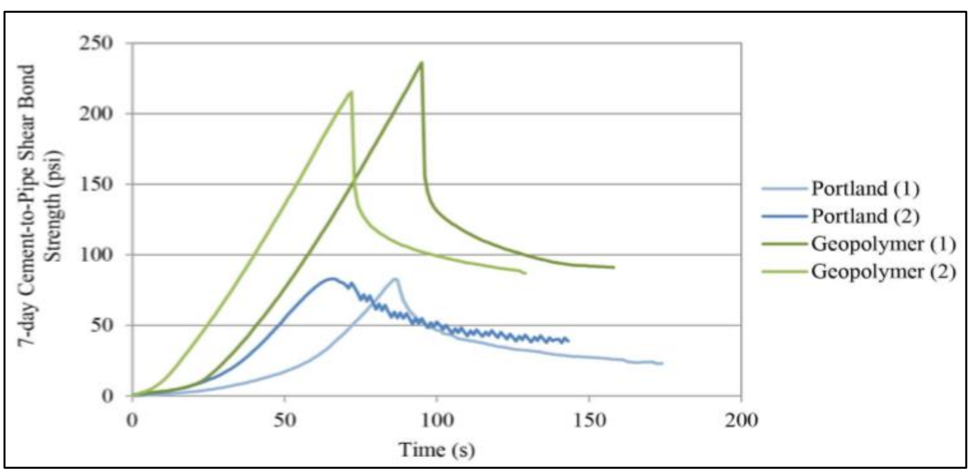

Figure 3.14. Cement to pipe shear bond strength at 170 ˚F on day 7 (Liu et al., 2017)

3.1.5. Bulk Shrinkage. The bulk shrinkage is defined as the decreasing of the volume of the cement after applying some forces on it for some time. It is considered one of the most important parameters to review for cementing materials.

A few studies have been done to examine the bulk shrinkage for the geopolymer cement. Khalifeh et al., (2014) prepared three different samples of class F fly ash geopolymer in order to measure the bulk shrinkage. Each sample consisted of different sodium hydroxide concentrations (6 M, 8 M, and 10 M). As can be seen in Figure 3.15, as the concentration of sodium hydroxide decreased, the bulk shrinkage decreased.

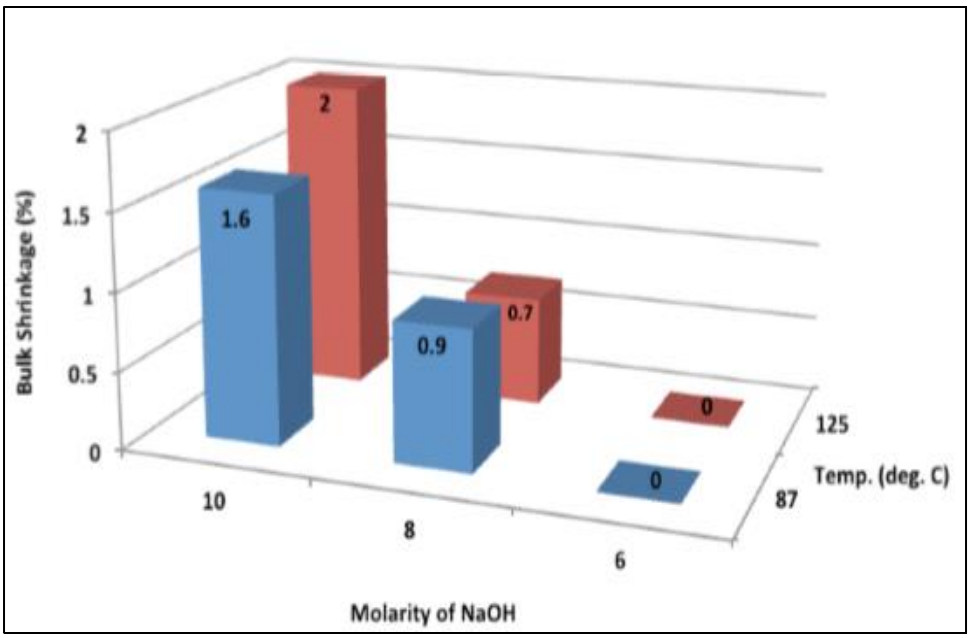

Figure 3.15. Bulk shrinkage results (Khalifeh et al., 2014)

Khalifeh et al. (2015) also investigated the effect of different alkali solution on the geopolymer shrinkage. Their result shows that the range of the percentage of shrinkage is 0.5 – 2.0%. Table 3.6 shows their results.

Table 3.6. Autogenous shrinkage of the geopolymer samples (Khalifeh et al., 2015)

Sample	Alkali solution / alkali silicate solution ratio by weight	Liquid/solid ratio by weight	Shrinkage factor (%)
1	8M $NaOH/Na_2OSiO_2$: 1	0.42	0.5
2	8M $NaOH/Na_2OSiO_2$: 0.35	0.48	2.0
3	8M $NaOH/K_2OSiO_2$: 1	0.42	0.5
4	8M $NaOH/K_2OSiO_2$: 0.4	0.43	0.8
5	6M KOH/Na_2OSiO_2 : 1	0.42	0.5
6	6M KOH/Na_2OSiO_2 : 0.35	0.8	1.3
7	4M KOH/Na_2OSiO_2 : 0.41	0.57	2.00
8	4M KOH/K_2OSiO_2 : 0.33	0.50	N/A
9	4M KOH/K_2OSiO_2 : 0.43	0.51	2.0
10	4M KOH/K_2OSiO_2 : 0.43	0.46	2.0
11	4M KOH/K_2OSiO_2 : 0.35	0.48	N/A
12	4M KOH/K_2OSiO_2 : 0.33	0.47	N/A

In 2017, a comparison between the geopolymer and Portland cement has been done by Salehi et al. (2017). Figure 3.16 shows their results for this comparison. Also, in Figure 3.17, bulk shrinkage can be observed. Their results indicate that the percentage of shrinkage for geopolymer mixtures is lower than the percentage of shrinkage for Portland cement at temperatures of 150 ˚F and 200 ˚F.

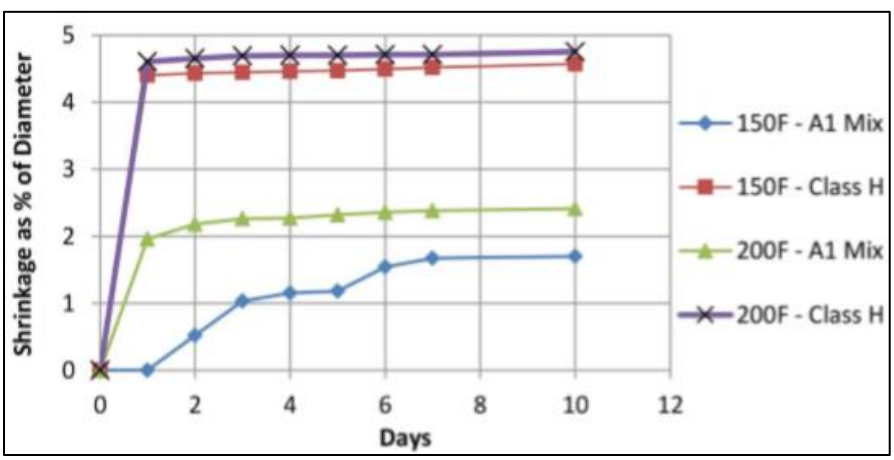

Figure 3.16. Shrinkage results after 10 days (Salehi et al., 2017)

Figure 3.17. Shrinkage results of after 12 hours (Salehi et al., 2017)

3.1.6. Thickening Time Tests. The thickening time is an important test to simulate the slurry pumping. The slurry consistency Bc is obtained by using an appropriate consistometer depending on the temperature and pressure. The thickening time is the time required to reach the upper limit of pumpability which is, 100 Bc.

Researchers have recently begun studying the geopolymer cement properties in order to use it in plug and abandonment operations. There are only a few studies done in this area. Salehi et al., (2016) used different mixtures by changing the curing conditions and also, changing alkali content, silica content, water to binder ratio, and alkali to fly ash ratio. Their result showed that the temperature had a strong effect on thickening time of fly ash based geopolymer mixtures as is shown in Figure 3.18. By added an in-house newly developed mix of retarders and superplasticizers, the thickening time was more than 4 hours for all mixtures.

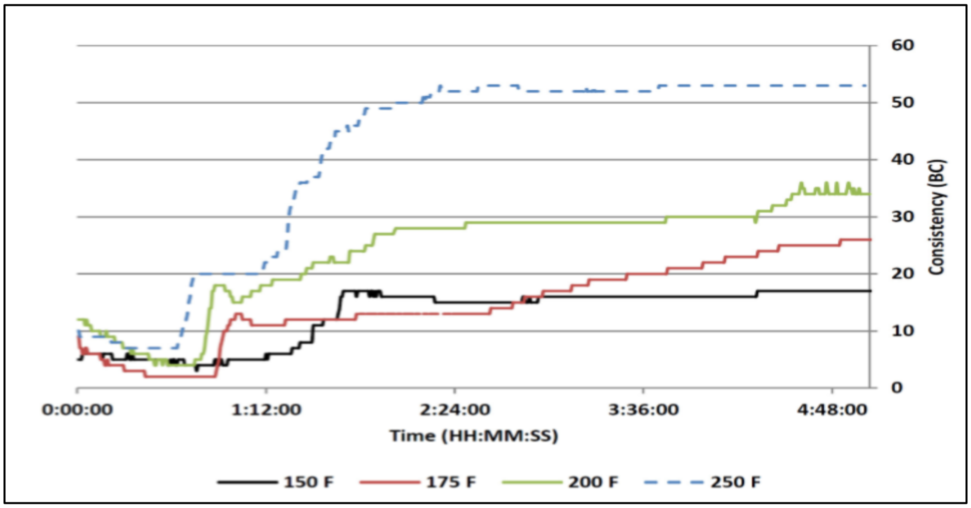

Figure 3.18. Thickening time results at different temperatures (Salehi et al., 2016)

3.1.7. Durability Test. A few studies has been done to test the durability of geopolymer to see how it can resist chemical attacks, Salehi et al., (2016). Results showed that the percentage of loss of geopolymer was less than 7%. In comparison, it became 9.1% in Portland cement. In general, their tests showed that the geopolymer had better durability, in presence of chemical attacks, than class H Portland cement.

3.1.8. Acid Resistance. Uehar, M. (2010) found that the geopolymer has better acid resistance properties than OPC. After four months of exposure to acid, The OPC collapsed, however, the geopolymer was not affected.

3.2. DRILLING FLUIDS CONTAMINATION OF GEOPOLYMER

All the work previously explained was performed on geopolymer alone. In the section, geopolymer contamination with drilling fluid will be discussed. There are few studies have been published about drilling fluids contaminations with geopolymer in oil and gas wells. In these papers, they investigated the effects of drilling fluids on geopolymer rheological and mechanical properties.

When Portland cement is contaminated by syhntatic base mud (SBM) the integrity of cement is impacted significantly (Aughenbaugh, et al., 2014). Aughenbaugh, et al., (2014) investigated the impact of SBM on the integrity of Portland cement. They used three different types of Portland cement including two types of class H Portland cement and API class C Portland cement. Two different methods were used to measure the compressive strength using different ratios of contamination including 5, 10, and 15 volume percent at 170 ˚F and 3000 psi including:

- Cured at curing chamber and crushed after 48 hours
- Cured in ultrasonic cement analyzer for 48 hours.

Figure 3.19 shows the compressive strength results of Aughenbaugh, et al. (2014) for different types of cements with different ratios of SBM contamination. Increasing the SBM weight percent resulted in decreasing in compressive strength.

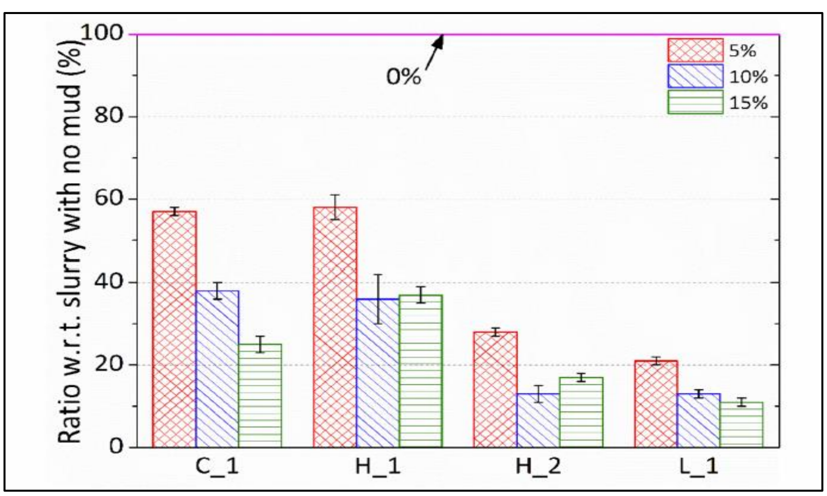

Figure 3.19. Compressive strength results of different type of cement with different ratios of SBM contamination (Aughenbaugh, et al., 2014)

Liu, et al. (2016) used three different types of fly ash class F based geopolymer to study the effect of SBM on these material. They use 2”× 2” cubes cured at high temperature, 170 ˚F, and high pressure, 3000 psi. Figure 3.20 shows the compressive strength results of Liu, et al. (2016) for geopolymer and Portland cement with different SBM ratios. The geopolymer strength decreased as the SBM increased. However, a significant decrease was observed in Portland cement strength when contaminated with SBM. After 30 volume percent of SBM was added to Portland cement, the compressive strength was not measurable. Also, SBM impacted the Portland cement viscosity; the viscosity increased as SBM ratios increased.

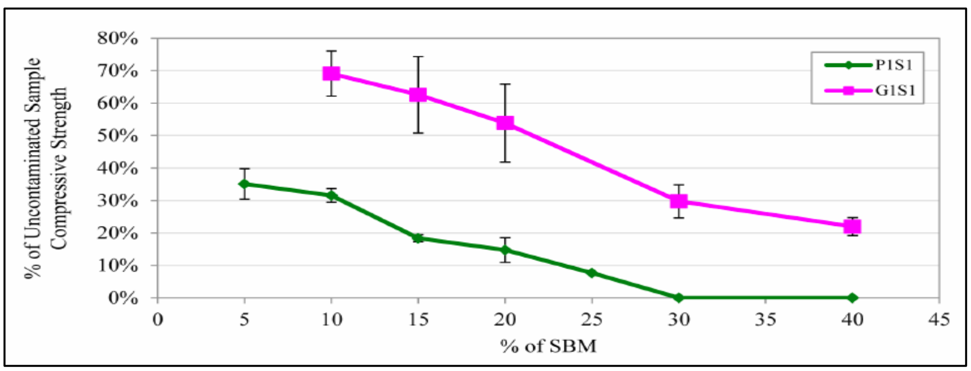

Figure 3.20. Compressive strength results for geopolymer and Portland cement with different SBM ratios (Liu, et al., 2016)

Figure 3.21 shows the rheological properties results of Liu, et al. (2016) of Portland cement and geopolymer with different SBM ratios. SBM had a negative effect on Portland cement rheological behavior however, SBM improved the geopolymer rheological behavior. Figure 3.22 shows the thickening time results of Liu, et al. (2016) of geopolymer with different SBM ratios at 125 ˚F. As the SBM volume percent increased the thickening time increased.

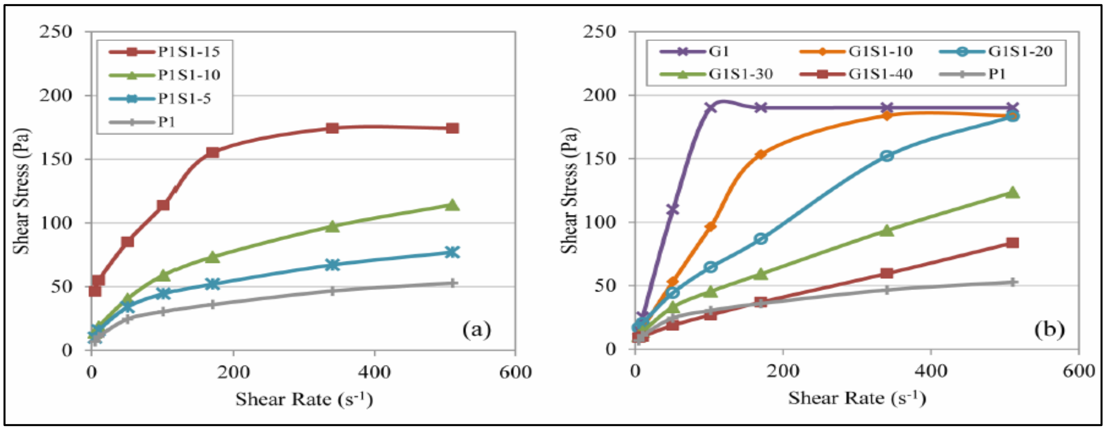

Figure 3.21. Rheological properties results of Portland cement and geopolymer with different SBM ratios (Liu, et al., 2016)

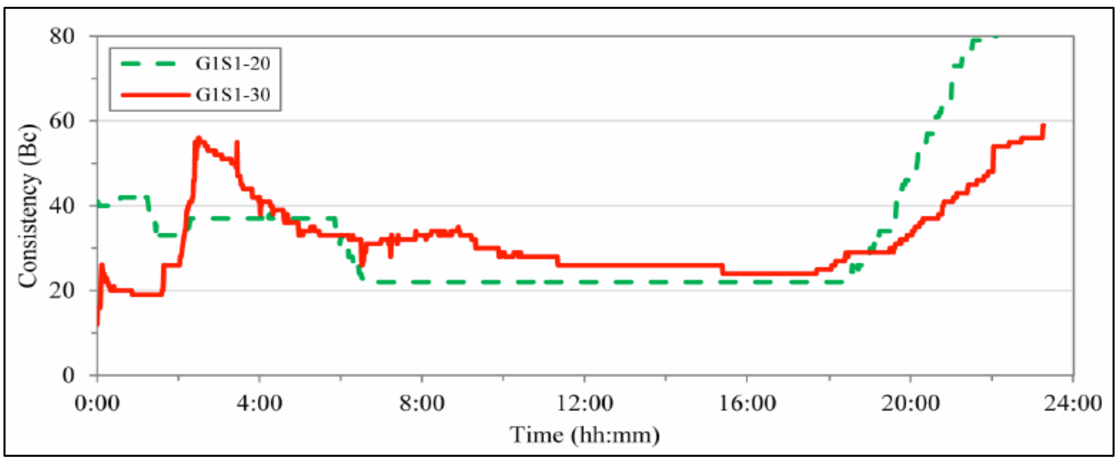

Figure 3.22. Thickening time results of geopolymer with different SBM ratios at 125 ˚F (Liu, et al., 2016)

Liu, et al. (2017) investigated the effect of SMB on geopolymer hybrid using different types of fly ash class F with different types of activations. Figure 3.23 shows the effect of pressure on thickening time. Increasing the pressure resulted in decreasing in geopolymer hybrid pumping time (Liu, et al., 2017). They found that SBM had negative effects on geopolymer strength; as SBM volume percent increased, the geopolymer strength decreased.

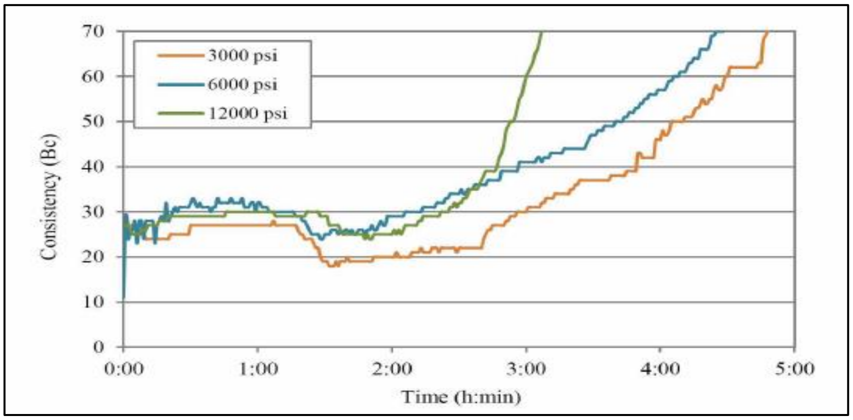

Figure 3.23. The effect of pressure on thickening time (Liu, et al., 2017)

Salehi, et al. (2018) investigated the effect of oil based mud (OBM) on the geopolymer and Portland cement strengths. Different ratios of OBM were used including 0%, 5%, and 10% by mass. Figure 3.24 shows the compressive strength results of Salehi, et al. (2018) of geopolymer and Portland cement with different OBM ratios. They found that OBM had a significant impact on Portland cement, however it had a slight impact on geopolymer strength. The reduction on Portland cement strength was 35% compared to geopolymer which only lost 5% of its strength when 5 % by mass of OBM was introduced.

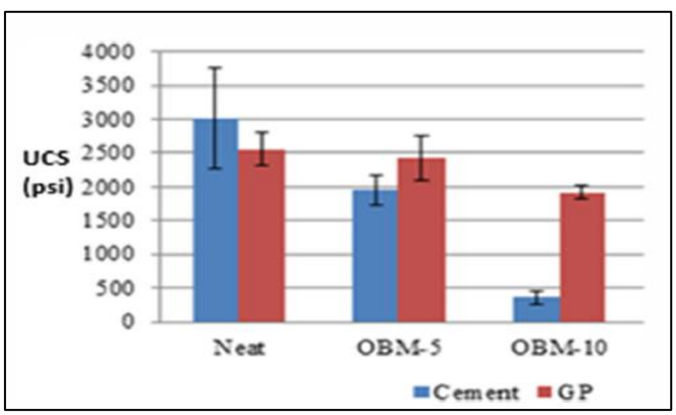

Figure 3.24. Compressive strength results of geopolymer and Portland cement with different OBM ratios (Salehi, et al., 2018)

PAPER

I. NEW FORMULATION OF FLY ASH CLASS C BASED GEOPOLYMER FOR OIL WELL CEMENTING

ABSTRACT

One of the most important steps in the drilling and completion operation is oil well cementing to provide wellbore integrity. Currently, Portland cement is mainly used in the oil industry, however it has many drawbacks including operational and environmental problems. Fly ash based geopolymer cement has recently gained more attention due to its low cost and environmental friendliness. This research aims to obtain a new formulation of class C fly ash based geopolymer cement to be used as an alternative to Portland cement in oil and gas cementing. Twenty four different geopolymers were prepared, and compared to decide which will be the optimum formulation to use. The alkaline activator to fly ash ratios used include 0.2, 0.4, and 0.8, the sodium hydroxide to sodium silicate ratios include 0.25, 0.5, 1, and 2, for three different sodium hydroxide concentration thus having 5, 10, and 15 molarity. The optimum formulation was chosen based on five different API recommended tests, including rheology, density, compressive strength, fluid loss test and stability tests which are sedimentation test and free fluid test. The optimum formulation was then compared to Portland cement using all the tests mentioned. Based on our results, increasing sodium hydroxide concentration resulted in an increase in compressive strength and showed a slight decrease in the plastic viscosity. However, increasing in the alkaline activator to fly ash ratios increased plastic viscosity, thus, the workability of the slurry was

reduced. Increasing in sodium silicate to sodium hydroxide ratio decreased the fluid loss significantly. The optimum design of geopolymer, which had lower fluid loss, reasonable compressive strength with an acceptable density and viscosity, was selected. Then the optimum design was compared to Portland cement. Compressive strength of the optimum design showed better results than neat Portland cement. Unlike neat Portland cement, which needs fluid loss additives, the new formulation of geopolymer investigated in this study showed fluid losses lower than 100 ml in 30 minutes when tested using a low pressure, low temperature filtrate loss tester. The higher mechanical strength and durability of geopolymer using fly-ash Class C compared to Portland cement is very promising for achieving long-term wellbore integrity goals and meeting regulatory criteria for zonal isolation. These results indicate that fly ash class C based geopolymer has the potential to be an environmentally friendly alternative to Portland cement when cementing oil wells.

1. INTRODUCTION

One of the important processes during the drilling and completion of the wells is primary cementing to provide full zonal isolation, which prevents the fluid migrations between the formation and wells. The main goal of primary cementing is to provide full zonal isolation. If zonal isolation is lost, it could result in severe operational difficulties and huge environmental issues as well as high remedy costs. Although Portland cement has been used for many years for cementing operations, many failures still occur. Failures including radial cracks within the cement sheath, micro-annuli at the interfaces of the cement, and channels through the cement matrix (Bois et al., 2012). Recently, a new cost effective and environmentally friendly material has come to light that has properties similar to Portland cement; this material is called geopolymer. Geopolymer was first researched by Davidovitts, who began searching for a non-flammable, non-combustible construction material after the fire in France in 1970. Geopolymer consists of fly ash that is activated by sodium or potassium hydroxide (NaOH, KOH). The source of fly ash is power plants. These power plants burn coal and produce an enormous amount of fly ash. Instead of wasting this fly ash, it can be used to form geopolymer. The thermal reactions between fly ash and the alkaline activator form the geopolymer. In other words, geopolymer can be defined as the reaction between the fly ash and the alkaline activator, which could be sodium hydroxide (NaOH) or potassium hydroxide (KOH) in the presence of an additional source of silicate, other than the fly ash, which is sodium silicate (Na2SiO3) or potassium silicate (K2O3Si). The result of this reaction is geopolymer. Geopolymer has many advantages over Portland cement, including that geopolymer is cheaper and more environmentally friendly. Since fly ash is a by-product of coal combustion, it is extremely cheap to acquire. Regarding the environmental impacts, Portland cement has a huge environmental effect due to its manufacturing process, which requires burning a huge amount of fuel and decomposition of limestone, thus causing enormous volumes of carbon dioxide (CO2) emissions (Kong and Sanjayan., 2008). In addition, geopolymer has another advantage compared to Portland cement, such as higher compressive strength and less fluid loss. Portland cement consists of calcium hydroxide and calcium silicate, while geopolymer consists of alumino-silicate gel (Salehi et al., 2016).

In the last few years, researchers have studied geopolymer properties to be used as an alternative to Portland cement. A few papers were published in this area showing good results to consider geopolymer as a replacement to Portland cement. Reasonable compressive strength geopolymers can be produced at different NaOH concentrations and different curing conditions (Bakkali et al., 2016). The compressive strength of geopolymer increases when higher concentrations of sodium hydroxide were used. The ratio of alkaline activator to fly ash has impacts on the compressive strength. As the alkaline activator to fly ash ratios increase, the compressive strength increases (Abdullah, et al., 2012). Nasvi (2012) used geopolymer and Portland cement class G to compare the mechanical behavior at different curing temperatures. An investigation of low calcium fly ash (class F) was done by Sugumran (2015) to study the effects of water ratios and sodium hydroxide ratios. Investigations have been done by Suppiah (2016) to examine the compressive strength of geopolymer cement utilizing different sodium hydroxide concentrations and different ratios of silicate to hydroxide. Their results showed that as sodium hydroxide concentrations increase, compressive strength increases. Furthermore, another investigation of using low calcium fly ash (ASTM class F) was performed by Salehi (2016), who made a comparison between geopolymer and Portland cement; it showed that the compressive strength of geopolymer has high improvement after seven days compared to Portland cement. Moreover, the results showed that geopolymer has a higher bond strength than Portland cement, similar to the results that were obtained by Liu in 2017. Besides bonding strength, Liu has compared other properties, including, but not limited to, compressive strength between geopolymers, geopolymer hybrid and Portland cement. In terms of viscosity and density, viscosity of geopolymer is directly proportional to sodium hydroxide concentrations. The viscosity increases with increasing sodium hydroxide concentrations, and the density increases as the ratios of fly ash to alkaline activator increase (Suppiah, et al., 2016). Furthermore, Salehi (2016) studied the effects of different temperature on the thickening time. According to Uehar (2010), geopolymer has better acid resistance than Portland cement. In addition, there are other properties that are used to characterize geopolymer including thermal stability, low surface roughness, and durability (Khalifeh, 2014). Most previous work was done on class F geopolymer, and most of it was focused on plugging and abandonment operations.

This paper aims to investigate the performance of using new fly-ash Class C as an alternative to Portland cement for oil well cement applications. Different ratios of alkaline activator to fly ash (AA/FA), sodium silicate to sodium hydroxide (SS/SH), and sodium hydroxide concentrations were used to choose the optimized design depending on the rheology, density, compressive strength, and fluid loss. Other tests were done to the optimized geopolymer to compare it with Portland cement.

2. EXPERIMENTAL DESCRIPTION

2.1. MATERIALS

2.1.1. Fly Ash. There are two types of fly ash: Class C and Class F. According to the American Society for Testing and Materials (ASTM), the differences between these two types is that Class C has a higher content of calcium oxide (CaO) than Class F, so fly ash Class C is also known as high calcium fly ash, whereas fly ash Class F is known as a low calcium fly ash.

Fly ash Class C was used in this study. X-ray fluorescence (XRF) was used to determine the chemical compositions of the fly ash. The result of XRF showed that the amount of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) is higher than 50%, which according to ASTM C 618 is fly ash Class C. Table 1 shows the compositions of fly ash that were obtained from X-ray fluorescence (XRF).

Table 1. The compositions of fly ash

Element	**Concentration (%)**
SiO_2	28.93
Al_2O_3	14.82
Fe_2O_3	6.40
CaO	39.80
MgO	4.86
Na_2O	1.10
K_2O	0.56
Other	2.63

2.1.2. Sodium Hydroxide (NaOH). The purity of sodium hydroxide is 96%. Different concentrations were prepared by weighing dry powder. This sodium hydroxide powder was added to a certain amount of distilled water and hand stirred until it was fully dissolved. Then, extra distilled water was added until the desired concentration was reached. Sodium hydroxide solution was mixed with sodium silicate solutions for the geopolymer preparations.

2.1.3. Sodium Silicate (Na_2SiO_3). Sodium silicate, also known as water glass, was obtained from PQ Corporation. Sodium silicate is an important material to provide another source of silicate (other than fly ash) to the mixture.

2.1.4. Portland Cement. American Petroleum Institute (API) Portland cement class H, which was obtained from Haliburton, was used in this study. X-ray fluorescence (XRF) was used to determine the chemical compositions of the Portland cement. Table 2 shows the compositions of Portland cement class H that were obtained from XRF.

Table 2. The compositions of Portland cement

Element	Concentration (%)
SiO_2	20.36
Al_2O_3	3.17
Fe_2O_3	6.19
CaO	65.72
MgO	1.32
SO_3	2.26
K_2O	0.43
Other components	0.55

2.2. GEOPOLYMER PREPARATION PROCEDURE

Before start mixing the geopolymer, alkaline solution was prepared by mixing sodium hydroxide and sodium silicate solutions. Then the geopolymer was mixed. All geopolymer slurries were mixed at ambient temperature and atmospheric pressure. First, tap water was added to the mixer, then the fly ash was added and the mixing started for 10 seconds at low speed. After that, the alkaline solution, which is a mixture of sodium silicate and sodium hydroxide, was added. After adding the alkaline solution, the mixture was mixed for 10 seconds at low speed and 30 seconds at high speed. Twenty four samples were prepared to measure rheology, density, and fluid loss, and another twenty four samples were prepared to measure the compressive strength. Different ratios of alkaline activator to fly ash (AA/FA) (0.2 and 0.4), sodium silicate to sodium hydroxide (SS/SH) (0.25, 0.5, 1, and 2), and sodium hydroxide concentrations (5 M, 10 M, and 15 M) were investigated in this study in order to select the optimum design. All geopolymer slurries have a water ratio of 33%. Table 3 shows the mix designs that were investigated in this study for different sodium hydroxide concentrations. Along with the previous ratios mentioned, an additional alkaline activator to fly ash ratio was used to investigate the impacts of increasing alkaline activator to fly ash ratio; the new ratio was (AA/FA) 0.8, (SS/SH) 1, and NaOH 5, 10, 15 M.

Table 3. Geopolymer mix designs for different ratios of SS/SH and AA/FA

AA/FA	**FA (gm)**	**SS/SH**	**SH Solution (gm)**	**SS Solution (gm)**
0.2	**600**	0.25	96	24
		0.5	80	40
		1	60	60
		2	40	80
0.4	**600**	0.25	192	48
		0.5	160	80
		1	120	120
		2	80	160
0.8	**600**	1	240	240

2.3. PORTLAND CEMENT PREPARATION PROCEDURE

Portland cement was mixed according to API recommendations. All Portland cement slurries were mixed at ambient temperature and atmospheric pressure. First a distilled water was poured in the blender and mixed at lower speed for 15 seconds while dry cement was added to the blender. After that, the blender was covered and was left for 35 seconds at high speed.

2.4. EXPERIMENTAL METHODOLOGY

This section is a description of the test procedures that were done in order to find the optimum design of geopolymer. These tests include density, rheology, compressive strength, and fluid loss. Stability tests, including free fluid tests and sedimentations tests, were done to make a comparison between the optimized geopolymer and Portland cement.

2.4.1. Density and Rheology. The rheology was studied due to the importance of understanding the behavior of geopolymer. Twenty four samples were prepared with different sodium hydroxide concentrations (5M, 10M, and 15M), sodium silicate to sodium hydroxide ratios (SS/SH) (0.25, 0.5, 1, and 2), and alkaline activator to fly ash ratios (AA/FA) (0.2 and 0.4). Then, the density was measured using standard mud balance. After that, an Ofite viscometer was used to obtain the rheology behavior for these samples. All the rheology and density tests were done at atmospheric pressure and room temperature.

2.4.2. Compressive Strength Test. Compressive strength is an important factor to investigate the strength of the geopolymer. In this study, twenty four samples of all the geopolymer designs with different ratios of alkaline activator to fly ash ratios, sodium silicate to sodium hydroxide, and sodium hydroxide concentrations were used to determine the strength of geopolymer. The slurries were poured in 2×2×2 in. molds and placed in a water bath to be cured under atmospheric pressure and room temperature for 24 hours.

2.4.3. Fluid Loss Test. Fluid loss tests have been conducted to all the geopolymer slurries to test the ability of geopolymer to retain water. In order to measure the fluid loss, twenty four samples of all the geopolymer designs with different ratios were prepared. The fluid loss was measured by a low pressure low temperature filtrate cell (LPLT) at 100 psi, and room temperature.

2.4.4. Stability Test. Stability tests are another important parameter to ensure that the cement maintains its desired properties. In this study, free fluids and sedimentation tests were performed to test the stability of the optimum design. In order to perform the free fluid test, 250 ml of geopolymer was left in a graduated cylinder for 2 hours. The sedimentation test was done by preparing a sample of geopolymer and letting it set for 24 hours in a 7.9 in. in length and 1 in. in diameter mold in accordance to (API RP 10B-2 2013). The sample was cut into six segments including top, bottom, and four segments in between, and the weight of every segment in air and water was taken by using the setup in Figure 1. The setup is composed of high precision digital balance connected to a 1000 ml transparent beaker filled with water. The sample is weighed before and after suspension in water. The density then calculated based on the change in weight using the equations provided below:

$$\rho = \frac{Wt_a}{Volume} \quad \text{(1)}$$

$$V = \frac{Wt_a - Wt_w}{\rho_w} \quad \text{(2)}$$

where ρ is the density in gm/cm^3, Wt_a is the weight in air in gm, Wt_w is the weight in water in gm, ρ_w is the water density in gm/cm^3,and V is the volume of the sample, based on the change in weight and density, in cm^3.

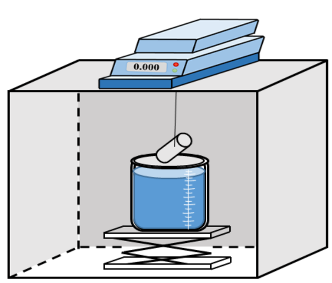

Figure 1. Mass measurement setup

2.5. RESULTS AND DISCUSSIONS

Geopolymer samples were conducted to choose the optimum design based on rheological behavior, density, compressive strength, and fluid loss. Additionally, three samples were prepared with different sodium hydroxide concentrations (5 M, 10 M, and 15 M) using the ratio of alkaline activator to fly ash (AA/FA) = 0.8 and sodium silicate to sodium hydroxide ratio (SS/SH) = 1 to investigate the effects of increasing alkaline activator to fly ash ratio (AA/FA) ratios. Figure 2 shows the geopolymer mixture for alkaline activator to fly ash ratio (AA/FA) = 0.8, sodium silicate to sodium hydroxide (SS/SH) = 1, and different sodium hydroxide concentrations. The result of this ratio showed that geopolymer sets in an extremely rapid manner, usually taking less than 10 seconds. The reason is that increasing the ratio of alkaline activator to fly ash resulted in increase of the amount of silicate solution in the mixture. This increase results in a higher rate of reaction between silicate and sodium hydroxide which accelerates silicate gel formation (Suppiah, et al., 2016).

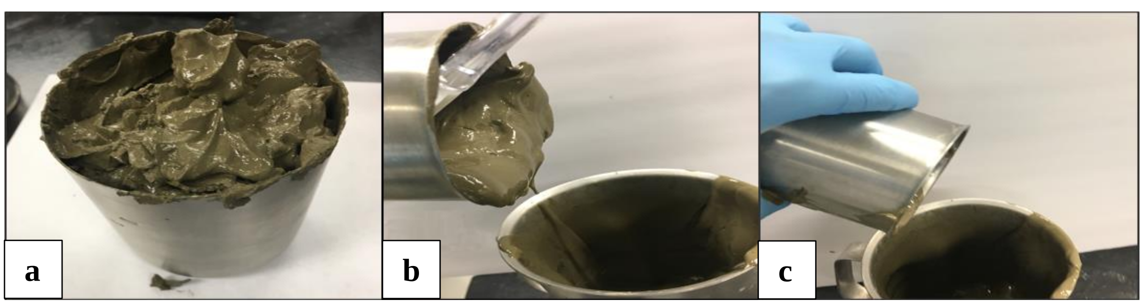

Figure 2. Geopolymer mixture for (AA/FA) = 0.8, (SS/SH) = 1, and different sodium hydroxide concentrations, a) 5 M, b) 10 M, c) 15 M

2.5.1. Density and Rheology Results. Density results for different alkaline activator to fly ash ratios (AA/FA) and different sodium hydroxide concentrations for sodium silicate to sodium hydroxide ratio (SS/SH) = 1 are shown in Figure 3. All geopolymer samples that were investigated showed that geopolymer had regular weight cement. There is no noticeable effect of sodium hydroxide concentrations on the density; however there are slight effects of changing the alkaline activator to fly ash ratios. This indicates that alkaline activator to fly ash ratios are inversely proportional to the density; as the alkaline activator to fly ash ratios increase, the density slightly decreases. This means when the amount of fly ash was higher, the density increases. As more alkaline activator was introduced to the mixture, more bubbles were formed, which creates an unstable system (Suppiah, et al., 2016).

Figure 4 shows shear stress versus shear strain for Portland cement and geopolymer slurries with different sodium silicate to sodium hydroxide ratios (SS/SH). The result of the rheology test showed that most geopolymer samples behave in a way similar to the Portland cement. Although the geopolymer has less viscosity than Portland cement, it has a similar manner of rheology behavior.

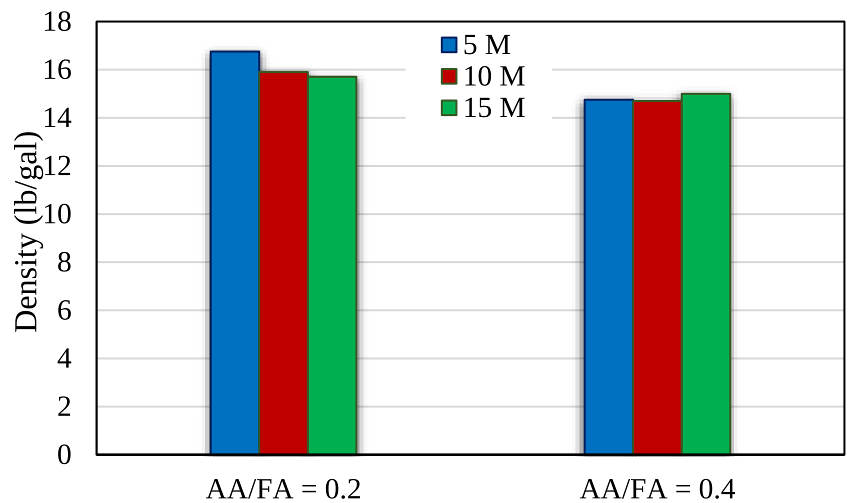

Figure 3. Density for different AA/FA ratios and different SH concentrations for SS/SH=1

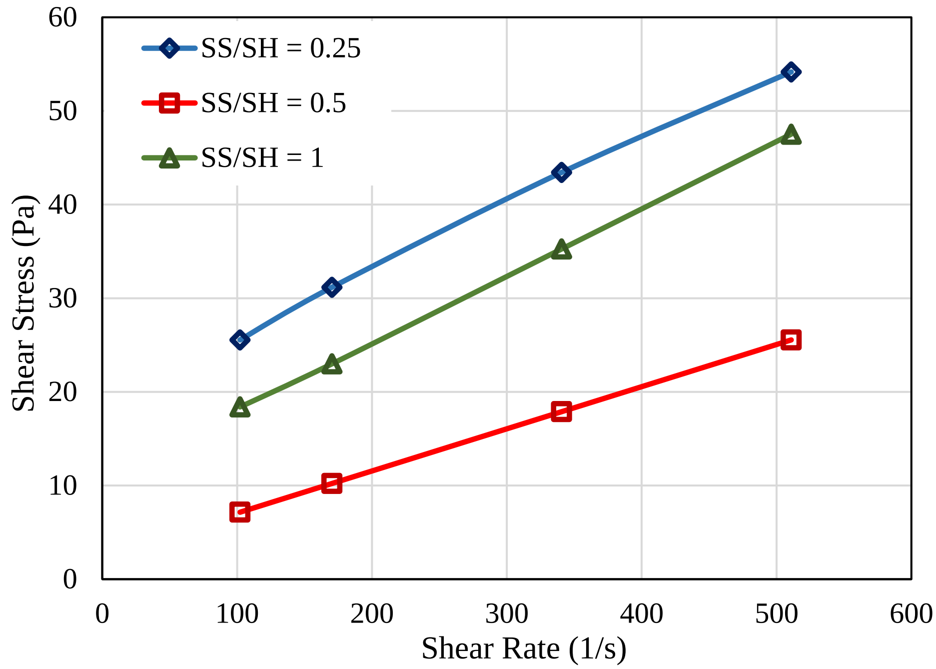

Figure 4. Shear stress vs. shear rate for different SS/SH ratios for the concentration of 10 M of sodium hydroxide and AA/FA = 0.4 and Portland cement

Plastic viscosity is an important factor to determine the cement workability. The plastic viscosity was measured using the Ofite viscometer by reading θ 600 and θ 300 and plastic viscosity was obtained by using the following equation:

PV= θ600- θ300………………………………………………………………………(3)

Figure 5 shows the plastic viscosity results for different alkaline activator to fly ash ratios (AA/FA) with different sodium hydroxide concentrations at a sodium silicate to sodium hydroxide ratio (SS/SH) = 1. The results showed that an increase of alkaline activator to fly ash ratios (AA/FA) resulted in an increase in plastic viscosity. However, sodium hydroxide concentrations are inversely proportional to the plastic viscosity. As the sodium hydroxide concentrations increase, the plastic viscosity has a slight decrease, which has an opposite trend from the results found by Suppiah et al., (2016). The plastic viscosity of the ratio of alkaline activator to fly ash (AA/FA) = 0.4 and sodium hydroxide concentration = 5 M could not be measured because it has a very short setting time.

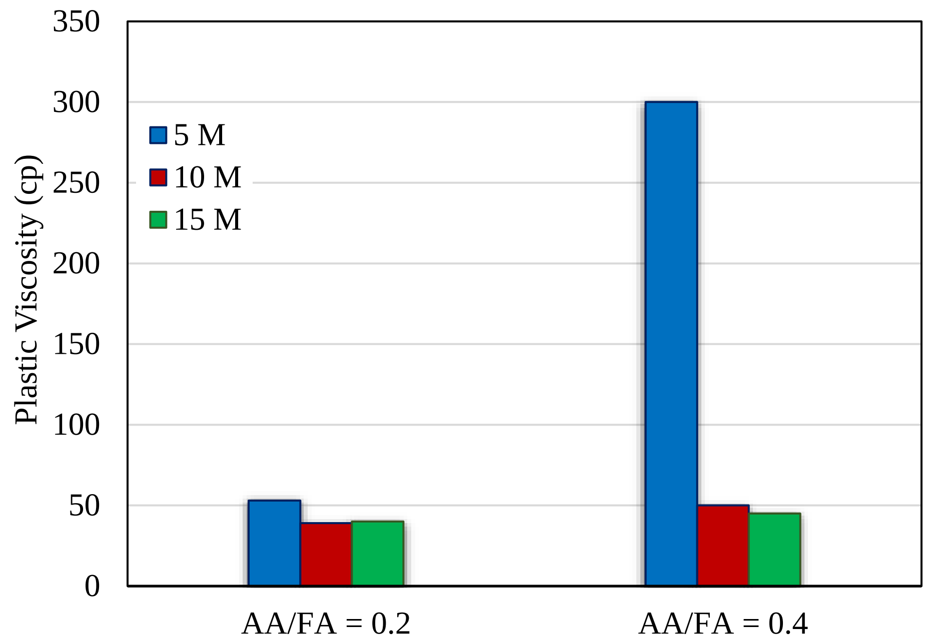

Figure 5. Plastic viscosity results for different AA/FA ratios with different sodium hydroxide concentrations at SS/SH = 1

2.5.2. Compressive Strength Results. Figure 6 shows the compressive strength measurements at different SS/SH ratios and different concentrations of sodium hydroxide with AA/FA = 0.2. Compressive strength of different SS/SH ratios at sodium hydroxide = 10M with AA/FA = 0.4 is presented in Figure 7. The laboratory results showed that increasing sodium hydroxide concentrations would positively affect the compressive strength, and thus, increases in sodium hydroxide concentrations led to an increase in compressive strength. The results indicated that for the sodium hydroxide to sodium silicate (SS/SH) ratio = 0.25, the compressive strength increased about 40% when increasing the concentration of sodium hydroxide from 5M to 10M, and the compressive strength was doubled when the sodium hydroxide concentration was increased from 10M to 15M. Leaching of silicate (Si) and aluminum (Al) starts when fly ash contacts the sodium hydroxide solution. Therefore, increasing sodium hydroxide concentration results in high leaching of Si and Al ions in the sodium hydroxide solution, which in turn generates higher compressive strength (Rattanasak and Chindaprasirt., 2009). The higher compressive strength of geopolymer is due to the alumino-silicate gel, which formed due to geopolymerization process (Abdullah et al., 2012).

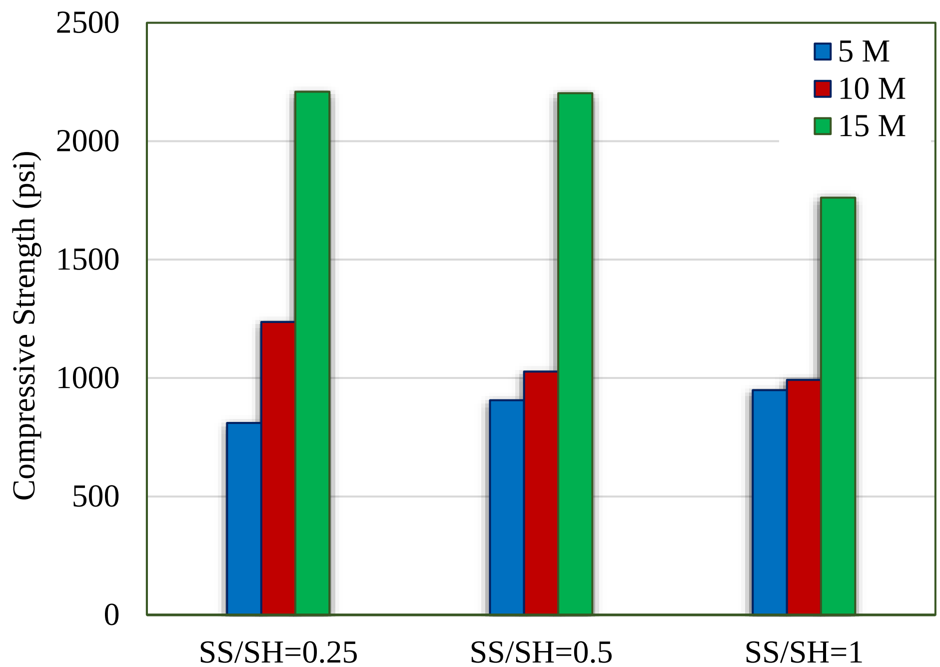

Figure 6. Compressive strength of different SS/SH ratios and different concentrations of sodium hydroxide with AA/FA = 0.2

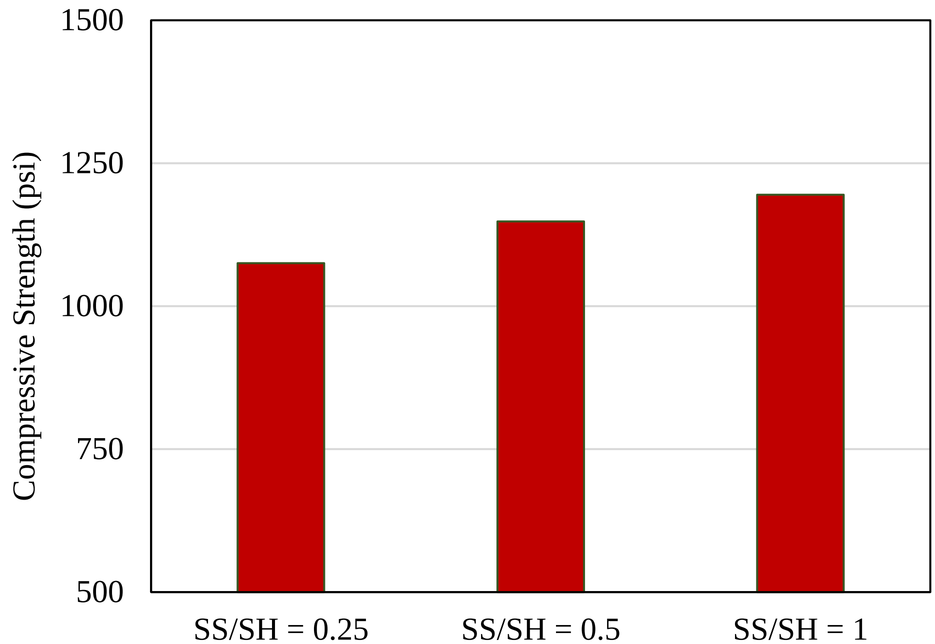

Figure 7. Compressive strength of different SS/SH ratios at sodium hydroxide = 10M with AA/FA = 0.4

2.5.3. Fluid Loss Test Results. Changing in the cement slurry properties and cracks within the cement formations are one of the problems that caused due to the loss of fluid from the cement slurry. Fluid loss additives is used to control the fluid loss. The obtained results showed that alkaline activator to fly ash ratios have small impacts. As alkaline activator to fly ash ratios (AA/FA) increase, the volume of the fluid loss decreases. Figure 8 shows that for the alkaline activator to fly ash ratio 0.4 with sodium hydroxide (SH) concentration 10M showed the lowest fluid loss volume in 30 minutes, which was 93 ml. The reason for the reduction of the volume of fluid loss is due to the huge availability of silicates (Si). These silicates react with aluminum (Al) and form alumino-silicate gels (Suppiah et al., 2016). This result indicates that geopolymer has less fluid loss than Portland cement. According to API, geopolymer does not require any fluid loss additives in contrast of Portland cement. When cement loses water, its properties change and the possibility increases to have channels and cracks within the cement formation. Geopolymer can retain its properties since it has a low fluid loss compared to Portland cement, which would reduce the probability of having channels inside the cement.

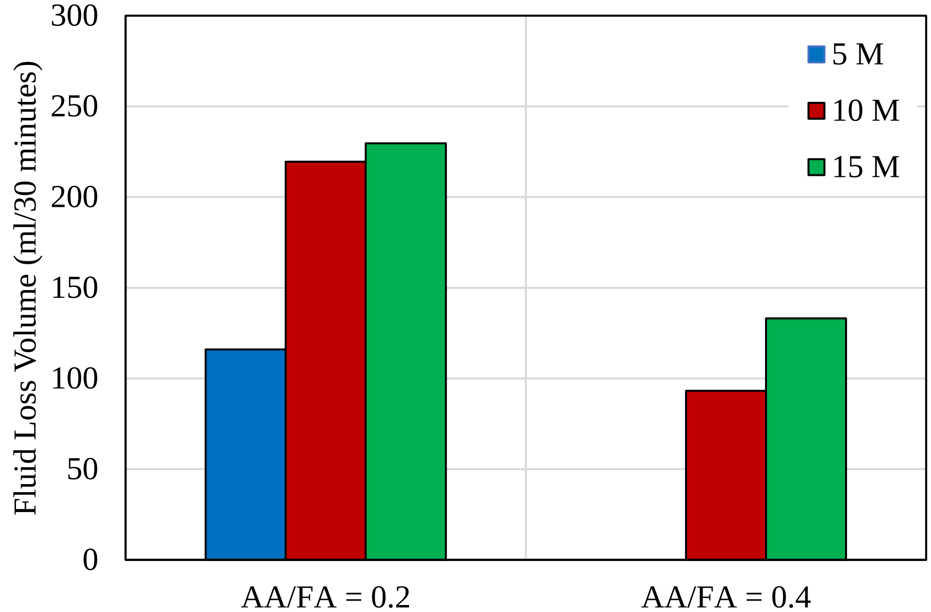

Figure 8. Fluid loss for different AA/FA ratios and SH concentrations for SS/SH = 1

2.5.4. Optimized Geopolymer Slurry. Based on the results of rheology, compressive strength, and fluid loss test, the optimum ratios of sodium silicate to sodium hydroxide, alkaline activator to fly ash, and sodium hydroxide concentration, were 1, 0.4, and 10 M, respectively. For all slurries, the density and rheology results were in the same range. Although, the optimized geopolymer did not have the highest compressive strength, it was still higher than Portland cement. Also, it provided the lowest fluid loss, which was less than 100 ml in 30 minutes; this, according to API, does not require any fluid loss additives. This indicates that this system can retain its properties since it has a low fluid loss, which would reduce the probability of having channels within the cement sheath.

2.5.5. Stability Test Results. In this study, free fluids and sedimentation tests were performed to test the stability of the optimum design and Portland cement. After the optimized geopolymer and Portland cement was left for two hours in a 250 ml graduated cylinder, the volume of free fluids for Geopolymer was 0. However, the volume of free water for Portland cement was 5.7 ml, it shown in Figure 9. The free fluid portion for Portland cement was 2.28%. As the results showed, geopolymer had not lost any water during this time compared to Portland cement, which had 2.28% of free fluid. This indicates that geopolymer can hold the water, which keeps its properties from changing; this will reduce the potential of having channels during cementing operations. Increasing in the free fluids amount have negative effects on cement slurries properties such as the effective density which decreases as the fee fluids increase. This could reduce the hydrostatic pressure which leads to increase the probability of having channels within the cement (Webster and Eikerts., 1979).

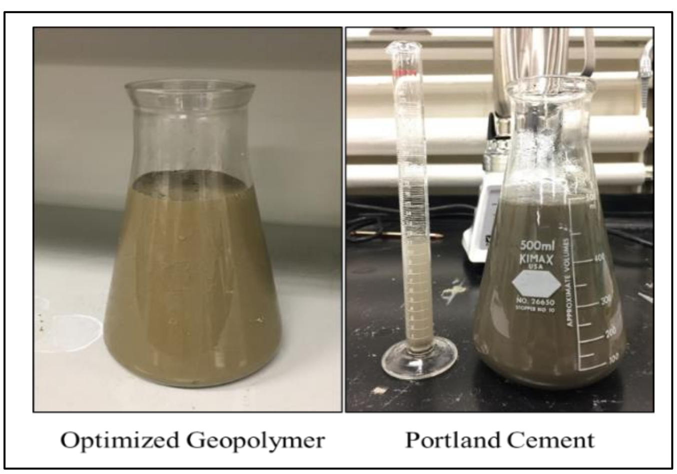

Figure 9. Free fluids test

The sedimentation test was done by preparing a sample of geopolymer and letting it set for 24 hours in a 7.9 in. in length and 1 in. in diameter cylindrical mold. Table 4 shows the results of the sedimentation test. The difference in density for the optimized geopolymer sample was 0.008 gm/cc, which is very low compared to 0.028 gm/cc for the Portland cement. This indicates that there are no particles settling for the optimized geopolymer.

Table 4. Sedimentation test results of Portland cement and geopolymer cured at room temperature 24℃ and Atmospheric pressure

	Downgrade (mm)	$\boldsymbol{\Delta\rho}$ $\left(\frac{gm}{cm^3}\right)$
Optimized Geopolymer	1.95	0.008
Portland Cement	3.30	0.028
API Limits	**5.00**	**0.060**

where $\boldsymbol{\Delta\rho}$ is the change in the specific density.

3. COMPARISON BETWEEN THE OPTIMIZED GEOPOLYMER AND PORTLAND CEMENT

Figure 10 shows the comparison in rheology behavior between the optimized geopolymer and Portland cement. The density investigations showed that the optimized geopolymer had regular weight cement. The optimized geopolymer showed a behavior similar to the Portland cement in terms of rheology.

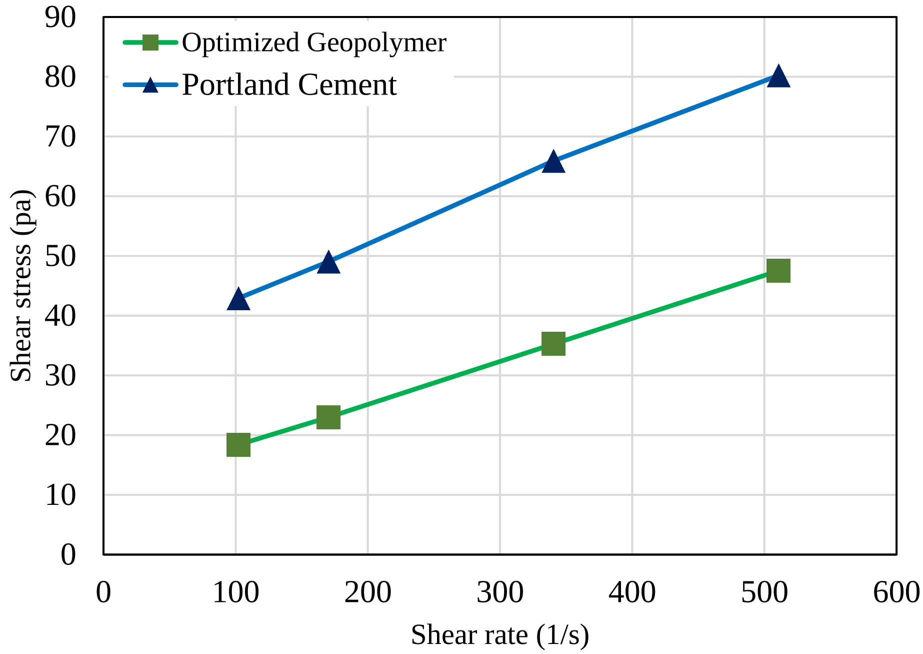

Figure 10. Comparison in rheology behavior between the optimized geopolymer and Portland cement

Figure 11 shows a comparison in compressive strength between the optimized geopolymer and Class H Portland cement. The obtained results showed that the optimized geopolymer has a higher compressive strength than Portland cement. These results show that geopolymer can withstand harsher downhole conditions.

Figure 12 shows a comparison in fluid loss between the optimized geopolymer and Portland cement. The results also show that the optimized geopolymer has lower fluid loss than Portland cement after 30 minutes, which is due to the alumino-silicate gels that formed as a result of the reaction between silicate (Si) and aluminum (Al). These results showed that optimized geopolymer has the ability to keep its water which would reduce the probability of having channels inside the cement.

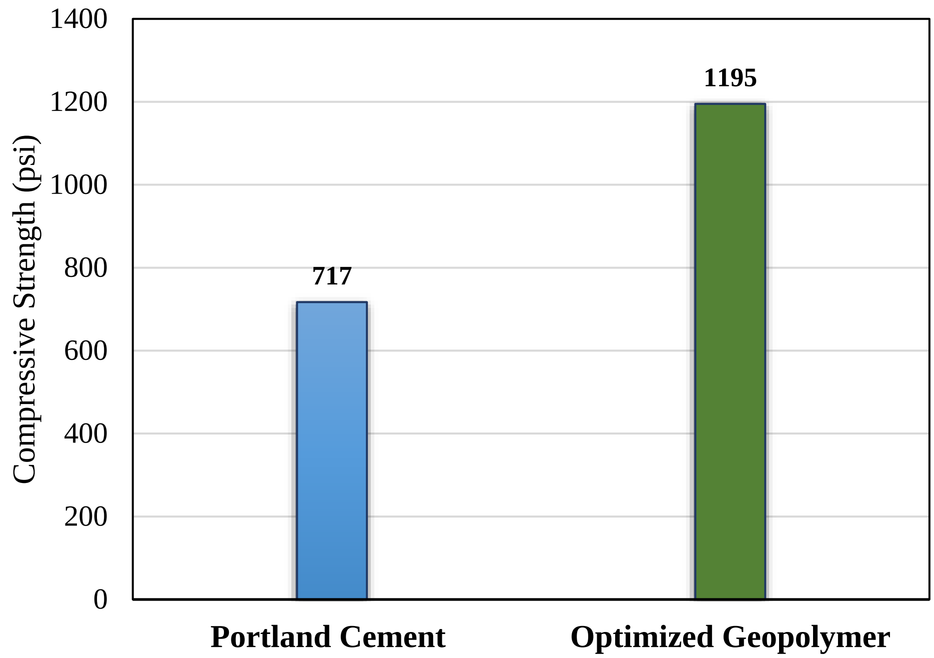

Figure 11. Comparison in compressive strength between the optimized geopolymer and Portland cement

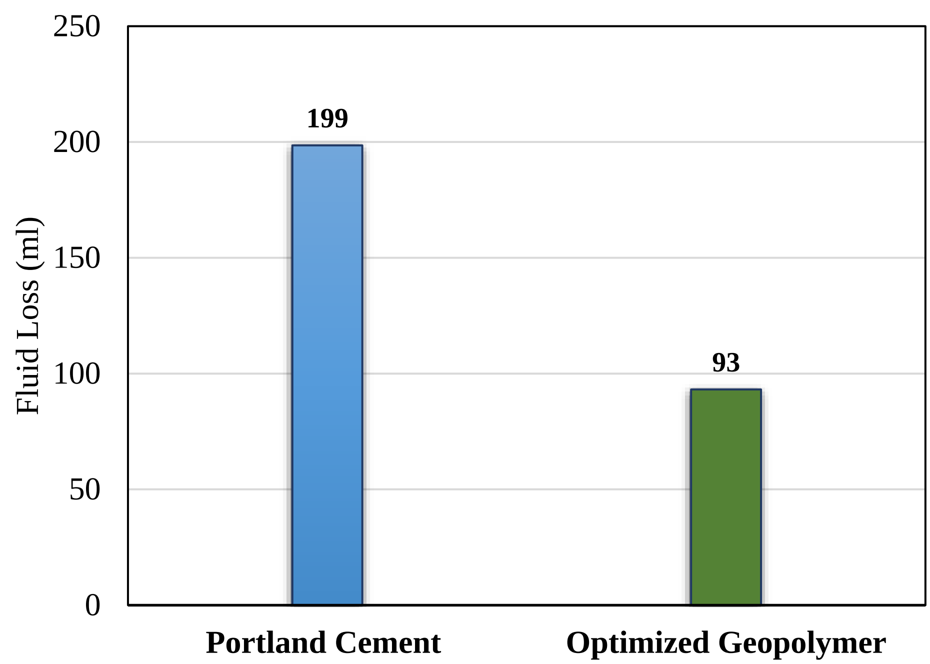

Figure 12. Comparison in fluid loss between the optimized geopolymer and Portland cement

4. CONCLUSION

The optimum ratios of sodium silicate to sodium hydroxide, alkaline activator to fly ash, and sodium hydroxide concentration were 1, 0.4, and 10 M, respectively. These ratios were obtained based on the results of the rheology, compressive strength, and fluid loss tests. This optimum design provides a higher compressive strength when compared to Portland cement and behaves in a similar manner. In addition, this system can retain its properties as it has low fluid loss, which would reduce the probability of having channels within the cement sheath.

- Sodium hydroxide concentrations are inversely proportional to the plastic viscosity; as the sodium hydroxide concentrations increases, plastic viscosity has a slight decrease.
- Sodium hydroxide concentrations positively affect the compressive strength. As sodium hydroxide concentrations increase, the compressive strength increases, which is due to high leaching of silicate (Si) and aluminum (Al) ions in higher sodium hydroxide concentrations.
- Sodium silicate to sodium hydroxide ratios increasing results in a decrease in fluid loss, which is due to the alumino-silicate gels that formed due to the high availability of silicates.
- Stability tests indicate that there is no free fluid and particles settling for the optimized geopolymer.
- The optimized geopolymer has a higher compressive strength than Portland cement.
- The optimized geopolymer has a lower fluid loss than Portland cement in 30 minutes

NOMENCLATURE

kg/m^3	=	Kilogram per meter cube.
psi	=	Pounds per square inch.
lb/gal	=	Pounds per gallon.
°C	=	Degree Celsius.
BWOC	=	By weight of cement.
V_{FF}	=	Volume of free fluids, ml.
V_i	=	Initial volume of cement, ml.
Φ	=	Free fluids content, vol%.
m	=	Mass of cement, gm, kg.
d_{rel}	=	Relative density, frac.
ρ	=	Gram per cubic centimeter, Pounds per gallon.

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II. INVESTIGATING RHEOLOGICAL AND MECHANICAL PERFORMANCE OF GEOPOLYMER CEMENT IN PRESENCE OF WATER BASED DRILLING FLUID

ABSTRACT

Oil well cementing is one of the most important steps in drilling and completion processes and providing a full zonal isolation which is the most important features in the oil cementing. Traditionally, Portland cement is used for oil cementing operations, however, a few years ago, a new cost-effective material came to light called geopolymer. In this research, a fly ash class C based geopolymer was used. This research investigates the effect of drilling fluid contamination with geopolymer cement to understand its impact on geopolymer rheological and mechanical performance. Initially, the optimized geopolymer was prepared and mixed with different drilling fluid ratios, including 0%, 5%, and 10% by weight of cement. Same percentages were added to Portland cement to compare it with the geopolymer. Four tests were conducted to determine the effects of drilling fluids including: rheology, density, fluid-loss, and compressive strength for different curing time (1 day, 3 days, and 7 days). Results showed that drilling fluids enhanced the geopolymer rheological behavior by improving geopolymer viscosity and reducing the fluid loss. In contrast, mixing the drilling fluid with Portland cement had a negative effect on rheological behavior as well as fluid loss. Mixing the drilling fluid with Portland cement increased the fluid loss significantly. Furthermore, drilling fluids reduced the geopolymer viscosity which facilitates the pumping operation during the cementing. In term of compressive strength, as the amount of drilling fluids increased, the compressive

strength of geopolymer was not significantly affected. After 3 days curing time, geopolymer lost about 8.5% of its strength when 5% of drilling fluids weight percent was added. Whereas, Portland cement has lost 38.4% of its strength when 5% of drilling fluids weight percent was added. After 7 days curing time, geopolymer lost about 23% of its strength when 5% of drilling fluid by weight of cement was added. However, Portland cement lost 49% of compressive strength in the same condition. These results are very promising since geopolymer showed a better rheological and mechanical performance than Portland cement.

1. INTRODUCTION

Cementing is one of the most important processes during the drilling and completion of the wells. The primary function is preventing the fluid migrations between the formations and wells to provide full zonal isolation. Severe operational difficulties and huge environmental issues as well as high remedy costs could be a result of losing zonal isolation. Portland cement has been used for many years for cementing process. Radial cracks within the cement sheath, micro-annuli at the interfaces of the cement, and channels through the cement matrix are challenges facing Portland cement (Bois, et al., 2012; Alkhamis, & Imqam, 2018). Lately, a new material, called geopolymer, has been investigated to be used as an alternative to Portland cement. Geopolymer is a result of the reaction between fly ash, which is a by-product of coal combustion in power plants, and alkaline activator, which is a mixture of sodium or potassium hydroxide (NaOH, KOH) and sodium silicate (Na_2SiO_3) or potassium silicate (K_2O_3Si).

Geopolymer has many advantages over Portland cement, which makes it more appealing to use. The two main advantages that make geopolymer a better candidate compared to Portland cement are:

- **Geopolymer is More Cost Effective**: The main component of geopolymer is fly ash. Fly ash is produced as a byproduct of coal burning, and since it has not major market, it is extremely cheap to acquire. Portland cement however, requires specific ingredient that are relatively expensive to acquire, compared to geopolymer (American Coal Ash Association, 2003).
- **Geopolymer is More Environmentally Friendly**: Since geopolymer is composed mainly of fly ash, it encourages the use of a byproduct waste material, which in turn prevents these material from being placed in landfills. Portland cement has a huge environmental effect due to its manufacturing process, which requires burning a huge amount of fuel and decomposition of limestone, thus causing enormous volumes of carbon dioxide (CO_2) emissions (Kong D. L. Y., and Sanjayan J. G., 2008).

Recently, geopolymer properties have been studied in hope that it can be applied as an environmentally friendly replacement to Portland cement. Contaminated cement slurry with drilling fluids is considered one of the major cause of the oil cementing failures (Morgan, & Dumbauld, 1952; Aughenbaugh, et al., 2014). In the last a few years, a few papers studied the effect of the drilling fluids on the geopolymer slurries. However, many research studies showed that geopolymer can be an appropriate environmental alternative to Portland cement in oil and gas wells. Bakkali, et al. (2016) indicated that geopolymer provides a dependable compressive strength at different sodium hydroxide (NaOH) concentrations and different curing conditions. Sodium hydroxide concentrations positively affect the compressive strength. The higher compressive strength of geopolymer is due to the alumino-silicate gel, which formed due to geopolymerization process (Abdullah, et al., 2012). As sodium hydroxide concentrations increase, the compressive strength increases. Also, the compressive strength is strongly affected by the ratio of alkaline activator to fly ash. Increasing the alkaline activator to fly ash ratios resulted in an increase in the geopolymer strength (Al-Bakri, et al., 2012). Nasvi, et al. (2012) studied the mechanical properties of geopolymer and Portland cement class G at different curing temperature. Suppiah, et al. (2016) studied the effects of using different silicate to hydroxide ratios and different sodium hydroxide concentrations on compressive strength. Their results showed that increasing in sodium hydroxide concentrations resulted in an increase in compressive strength. Thermal stability, low surface roughness, and durability are also used to characterize geopolymer (Khalifeh, et al., 2014). According to Uehar, M., (2010), geopolymer has better acid resistance than Portland cement. Ahdaya, et al. (2019) selected the optimum design of geopolymer by changing the sodium hydroxide concentrations, sodium silicate to sodium hydroxide ratios, and alkaline activator to fly ash ratios until the best properties were achieved.

One of the main challenges facing geopolymer is the pumping processes and early strength. In 2016, a retarder was added to achieve a 4 hour thickening time for the optimized geopolymer. Geopolymer has better durability compared to Portland cement when exposure to acid environment (Salehi, et al., 2016). There is not significant influences on the cement slurry properties when the cement slurries are mixed with low concentrations of untreated mud (Morgan, B. E., and Dumbauld, G. K., 1952). According to El Sayed, (1995), Portland cement, in 24 hr. curing time, lost about 80% of its strength when a high concentration of drilling fluids were introduced. Also, Bradford, (1982) studied the effect of drilling fluids on Portland cement, his result indicated that Portland cement lost about 44% of its strength. Mixing the synthetic-based mud (SBM) with Portland cement also reduced its strength (Aughenbaugh, et al., 2014). Sufficient compressive strength and acceptable rheological behavior are obtained when mixing the synthetic-based mud (SBM) with geopolymer (Liu, et al., 2016). Also, the pumping time was significantly accelerated when mixing the SBM with geopolymer (Liu, et al., 2017). Most previous work was done by mixing fly ash class F based geopolymer and Portland cement with the synthetic-based mud (SBM).

This research studies the mixing of fly ash class C based geopolymer with drilling fluid as a means to investigate the rheological and mechanical performance of geopolymer cement in presence of water based drilling fluid. Rheological factors studied include slurries' viscosity, density, rheology behavior, and fluid loss to investigate the slurries' basic properties. Mechanical performance of both geopolymer and Portland cement was indicated using compressive strength test.

2. CHEMISTRY OF GEOPOLYMER

Geopolymers are synthesized by reacting an aluminosilicate source, such as fly ash, with the alkaline activator, which is a mixture of the sodium hydroxide and sodium silicate. This reaction will yield a polymeric bond between the silicate, oxygen, and the aluminum as shown in equation below (Davidovits, 1994):

$$n(Si_2O_5, Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{NaOH,KOH} n(OK)_3 - Si - O - \begin{array}{c} (-) \\ Al \\ | \\ (OH)_2 \end{array} - O - Si - (OH)_3$$

The SiO4 and the AlO4 are combined covalently by sharing the oxygen atoms. The aluminum ions create a negative charge, which is neutralized by the sodium, potassium, and lithium positive ions, which occupy the cavities present in the geopolymer framework. This is shown in the chemical reaction below (Davidovits, 1994; Yong, et al., 2015):

$$n(OK)_3 - Si - O - \begin{array}{c} (-) \\ Al \\ | \\ (OH)_2 \end{array} - O - Si - (OH)_3 \xrightarrow{NaOH,KOH} (Na, K)^{(+)} - (-\begin{array}{c} | \\ Si \\ | \\ O \\ | \end{array} - O - \begin{array}{c} | \\ Al \\ | \\ O \\ | \end{array} - O - \begin{array}{c} | \\ Si \\ | \\ O \\ | \end{array} - O) + 4nH_2O$$

3. EXPERIMENTAL DESCRIPTION

3.1. MATERIALS

3.1.1. Fly Ash. Fly ash Class C was used in this study. The chemical composition of the fly ash was determined by using X-ray fluorescence (XRF). The result of XRF showed that the amount of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) is higher than 50%, which, according to American Society for Testing and Materials (ASTM C 618), proves that it is fly ash Class C. Table 1 shows the composition of fly ash that were obtained from X-ray fluorescence (XRF).

Table 1. The chemical composition of fly ash

Element	Concentration (%)
SiO_2	28.93
Al_2O_3	14.82
Fe_2O_3	6.40
CaO	39.80
MgO	4.86
Na_2O	1.10
K_2O	0.56
Other components	2.63

3.1.2. Sodium Hydroxide (NaOH). Sodium hydroxide with purity of 96% was used in this study. Sodium hydroxide with concentrations of 10 M was used in this study. Sodium hydroxide solution was prepared by 400 gm of dry powder and then adding this amount to a 500 ml of distilled water and hand stirred until it was fully dissolved. Then, extra distilled water was added until the total volume reached 1 liter.

3.1.3. Sodium Silicate (Na_2SiO_3). Sodium silicate, also known as water glass, was obtained from PQ Corporation.

3.1.4. Portland Cement. American Petroleum Institute (API) Portland cement class H was used in this study. The chemical composition of the Portland cement was determined using X-ray fluorescence (XRF). The composition of Portland cement class H, obtained from XRF, is shown in Table 2.

Table 2. The chemical composition of Portland cement

Element	**Concentration (%)**
SiO_2	20.36
Al_2O_3	3.17
Fe_2O_3	6.19
CaO	65.72
MgO	1.32
SO_3	2.26
K_2O	0.43
Other components	0.55

3.1.5. Drilling Fluids. In this study, water base mud was used. The drilling fluid was prepared by adding bentonite to water and leaving it for prehydration for 24 hours. Following that, xanthan gum (XG) was added and mixed for 10 minutes. After that, Low Viscosity Polyanionic Cellulose (PAC-LV) was added and mixed for another 10 minutes. Then, the density was measured. Barite was added to keep the drilling fluid's density at a constant value of 9.5 lb/gal. Drilling fluids properties are shown in Table 3.

Table 3. Drilling fluids properties

Plastic Viscosity	**Density**	**Gel Strength at** 10 Sec	**Gel Strength at** 10 min
17	9.5	15	28

3.2. EXPERIMENTAL METHODOLOGY AND PROCEDURE

This section is a description of geopolymer and Portland cement preparation procedure as well as test procedures that were done in order to investigate the effects of drilling fluids on geopolymer and Portland cement. These tests include density, rheology, fluid loss, and compressive strength using different curing time. After prepared the drilling fluids, geopolymer slurries were prepared and mixed with different drilling fluid ratios, including 0%, 5%, and 10% by weight of cement (BWOC). These drilling fluids ratios were also mixed with Portland cement slurries to investigate the effects of drilling fluids on Portland cement properties and made comparison between Portland cement and geopolymer.

3.2.1. Geopolymer Preparation Procedure. All geopolymer slurries were mixed at ambient temperature and atmospheric pressure. The blender was filled with the tap water firstly, after that, the fly ash class C was added and mixed at low speed for 10 seconds. Then, the alkaline solution, which is a mixture of sodium silicate and sodium hydroxide, was added. After adding the alkaline solution to the blender, the mixture was mixed for 10 seconds at low speed and 30 seconds at high speed. This slurry was poured in cubic molds and cured for 24 hours to be used in compressive strength measurement. The basic components of geopolymer are shown in Figure 1. Initially, thirty different geopolymer batches were prepared with different ratios of alkaline activator to fly ash (AA/FA), sodium silicate to sodium hydroxide (SS/SH), and different sodium hydroxide concentrations. Following an extensive analysis including compressive strength, rheology, density, and fluid loss. The optimized geopolymer design had a reasonable compressive strength, lower fluid loss, and acceptable rheological behavior. Table 4 shows the geopolymer mix design.

Table 4. Geopolymer mixing design

AA/FA	FA (gm)	SS/SH	SH Solution (gm)	SS Solution (gm)
0.4	600	1	60	60

AA Alkaline Activator FA Fly Ash

SS Sodium Silicate SH Sodium Hydroxide

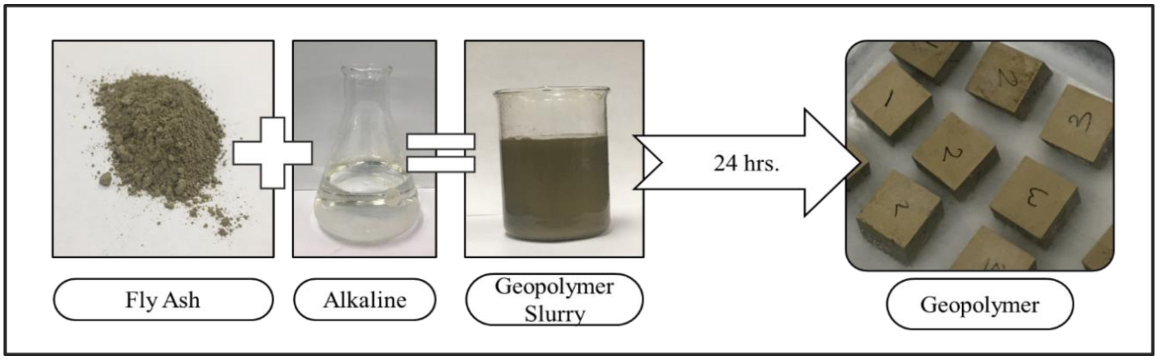

Figure 1. Reaction of fly ash with alkaline activator to produce geopolymer

3.2.2. Portland Cement Preparation Procedure. Portland cement was mixed according to API recommendations. All Portland cement slurries were mixed at ambient temperature and atmospheric pressure. The blender was filled with the distilled water and mixing commenced at low speed for 15 seconds. During the 15 seconds, the dry cement was added to the blender. Then, the blender was covered and mixing continued for 35 seconds at high speed. The Portland cement mix design is presented in Table 5.

Table 5. Portland cement mixing design

	Mass (percent by weight of cement BWOC)
Class H Cement	100
Distilled Water	38

A low speed blender was used to mix the drilling fluids with the cement slurries. Five and ten percent by weight of cement of drilling fluids was added to the cement slurries. The total weight of the slurry after adding the weight percent of drilling fluids was maintained similar to the slurry containing no drilling fluids in order to compare the results. Finally, the mixture was mixed at low speed, 400 rpm, for 30 seconds.

3.2.3. Density and Rheology. The rheology was studied due to the importance of understanding the behavior of geopolymer and Portland cement when interacting with drilling fluids. The density was studied to investigate the impacts of mixing the drilling fluids on the slurries densities. Then, the density was measured using a standard mud balance. After that, an Ofite viscometer was used to obtain the rheology behavior for these samples. All the rheology and density tests were done at atmospheric pressure and room temperature.

3.2.4. Compressive Strength Test. Compressive strength is an important factor to investigate the strength of the geopolymer. In this study, geopolymer strength and Portland cement strength were tested after the slurries were mixed with different drilling fluids ratios to study the effect of these additives on the compressive strength. All geopolymer slurries were mixed at ambient temperature and atmospheric pressure. Then, the geopolymer slurries were mixed with drilling fluids. The mixture was poured in 2×2×2 in. molds and placed in a water bath to be cured under atmospheric pressure and room temperature for different curing time (1 day, 3 days, and 7 days). Similar procedure was done to Portland cement.

3.2.5. Fluid Loss Test. Fluid loss test is an important test in order to understand how much water will be lost to the formation during the cementing operation; in other words, to test the ability of cement to retain its water. The fluid loss was measured by a low-pressure low-temperature filtrate cell (LPLT) using 100 psi pressure, and room temperature.

3.3. RESULTS AND DISCUSSIONS

3.3.1. Density Measurement Results. Mixing the drilling fluids with cement slurries did not affect the density significantly on both materials, geopolymer and Portland cement. Figure 2 shows the densities of geopolymer and Portland cement with different ratios of drilling fluids. As the drilling fluids weight percentage increased the density decreased slightly; the density of these slurries still remained within the regular weight cement density range of 14 to 17 lb/gal (Pang, et al., 2014). Geopolymer density was 14.7 lb/gal when no drilling fluid was added compared to 14.3 lb/gal when 10 weight percent drilling fluid was added. The slight decrease that happened to the density was due to adding the drilling fluid that has a lower density compared to the geopolymer and Portland cement slurries. This resulted in a reduction in the cement slurries density.

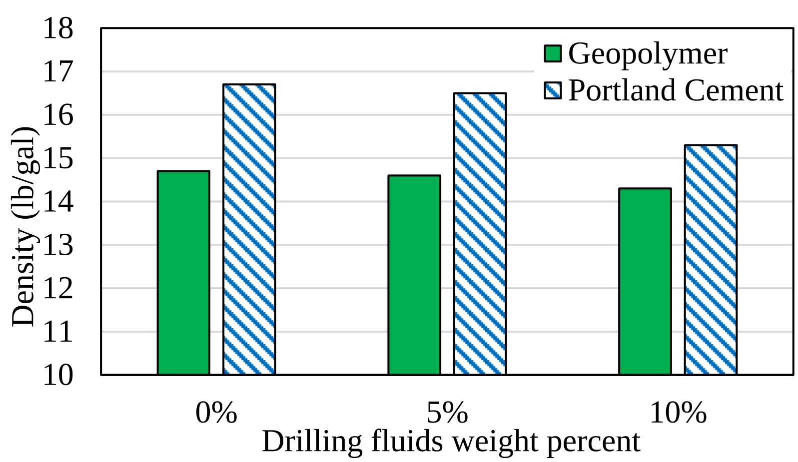

Figure 2. Density of geopolymer and Portland cement slurries after adding drilling fluids

3.3.2. Rheology Results. Plastic viscosity is an important factor to determine the cement flowability. The plastic viscosity was measured using Ofite viscometer.

Figure 3 shows the result of the viscosity of geopolymer and Portland cement after adding drilling fluids. The results of the rheology test showed that mixing the drilling fluids with geopolymer decreased its viscosity which increase the slurries workability. However, mixing the drilling fluids with Portland cement resulted in an increase in the viscosity. Increasing the amount of drilling fluid was directly proportional to Portland cement viscosity. Increasing in the amount of the drilling fluids resulted in an increase in the viscosity of Portland cement slurries, which will affect the cement slurries workability. Viscosity is important during the pumping processes. Decreasing on the viscosity will facilitate the pumping processes and also reduce the pumping operations cost due to the lower pump power needed to pump the lower viscosity slurry (Alzgoul, 2014).

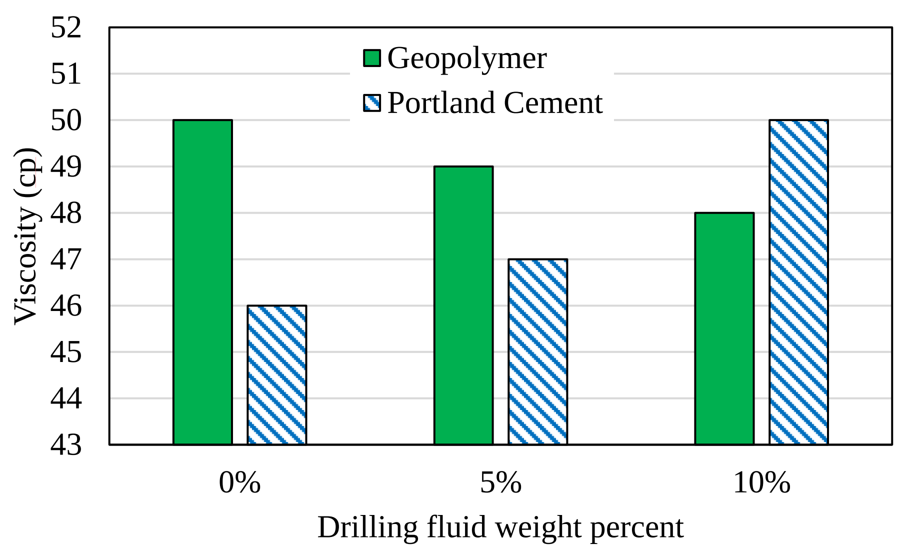

Figure 3. Viscosity of geopolymer and Portland cement slurries using different drilling fluid weight percent

The flow curves for the geopolymer, geopolymer plus 5% BWOC of drilling fluids, and geopolymer plus 10% BWOC of drilling fluids at room temperature (24˚C) are very close to straight lines. Figure 4 and Figure 5 show shear stress verses shear rate using different drilling fluid weight percent for geopolymer and Portland cement. These results indicate that there is a small effect on the rheological behavior of geopolymer, however, the rheological behavior still in the acceptable level. Mixing drilling fluids with geopolymer reduced the shear rate verses shear stress which helps during the pumping processes. In other words, drilling fluids can reduce the cost of pumping during cementing operations due to its effect on geopolymer slurries. However, mixing drilling fluids with Portland cement can cause an enormous problems. Drilling fluids have a negative effects on the rheological behavior of Portland cement, it increases the viscosity and makes the slurry very thick which will affect the pumping processes and causes many problems during the cementing operations.

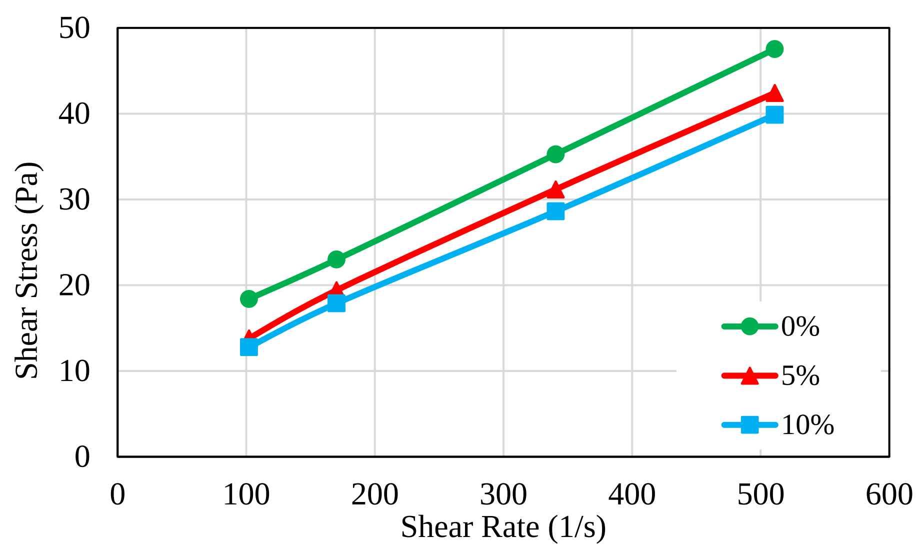

Figure 4. Shear stress verses shear rate using different drilling fluid weight percent at room temperature for geopolymer

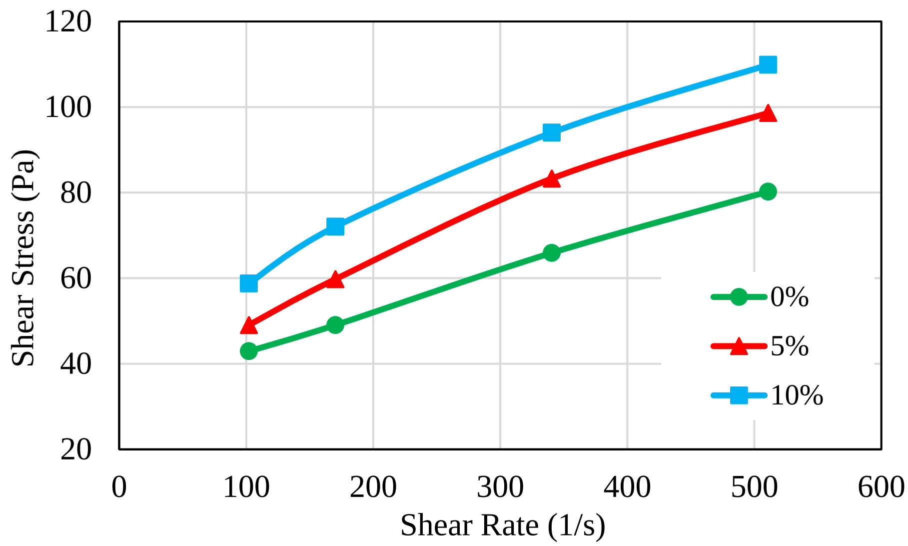

Figure 5. Shear stress verses shear rate using different drilling fluid weight percent at room temperature for Portland cement

3.3.3. Compressive Strength Results. Geopolymer and Portland slurries were prepared and mixed with different ratios by weight of cement of drilling fluids using a low speed mixer. The mixtures were poured in 2*2*2 cubic molds and were cured in water bath at room temperature, and atmospheric pressure. Compressive strength was measured at different curing times (1 day, 3 days, and 7 days). Figure 6 show compressive strength of geopolymer and Portland cement after 1, 3, and 7 days. The laboratory results showed that curing time positively affects the compressive strength. The obtained results showed that geopolymer has early strength compared to Portland cement, 1195 and 717 psi respectively. However, with time, the geopolymer compressive strength increased at a lower rate compared to Portland cement. After 3 and 7 days, Portland cement had higher compressive strength, 3441 and 4610 psi respectively, compared to 2330 and 3085 psi of geopolymer strength.

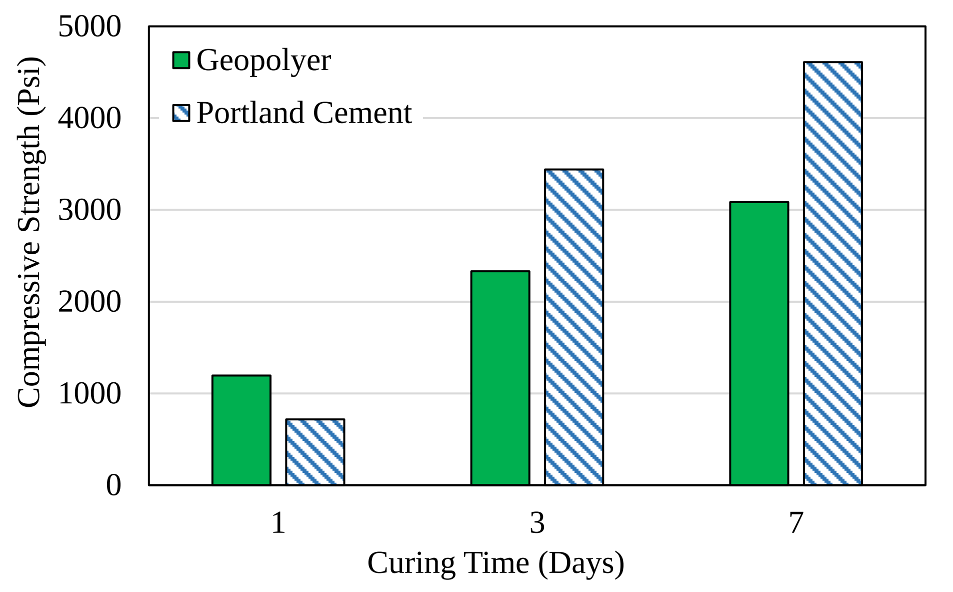

Figure 6. Compressive strength of geopolymer and Portland cement after 1, 3, and 7 days for no drilling fluid

Even after mixing geopolymer with drilling fluid, the compressive strength of geopolymer remained high. Portland cement however lost a large percentage of its compressive strength when mixed with the same weight percent of drilling fluids. This is an indication that geopolymer cement is much more compatible with drilling fluids compared to Portland, and thus geopolymer can be considered a better alternative to Portland cement. Compressive strength results for geopolymer and Portland cement after 1, 3, and 7 days using 10 weight percent of drilling fluid are shown in Figure 7. When the slurries were mixed with drilling fluids, the obtained results showed that geopolymer has higher compressive strength compared to Portland cement. After a one day curing time, geopolymer strength was 935 psi compared to 476 psi for Portland cement strength.

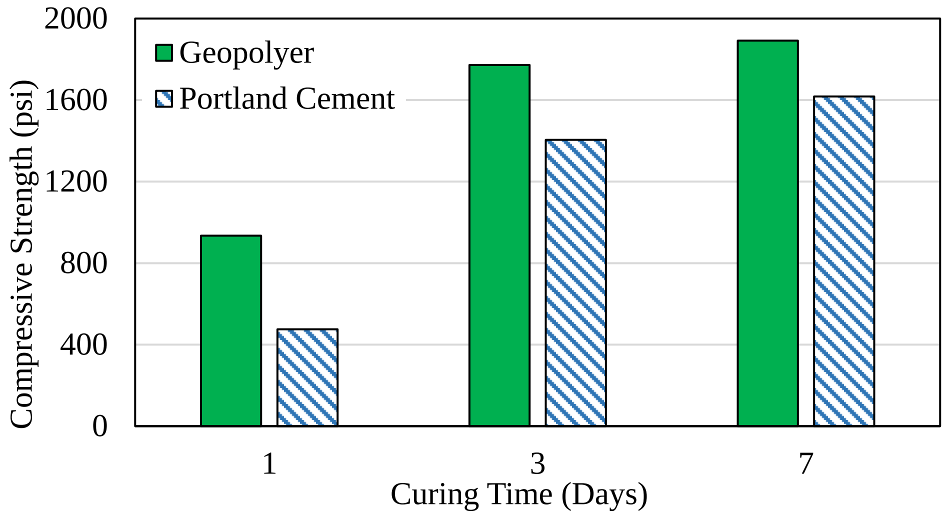

Figure 7. Compressive strength of geopolymer and Portland cement after 1, 3, and 7 days using 10 weight percent of drilling fluid

Referring to Figure 6 and Figure 7, the reduction of compressive strength of geopolymer and Portland cement after 1 day, 3 days, and 7 days curing time with different drilling fluids weight percent is shown in Figure 8, Figure 9, and Figure 10. After a one day curing time, drilling fluids with 5 and 10 weight percent exhibited an 8 and 20 % reduction in compressive strength respectively.

For Portland cement however, adding 5 and 10 weight percent drilling fluid resulted in a decrease in compressive strength by 9 and 34 % respectively. After 3 days curing time, geopolymer lost only 8.5 and 23.9 % of its strength when mixed with 5 and 10 % of drilling fluids weight percent respectively. However, Portland cement had a huge decrease in compressive strength when mixed with 5 % and 10 % of drilling fluids weight percent, with a 38.4 % and 59.2 % loss of its strength, respectively. After 7 days curing time, geopolymer strength decrease slightly more reaching 24 % reduction for 5 weight percent drilling fluids compared to Portland cement which exhibited 49 % reduction when exposed to 5 weight percent drilling fluids. Adding drilling fluids to the slurry will result in an increase in the water overall percentage, since drilling fluid is composed of a high percentage of water; this increased water percentage will impact the cement slurries properties (Bourgoyne, et al., 1991; Donham, & Young, 2009).

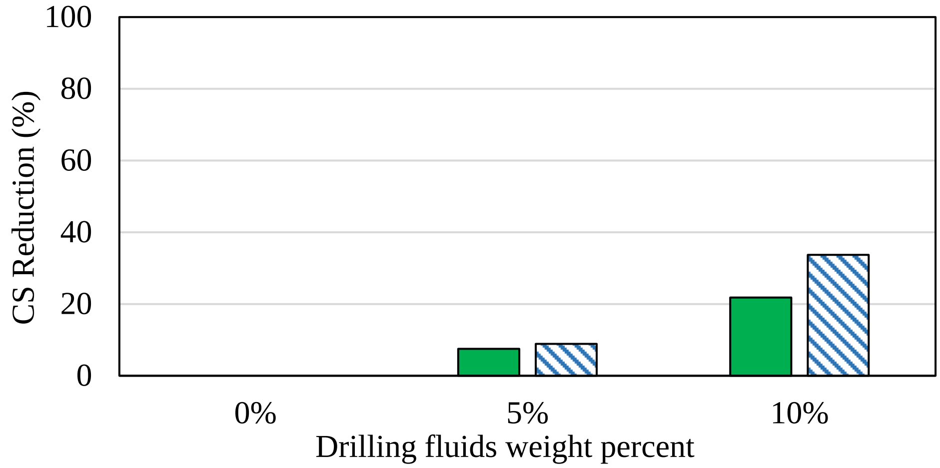

Figure 8. Reduction of compressive strength of geopolymer and Portland cement after 1 day

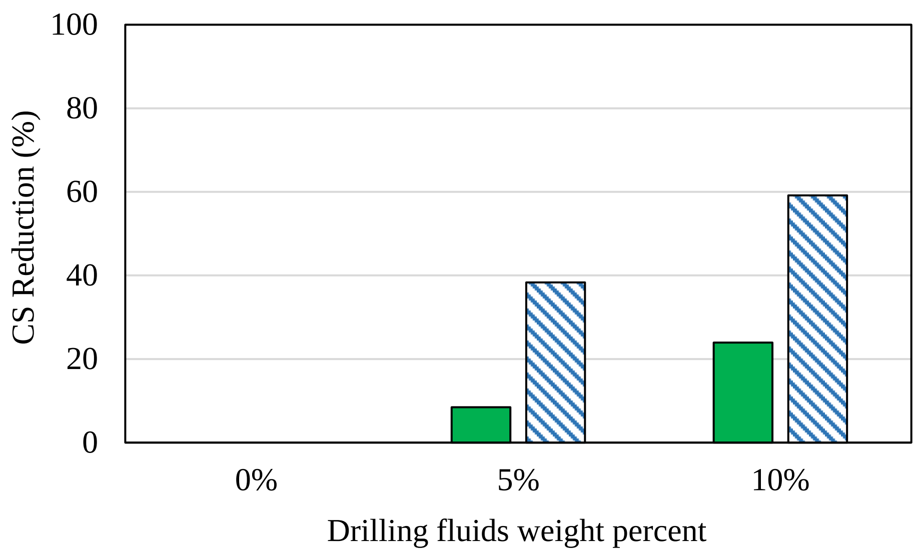

Figure 9. Reduction of compressive strength of geopolymer and Portland cement after 3 days

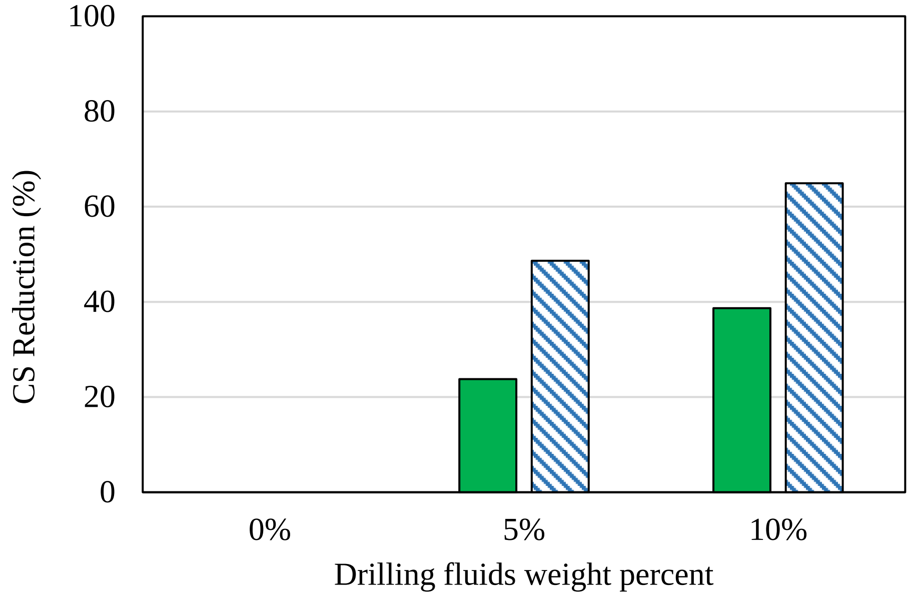

Figure 10. Reduction of compressive strength of geopolymer and Portland cement after 7 days

3.3.4. Fluid Loss Test Results. Cement properties can be strongly affected by losing its water, which will increase the possibility of having cracks and channels within the cement. The fluid loss was measured by a low pressure low temperature filtrate cell (LPLT). The geopolymer slurries were prepared and mixed with the drilling fluids and were poured at the cell. The cell was pressurized at 100 psi using air pressure. The measurement was taken every one minute, for accuracy, for 30 minutes or until the water stopped, following API recommendations. If the time did not reach 30 minutes, the following equation was used to obtain the fluid loss volume:

$$API\ fliud\ loss = 2\,V_t\sqrt{\frac{300}{t}} \qquad (1)$$

where V_t is the volume of filtrate at the time air blows through, in ml, and t is the elapsed time, in minutes.

Figure 11. Shows geopolymer fluid loss with different drilling fluids weight percent. These obtained results showed that drilling fluids concentrations are inversely proportional to the fluid loss. This indicates that drilling fluids can work as fluid loss additives. As drilling fluid weight percent increases the geopolymer fluid loss decreases. Geopolymer had 93 ml fluid loss in 30 minutes when no drilling fluids was added compared to only 80 ml fluid loss in 30 minutes when 10 weight percent drilling fluid was added. This reduction is due to the drilling fluids containing bentonite which contain aluminum and silicate; the aluminum and silicate were induced by the sodium hydroxide during the polymerization process. These silicates react with aluminum (Al) and form alumino-silicate gels (Suppiah, et al., 2016).

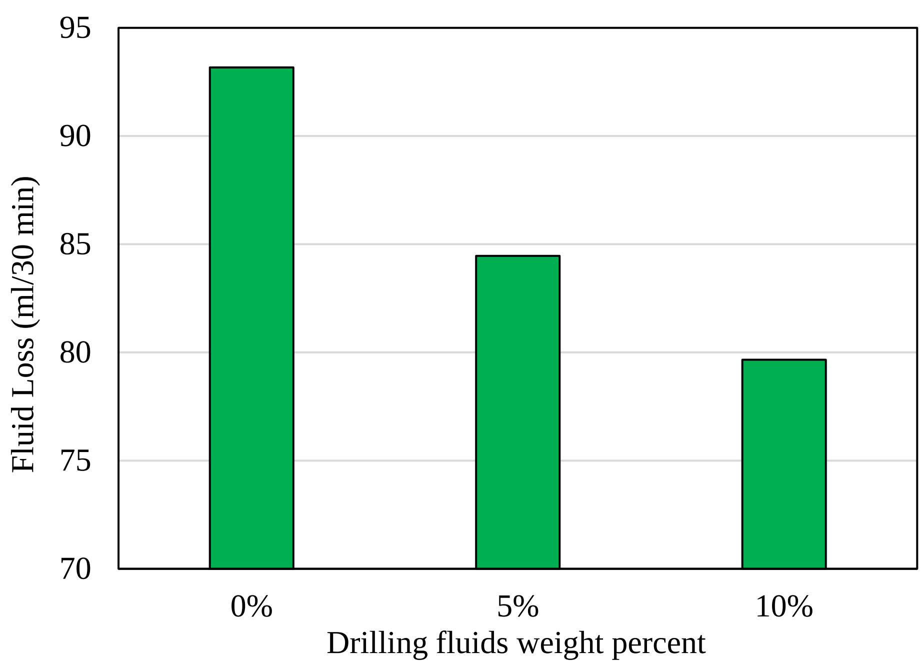

Figure 11. Geopolymer fluid loss with different drilling fluids weight percent

However, mixing drilling fluids with Portland cement resulted in a significant increase on the fluid loss, more than 500 ml in 30 minutes when mixed with 10 percent of drilling fluids weight percent. Figure 12 shows Portland cement fluid loss with different drilling fluids weight percent. Increasing the weight percent of the drilling fluids lead to a huge amount of fluid loss due to the water that was introduced to the mixture by drilling fluids. In Portland cement, no sodium hydroxide is present, thus no reaction will occur between the Portland cement and the bentonite, and since the drilling fluid is mainly composed of water, the fluid loss volume will increase.

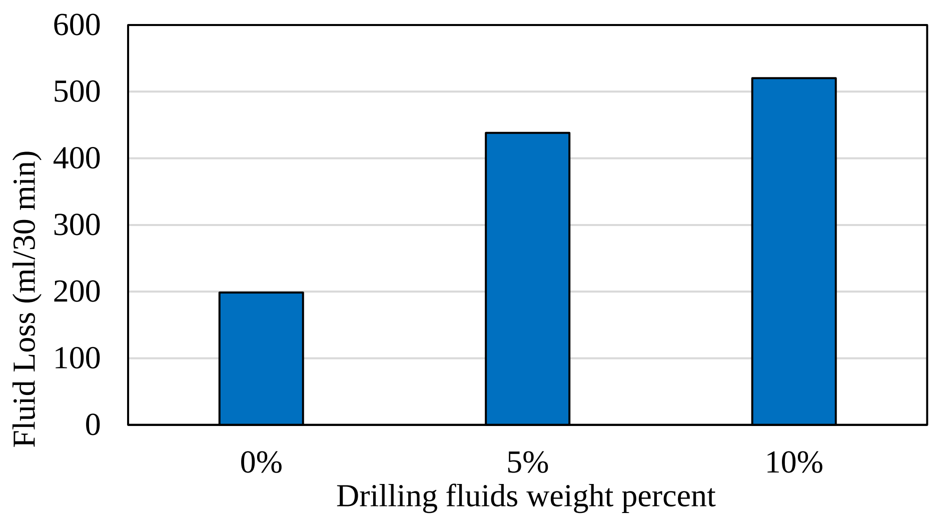

Figure 12. Portland cement fluid loss with different drilling fluids weight percent

4. CONCLUSION

Geopolymer has recently attracted attention because it is a cost-effective material and has less environmental impacts compared to Portland cement. By studying the drilling fluid contamination effects on geopolymer and Portland cement, it was observed that the drilling fluid with the geopolymer enhanced the geopolymer properties and undermine the properties of Portland cement. The drilling fluids improved the injectivity of the geopolymer without any significant effects on mechanical properties. In contrast, mixing drilling fluids with Portland cement had a negative impact on the Portland cement properties and reduced the compressive strength significantly. A summary of the conclusion are listed below:

- A slight decrease was observed in the cement slurries density when mixed with drilling fluids in both materials, geopolymer and Portland cement. As the drilling fluids weight percentage increased the density decreased slightly.
- Drilling fluids concentrations are inversely proportional to the geopolymer viscosity. As drilling fluids weight percent increased the viscosity of geopolymer decreased. However, the viscosity increased rapidly as the amount of drilling fluid in Portland cement slurry increased.
- Drilling fluid improved the geopolymer injectivity.
- Geopolymer showed higher compressive strength when exposed to drilling fluids compared to Portland cement.
- As the amount of drilling fluids increased, the compressive strength of geopolymer was not significantly affected. However, increasing the amount of the drilling fluids resulted in a significant decrease in the Portland cement strength.
- Mixing drilling fluids with geopolymer reduced the fluid loss. However, Portland cement fluid loss significantly increased when drilling fluids were introduced, which could impact the cement slurry properties.

NOMENCLATURE

V_t	=	Volume of filtrate in ml.
t	=	Elapsed time in minutes.
psi	=	Pounds per square inch.
lb ⁄ gal	=	Pounds per gallon.
°C	=	Degree Celsius.
BWOC	=	By weight of cement.
Na_2SiO_3	=	Sodium silicate
K_2O_3Si	=	Potassium silicate.
NaOH	=	Sodium hydroxide.
KOH	=	Potassium hydroxide.
PV	=	Plastic viscosity.
m	=	Mass of cement, gm, kg.
ρ	=	Gram per cubic centimeter, pounds per gallon.
LPLT	=	low pressure low temperature fluid loss test
AA	=	Alkaline activator.
FA	=	Fly ash.
SS	=	Sodium silicate.
SH	=	Sodium hydroxide.
CS	=	Compressive strength.

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SECTION

4. CONCLUSIONS AND RECOMMENDATIONS

4.1. CONCLUSIONS

This thesis provides a novel development of fly ash class C based geopolymer to be used in oil and gas wells. In first paper, different ratios were investigated. The selection of the optimum formulation was based on five different tests, including rheology, density, compressive strength, fluid loss test, and stability tests (sedimentation test and free fluid test). Then, a comparison between the optimum mix design and Portland cement was done using the same tests. The obtained results showed the following:

- Sodium hydroxide concentrations are inversely proportional to the plastic viscosity; as the sodium hydroxide concentrations increase, plastic viscosity has a slight decrease.
- Sodium hydroxide concentrations positively affect the compressive strength. As sodium hydroxide concentrations increase, the compressive strength increases.
- Increasing sodium silicate to sodium hydroxide ratios results in a decrease in fluid loss.
- Stability tests indicate that there is no free fluid and particle settling for the optimized geopolymer.
- The optimized geopolymer has a higher compressive strength than Portland cement.
- The optimized geopolymer has a lower fluid loss than Portland cement after 30 minutes.

The optimum ratios of sodium silicate to sodium hydroxide, alkaline activator to fly ash, and sodium hydroxide concentration were 1, 0.4, and 10 M, respectively. In the second paper of this thesis, the effect of drilling fluids on geopolymer and Portland cement has been investigated. By studying the drilling fluid effects on geopolymer and Portland cement, it was observed that mixing the drilling fluid with the geopolymer enhanced the rheological performance of geopolymer without a significant impact on its mechanical performance. A summary of the conclusions is listed below:

- A slight decrease occurred in the cement slurry density when mixed with drilling fluids in both materials, geopolymer and Portland cement.
- Drilling fluid concentrations are inversely proportional to the geopolymer viscosity. As the drilling fluids' weight percent increased, the viscosity of geopolymer decreased. However, the viscosity increased rapidly as the amount of drilling fluid in Portland cement slurry increased.
- Drilling fluid improved the geopolymer injectivity.
- Geopolymer showed higher compressive strength when exposed to drilling fluids compared to Portland cement.
- As the amount of drilling fluids increased, the compressive strength of geopolymer was not significantly affected. However, increasing the amount of the drilling fluids resulted in a significant decrease in the Portland cement strength.
- Mixing drilling fluids with geopolymer reduced the fluid loss; however, Portland cement fluid loss significantly increased when drilling fluids were introduced.

4.2. RECOMMENDATIONS

In this work, geopolymer and Portland cement were studied to better understand the behavior of these materials. Regarding geopolymer, this research studied the effect of the ratios of sodium silicate to sodium hydroxide, alkaline activator to fly ash, and sodium hydroxide concentrations on geopolymer properties. The following tests are recommended:

1. Testing thickening time for both materials, geopolymer and Portland cement.
2. Testing both materials using different curing temperatures and pressures to simulate the downhole conditions.
3. Measuring the tensile strength to examine the mechanical properties for both materials.
4. Measuring the Young's modulus and Poisson's ratio to understand the elastic behavior of both materials.
5. Investigating the effect of carbon dioxide (CO_2) on geopolymer at different temperatures and different pressures.

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