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# Evaluation of Class F Fly Ash-Based Alkali-Activated Materials for Civil and Petroleum Engineering Applications

# APPROVED BY SUPERVISING COMMITTEE:

Eric van Oort, Supervisor

Maria Juenger, Co-Supervisor

Moneeb Genedy

# Evaluation of Class F Fly Ash-Based Alkali-Activated Materials for Civil and Petroleum Engineering Applications

by

## **Cameron Rae Horan**

### Thesis

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## Dedication

I would like to dedicate this work to my parents, John and Angie, and my two brothers, Codie and Carson. Thank you for the support and advice provided along my entire journey.

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First and foremost, I want to give all the glory to God. None of this would be possible without Him directing my path. God works in mysterious ways and sometimes contrary to what we think, for that I am extremely grateful.

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### Abstract

# Evaluation of Class F Fly Ash-Based Alkali-Activated Materials for Civil and Petroleum Engineering Applications

Cameron Rae Horan, M.S.E

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Supervisors: Eric van Oort, Maria Juenger

Advancements in technology have allowed oil, gas and geothermal well construction in into progressively more challenging subsurface environments, with deeper depths, higher temperatures and pressures, etc. With this progress arises the need for well cementing solutions that can perform better than ordinary portland cement (OPC), with an ability to better handle high pressure / high temperature (HPHT) conditions while possessing a more tolerant chemical composition to drilling mud contamination. Faulty cement jobs due to poor performance of OPC have allowed for the occurrence of micro annuli, putting many wells at risk of a well integrity failure. Such a failure compromises zonal isolation, which can in turn lead to high costs for repair that have not typically been factored into operating budgets. Likewise, civil infrastructure durability has become a key concern for much of the United States due to aging structures and the deterioration of OPC concrete with time. While performance concerns pose a significant risk, the CO<sub>2</sub> emissions associated with OPC production are also at the forefront of concerns about climate change.

The topic of this report is alkali-activated materials (AAM) or geopolymers, produced from fly ash, which are currently investigated for use as OPC alternatives. They are of interest because suitable strengths and rheological behaviors have been observed when these materials are subjected to elevated temperatures or mud contamination.

To understand the effects of various activators and fly ash compositions on geopolymer formulations, a variety of tests have been conducted at different temperature and pressure conditions. These tests include measurements of rheological behavior, set time, unconfined compressive strength (UCS), tensile strength, and bond strength. As a result of this testing, it has been shown that geopolymers exhibit desirable rheological profiles and set times for a variety of different applications. Their compressive strength was also shown to be equivalent to - or greater than - OPC for most formulations. Furthermore, their tensile strengths and bond strength profiles were often found to be better than OPC. Ultimately, with this research, geopolymers are shown to be viable and appropriate alternatives to OPC for both the oil, gas and geothermal well construction as well as the civil infrastructure industry. An added benefit of geopolymers is that the base material is a waste material, with no further release of  $CO_2$  in manufacturing.

Thus, there is the opportunity to utilize a new material for cementation purposes that outperforms OPC while decreasing environmental impacts.

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### **CHAPTER 1.** INTRODUCTION

#### **1.1 MOTIVATION**

The process by which ordinary portland cement (OPC) is produced emits greenhouse gasses to the atmosphere. The most common gas associated with the production of OPC is carbon dioxide (CO<sub>2</sub>). OPC production also requires consumption of large amounts of energy, which contributes significantly to environmental pollution through additional CO<sub>2</sub> emissions. In 2000, the global figure for CO<sub>2</sub> emissions from cement production neared 829 million metric tons (Jayaraman & Smith, 2004) while in 2019 alone, the U.S. cement industry emitted an estimated 65.4 million metric tons of CO<sub>2e</sub> (*EPA Facility Level GHG Emissions Data*, 2019). Additionally, with demand for OPC expected to increase from several industries, particularly within the construction and oil and gas sectors, and no reliable alternative to replace OPC entirely, the CO<sub>2</sub> emissions from the cement industry will likely be unchanged. Thus, there is a need for materials that can meet (and preferably improve upon) the performance of OPC to lessen the environmental footprint of cement related projects.

Fly ash is a common material that is as a partial substitution OPC in concrete mixtures helping to reduce the environmental impact of cement related projects. Incorporating fly ash with OPC can not only lower the amount of CO<sub>2</sub> emitted, but it has been shown to improve the properties of concrete. For example, fly ash increases durability, improves workability, reduces porosity, and can mitigate aggregate alkali-silica reactions (*Using Fly Ash in Concrete*, 2010). Furthermore, fly ash is a waste product generated from the combustion of coal in coal-powered electrical generation plants. Typically disposed of in landfills, this material is often available for a lower cost than OPC.

However, OPC is never completely replaced by fly ash because most fly ashes are not hydraulic materials which do not react with water spontaneously.

Construction industries are the main consumer of OPC, as mentioned previously. In 2013, 70% of OPC produced in the U.S. was sent to ready-mix concrete companies (*Cement Industry Overview*, 2013). OPC is used in numerous projects that range from buildings and roads to dams and pipes, but it is not as indestructible as some may think. The U.S. highway system is in a state of decline as the bridges and roads continue to deteriorate with little to no preservation being done. The American Society of Civil Engineers (ASCE) found 7.5% of the bridges to be structurally deficient and 42% to be at least 50 years old (ASCE, 2021a). Likewise, ASCE found that 43% of the roadways are in poor condition (ASCE, 2021b). The volume of traffic is only expected to increase as the infrastructure continues to deteriorate. OPC has proven to be a reliable material, but with the number of projects needing to be undertaken and the environmental impact causing serious concern, fly ash could be a viable solution as an alternative cementitious material. Fly ash, however, continues to be an underutilized material. As an example, 40.4% of the fly ash produced in 2019 was not recycled (Adams, 2020).

Another possibility for the implementation of fly ash as a cementitious material lies within the oil and gas industry. Well cementing takes place at various downhole conditions (i.e., curing temperature and pressure). The integrity of the cement is critical to provide safe operations during the production and safe abandonment after decommissioning. Durability and bond strength are key parameters in the cementing material. Subjected to abnormal conditions for its entire life, the cement must prevent reservoir fluids from reaching the surface and maintain effective zonal isolation.

Advancements in the oil and gas industry have allowed for even deeper, more higher temperature environments to be explored and produced along with the development of hydrocarbon plays. With this observation comes the need for a cement alternative that can handle both regular and high temperature / high pressure (HTHP) conditions. It would also be beneficial if this material would possess a higher tolerance by non-aqueous drillings fluids (NADF) such as oil- or synthetic- based muds (OBM / SBM). While the use of OPC has been a norm in the industry, OPC cements have been found to have strength retrogression when subjected to temperatures above the critical temperature of 110 °C (230 °F) (Pernites & Santra, 2016). In addition to the issue posed by high temperatures for OPC slurries, there are many more parameters that must be considered when observing the strength of the cement slurry. Specifically, contamination by the drilling mud has been known to cause adverse effects to the OPC slurry resulting in a loss of zonal isolation and possibly a well cementing failure (Liu et al., 2019).

Wells are not only becoming more advanced in design, but also many wells are either in or nearing their abandonment phase. As energy demands increase, the oil and gas sector continues to explore new areas, creating new wells and abandoning old ones. Additionally, geothermal energy is being targeted as a new source of energy that involves challenging well conditions in which the cement is prone to deterioration from high temperatures. The number of producing wells in the U.S. in 2019 was 969,140 (*US Oil and Gas Wells by Production Rate - U.S. Energy Information Administration (EIA)*, 2020). While this is a considerable amount, a greater number of wells are in the abandonment category. It is estimated that there are between 2.3 to 3 million abandoned wells in the U.S. (Townsend-Small et al., 2016). These abandoned wells include both plugged and unplugged wells, both of which presenting a risk of emitting methane into the atmosphere, with the latter posing the highest risk of leaking. This is cause for concern due to methane being a more potent greenhouse gas than CO<sub>2</sub> and most of the wells today are cemented and continue to be cemented with a form of OPC cement. To lessen the impact of these problems, there is a need for a cement that can replace OPC and perform better from a zonal isolation perspective.

Geopolymers are an alkali-activated material that are typically comprised of metakaolin or coal fly ash as precursors. This aluminosilicate precursor reacts with an alkaline activator explaining the term, "alkali-activated material" (AAM) used to describe the reaction product. Classic alkaline activators can include, but are not limited to, sodium hydroxide (NaOH), potassium hydroxide (KOH), or also a combination of hydroxide / silicate solutions. The associated reactions differ from that of OPC considerably. OPC utilizes a water based hydration reaction to form calcium silicate hydrate, while the geopolymer forms through a polymerization process resulting in a pseudo-zeolitic network structure (Provis and van Deventer, 2014). This creates a N-A-S-(H)-type gel that produces Si-O-Al bonds and eventually leads to some degree of crystallinity, forming the hardened cement (Provis & Bernal, 2014).

The consortium on **Co**nstruction, **D**ecommissioning, and **A**bandonment (CODA) at the University of Texas at Austin has done research primarily on alkali activation of low-calcium Class F fly ash. It has been shown that the geopolymers made with Class F fly ash perform well when contaminated with either OBM or SBM (Liu et al., 2019). It was observed that the geopolymer does indeed have a more tolerant chemical composition than that of OPC when contaminated with drilling mud. This study also indicated that geopolymers of this type can be used to solidify NADFs (Liu et al., 2019). As this type of geopolymer continues to be studied, it is clear that there could be potential for a future use of geopolymer / mud combination (hybrid) materials.

While there is some evidence that geopolymers can be an alternative for OPC in both the civil and petroleum industries, both the liquid and solid properties of the material need to be evaluated further. Rheology, pump time, set time, and strength tests are just a few of the many tests that can be conducted on cements. Past research, for example Liu (2017) and Mundra (2021), have produced viable results for these parameters allowing the geopolymer to be used potentially for civil infrastructure and for the construction and abandonment of wells. Not only is the geopolymer beneficial there, but it has also been concluded that it is better for the environment with regards to  $CO_2$  production. Likewise, as research continues to advance, the knowledge of geopolymer interactions within practical oil well applications and civil engineering will continue to improve. Thus, the knowledge of the significance of individual constituents in the geopolymer along with liquid and solid properties lack the understanding that will be needed.

#### **1.2 RESEARCH OBJECTIVE**

In this study reported here, the objective was to conduct research toward the development of optimum Class F fly ash-based geopolymer formulations for various well conditions and construction applications. While testing was based on methods set forth by the American Petroleum Institute (API), formulations were also analyzed for use within civil engineering applications. To determine what formulations are appropriate for each application, the type of activator was varied in the mix proportions and then tested to allow for a better understanding of the geopolymer when subjected to elevated temperature and pressure conditions, as shown in Figure 1.1. The limits for temperature and pressure were chosen based on typical operating conditions observed in the field, which are shown in Table 1.1 and discussed later. Prior research by Liu (2017) and Mundra (2021) investigated the effects of temperature and pressure on fluid and solid properties. This work was expanded upon with a wider range of temperatures and pressures, as well as studying the effects of fly ash variability. This research focused on the mechanical properties (i.e., compressive strength, bond strength, and tensile strength) and the fluid properties

(viscosity and set time) of geopolymers with the compositions and curing conditions illustrated in Figure 1.1. Previous work from Liu (2017) and Mundra (2021) guided the key question on which formulation would perform best at what conditions. The specific questions to be of concern during this research were:

- 1. What alkaline activator provides the best well cement for given oil and gas well conditions?
- 2. What alkaline activator provides the best cement for civil engineering applications?
- 3. Where are the temperature and pressure limits for each type of cement (see Figure 1.1)?
- 4. What are the fluid rheology and pumpability / pouring properties of the geopolymer slurry?
- 5. What are the solid properties of the geopolymer when cured under specified conditions?
- 6. How do the differing amounts of calcium oxide (CaO) in the Class F fly ashes change the fluid and solid properties of the cement?



LSH: Liquid Sodium Hydroxide; SSS: Solid Sodium Silicate LSS: Liquid Sodium Silicate; LPS: Liquid Potassium Silicate SPS: Solid Potassium Silicate; LPH: Liquid Potassium Hydroxide

Figure 1.1: Expected Geopolymer Activation Profiles as a Function of Temperature and Pressure based on prior Research.

Condition	1	2	3	4
	76.67°C	135°C	204.44°C	76.67°C
Temperature	(170°F)	(275°)	(400°F)	(170°F)
	20.68 MPa	20.68 MPa	20.68 MPa	0.101 MPa
Pressure	(3000 psig)	(3000 psig)	(3000 psig)	(14.7 psia)

 Table 1.1:
 Testing Conditions selected for this Research.

#### **1.3 DESCRIPTION OF CHAPTERS**

The following chapter, Chapter 2, provides some insight on prior investigations dealing with AAMs. Studies associated with rheology and mechanical properties are examined with a brief description of geopolymers provided. Chapter 3 covers the materials and methods that were utilized in the research presented here. The fly ash types are discussed with each samples' particle size distribution and oxide composition being provided. Preparation of the samples and explanations of the testing procedures for rheology, set time, compressive strength, tensile strength, and bond strength are also provided. In Chapter 4, the research results are provided and discussed. Finally, in Chapter 5, the conclusions of the research findings are listed and the recommendations for future work are proposed.

### **CHAPTER 2.** BACKGROUND

#### 2.1 FLY ASH FOR AAM

Most materials utilized for the solid precursor in AAMs are waste products often derived from industrial processes, but there are several naturally occurring materials that can also be utilized. However, any material that is high in reactive silica and alumina content can be applied to alkali activation (Bernal et al., 2016).

One of the most common materials used with alkali activation is fly ash. Fly ash is a waste product retained in the baghouse of electrical generation plants that burn coal. In the U.S., the classification of fly ash is categorized into two types, Class C and Class F, where Class C is from the combustion of lignite / sub-bituminous coal (low grade) and Class F is from the combustion of anthracite / bituminous coal (high grade). ASTM C618-19 (ASTM, 2019) provides the requirements for each of these fly ash types where a major distinction between the two types of fly ash is the amount of CaO. Class F fly ash is a low calcium material comprised of 18% or less CaO while Class C fly ash is generally higher in calcium content with CaO greater than 18%. Additionally, the limit for the combined total of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>) for Class F fly ash is a minimum of 70% and for Class C fly ash is a minimum of 50%. Figure 2.1 provides a comparison of the amount of silica, alumina, and iron oxide in both types of fly ash to that of OPC.



Figure 2.1: Approximate Compositions of OPC, Class C Fly Ash (FA), and Class F Fly Ash (FA).

Due to the high amount of silica and alumina contained in Class F fly ash and the high thermal stability observed by Kong et al. (2007) of Class F fly ash pastes, it was selected as the aluminosilicate material of choice in this research. Liu (2017) and Mundra (2021) also found that Class F fly ash-based geopolymers exhibited desirable rheological properties, with the possibility for use in well cementing. Thus, the focus of this research was on AAMs based on the activation of Class F fly ash obtained from several different sources. The rest of this Chapter will focus exclusively on Class F fly ash-based systems.

#### **2.2 GEOPOLYMER CLASSIFICATION AND PROCESS**

The term AAM covers a broad range of materials associated with alkaline activation including geopolymers. Geopolymers are a category of AAMs that are made with an aluminosilicate material low in calcium content as shown in Figure 2.2 (Provis and van Deventer, 2014). Types of aluminosilicate precursor materials that are considered under this category are Class F fly ashes and calcined clays.



Figure 2.2: Classification of AAMs\* (Provis and van Deventer, 2014).

Precursor materials for geopolymers are aluminosilicate-rich and activated by an alkali metal solution in hydroxide or silicate form. The associated solutions have a high pH to allow for the dissolution of the fly ash particles, beginning the activation process. As

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dissolution and rearrangement occurs, precipitation takes place, where there is an initial phase in which the gel has a high aluminum content with bonds of Si-O-Al and a later phase in which the silicon concentration of the gel increases and Si-O-Si bonds form (Provis & Bernal, 2014). This occurs due to the Si-O-Al bonds being weaker and more readily converted to Si-O-Si bonds (Duxson & Provis, 2008).

Unlike OPC, where calcium plays a significant role in the formation of strength providing reaction products, geopolymers rely mainly on silica and alumina for gel formation. Therefore, in high calcium AAM systems, the main binding phase is the C-(A)-S-H phase, whereas in low calcium AAM systems the N-A-S-(H) phase dominates (Provis and van Deventer, 2014; Juenger et al., 2011). While reaction product formation is dependent on calcium content, both types can occur in either AAM system when the constituents of each phase are present in the original aluminosilicate material. However, the primary gel type will be as described above. Figure 2.3 provides a generalized representation of the alkali activation process for AAM systems.



Figure 2.3: Generalized AAM Activation Process\* (Juenger et al., 2011).

Since the geopolymer activation process is highly complex and ongoing research is still being pursued to help clarify it, only a brief description is provided in the following to give some insight into what a geopolymer is and how it is being referenced within this research. The activation process is generalized considerably as it is outside the scope of this research and can vary with the type of material and activator being used.

#### 2.3 ACTIVATION

Class F fly ash is generally mixed with some combination of alkali metal hydroxides and / or silicates creating the geopolymer as previously mentioned. There has also been work completed with sodium aluminate solutions as activators for geopolymers but to a lesser extent (Provis et al., 2014). It is also important to understand that geopolymer

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activation often requires high molar concentrations, where the optimum molarity has been a matter of discussion in order to provide the highest strength geopolymer (Ahmari & Zhang, 2015). In addition to Ahmari & Zhang (2015), Aughenbaugh (2013) provided research on desirable activator concentrations, activators, and proportioning ratios, but total understanding of these variables with respect to Class F fly ash-based geopolymers, especially at elevated temperature and pressure conditions, has yet to be adequately developed.

#### 2.3.1 ALKALINE HYDROXIDE ACTIVATION

Hydroxide solutions are the most common activators in generating geopolymers, but there are several different types of hydroxides that can be used. These usually consist of sodium (most prevalent) or potassium (specialties), but rubidium, lithium, and cesium hydroxides have also been utilized (Provis & Bernal, 2014). The latter three have been used significantly less due to limitations in real-world applications along with cost. Likewise, there is little known about these alkaline hydroxide activators. Still, alkaline hydroxide solutions as a whole provide several benefits that are useful to cementing applications. Prior research has found that hydroxides have a great degree of stability at higher temperatures (Provis & Bernal, 2014; Kong, Sanjayan, & Sagoe-Crentsil, 2007; Bakharev, 2005). This allows for geopolymer cements to be used in high temperature applications such as steam injection or extreme depth wells. Rheological properties of cements with these solutions have also been shown to exhibit more favorable properties versus cements activated with silicate solutions (Provis & Bernal, 2014). It should also be mentioned that hydroxide solutions result in a more permeable cement than silicate-activated geopolymers (Provis & Bernal, 2014).

#### **2.3.2 ALKALINE SILICATE ACTIVATION**

Silicate solutions are becoming increasingly more desirable to the industry due to the potential for increased cement durability in extreme conditions, but little is known about the effects at elevated temperature and pressure conditions. These solutions usually can be made from solid or liquid silicates with either sodium or potassium as the alkali cation. Geopolymers formed by silicate activation are generally more viscous than geopolymers that contain hydroxide solutions (Provis & Bernal, 2014). Sodium and potassium alkaline silicate activators also show differences when compared on viscosity and rheological properties. Potassium silicate-activated geopolymers are superior to the sodium silicate-activated geopolymers by yielding higher strengths, and also by having a lower viscosity and better rheology when in paste form (Provis & Bernal, 2014; Sabitha, Dattatreya, Sakthivel, Bhuvaneshwari, & Sathik, 2012). Another benefit of the increased silicate concentrations is strength. Compressive strengths have been shown to be directly related to the amount of silicate present in the geopolymer mixture (Ma et al., 2012; Komljenović, Baščarević, & Bradić, 2010).

#### **2.4 CURING CONDITIONS**

Class F fly ash-based geopolymers tend to have slow strength development at room temperatures providing and often need thermal curing (Provis & Bernal, 2014). Indeed, studies by Somna et al. (2011) and Kumar & Kumar (2011) have shown that it is possible to cure geopolymer samples at low temperatures, but the duration of curing is longer and grinding of the fly ash may be needed. Thus, to achieve optimum strength, the ideal curing temperature for Class F fly ash-based geopolymers has been found to be at 75°C (167°F) to 80°C (176°F), while the optimum curing temperature for geopolymers in general is 40°C (104°F) to 90°C (194°F) (Ahmari & Zhang, 2015).

#### 2.4.1 CURING CONDITIONS – CONSTRUCTION INDUSTRY

Since curing conditions for Class F fly ash-based geopolymers typically require elevated temperatures much higher than most natural climates provide, ready-mix applications are usually not a viable option. However, the precast industry utilizes a lowpressure steam curing process where temperatures typically range from 48.89°C (120°F) to 60°C (140°F) with a maximum temperature of 71.11°C (160°F). Therefore, precast operations can readily produce geopolymer products.

#### 2.4.2 CURING CONDITIONS – PETROLEUM INDUSTRY

The conditions for oil and gas wells are far more variable than conditions in precast operations, providing a considerable number of opportunities for different geopolymer formulations to be implemented. Temperatures can range from 0°C (32°F) to greater than 200°C (392°F) with pressures ranging from atmospheric pressure to greater than 140 MPa (~20,300 psi) (Liska et al., 2019). API SPEC 10A (2019) also provides performance requirements for OPC based cements cured at 38°C (100°F) up to 160°C (320°F), illustrating the elevated temperature conditions that could be taken advantage of for activating and curing Class F fly ash-based geopolymers.

While API SPEC 10A (2019) fits many oil and gas wells, there are much more extreme conditions that can be encountered, as shown in Figure 2.4. Geopolymer use in HPHT areas remains to be explored. However, geopolymers have shown good thermal stability within other applications where temperatures are much higher than in Figure 2.4 (Colangelo et al., 2017; Kong, Sanjayan, & Sagoe-Crentsil, 2007). For example, geopolymers have shown increased strength when subjected to the extreme conditions. In particular, geopolymers made with fly ash have shown the greatest increase in strength compared to geopolymers made with metakaolin (Kong et al., 2007). Table 2.1 shows the

relationship between metakaolin and fly ash geopolymers in which one sample of each was subjected to 800°C while the other was left unchanged where metakaolin showed strength retrogression while fly ash continued to gain strength and cure.



Figure 2.4: Schlumberger HPHT Classification System\* (after Smithson, 2016).

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Compressive Strength			
Dia dan Tana	Linewneed	Temperature	
Binder Type	Unexposed	Exposed	
Madalas al'u	38.5 MPa	25.4 MPa	
Metakaolin	(5580psi)	(3680psi)	
Elv. Ash	59.0 MPa	62.8 MPa	
	(8560 psi)	(9100 psi)	

Table 2.1:Relationship between Exposure to 800°C and No Exposure to 800°C\*<br/>(Kong, Sanjayan, & Sagoe-Crentsil, 2007).

#### **2.5 GEOPOLYMER PROPERTIES**

For geopolymers to be considered for industrial applications, it must be shown that they exhibit properties that compare favorably with those of OPC. Viscosity and set time are often discussed with relation to how pumpable a mix is and the duration that it remains pumpable. Other typical properties of concern are compressive, tensile, and bond strength. These mechanical properties need to be sufficient for the standards of the industry where the geopolymer will be used. Various studies have been completed on each of these properties and are discussed further next.

#### 2.5.1 VISCOSITY

As previously mentioned, it has been determined that activating geopolymers with sodium hydroxide or silicate tends to provide a much higher viscosity than desired. Recently, Barneoud-Chapelier et al. (2020) and Mundra (2021) verified this and have also shown that potassium-activated geopolymers exhibit a much lower viscosity than sodium-activated geopolymers. The previous research also showed that reductions in viscosity can

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be made through increases in water content. Another potential solution to high viscosity is to add polycarboxylate ether (PCE), a dispersant, which when added to the sodiumactivated geopolymers reduces the yield stress (Mundra, 2021). Other research has investigated the effects of mud contamination on geopolymer properties and has shown that mud contamination can either increase or decrease the viscosity (Mundra, 2021; Liu et al., 2019). Apart from the formulation becoming unpumpable, high viscosity can lead to adverse effects on other formulation properties and must be tailored to the specific field application.

#### **2.5.2 SET TIME**

Set time is a function of the formulation composition and environmental conditions of the cementing job being attempted, and the ideal set time is determined by the type of job. Precast concrete applications may require a set time that is completely different from that of a primary cementing job. Likewise, set times for deep casing strings are going to be very different than set times for shallow casing strings due to the amount of time required for placement of the cement in the appropriate location, and the optimum time for curing before drilling operations resume. As previously discussed, the set time of geopolymers has been shown to decrease with a decrease in particle size because the increased surface area of the solid precursors results in increased reaction rates (Kumar & Kumar, 2011; Somna et al., 2011). However, the main characteristic of fly ash that affects set time is the calcium content, because this can interfere with the polymerization process (Wattimena & Hardjito, 2017). Mundra (2021) and Pacheco-Torgal et al. (2014) showed that increasing CaO content of fly ash decreased the set times of geopolymers. Liu et al. (2019) also showed that set time at low temperatures of 51.67°C (125°F) can be extended with mud contamination or decreased with an increase in pressure. However, other work done on mud contamination showed a decrease in set time as a result of contamination (Mundra, 2021). These studies demonstrated a range of set times anywhere from 2 hours to 24 hours. These results demonstrate the necessity for further experimentation into set time behavior and modification elevated temperature and pressure conditions.

#### **2.5.3 COMPRESSIVE STRENGTH**

One major advantage of using OPC is the relatively high compressive strength achieved across a variety of specified curing conditions. This has allowed OPC to become so successful as a building material. Class F fly ash-based geopolymers have been shown to achieve compressive strengths similar to OPC but only when cured at elevated temperatures. Values of compressive strength reported for geopolymer mortar and concrete have been in excess of 100 MPa (~14,500 psi) and 70 MPa (~10,100 psi) respectively (Van Deventer et al., 2012). Additionally, the greater the increase in the curing temperature, the greater the compressive strength (Rai et al., 2018). On the contrary, Nasvi et al. (2012) found that after curing above 60°C (140°F) for certain formulations, compressive strength was reduced. Bakharev (2005) showed that higher concentrated alkali silicate-activated geopolymers gained strength more rapidly when cured at 75°C (167°F) versus alkaline hydroxide-activated geopolymers.

Furthermore, the duration of curing does not appear to have the same beneficial effect on compressive strength of geopolymers as OPC. Mehta & Siddique (2017) have shown that geopolymers tend to have high early strength development where 97% of the 28 day strength was achieved at 7 days versus 70% of the 28 day strength for OPC. While the most appropriate curing temperature and duration for each formulation is still under evaluation, the observed compressive strengths are sufficient for geopolymers to be used.
Higher compressive strengths have also been associated with an increase in CaO content (Pacheco-Torgal et al., 2014). One study blended a low calcium Class F fly ash with a high calcium Class C fly ash to determine the effects of increasing amounts of calcium on the compressive strength of the geopolymer (Canfield et al., 2014). This study showed when only Class F fly ash was used, the geopolymer had a 20 MPa (2900 psi) compressive strength. However, when 60% of the Class F fly ash was replaced with Class C fly ash, the compressive strength of the geopolymer increased to 87.6 MPa (12,700 psi). Thus, the amount of calcium in the precursor material can significantly increase affect the compressive strength.

### **2.5.4 TENSILE STRENGTH**

The tensile strength of OPC cement is generally too low for direct tensile loading causing the need for additional materials to be incorporated into the project design. Syarif et al. (2018) found that the tensile strength of OPC mortar was 2.01 MPa (292 psi) corresponding to literature values found in Nelson and Guillot (2006), with the actual value being dependent on the compressive strength. Thus, the higher the compressive strength, the higher the tensile strength. In the oil and gas sector, there are no specifications for tensile strength of cements. However, it is known that lack of tensile strength is the cause of several zonal isolation issues and has been of concern since the 1920s when latex was introduced to cements to help increase tensile strength (Nelson and Guillot, 2006).

AAMs have been found to have higher tensile strength compared to OPC (Provis and van Deventer, 2014). Literature suggests that the ratio of splitting tensile strength to compressive strength for geopolymer concrete is 7.8% to 8.2% (Pacheco-Torgal et al., 2014). Another study focusing on Class G OPC has found this ratio to be 10% (James & Boukhelifa, 2008). Many factors can contribute to these conflicting values such as curing conditions or activator selection, as mentioned in prior sections. To provide a complete comparative analysis, more research must be completed. As will be shown later, however, geopolymer tensile strength behavior is quite promising when compared to OPC.

### **2.5.5 SHEAR BOND STRENGTH**

Tensile strength is not the only mechanical property that can be improved upon to mitigate zonal isolation concerns. The cement bond with the casing is a critical property preventing the creation of a micro-annulus and maintaining the integrity of the well. The shear bond strength for OPC at 20°C (68°F) is around 6.90 MPa (1000 psi) (Nelson and Guillot, 2006). It is important to note that this testing has been done at conditions that are free of contaminants. As previously shown, mud contamination on OPC has negative effects on compressive strength. This has also been observed with the shear bond strength by Evans & Carter (1962) and Liu (2017) where values became less than 0.69 MPa (100 psi).

Geopolymers have shown to be promising materials for bonding applications in several different industries. Within infrastructure, geopolymers are proven to be effective repair materials for concrete, brick, and stone due to the high quality of bonding observed (Davidovits, 2002). This may translate to superior bonding well with the formation and casing in petroleum operations as well. For example, a study on Class C fly ash-based formulations demonstrated shear bond strengths from 5.26 MPa (763 psi) to 7.81 MPa (1132 psi) (Shah, 2004). Another study by Liu (2017) showed that Class F fly ash-based geopolymers had shear bond strengths greater than 1.38 MPa (200 psi), and when contaminated with mud, had shear bond strengths that remained higher than the Class H OPC. The benefit offered by geopolymers over OPC-based cements is evident as in most cases the geopolymers provide higher shear bond strengths than OPC. However, as

mentioned in the description of other properties, further testing should be conducted to better understand the performance of each source material and associated formulation.

#### **2.6 APPLICATIONS**

Due to the high variation in fly ash composition and sufficient properties observed, Class F fly ash-based geopolymers have the potential to be incorporated into many different cementing projects. These projects can consist of civil engineering-related projects like precast operations or petroleum-related projects such as primary and remedial cementing. The following sections will present some of the projects that are associated with these two industries to provide an account for where the implementation of geopolymers currently stands and could be considered in the future.

### 2.6.1 APPLICATIONS – CONSTRUCTION INDUSTRY

AAMs have been utilized historically for a wide variety of applications. As a result of their fireproof characteristic, many industries have incorporated the use of them for the development of new products. Fireproof panels and other shields have been designed out of geopolymers (Davidovits, 2002). Pavements made from AAMs have also been pursued (Provis and van Deventer, 2014; Davidovits, 2002). A company in Australia has developed a binder called E-Crete which has been standardized for non-structural applications and is being explored for structural applications (Provis and van Deventer, 2014). Along with Australia, Russia and China have completed several significant infrastructure projects using AAMs (Provis and van Deventer, 2014), creating buildings, retaining walls, and bridges. While there are many projects that can and have utilized AAMs, the current use of AAMs in the civil industry is believed to have reached its full potential. The fact that many Class F fly ash-based geopolymer formulations requiring thermal curing has limited the options for implementation as indicated earlier.

### **2.6.2 APPLICATIONS – PETROLEUM INDUSTRY**

While the environment for implementing Class F fly ash-based geopolymers in the petroleum industry is much more favorable than the construction industry since oilfield cements harden by thermal curing, few projects have utilized geopolymers. In the study previously discussed by Shah (2004), two wells were chosen to be candidates for plugging operations applying Class C fly ash-based slurries. However, the outcome of that procedure is unknown. Class F fly ash-based geopolymers are also being considered for multiple types of cement jobs within the CODA consortium. Yard trials are being conducted with a well cementing company to determine the most appropriate formulation for a field trial in Canadian well construction and abandonment operations in the future. The result of this research supports this field trial preparation, and will hopefully create additional opportunities for field use.

# **CHAPTER 3.** MATERIALS AND METHODS

## **3.1 MATERIALS**

## **3.1.1 FLY ASH COMPOSITION**

The aluminosilicate precursor material chosen for this research was Class F fly ash according to ASTM C618-19 (ASTM, 2019) due to the desirable rheological properties, set times, and strengths that have been observed when alkali-activated. Nine different fly ash samples were chosen to be studied in this research, and XRF analysis was performed on each fly ash sample to determine the complete oxide composition of the fly ash. This testing was performed in accordance with ASTM C311 by Wyoming Analytical Laboratories, Inc., and the results for the oxide composition, moisture, and loss on ignition (LOI) are presented in Table 3.1. The fly ash name is also included in Table 3.1 with the abbreviation used throughout the remainder of the Chapters.

Un- beneficiated Georgetown (GTUFA)	Battle River (BRFA)	Kingston (KIFA)	Georgetown (GTFA)	Craig (CRFA)	Delta (DLFA)	San Miguel (SMFA)	Cumberland (CUFA)	Newburg (NBFA)	Sample I.D.
48.81	56.23	40.54	53.73	48.91	52.25	53.12	49.37	44.67	$SiO_2$
25.28	21.59	17.78	27.55	20.28	17.05	19.05	20.81	23.17	Al <sub>2</sub> O <sub>3</sub>
8.90	4.55	12.22	9.95	4.91	4.51	1.97	15.96	24.21	Fe <sub>2</sub> O <sub>3</sub>
82.99	82.37	70.54	91.24	74.10	73.80	74.14	86.15	92.06	(SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> )
2.01	8.55	8.10	2.22	8.50	7.24	4.42	4.66	3.15	CaO
0.92	1.34	1.90	1.00	2.37	1.71	0.85	1.88	0.76	MgO
1.76	4.21	2.04	1.95	1.40	2.44	4.53	2.29	1.02	Alkalis (Na <sub>2</sub> O+ 0.658K <sub>2</sub> O)
0.24	0.29	1.62	0.37	0.31	0.72	0.30	1.95	0.62	$SO_3$
1.94	1.75	1.79	2.15	2.55	1.41	1.32	1.46	1.65	Other Oxides
0.46	0.18	0.33	0.04	0.15	0.24	0.24	0.18	0.22	Moisture
9.34	0.89	13.42	0.37	10.35	12.27	13.76	0.93	0.42	LOI

 Table 3.1:
 Oxide Composition, Moisture, and LOI of Fly Ash Samples (Wt %).

## **3.1.2 FLY ASH SOURCE LOCATION**

The nine fly ash samples were chosen with the intent to test fly ash materials from different parts of the United States to elucidate their variety in fluid and hardened geopolymer properties. This was also done to understand the possibility of using that source for future well construction in nearby locations. One sample was also obtained from a powerplant in Battle River, Alberta, Canada. The specific locations for the United States based sources are shown in Figures 3.1 and 3.2.



Figure 3.1: Fly Ash Source Locations from SEFA\* (Source Locations, 2021).

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Figure 3.2: Fly Ash Source Locations from Boral\* (Locations / Boral Resources, 2021).

## **3.1.3 FLY ASH PARTICLE SIZE DISTRIBUTION**

The particle size of the fly ash is known to affect both fluid and hardened properties, as mentioned previously. Thus, the particle size distribution (PSD) of each fly ash was measured using a Mastersizer 2000 particle size analyzer with a Hydro 2000MU accessory unit. Isopropyl alcohol was used as a dispersant with a refractive index of 1.39. Isopropyl alcohol was chosen because it prevents the fly ash particles from hydrating during the PSD measurement. The refractive index and absorption values for the fly ash were determined to be 1.56 and 1, respectively from findings in literature for Class F fly ash (Jewell and Rathbone, 2009). The testing procedure used for the PSD analysis of each fly ash was as follows:

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Step 1. Properly circulate the isopropyl alcohol at 2300 rpm.

Step 2. Add fly ash until obscuration reaches 5% to 15%.

Step 3. Turn on ultrasonic probe for 30 seconds at setting 10.

Step 4. Wait 5 minutes after sonication is complete.

Step 5. Run test for five times and take average data for PSD.

The results of the PSD analysis for all fly ash samples can be seen in Figures 3.3, 3.4, and 3.5. All fly ash samples demonstrated an approximately unimodal distribution except GTFA. The summarized results of the PSD analysis for each fly ash can be seen in Table 3.2.



Figure 3.3: Percent volume PSD for BRFA, CRFA, and CUFA.



Figure 3.4: Percent volume PSD for DLFA, GTFA, and GTUFA.



Figure 3.5: Percent volume PSD for KIFA, NBFA, and SMFA.

Sample I.D.	d <sub>10</sub> (μm)	d <sub>50</sub> (µm)	d <sub>90</sub> (µm)	Specific Surface Area (m <sup>2</sup> /g)
NBFA	2.879	16.835	58.874	0.429
CUFA	1.807	14.132	69.282	0.512
SMFA	4.783	25.618	108.177	0.289
DLFA	2.609	20.969	79.425	0.39
CRFA	2.007	17.400	74.195	0.459
GTFA	2.458	16.556	104.689	0.437
KIFA	3.077	13.893	56.084	0.434
BRFA	2.298	20.505	117.278	0.413
GTUFA	3.676	34.997	176.805	0.287

Table 3.2:PSD Quantitative Results for all Fly Ash Samples.

# **3.1.4 PORTLAND CEMENT**

In order to compare the geopolymer testing results to OPC, Class H Portland cement (API 10A, 2019) was used. The chemical composition provided by the supplier for the Class H cement is given in Table 3.3.

 Table 3.3:
 Oxide Composition and LOI of Class H cement (Wt %).

Sample I.D.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O <sub>eq</sub>	SO <sub>3</sub>	LOI
OPC	22.1	4.5	2.7	64.4	2.5	2.0	2.8	1.1

# **3.1.5** ALKALINE ACTIVATORS

This research studied the properties of hydroxide- and silicate-activated geopolymers. Liquid potassium hydroxide (LPH) and liquid sodium hydroxide (LSH) solutions were made using reagent grade pellets (Fisher Chemical) dissolved in deionized (DI) water with resistivity of 18 M $\Omega$ -cm. The silicate activators used were liquid potassium silicate (LPS), solid potassium silicate (SPS), liquid sodium silicate (LSS), and solid sodium silicate (SSS) supplied by PQ Corporation. The typical silicate properties can be found in Tables 3.4 and 3.5.

Table 3.4:Solid Silicate Properties.

PQ Silicate Name	Wt Ratio SiO <sub>2</sub> :M <sub>2</sub> O	Wt % M <sub>2</sub> O	Wt % SiO <sub>2</sub>	Wt % H <sub>2</sub> O	Density (g/cm <sup>3</sup> )	Particle Size
KASOLV 16	1.60	32.5	52.8	14.5	0.69	99% thru 40 mesh
GD	2.00	27.0	54.0	18.0	0.73	75% thru 100 mesh

Table 3.5:Liquid Silicate Properties.

PQ Silicate	Wt Ratio	Wt %	Wt %	Density	Viscosity (ops)
Name	SiO <sub>2</sub> :M <sub>2</sub> O	$M_2O$	SiO <sub>2</sub>	$(g/cm^3)$	viscosity (cps)
KASIL 6	2.10	12.7	26.5	1.38	1050
Ν	3.22	8.9	28.7	1.38	180

### **3.2 METHODS**

### **3.2.1 MIXING AND PREPARATION – GEOPOLYMER SLURRY**

To make geopolymer slurries, hydroxide solutions were prepared to the desired concentration by adding the hydroxide pellets to the DI water. This solution was then allowed to cool to room temperature before adding the fly ash to the solution and stirring together completely by hand, making sure that no dry clumps of fly ash particles remained. The geopolymer slurry was then mixed with a paddle stirrer on a drill press at 850 rpm for 35 seconds. This procedure is how the LPH and LSH slurries were made.

When using silicate activation, the process was very similar. However, the introduction of the silicates to the solution happened in several different times. For this research, both liquid and solid silicates were added as the fly ash was being mixed with solution. For liquid silicates, they were added to a previously prepared hydroxide solution and stirred for 30 seconds with a magnetic stirrer to allow for good dispersion before combining with fly ash. The solid silicates were added to the dry fly ash and mixed in by hand until no silicate was seen. After this, the fly ash (liquid silicate case) or fly ash-silicate combination (solid silicate case) was then added to the liquid hydroxide solution and the mixing process followed as described for LPH and LSH.

### 3.2.2 MIXING AND PREPARATION – OPC SLURRY

OPC slurries were prepared in accordance with API RP 10B-2 (2019). DI water was mixed with Class H Portland cement at the desired ratio and then placed in an appropriate high shear mixer for the 35 seconds.

### **3.2.3 MIX PROPORTIONS**

The concentration of the solutions for this research, LPH and LSH, were 8 M as it has been found in literature that 8 M solutions provide a practical and efficient means of activation (Ahmari & Zhang, 2015; Aughenbaugh, 2013). The water to solids ratio (W/S) for all mixes was set at 0.33 as previous work has shown W/S from 0.30 to 0.36 for Class F fly ash-based geopolymers activated with potassium or sodium alkaline solutions provides appropriate rheological properties (Mundra, 2021). Please note that the W/S considers the addition of water from the respective silicate with the original DI water while solids are considered hydroxide pellets, fly ash, and the solid portion of the silicates.

Proportioning of the silicates was based on previous work done by Liu (2017) and Mundra (2021). The SiO<sub>2</sub> / M<sub>2</sub>O ratio (M signifies K or Na) for potassium and sodium activation was set at 0.12. The M<sub>2</sub>O / FA ratios for potassium and sodium activation were set at 0.2 and 0.1, respectively. Additionally, a second M<sub>2</sub>O / FA ratio of 0.2 for sodium activation was studied only for NBFA, CUFA, and SMFA. A summary of the mix proportions can be found in Table 3.6.

OPC was mixed with DI water based on a water by weight of cement (bwoc) ratio equal to 0.385. This ratio can also be referred to as the water to cement ratio (W/C) which is equivalent to the W/S. Only OPC and DI water were used for the OPC mix.

MIX I.D.	Activator	W/S	SiO <sub>2</sub> /M <sub>2</sub> O	M <sub>2</sub> O/FA
LPH	8 M Liquid Potassium Hydroxide	0.33		
LPS	Liquid Potassium Silicate (KASIL 6)	0.33	0.12	0.2
SPS	Solid Potassium Silicate (KASOLV 16)	0.33	0.12	0.2
LSH	8 M Liquid Sodium Hydroxide	0.33		
LSS	Liquid Sodium Silicate (N)	0.33	0.12	0.1
SSS	Solid Sodium Silicate (GD)	0.33	0.12	0.1
0.2LSS	Liquid Sodium Silicate (N)	0.33	0.12	0.2
0.2888	Solid Sodium (GD)	0.33	0.12	0.2
OPC	DI Water	0.385		

Table 3.6: Mix Designs.

#### **3.2.4 Rheology**

Rotational viscometer testing allows for the rheological properties of the slurry to be determined, which can be important in deciding how pumpable a mix is. Following the recommended practices of API RP 10B-2 (2019), the geopolymer slurry was prepared and placed in the rotational viscometer. An F1.0 spring and an R1B1 rotor and bob configuration were used. The test was then performed to measure the viscosity of the slurry. Comparing shear stress versus shear rate lets the slurry be categorized as a specific fluid type (Bingham, Herschel – Bulkley, etc.) and aids in the determination of the viscosity of the slurry by measuring the slope. In this work, all geopolymer slurries were modeled as Herschel–Bulkley fluids to determine the rheological constants and compared to OPC. The model in Equation 3.1 was used:

$$\tau = \tau_{\nu} + k \times \gamma^n \qquad Equation 3.1$$

where:

 $\tau$  is the shear stress in Pa (lbf/100ft<sup>2</sup>)  $\tau_y$  is the yield stress in Pa (lbf/100ft<sup>2</sup>) *n* is the flow behavior index, dimensionless  $\gamma$  is the shear rate in s<sup>-1</sup>

*k* is the consistency index in Pa.s<sup>n</sup> (lbf.s<sup>n</sup>/100ft<sup>2</sup>)

# **3.2.5 SET TIME**

To determine the set time and pumpable limits of geopolymer slurries, the recommended practices of API RP 10B-2 (2019) were followed. A pressurized consistometer was used, where the geopolymer slurry sample was poured into the slurry container. Once placed in the slurry container and sealed with all required components of

the container assembly, it was loaded into the consistometer. After all preparation was complete, the test was initialized so the set time could be determined. The set time was determined by the amount of time it takes for the slurry to reach a consistency of 70  $B_c$  (Bearden units) based on equivalent values for the torque applied to the paddle. Acceptable set times vary with the application, so geopolymer set times were compared to set times of OPC.

Geopolymer slurries were subjected to four different testing schemes based of temperature and pressure. Figures 3.6 and 3.7 show the initial timeframe for each scheme. All schemes had an initial starting temperature of 23°C (room temperature). The last scheme, labeled as Scheme 4, was developed for analyzing the set time of the geopolymer slurry when subjected to a condition like that of a precast operation. The other three schemes are designed for well cementing operations. Bottomhole circulating temperature (BHCT) was determined from API RP 10B-2 (2019), and the bottomhole pressure (BHP) was set at 20.68 MPa (3000 psi) due to the limits of the curing chamber. Once the final conditions had been met, the consistometer testing ran until the consistency reached 70 Bc. The specific parameters can be seen in Table 3.7. Please note that all schemes started from 101.1kPa (atmospheric pressure). However, Schemes 1, 2, and 3 jumped up to an initial pressure of 6.89 MPa (1000 psi) once the test was started.



Figure 3.6: Initial Temperature Profiles for Set Time Testing Schemes (for first 250mins).



Figure 3.7: Initial Pressure Profiles for Set Time Testing Schemes (for first 250 mins).

Sahama	Initial	Final	Ramp	Initial	Final	Ramp	
Scheme	Temp.	Temp.	Time	Pressure	Pressure	Time	
1	23°C	51.67°C	120 mins	6.89 MPa	20.68 MPa	120 mins	
	(73.4°F)	(125°F)	120 111113	(1000 psig)	(3000 psig)	120 111118	
2	23°C	100°C	150 mins	6.89 MPa	20.68 MPa	150 mins	
	(73.4°F)	(212°F)	150 mms	(1000 psig)	(3000 psig)	150 11115	
3	23°C	135°C	180 mins	6.89MPa	20.68 MPa	180 mins	
	(73.4°F)	(275°F)	100 111113	(1000 psig)	(3000 psig)	100 111115	
4	23°C	76.67°C	100 mins	101.1 kPA	101.1 kPA	100 mins	
	(73.4°F)	(170°F)	100 111115	(14.7 psia)	(14.7 psia)	100 111115	

 Table 3.7:
 Consistometer Parameters for Set Time Testing Schemes.

#### **3.2.6** Atmospheric Pressure Curing

Atmospheric pressure curing was done in order to replicate curing conditions in a precast concrete operation with conditions slightly warmer than currently used in the industry. Cylindrical samples were cast in molds and cured in water baths at 76.67°C (170°F) for 3, 7, and 28 days. Once the desired curing time was reached, the samples were demolded and tested. Three replicate samples were made for each test for each geopolymer formulation at each curing time. All results were compared to OPC values cured at the same conditions, and three replicates were also performed in this case for all tests.

### **3.2.7 PRESSURIZED CURING**

Pressurized curing was done in order to simulate downhole well conditions. This curing was done according to API RP 10B-2 (2019). Similar to the atmospheric curing procedure, only 3 cylindrical samples of each mix were made. These samples were only cured for 3 days, and curing conditions were based on the BHCT, BHP, and bottomhole

static temperature (BHST). The initial temperature profiles for Schemes 1, 2, and 3 (same labeling as above) are shown in Figure 3.8 while the pressure profile was set constant (initial and final pressures) for all three schemes at 20.68 MPa (3000 psi) due to the limits of the curing chamber. The specific parameters can be seen in Table 3.8. OPC was also cured in these conditions and compared to the geopolymers.



Figure 3.8: Initial Temperature Profiles for Curing Chamber (for first 1000 mins).

Sahama	Initial	DUCT	Ramp	DUCT	Ramp	Constant
Scheme	Temp.	DICI	Time	рцэт	Time	Pressure
1	23°C	51.67°C	120 mins	76.67°C	600 mins	20.68 MPa
	(73.4°F)	(125°F)	120 111115	(170°F)	000 111113	(3000 psig)
2	23°C	100°C	150	135°C		20.68 MPa
_	(73.4°F)	(212°F)	150 mins	(275°F)	600 mins	(3000 psig)
3	23°C	135°C		204.44°C		20.68 MPa
	(73.4°F)	(275°F)	180 mins	(400°F)	600 mins	(3000 psig)

 Table 3.8:
 Curing Chamber Parameters for Temperature and Pressure.

### **3.2.8 UNCONFINED COMPRESSIVE STRENGTH (UCS)**

The UCS test provides the compressive strength at which the material fails with no confining support. UCS testing was performed on geopolymer and OPC cylinders (5.1 cm (2 in) diameter  $\times$  10.2 cm (4 in) length) in accordance with ASTM C39/C39M (2021). Plastic molds were used for atmospheric curing while brass molds were designed for pressurized curing and can be seen in Figure 3.9. After the sample was demolded, it was placed in an appropriate load frame specified in the standard and then preloaded to 1.11 kN (250 lbf) after which the load was applied at a uniform load rate of 0.331 MPa/s (48 psi/s) until complete failure. The UCS was determined by Equation 3.2:

$$UCS = \frac{P}{A}$$
 Equation 3.2

where:

UCS is the unconfined compressive strength in MPa (psi)

*P* is the maximum load in MN (lbf)

A is the average cross – sectional area in  $m^2$  (in<sup>2</sup>)



Figure 3.9: Mold Assembly designed and used for Curing Chamber.

# **3.2.9** TENSILE STRENGTH (BRAZILIAN SPLIT TENSION TEST)

Guided by ASTM C496 (2017), splitting tensile test for cylindrical concrete specimens, the splitting tensile strength of the geopolymer and OPC cylinders (5.1 cm (2 in) diameter  $\times$  10.2 cm (4 in) length) were determined. The loading frame designed for this testing is shown in Figure 3.10. The importance for tensile strength has not been heavily stressed in the oil well cementing field, thus this testing procedure was used to determine the tensile strength of the geopolymer and OPC samples. The cylindrical sample was placed in the load frame on its long side and preloaded to 0.445 kN (100 lbf) after which the load was applied at a uniform load rate of 0.083 MPa/s (12 psi/s) until complete failure occurred. This allows for the center of the sample to be in complete tension where a tensile fracture is created, and the equivalent load is recorded as the load causing tensile failure.

Applying that value to Equation 3.3 results in the splitting tensile strengths of the geopolymer sample. The calculated splitting tensile strengths of the geopolymer samples were then compared to OPC samples.

$$T = \frac{2P}{\pi ld}$$
 Equation 3.3

where:

T is the splitting tensile strength in MPa (psi)P is the maximum load in MN (lbf)l is the average length in m (in)d is the average diameter in m (in)



Figure 3.10: Test Setup for Splitting Tensile Test.

# **3.2.10 SHEAR BOND STRENGTH**

To determine the shear bond strength of the geopolymer and OPC to steel, a pushout procedure was designed following work completed by Liu (2017) and Genedy et al. (2017). For non-pressurized curing, this consisted of placing the slurry into a PVC pipe section that was attached to a stainless steel base creating the mold. A polished stainless steel rod was then positioned in the center of the mold, and the slurry was placed in the mold around the rod. Once the slurry hardened at the desired curing conditions for the desired time, the sample-mold assembly without the base was placed into a loading machine for the pushout test. The rod was preloaded to 1.11 kN (250 lbf), after which the load was applied at a uniform load rate of 0.055 MPa/s (8 psi/s). When the assembly failed, the max loading value was recorded and used to calculate the bond strength of geopolymers and OPC by Equation 3.4. The design of the assembly can be seen in Figure 3.11. For pressurized curing, the process was the same except that the samples were cured in the brass cylindrical molds previously shown. All load rates, sample dimensions, and rod diameters were kept the same.

$$BS = \frac{P}{\pi ld}$$
 Equation 3.4

where:

BS is the shear bond strength in MPa (psi)P is the maximum load in MN (lbf)l is the average length sample cover rod in m (in)

d is the average diameter of the rod in m (in)

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Figure 3.11: Diagram of the Shear Bond Strength Assembly.

# **CHAPTER 4.** RESULTS AND DISCUSSION

## 4.1 RHEOLOGY

As discussed in Chapter 3, nine different Class F fly ash samples with various alkaline activators were evaluated for use as geopolymers. Rheological constants were first determined for each fly ash and activator combination to understand how the different fly ashes and activators impact geopolymer rheology. The shear stress versus shear rate plot and Herschel-Bulkley rheological constants from rheology testing for each fly ash are given below supplemented with a discussion of the results. The dial readings for the 300 rpm and 100 rpm shear rates are also presented. This has been provided as desirable slurries for well cementing should have dial readings less than 200 at 300 rpm and dial readings less than 100 at 100 rpm. In civil engineering industries, there are no acceptable limits because pumping of concrete involves the inclusion of aggregate. Direct comparison is therefore difficult. However, the formulations have been compared to OPC since it is typically used. All results are the average of three tests with error being determined by a T-distribution considering a 95% confidence interval.

### 4.1.1 NBFA

The rheology of NBFA formulations fell into two distinct groups, as seen in Figure 4.1. The sodium-activated formulations were very viscous, and only the LSH slurry could be tested past 100 rpm with the equipment. However, the potassium-activated formulations were far less viscous and displayed a more desirable behavior for well cementing operations with dial readings in the range of 200 and 100 for 300 rpm and 100 rpm, respectively. While the rheological behaviors of geopolymer formulations with LPH, LPS, and SPS were more desirable when compared to the sodium-activated formulations, these formulations remained slightly more viscous at higher shear rates compared to OPC. This

can be observed from all the geopolymer formulations having a flow index (n) of approximately 1. Thus, these formulations could be considered Bingham plastic fluids (0.95 < n < 1.05) with a different shear thinning behavior then OPC.



Figure 4.1: Shear Stress vs. Shear Rate for NBFA and OPC Mixes.

	LSH	0.2LSS	LSS	0.2SS	SSS
Ty (Pa)	2.87±0.21	1.38±0.09	1.05±0.72	2.10±1.01	4.31±2.40
k (Pa.s <sup>n</sup> )	0.84±0.30	2.71±0.46	2.04±0.48	3.74±0.43	1.69±0.51
п	$1.00\pm0.05$	0.99±0.00	$1.00\pm0.01$	$0.98 \pm 0.01$	1.02±0.05
300 rpm	N/A	N/A	N/A	N/A	N/A
100 rpm	292±26	N/A	N/A	N/A	N/A
	Potassium-A	ctivated Mixe	es		
	LPH	LPS	SPS	OPC	
Ty (Pa)	2.62±0.98	0.57±0.93	3.20±1.05	6.70±0.37	
k (Pa.s <sup>n</sup> )	0.18±0.09	0.19±0.05	0.22±0.04	3.87±0.73	
п	1.02±0.08	1.01±0.10	1.04±0.04	$0.46 \pm 0.06$	
300 rpm	210±61	210±85	298±33	133±29	
100 rpm	72±20	70±23	99±9	77±8	

 Table 4.1:
 Rheological Properties and Dial Readings for NBFA and OPC Mixes.

### 4.1.2 CUFA

All formulations made with CUFA showed reduced viscosities compared to the corresponding formulations made with NBFA, as shown in Figure 4.2. CUFA-based geopolymers made with LPH, LPS, and SPS had favorable rheological behaviors for well cementing, with shear stress values consistently below OPC for the entire duration of the test and dial readings below 100 for both 300 rpm and 100 rpm readings. Furthermore, geopolymers made with LPH and SPS had YPL shear thinning behaviors, with lower flow indices (n=0.87) than the other formulations (n~1). The sodium-activated formulations, LSH, LSS, and SSS, also showed to be potential well cementing candidates at low shear rates with 100 rpm dial readings of 92, 160, and 169, respectively. However, the CUFA formulations made with 0.2LSS and 0.2SSS proved to be too viscous and could not be tested at 100 rpm or higher.



Figure 4.2: Shear Stress vs. Shear Rate for CUFA and OPC Mixes.

Table 4.2:	Rheological Prop	erties and Dial R	eadings for	CUFA and	OPC Mixes.
	<i>, , , ,</i>		<b>1</b>		

	Sodium-Activated Mixes								
	LSH	0.2LSS	LSS	0.2SS	SSS				
Ty (Pa)	7.05±2.09	0.87±0.10	1.82±0.68	7.25±0.24	10.39±0.30				
k (Pa.s <sup>n</sup> )	0.29±0.03	$1.04 \pm 0.07$	0.46±0.06	1.18±0.04	0.53±0.04				
п	0.96±0.02	$1.01 \pm 0.00$	$1.01 \pm 0.01$	$0.98 \pm 0.00$	0.97±0.01				
300 rpm	235±15	N/A	N/A	N/A	N/A				
100 rpm	92±3	N/A	160±13	N/A	169±5				
	Potassium-A	ctivated Mixe	es						
	LPH	LPS	SPS	OPC					
Ty (Pa)	5.12±1.26	0.32±0.32	4.43±0.46	6.70±0.37					
k (Pa.s <sup>n</sup> )	0.16±0.04	0.09±0.01	0.21±0.01	3.87±0.73					
п	0.87±0.01	0.98±0.02	$0.87 \pm 0.00$	$0.46 \pm 0.06$					
300 rpm 78±21		81±3	103±2	133±29					
100 rpm	37±9	28±1	45±1	77±8					

## 4.1.3 SMFA

The SMFA formulations behaved very similar to those with NBFA. The shear stress vs. shear rate plots are shown in Figure 4.3, where a clear distinction is shown between sodium-activated formulations and potassium-activated formulations. All sodium silicate-activated formulations had high viscosities; LSH had slightly lower viscosity but still too high for well cementing operations with a 100 rpm dial reading of 312. By contrast, the potassium-activated formulations appeared to be far better options for well cementing and had desirable properties that overlapped with OPC for the most part. The dial readings for CUFA with potassium activation were less than 100 for both 300 rpm and 100 rpm readings. The rheological properties and dial readings shown in Table 4.3 are also similar those for NBFA values.



Figure 4.3: Shear Stress vs. Shear Rate for SMFA and OPC Mixes.

1.0						
		LSH	0.2LSS	LSS	0.2SS	SSS
	Ty (Pa)	2.94±0.43	1.17±1.51	0.54±0.46	3.72±1.10	2.86±0.28
	<i>k</i> (Pa.s <sup>n</sup> )	0.79±0.10	4.94±2.21	2.15±0.31	5.16±0.56	1.86±0.33
	п	1.03±0.02	1.03±0.02	$1.04 \pm 0.00$	$1.01 \pm 0.02$	$1.02\pm0.00$
	300 rpm	N/A	N/A	N/A	N/A	N/A
	100 rpm	312±4	N/A	N/A	N/A	N/A
		Potassium-A	ctivated Mixe			
		LPH	LPS	SPS	OPC	
	Ty (Pa)	1.88±0.22	$0.88 \pm 0.44$	2.68±0.65	6.70±0.37	
	k (Pa.s <sup>n</sup> )	0.16±0.04	0.15±0.03	0.20±0.06	3.87±0.73	
	п	$1.00\pm0.05$	1.07±0.02	$1.05 \pm 0.07$	$0.46 \pm 0.06$	
	300 rpm	161±15	227±25	282±41	133±29	
	100 rpm	56±4	72±8	92±7	77±8	

 Table 4.3:
 Rheological Properties and Dial Readings for SMFA and OPC Mixes.

## 4.1.4 DLFA

The DLFA formulations showed a wide range of variability between sodiumactivated formulations and potassium-activated formulations, as shown in Figure 4.4. DLFA with LSS developed a shear thickening behavior at low shear rates and had a significantly higher yield stress, while DLFA with LSH and SSS resembled Bingham plastic fluids but were characterized as Herschel-Bulkey fluids with flow indices of n=0.97. All sodium silicate-activated formulations had dial readings too high for well cementing, while DLFA with LSH could potentially be utilized at low shear rate since the dial reading at 100 rpm was 142. As also seen with the CUFA, the LPH, LPS, and SPS formulations had more desirable behaviors where the shear stress was constantly below OPC. Dial readings were within the limits for well cementing at low and high shear rates, and DLFA with LPH also showed to be shear thinning with a flow index of 0.88. Table 4.4 provides further details about the rheological properties and dial readings for DLFA.



Figure 4.4: Shear Stress vs. Shear Rate for DLFA and OPC Mixes.

	]				
	LSH	LSS	SSS		
Ty (Pa)	4.17±0.66	37.93±10.17	5.30±0.12		
k (Pa.s <sup>n</sup> )	0.48±0.17	0.12±0.15	0.77±0.02		
п	0.97±0.01	1.37±0.29	0.97±0.01		
300 rpm	N/A	N/A	N/A		
100 rpm	142±38	321±11	232±9		
	LPH	LPS	SPS	OPC	
Ty (Pa)	2.71±0.40	1.21±0.48	2.63±0.03	6.70±0.37	
k (Pa.s <sup>n</sup> )	0.18±0.07	0.13±0.13	$0.18 \pm 0.02$	3.87±0.73	
n	0.88±0.03	0.96±0.14	0.93±0.02	0.46±0.06	
300 rpm	90±18	94±13	124±3	133±29	
100 rpm	37±9	34±15	48±1	77±8	

 Table 4.4:
 Rheological Properties and Dial Readings for DLFA and OPC Mixes.

## 4.1.5 CRFA

The CRFA formulations had rheological profiles that were similar to DLFA, excluding LSS, as shown in Figure 4.5. CRFA made with LPH, LPS, and SPS were slightly less viscous compared to DLFA and had dial readings less than 100 for both, 300 rpm and 100 rpm readings. These formulations had shear stress values that remained below OPC, and CRFA made with LPH exhibited shear thinning properties once again with a flow index of 0.89. Likewise, CRFA made with LSH, LSS, and SSS were all less viscous than DLFA sodium-activated formulations. The rheological properties and dial readings listed in Table 4.5 show that the sodium-activated formulations could potentially be used for well cementing operations when slow shear rates are used with 100 rpm dial readings averaging a value of 150.



Figure 4.5: Shear Stress vs. Shear Rate for CRFA and OPC Mixes.

	LSH	0.2LSS	LSS		
Ty (Pa)	5.94±1.62	$1.52 \pm 1.36$	6.89±0.67		
k (Pa.s <sup>n</sup> )	0.41±0.14	0.47±0.02	0.69±0.14		
n	0.95±0.03	$1.02 \pm 0.01$	$0.96 \pm 0.01$		
300 rpm	310±44	N/A	N/A		
100 rpm	117±18	178±21	195±45		
	LPH	LPS	SPS	OPC	
Ty (Pa)	3.67±0.09	$0.29 \pm 0.22$	2.38±0.12	6.70±0.37	
$k(\mathbf{Pas}^{n})$	$0.15 \pm 0.02$	$0.00 \pm 0.01$	$0.14 \pm 0.01$	$287\pm072$	
$\kappa$ (1 a.s.)	$0.13\pm0.02$	$0.08\pm0.01$	$0.14\pm0.01$	$3.07\pm0.73$	
$\frac{\kappa (1 a.s)}{n}$	0.13±0.02 0.89±0.03	0.08±0.01 0.99±0.02	0.14±0.01 0.92±0.01	0.46±0.06	
$\frac{n}{300 \text{ rpm}}$	0.13±0.02 0.89±0.03 81±5	0.08±0.01 0.99±0.02 72±7	0.14±0.01 0.92±0.01 93±2	0.46±0.06 133±29	

 Table 4.5:
 Rheological Properties and Dial Readings for CRFA and OPC Mixes.

### 4.1.6 GTFA, KIFA, BRFA, AND GTUFA

LPH was the only formulation studied for these fly ashes due to limited amounts of the material available. These formulations were studied for high temperature applications only, but have been included in this section for the sake of completeness.

LPH formulations involving GTFA, KIFA, BRFA, and GTUFA did not seem to follow any specific pattern. Figure 4.6 shows that only GTFA and KIFA had similar rheology profiles. However, KIFA had a flow index of n=0.64 while GTFA had a flow index of 1.07 with a linear profile. The BRFA formulation showed a favorable viscosity profile and therefore has the potential to be a desirable well cement with dial readings at 300 rpm and 100 rpm below 100. On the contrary, the GTUFA formulation had a very high viscosity and was unable to be tested at 300 rpm. Table 4.6 provides a comparison of the rheological properties and dial readings for each fly ash sample made with LPH compared to OPC.



Figure 4.6: Shear Stress vs. Shear Rate for OPC and LPH with GTFA, KIFA, BRFA, and GTUFA.

Table 4.6:Rheological Properties and Dial Readings for OPC and LPH with GTFA,<br/>KIFA, BRFA, and GTUFA.

	GTFA	KIFA	BRFA	GTUFA	OPC
Ty (Pa)	3.81±1.03	11.37±0.71	2.03±0.11	2.79±0.59	6.70±0.37
k (Pa.s <sup>n</sup> )	$0.15 \pm 0.05$	1.78±0.59	0.11±0.00	0.83±0.10	3.87±0.73
п	$1.07 \pm 0.05$	0.64±0.09	0.92±0.01	0.95±0.00	0.46±0.06
300 rpm	243±14	208±41	72±4	N/A	133±29
100 rpm	80±5	111±9	28±1	217±22	77±8

## 4.1.7 IMPACT OF FLY ASH AND ACTIVATOR PROPERTIES ON RHEOLOGY

The CaO in the fly ash has been found in the literature to be a key contributor to geopolymer rheology, but this was not observed in this study (Mundra, 2021; Wattimena & Hardjito, 2017; Provis, 2014). For example, BRFA has the greatest amount of CaO at 8.55%, yet yielded the lowest viscosity LPH formulation of the nine different fly ash

samples being compared. This same occurrence can be seen when looking at the sodiumactivated formulations of the CUFA (CaO = 4.66%) compared to the SMFA (CaO = 4.42%). Figure 4.7 shows the trend for all LPH formulations where dial readings at 300 rpm were initially decreasing as the amount of CaO in the fly ash increased. However, at CaO contents greater than 4.5%, the dial readings changed little or increased with no clear pattern observed. Thus, there appears to be no significant correlation between the amount of CaO in the fly ash samples and the rheological profiles of the geopolymer formulations.



Figure 4.7: 300 rpm Dial Reading vs. CaO Percent for all Fly Ashes with LPH.

The particle size and specific surface area are two other properties of fly ash that have been shown to affect the rheological profile of the geopolymer formulation Wattimena & Hardjito, 2017; Bentz et al., 2012). It has been shown that finer (higher specific surface area and smaller particle size) fly ash samples resulted in less viscous formulations (Wattimena & Hardjito, 2017). Once again, it appears that this is not the case for the fly ash samples chosen in this research. The CUFA is the finest fly ash sample in this research and produced many low viscosity formulations with both sodium and potassium activation. However, KIFA and CRFA made with LPH have specific surface areas of 0.434 m<sup>2</sup>/g and 0.459 m<sup>2</sup>/g, respectively, and similar PSDs, but the resulting LPH formulations have significantly different rheologic profiles. Figure 4.8 shows the specific surface area of all fly ash samples made with LPH compared to the 300 rpm dial readings and the trend is similar to CaO percent vs. 300 rpm dial reading. Initially, the higher specific surface area fly ashes have higher dial readings and as the specific surface area decreases the dial readings decrease. However, this behavior changes near the specific surface area of 0.425 m<sup>2</sup>/g, where the dial readings remain at similar values or increase with increasing surface area.



Figure 4.8: 300 rpm Dial Reading vs. Specific Surface Area for all Fly Ashes with LPH.

One other important parameter that can determine the behavior of the rheological properties is the activator (Provis & Bernal, 2014). In this research, as expected, the sodium-activated formulations were always more viscous than the potassium-activated formulations for each fly ash sample. Furthermore, it was shown that sodium silicate activation provided an increase in the viscosity of the formulations compared to sodium
hydroxide activation. The addition of more sodium hydroxide and silicate in the case of 0.2LSS and 0.2SSS appeared to increase the viscosity even further. The opposite, however, was shown in potassium silicate activation where all potassium activated mixes had similar rheological profiles.

#### 4.1.8 SUMMARY AND DISCUSSION

After observing the different rheological profiles from all the fly ash and activator combinations, it is clear that no single characteristic of the formulation dictates the outcome of the rheology profile. Considering the dial readings and rheological profiles observed, there are many potential geopolymer formulations that could be used for well construction purposes. Potassium activation appears to be preferable, because the geopolymers created were generally less viscous than those with sodium activation. There are several sodiumactivated formulations that also have the potential for use in well cementing if low shear rates are chosen. However, most sodium silicate formulations are too viscous and better suited for civil engineering purposes. Ultimately, all formulations could be used within civil engineering industries as the pumpable limits are less restrictive compared to well cementing.

# 4.2 SET TIME

The set time of each geopolymer formulation was determined with respect to several different temperature and pressure conditions to represent different downhole curing conditions. This was done to determine how long the formulation would remain pumpable at the specified conditions. Acceptable set times for well cementing can range from 1 hour to 9 hours depending on the job type and downhole environment (Mundra, 2021). For civil engineering applications, the set time was determined for analysis of how

long pumpability would exist for each formulation and compared to OPC, but an acceptable limit was not set. Mechanical properties were used to determine if a formulation was acceptable for civil engineering applications. A description of the results from each condition can be found below with a listing of the set times to follow. All results are the average of three tests with error being calculated from a T-distribution assuming a 95% confidence interval.

### **4.2.1 ATMOSPHERIC PRESSURE CONDITION**

Curing under atmospheric pressure condition was done to simulate the conditions in precast concrete operations. Table 4.7 provides the set times for NBFA, CUFA, SMFA, DLFA, and CRFA activated with a variety of different activators when subjected to the same conditions of 76.67°C ( $170^{\circ}$ F) and atmospheric pressure. Please note these fly ash samples were the only ones used for this testing due to inadequate amounts of the other fly ashes available. Sodium activation, both sodium silicate and sodium hydroxide, provided a narrow range of set times from 1 to 2 hours across all fly ash samples. This was very similar to the set time of OPC, which was 1.5 hours. It should also be noted that silicate activation of NBFA and SMFA resulted in initial consistency values above the pumpable limit of 70 Bc but as temperature increased, the consistency fell below 70 Bc. When looking at the set times of the potassium-activated mixes, there is greater variability between formulations. DLFA, CRFA, and SMFA made with LPS and CRFA made with SPS had very short set times compared to the rest of the results for potassium activation. LPH for all fly ash samples besides DLFA tended to have the longest set times, anywhere from 12 hours to never setting within a 24 hour period. As can be seen, there are a variety of set times for all activator and fly ash combinations that could be useful depending on the application for which it is proposed.

FA Source/Activator	NBFA	CUFA	SMFA	DLFA	CRFA
LSH	$1:31 \pm 3$	$1:35 \pm 4$	$1:04 \pm 1$	1:07 ± 3	$0:59 \pm 2$
LSS	$1:24 \pm 5*$	$1:26 \pm 1$	xx:xx	$1:04 \pm 1$	$0:53 \pm 2$
0.2LSS	$1:43 \pm 1*$	$1:32 \pm 6$	$1:04 \pm 1*$	N/A	N/A
SSS	$1:40 \pm 5^{*}$	$1:35 \pm 3$	xx:xx	$1:13 \pm 1$	$0:54 \pm 2$
0.2888	$1:45 \pm 2*$	$1:44 \pm 4$	xx:xx	N/A	N/A
LPH	$22:41 \pm 30$	:	$14:26 \pm 32$	$5:57 \pm 10$	$12:16 \pm 14$
LPS	$15:34 \pm 51$	$10:43 \pm 35$	$1:49 \pm 9$	$0:37 \pm 2$	$1:13 \pm 5$
SPS	$15:21 \pm 17$	$10:38\pm29$	5:07 ± 37	$11:59 \pm 22$	$3:12 \pm 2$

Table 4.7: Summary of Set Times at 76.67°C ( $170^{\circ}$ F) (hh:mm ± mm).

OPC 1:27 ± 2

\* denotes that FA Source/Activator initial consistency was above 70 Bc

--:-- denotes that FA Source/Activator never set within 24 hr. period

xx:xx denotes that FA Source/Activator too thick to test (beyond limits of machine)

N/A denotes that FA Source/Activator not tested

### 4.2.2 PRESSURIZED CONDITION – NBFA

To replicate downhole conditions more appropriately, the temperature and pressure profiles listed in Chapter 3 have been utilized for testing in this section. NBFA was the only fly ash sample that was chosen for this method based on prior findings (Mundra, 2021; Liu, 2017). Utilizing one fly ash sample allowed for all activators to be analyzed at three different temperature profiles in order to observe the effects of elevated temperatures on set time. Table 4.8 shows the results for the NBFA formulations at the different temperature conditions. At a relatively low (for oilfield purposes) BHCT of 56.67°C (125°F), no formulations would set within a 24 hour period. However, with the addition of sodium silicate, LSS and SSS eventually set at around 18 hours and 14 hours, respectively. When the BHCT was increased to 100°C (212°F), all formulations had set times within 7 hours and thereby have the potential to be used in various well cementing jobs. As found in the

set time results associated with atmospheric pressure conditions, the sodium-activated formulations had a very small range of set times, which were comparable to OPC. Likewise, the potassium silicate-activated formulations had a narrower range of set times, while LPH was significantly longer. Increasing the BHCT even further to 135°C (275°F) caused the LPH set time to decrease considerably to the point where all potassium-activated formulations set within 2.5 hours, which is still within the acceptable range for well cementing. The sodium-activated formulations were not tested at the highest temperature condition due to poor mechanical properties of cured specimens. This will be discussed in sections 4.3 and 4.4.

Table 4.8:Summary of Set Times for OPC and NBFA at Different Temperature<br/>Conditions (hh:mm  $\pm$  mm).

Mix	56.67°C/20.68 MPa	100°C/20.68 MPa	135°C/20.68 MPa
LSH - NBFA	:	$1:42 \pm 3$	N/A
LSS - NBFA	18:41 ± 54*	1:32 ± 3*	N/A
SSS - NBFA	$13:52 \pm 98*$	$1:38 \pm 7*$	N/A
LPH - NBFA	:	$6{:}43\pm14$	$2:35 \pm 1$
LPS - NBFA	:	$3:14 \pm 4$	$2{:}35\pm14$
SPS - NBFA	:	$3:30 \pm 9$	$2:32 \pm 3$
OPC	$1:50 \pm 2$	$1:22 \pm 1$	$1:16 \pm 4$

\* denotes that FA Source/Activator initial consistency was above 70 Bc

--:-- denotes that FA Source/Activator never set within 24 hr. period

N/A denotes that FA Source/Activator not tested

#### **4.2.3 PRESSURIZED CONDITION – LPH**

Further testing was completed on the LPH formulations with all nine fly ash samples at 135°C (275°F) after it was observed that NBFA with LPH had a 2.5 hour set time. Unlike the results from the atmospheric condition testing, the LPH results shown in Table 4.9 are all very similar. Average set times ranged from just over 3 hours to around 2

hours, while the KIFA formulation was outside the range with a set time of 45 minutes. Apart from KIFA and GTFA, all fly ashes showed the potential for use in well cementing with appropriate set times.

Fly Ash	135°C/20.68 MPa
CUFA	$3:08 \pm 2$
SMFA	$2:53\pm7$
DLFA	$1:54 \pm 9$
CRFA	$2:07 \pm 3$
GTFA	$2:43 \pm 18$
KIFA	$0:45 \pm 5$
BRFA	2:34 ± 13
GTUFA	XX:XX

Table 4.9: Summary of Set Times for LPH at  $135^{\circ}$ C (275°F) and 20.68 MPa (3000 psi) (hh:mm ± mm).

xx:xx denotes that FA Source/Activator too thick to test (beyond limits of machine)

## 4.2.4 IMPACT OF FLY ASH AND ACTIVATOR PROPERTIES ON SET TIME

The fly ash composition appeared to play a minor role in the length of the set time like results observed from the rheological profiles. The amount of CaO may have some impact on the set time at lower temperatures and pressure as shown by CRFA and DLFA formulations having the shortest set times of the five fly ash samples in Table 4.7. However, the SMFA showed similar results as CRFA and DLFA, even though it had only half the CaO content. At higher temperatures and pressure, the effect of different fly ash compositions on set time became less pronounced. Table 4.9 shows that eight different LPH formulations had set times within an hour of each other.

While the amount of CaO in the fly ash did not seem to affect the set time, the opposite was observed with activator type. Sodium activation, either hydroxide or silicate,

resulted in shorter set times across all fly ashes, while potassium-activated formulations yielded much longer set times in most cases. The use of silicate activators compared to hydroxide also had an influence on the set time, where all silicate formulations were observed to decrease set time except for the 0.2LSS formulations, 0.2SSS formulations, and DLFA made with SPS.

### 4.2.5 SUMMARY AND DISCUSSION

A number of formulations showed favorable set times for a variety of well conditions. At 100°C (212°F), all formulations had set times that could be used for well cementing applications based on the specific job. When the formulations were subjected to elevated temperature and pressure conditions, the set times were reduced significantly as expected, but could still be used in well cementing. Comparing to OPC, the set times for sodium activation were always in the same time frame as OPC, while potassium activation set times were in general considerably longer. The shorter set times of the silicate-activated formulations could be used for small civil engineering applications requiring short placement times, while potassium-activated formulations could be used for large scale applications requiring longer set times.

Generally, the set times of geopolymers at low temperatures (56.67°C (125°F)) were found unfavorable for use in any industry because no formulation set within 10 hours. Set times that are too long lead to additional non-productive time in oil and gas well construction. Likewise, set times that are too short will create placement issues and not allow enough time for pumping. However, many of the formulations tested at elevated temperatures provided reasonable set times for various well cementing applications and precast concrete operations. In short, the correct formulation needs to be chosen for the correct application, and the work described here demonstrates the importance of proper

cement job preparation with the appropriate testing of geopolymer base material and activator(s).

#### **4.3 UNCONFINED COMPRESSIVE STRENGTH**

Cylindrical specimens were cured at atmospheric conditions and at pressurized elevated temperature conditions, for different temperature profiles and for different lengths of time. This allowed for the analysis of the evolution of compressive strength for different fly ash and activator combinations when subjected to different curing conditions. In well cementing, a minimum compressive strength of 3.45 MPa (500 psi) is required before operations cane continue (Nelson and Guillot, 2006). Thus, formulations providing compressive strengths equal to or greater than this value were considered acceptable. For civil engineering applications, no specific compressive strength requirement for paste alone has been suggested, but comparison to the OPC standard were made. A description of the results for each fly ash sample and activator can be found here, accompanied by plots showing the unconfined compressive strength results. All results are the average of three samples with error being calculated from a T-distribution assuming a 95% confidence interval.

## 4.3.1 ATMOSPHERIC PRESSURE, 76.67°C (170°F)

# 4.3.1.1 NBFA

The NBFA had several formulations that developed strength rapidly by the first 3 days of curing. Figure 4.9 shows that LSH, LSS, SSS, and LPS had a UCS greater than 15 MPa (2176 psi) at 3 days. At 7 days, the UCS of LSH almost doubled compared to the 3 day value, to 30 MPa, while LSS had almost no strength gain over that period of time. Between 3 and 7 days, LPS seemed to decrease in strength and increase in variability. LPH

and SPS continued to gain strength but had UCS values less than 15 MPa (2176 psi). At 28 days, LSH had a UCS of 42 MPa (6092 psi), which was a 64% increase in strength from 3 days. LSS had a similar UCS but a smaller strength gain of 25% from 3 days to 28 days. Comparable to LSH, SSS had a 53% increase in strength from 3 days to 28 days. LPS had minimal strength gain from 7 days while LPH and SPS both had 28 day strengths around 15 MPa (2176 psi). The 0.2LSS and 0.2SSS formulations remained below 5 MPa (725 psi) for all ages.



Figure 4.9: UCS for OPC and NBFA at 3, 7, and 28 Days at 76.67°C.

#### 4.3.1.2 CUFA

The CUFA had only one formulation that had rapid strength development in the first 3 days. LSS had a UCS of 37 MPa (5366 psi) at 3 days, which was significantly higher than all other formulations. Figure 4.10 shows that all formulations besides LSS had UCS values of 25 MPa (3626 psi) or lower throughout 28 days and were relatively close to one another. LSS had a 28 day strength of 70 MPa (10,153 psi) and a 40% strength gain from 3 days. LPH and SPS achieved the highest strength of all other formulations with 50%

strength gain from 3 days. The LSH followed closely, with a strength gain of 45%. 0.2LSS and 0.2SSS had greater UCS values with CUFA than with NBFA, which were similar in magnitude to the other formulations.



Figure 4.10: UCS for OPC and CUFA at 3, 7, and 28 Days at 76.67°C.

# 4.3.1.3 SMFA

The SMFA had a similar response to the CUFA in which only a couple of formulations had significantly higher compressive strengths than the other formulations. Figure 4.11 shows that LSS developed a 53 MPa (7687 psi) UCS at only 3 days. LPS and LSH also had higher compressive strengths of 34 MPa (4931 psi) and 22 MPa (3191 psi), respectively. All other mixes had compressive strengths below 15 MPa (2176 psi) at 3 days. Once 7 days were reached, LPS had not developed any further strength, while LSH and SSS developed an additional 10 MPa (1450 psi) of compressive strength each. LSS had minor strength gain at 7 days. Looking further to 28 days, the results remained much the same from 7 days. However, LPS appeared to decrease in strength by a little more than 50% and LSS only had a 22% strength increase from 3 days to 28 days. Like CUFA, the

0.2LSS and 0.2SSS performed consistently with the other formulations but remained at much lower strengths than LSS and SSS.



Figure 4.11: UCS for OPC and SMFA at 3, 7, and 28 Days at 76.67°C.

# 4.3.1.4 DLFA

The DLFA exhibited a different response than seen by any of the other fly ash samples as shown in Figure 4.12. At 3 days, LPS had developed 27 MPa (3916 psi) of compressive strength while all other formulations had less than 15 MPa (2176 psi). At 7 days, the results for all formulations were very similar except LPS and SPS, which had gained 11 MPa (1595 psi) and 27 MPa (3916 psi), respectively. The other formulations finally began to gain more strength at 28 days of curing. LSH, LSS, and SSS all had 60% or more strength gain from 3 days onwards. LPH remained with the lowest strength of 21 MPa (3046 ps), while LPS had no strength gain from 7 days onwards. The SPS continued to increase in strength to 57 MPa (8557 psi), which was a 79% strength gain from 3 days onwards.



Figure 4.12: UCS for OPC and DLFA at 3, 7, and 28 Days at 76.67°C.

# 4.3.1.5 CRFA

The UCS responses provided by CRFA formulations were similar to NBFA. All formulations had developed a substantial amount of strength at 3 days that was 15 MPa (2176 psi) or greater. Figure 4.13 shows that no single formulation was superior throughout the entire duration of curing. LPH showed a minor strength reduction at 7 days, but then ended up with a 29 MPa (4206 psi) UCS at 28 days. LSS and SSS had a comparable strength evolution to LPS and SPS, where all four formulations had 28 day strengths between 47 MPa (6817 psi) and 54 MPa (7832 psi). LSH had a 54% strength increase from 3 days but remained lower than the other formulations with a 28 day UCS of 35 MPa (5076 psi). SSS and SPS had a 56% increase in strength from 3 days while LSS had a 46% increase. The LPS had significantly less strength gain, increasing only 29% from 3 days onwards.



Figure 4.13: UCS for OPC and CRFA at 3, 7, and 28 Days at 76.67°C.

### 4.3.2 NBFA – ELEVATED TEMPERATURE AND PRESSURE

Figure 4.14 provides the results of an investigation further into the effects of elevated temperature and pressure conditions that was carried out only on NBFA for 3 days. At 76.67°C (170°F), the results are similar to the results shown earlier with NBFA cured at atmospheric pressure conditions. When the temperature is increased to 135°C (275°F), all formulations had an increase in compressive strength compared to OPC, which had decreased in strength considerably. The 3 day UCS values for LSH, LSS, and SSS were the highest with compressive strengths above 32 MPa (4641 psi), while LPH, LPS, and SPS were between 16 MPa (2321 psi) and 25 MPa (3626 psi). The LSH formulation had a 74% strength increase from 76.67°C (170°F) to 135°C (275°F) which was noticeably larger than the other formulations. At 204.44°C (400°F), the sodium-activated formulations showed to be very weak. In contrast, LPH and SPS exhibited UCS values of 23 MPa (3336 psi) and 22 MPa (3191 psi), respectively, which were greater than samples cured at lower

temperatures. LPS underwent some strength retrogression, but LPH cured at 204.44°C (400°F) still had UCS above 10MPa (1450 psi). Likewise, the OPC compressive strength decreased even further from what was seen at 135°C (275°F) to 12 MPa (1740 psi).



Figure 4.14: UCS for OPC and NBFA at Elevated Temperature and Pressure Conditions at 3 Days.

## 4.3.3 LPH – ELEVATED TEMPERATURE AND PRESSURE

Once NBFA with LPH was found to have an increasing compressive strength at 204.44°C (400°F), LPH with the eight remaining fly ash samples was tested at the same condition. Figure 4.15 provides the findings of this testing with a wide variety of strengths being observed. The DLFA and CRFA behaved very similarly with strengths of 42 MPa (6092 psi). BRFA and KIFA also behaved similarly to each other with strengths near 30 MPa (4351 psi). The other fly ash samples showed lower strengths but were consistently higher than OPC.



Figure 4.15: UCS for OPC and LPH with Various Fly Ash Samples at 204.44°C at 3 Days.

# 4.3.4 IMPACT OF FLY ASH AND ACTIVATOR PROPERTIES ON UCS

Fly ash with high amounts of CaO have typically been associated with high compressive strengths due to the production of a binder which resembles that of high calcium systems like OPC or slag (Canfield et al., 2014; Provis and van Deventer, 2014). The results from this study show that CaO does influence the compressive strength. This can be seen when comparing the results of LPH with the nine different fly ash samples at elevated temperatures. DLFA and CRFA had identical compressive strengths and were two of the fly ash samples with the greatest amount of CaO. GTFA is a fly ash with a very low amount of CaO and it had the lowest compressive strength. However, the other fly ash samples show results that are not as easily explained on the basis of CaO content. BRFA and KIFA have similar amounts of CaO compared to DLFA and CRFA. Thus, the

behavior of each fly ash and activator combination had no clear trend based on CaO content.

Similarly, the results observed at low temperatures and atmospheric pressure curing had no correlation between fly ash samples or activator type and compressive strength. LPH and SPS made with CRFA had desirable UCS values, while the same activators used in DLFA showed lower strengths at 3 days. This same degree of variability also applies to the evolution of compressive strength. SPS made with DLFA had a 79% strength gain from 3 days while SPS made with SMFA only had 42% strength gain from 3 days. From the data collected, the variations observed cannot be explained by simply referencing the activator type. Hence, further analysis of the geopolymer material is needed.

### 4.3.5 SUMMARY AND DISCUSSION

Given that the minimum compressive strength for oil and gas well cement is 3.45 MPa (500 psi), most formulations offer the possibility of being used in well cementing operations. There also exists the likelihood of using many of these formulations for precast operations as the compressive strength was comparable to OPC throughout the curing cycle. LSH and LSS along with LPS typically provided the best early strength gain, while the solid silicates reacted slower while still producing comparable strengths later in the curing process. The greatest compressive strengths were governed by the particular fly ash sample and activator with no clear trend observed. However, LSH and LSS formulations generally had the highest UCS, while the other formulations typically had less strength. However, some formulations resulted in UCS values comparable to LSH and LSS.

When all formulations were subjected to further elevated temperatures, specifically 135°C (275°F), the compressive strengths were generated at a quicker rate and were of greater magnitude, indicating that the geopolymerization process was accelerated

significantly at elevated temperatures. However, like OPC, once a specific temperature was achieved, several formulations did not achieve as high compressive strength. At 204.44°C (400°F), all sodium-activated formulations had practically no compressive strengths with UCS values less than 2 MPa (290 psi). LPH and SPS had continued strength gain at this temperature while LPS decreased in strength at this temperature versus lower temperatures. Still, geopolymer formulations cured at elevated temperatures and pressures provided compressive strengths that were significantly greater than OPC in most cases.

## 4.4 TENSILE STRENGTH (BRAZILIAN SPLIT TENSION TEST)

Cylindrical specimens were cured at atmospheric pressure conditions and pressurized conditions for different temperature profiles for different lengths of time as described in Chapter 3. This allowed for the analysis of the evolution of tensile strength for different fly ash and activator combinations when subjected to different curing conditions. Also, acceptable values for tensile strength have not been standardized for well cementing, so values were compared to values from OPC since it is typically used. Likewise, no acceptable limit for tensile strength has been suggested for civil engineering applications, but comparisons with OPC were made here also. The tensile strength results for each fly ash sample and activator can be found below accompanied by a chart showing the tensile strength results. A discussion of the results follows. All results are the average of three samples with error being calculated from a T-distribution assuming a 95% confidence interval.

#### 4.4.1 ATMOSPHERIC PRESSURE, 76.67°C (170°F)

### 4.4.1.1 NBFA

All the NBFA formulations showed minor strength increase from 3 days to 28 days. Figure 4.16 shows that the tensile strength values were consistent within 1 MPa (145 psi) to 2 MPa (290 psi) for most formulations. As in compressive strength testing, the LPS showed a decrease in tensile strength at 28 days. SSS had the greatest tensile strength at 28 days and was comparable to OPC at all ages. All potassium-activated mixes resulted in a 28 day tensile strength of 0.7 MPa (102 psi) which was a decrease in tensile strength for LPS compared to 3 day and 7 day tensile strengths. 0.2LSS and 0.2SSS results followed the same trend shown in the compressive strength testing with very low tensile strengths.



Figure 4.16: Tensile Strength for OPC and NBFA at 3, 7, and 28 Days at 76.67°C.

# 4.4.1.2 CUFA

Most of the CUFA formulations were all within the same range of 1 MPa (145 psi) to 2 MPa (290 psi) like NBFA as shown in Figure 4.17. LSS had the highest tensile strength of 2 MPa (290 psi), and SSS was lower, with 1.6 MPa (232 psi) at 3 days. LSH had the

greatest strength gain of 42% from 3 days to 28 days, while LSS and SSS failed to gain anymore tensile strength after 3 days. 0.2LSS and 0.2SSS had similar tensile strengths to LSH at 3 days but did not gain a lot of additional strength with increased curing as well. All the potassium-activated formulations had 28 day tensile strengths of 1.25 MPa (181 psi), with SPS having the greatest strength increase of 0.6 MPa (87 psi) from 3 days.



Figure 4.17: Tensile Strength for OPC and CUFA at 3, 7, and 28 Days at 76.67°C.

## 4.4.1.3 SMFA

The SMFA tensile strength results were mostly in the range of 1 MPa (145 psi) to 2 MPa (290 psi), similar to NBFA and CUFA. However, Figure 4.18 shows that most of the formulations had significant strength gain from 3 days to 28 days. LSH had a 28 day tensile strength of 2.4 MPa (348 psi), which was comparable to OPC. This was a 67% strength increase from 3 days. LPH also had a considerable strength gain of 64% from 3 days. 0.2LSS, LSS, 0.2SSS, and SSS had 28 day strengths that were around 1.25 MPa (181 psi). The LPS formulation was the only formulation that displayed significant strength retrogression with time.



Figure 4.18: Tensile Strength for OPC and SMFA at 3, 7, and 28 Days at 76.67°C.

# 4.4.1.4 DLFA

The DLFA was another fly ash sample that demonstrated a noticeable strength increase from 3 days to 28 days. Figure 4.19 shows at 3 days all formulations had tensile strengths between 1 MPa (145 psi) and 1.5 MPa (218 psi). This was comparable to the OPC tensile strength value of around 1.5 MPa (218 psi). At 7 days, there appear to be minor strength increases for all formulations except SPS. SPS tensile strength increased 0.75 MPa (109 psi) from 3 days to 7 days. LSH, LSS, and SSS eventually developed 28 day tensile strengths equivalent to or exceeding the OPC tensile strength of 2.6 MPa (377 psi), while LSH had the greatest strength increase of 60% from 3 days. LPH tensile strength increased by 0.8 MPa (116 psi) while LPS and SPS maintained the same tensile strength from 7 days onwards.



Figure 4.19: Tensile Strength for OPC and DLFA at 3, 7, and 28 Days at 76.67°C.

# 4.4.1.5 CRFA

The CRFA had tensile strength results with a bit more variation between the formulations than other fly ashes. The range of tensile strength values shown in Figure 4.20 is between 1 MPa (145 psi) to 2.5 MPa (363 psi). Most results were also equivalent to or exceeding OPC tensile strength values across all ages. LSS, SSS, LPS, and SPS exhibited no strength gain from 3 days to 28 days. LSH and LPH did, however, show an increase in strength from 3 days. LPH had a 48% strength increase providing a 2.4 MPa (348 psi) tensile strength while LSH had a 36% strength increase providing a 2.15 MPa (312 psi) tensile strength.



Figure 4.20: Tensile Strength for OPC and CRFA at 3, 7, and 28 Days at 76.67°C.

### 4.4.2 NBFA – ELEVATED TEMPERATURE AND PRESSURE

Figure 4.21 provides the tensile strength results for NBFA when subjected to elevated temperatures and pressures. As with the compressive strength results, the tensile strength results for NBFA cured at 76.67°C ( $170^{\circ}F$ ) and 20.68 MPa (3000 psi) are similar to the results from the prior condition of 76.67°C ( $170^{\circ}F$ ) and atmospheric pressure. At 135°C ( $275^{\circ}F$ ), the tensile strength of all formulations increased, with LSS having the highest tensile strength of 2.72 MPa (395 psi). LSH and SSS followed, with very similar tensile strengths of 2.2 MPa (319 psi). The potassium-activated formulations continued to have lower tensile strengths than the sodium-activated formulations but sill equivalent to or greater than OPC. At 204.44°C ( $400^{\circ}F$ ), the sodium-activated formulations tensile strengths increased to 2.23 MPa (323 psi) and 1.82 MPa (264 psi), respectively. For the LPH, this was 85% higher than the tensile strength at 76.67°C ( $170^{\circ}F$ ). The LPS formulation decreased in



strength at 204.44°C (400°F) but was greater than the OPC tensile strength of 1 MPa (145 psi).

Figure 4.21: Tensile Strength for OPC and NBFA at Elevated Temperature and Pressure Conditions at 3 Days.

### 4.4.3 LPH – ELEVATED TEMPERATURE AND PRESSURE

Since LPH has provided such promising compressive and tensile strength results when cured at 204.44°C (400°F), the LPH formulations across the other eight fly ash samples were tested tensile strength. Figure 4.22 provides the tensile strength results of these formulations at 3 days, where the range is between 1.5 MPa (218 psi) to 2.5 MPa (363 psi). DLFA, CRFA, GTFA, KIFA, and CUFA all had similar tensile strength around 2.25 MPa (326 psi). BRFA, GTUFA, and SMFA had slightly less tensile strengths around 1.5 MPa (218 psi). All formulations had tensile strengths greater than OPC by 0.5 MPa (73 psi) or more.



Figure 4.22: Tensile Strength for OPC and LPH with Various Fly Ash Samples at 204.44°C at 3 Days.

## 4.4.4 IMPACT OF FLY ASH AND ACTIVATOR PROPERTIES ON TENSILE STRENGTH

When trying to see if the characteristics of the fly ash sample have any correlation to tensile strength values, it is best to look at the case of LPH with all fly ash samples at 204.44°C (400°F). It can be seen that the fly ash samples with the highest amount of CaO generally provided the highest tensile strengths. However, NBFA and CUFA have significantly lower amounts of CaO while providing almost the same tensile strength. To better illustrate the effects of CaO on tensile strength, Figure 4.23 shows the tensile to compressive (T/C) strength ratio for each LPH formulation. NBFA, CUFA and GTFA had the lowest amount of CaO while having the highest T/C ratio. However, SMFA also had a similar amount of CaO but was left with a lower T/C ratio comparable to that of the fly ash samples with the highest amounts of CaO. Likewise, GTUFA had a low amount of CaO but had a lower T/C ratio.



Figure 4.23: T/C for LPH with Various Fly Ash Samples at 204.44°C at 3 Days.

Furthermore, activator type also did not have any significant effects on the tensile strength of the formulations. At 76.67°C (170°F) and atmospheric conditions, the geopolymer formulations tend to have tensile strengths between 1 MPa (218 psi) and 2.5 MPa (363 psi) and the values were not specific to the fly ash sample or the activator type. As with compressive strength, the results at this condition appear to not unexplainable provided the current data in this research. Also, most of the results did not show substantial tensile strength development after 3 days, with some formulations decreasing their tensile strength over time.

At elevated temperatures and pressures, the results were found to be quite different. It was observed that tensile strength development was quicker when subjected to 135°C (275°F) and even greater for LPH and SPS at 204.44°C (400°F). LSH, LSS, and SSS were found to not exhibit useful tensile strengths at 204.44°C (400°F). Figure 4.24 shows the T/C ratios for each formulation at the different curing conditions. LPS had an increasing T/C ratio from lower temperature to higher temperature while SPS decreased slightly. At



135°C (275°F), all formulations had a very similar T/Cs around 6.5% to 7% which was double the T/C for OPC.

Figure 4.24: T/C for OPC and NBFA at Elevated Temperature and Pressure Conditions at 3 Days.

### 4.4.5 SUMMARY AND DISCUSSION

Overall, the tensile strength results support the use of geopolymers for use in well cementing and precast concrete operations, as most formulations had tensile strengths comparable to OPC. Specific precast concrete applications could also be targeted based on the amount of tensile strength desired or required. For instance, some formulations with higher T/C ratios could be better suited for infrastructure subjected to large amounts of tensile loading, while other formulations with lower T/C ratios and are better suited for significant compressive loading. The results at atmospheric conditions are consistently in the range of OPC values and much of the tensile strength is developed within the first 3 days of curing for most formulations. When subjected to elevated temperatures and

pressure, the geopolymer formulations provide further justification for use because tensile strength values were generally significantly higher than OPC values.

#### 4.5 SHEAR BOND STRENGTH

Specimens of the form described in Chapter 3 have been cured at atmospheric pressure conditions and pressurized conditions for different temperature profiles for different lengths of time. This allowed for the analysis of the evolution of shear bond strength for different fly ash and activator combinations when subjected to different curing conditions. Acceptable values for bond strength have not been standardized for well cementing, so values were compared to values from OPC since it is typically used. Likewise, no acceptable limit for bond strength has been suggested for civil engineering applications, but comparison with OPC were also made. A chart showing the shear bond strength results for each fly ash sample and activator can be found below accompanied with a discussion. All results are the average of three samples with error being calculated from a T-distribution assuming a 95% confidence interval. The 0.2LSS and 0.2SSS formulations were discontinued in this testing due to the poor performance observed with respect to tensile and compressive strengths.

## 4.5.1 ATMOSPHERIC PRESSURE, 76.67°C (170°F)

### 4.5.1.1 NBFA

The bond strength results for the NBFA formulations at 76.67°C (170°F) and atmospheric pressure are provided in Figure 4.25, which shows that little-to-no bond strength gain was recorded for most formulations. However, LSS had the greatest increase in strength of 53% from 3 days to 28 days. Furthermore, LSS had a 28 day strength of 1.66 MPa (241 psi), which was comparable to OPC. Also, LSH and SSS formulations were

found to have greater bond strengths than OPC for all three ages observed. LPS initially had a bond strength comparable to OPC at 3 days but declined to values similar to LPH and SPS by 28 days. LPH and SPS bonds strengths were below 1 MPa (145 psi) for all ages.



Figure 4.25: Bond Strength for OPC and NBFA at 3, 7, and 28 Days at 76.67°C.

## 4.5.1.2 CUFA

The CUFA formulations had greater bond strengths compared to NBFA, as shown in Figure 4.26. All formulations exhibited some degree of strength gain throughout the entire duration of curing. LPH had a minimal amount of strength gain, while SSS developed an additional 84% of bond strength from 3 days. Initially, LPS was the only formulation with a bond strength similar to OPC. However, the results at 28 days show that every formulation had developed bond strengths comparable to OPC, apart from LPH. In the case of LSH, LSS, SSS, and LPS, the bond strengths at 28 days were significantly higher than OPC.



Figure 4.26: Bond Strength for OPC and CUFA at 3, 7, and 28 Days at 76.67°C.

# 4.5.1.3 SMFA

The magnitude of the bond strengths for the SMFA formulations were similar to CUFA, except for the strength evolution with time. Figure 4.27 provides the bond strengths for SMFA, and it can be seen that a rapid gain in strength was observed for the sodium-activated formulations between 3 days and 7 days. The strength gains from 3 days to 7 days for LSH, LSS, and SSS was 40%, 51%, and 34%, respectively. At 28 days, the sodium-activated formulations showed a decrease in bond strength while it remained greater than OPC. In contrast, the potassium-activated formulations did not exhibit the same strength evolution pattern and instead gained or maintained strength as age increased. These formulations resulted in 28 day bond strengths that were less than OPC at 1.5 MPa (218 psi).



Figure 4.27: Bond Strength for OPC and SMFA at 3, 7, and 28 Days at 76.67°C.

# 4.5.1.4 DLFA

The DLFA formulations behaved a manner quite opposite to the SMFA. Figure 4.28 shows that LPS was the only formulation to generate a considerable amount of bond strength within 3 days. The sodium-activated formulations were all less than 0.5 MPa (73 psi) at 3 days with LSS showing no bond strength at all. LPH and LPS had similar bond strengths of 0.5 MPa (73 psi) but demonstrated a greater increase in strength with time compared to the other formulations. At 28 days, LPH had a 73% strength increase from 3 days to 28 days, while SPS also had a substantial strength increase of 68% over the same period. The LPS formulation showed no bond strength increase and had, in fact, decreased by 0.5 MPa (73 psi) from 3 days to 28 days. Eventually, SSS showed a significant amount of strength gain between 7 days and 28 days but still had a lower bond strength than the potassium-activated formulations and OPC. The potassium-activated formulations continued to have comparable bond strengths to OPC at 28 days.



Figure 4.28: Bond Strength for OPC and DLFA at 3, 7, and 28 Days at 76.67°C.

# 4.5.1.5 CRFA

The CRFA formulations seemed to follow no patterns observed in the other fly ash samples. Figure 4.29 shows that all potassium-activated formulations showed more strength gain than sodium-activated formulations at 3 days. The 3 day bond strengths were near 0.75 MPa (109 psi) for the sodium-activated formulations and 1.5 MPa (218 psi) to 2.5 MPa (363 psi) for the potassium-activated formulations. At 7 days and 28 days, LPS remained near 2 MPa (290 psi) with no additional strength gain. At 28 days, LSS, LPH, and SPS showed an increase in strength from 3 days of 65%, 64%, and 30%, respectively. In contrast, the LSH had an 87% strength increase from 3 days to 28 days while the SSS increase was even greater at 95%. All formulations developed 28 days bond strengths that were equivalent to OPC except LSH and SSS, which exhibited almost 3 times the bond strength of OPC.



Figure 4.29: Bond Strength for OPC and CRFA at 3, 7, and 28 Days at 76.67°C.

### 4.5.2 NBFA – ELEVATED TEMPERATURE AND PRESSURE

Figure 4.30 provides the bond strength results for elevated temperature and pressure testing performed only on the NBFA. The sodium-activated mixes were not tested at 204.44°C (400°F) due to the poor performance shown in tensile and compressive strength testing previously. At 76.67°C (170°F) and 20.68 MPa (3000 psi), the results were slightly different from what was seen at 76.67°C (170°F) and atmospheric pressure. All formulations had bond strengths around 1 MPa (145 psi), besides LPH, which was significantly lower. OPC had the highest bond strength at this condition at 3.5 MPa (508 psi). At 135°C (275°F), there was a substantial increase in bond strength in every formulation except LSH. LPS had the greatest bond strength of 8.8 MPa (1276 psi) which was an 84% increase compared to the lower temperature condition and 13.5 times the bond strength of OPC. LSS followed closely with 6.9 MPa (1001 psi), showing an 80% strength increase. SSS, LPH, and SPS all had significant bond strengths as well. The formulations were in the range of 3 MPa (435 psi) to 5 MPa (725 psi), which was considerably more

than OPC, which had 1 MPa (145 psi) of bond strength. At 204.44°C (400°F), all bond strengths of potassium-activated formulations were around 7.25 MPa (1052 psi). LPS showed a slight decrease in bond strength while LPH and SPS continued to experience strength gain. LPH and SPS had significant strength gain of 96% and 88%, respectively, from what was observed at 76.67°C (170°F). These formulations showed 11.5 times the bond strength of OPC, i.e., more than an order of magnitude improvement compared to OPC at these experimental conditions.



Figure 4.30: Bond Strength for OPC and NBFA at Elevated Temperature and Pressure Conditions at 3 Days.

# 4.5.3 LPH – ELEVATED TEMPERATURE AND PRESSURE

Due to the significant bond strengths shown with LPH and NBFA at 204.44°C (170°F) compared to OPC, further formulations were studied with the eight other fly ash samples and the bond strength results are shown in Figure 4.31. What can be seen is that only the GTFA had a bond strength comparable to NBFA, which was 8.7 MPa (1228 psi) and 13 times the bonds strength of OPC. The DLFA and GTUFA we the next closest

formulations with bonds strengths of 5 MPa (725 psi) and the CUFA was similar with 3.5 MPa (508 psi). All other fly ash samples showed bond strength that were less than 2 MPa (290 psi), but these were still noticeably better than OPC.



Figure 4.31: Bond Strength for OPC and LPH with Various Fly Ash Samples at 204.44°C at 3 Days.

### 4.5.4 IMPACT OF FLY ASH AND ACTIVATOR PROPERTIES ON BOND STRENGTH

When looking at the results from 76.67°C (170°F) and atmospheric pressure, there appears to be no clear trend between fly ash sample or activator. The SSS yielded the highest bond strength values for all fly ash samples except DLFA. Moreover, it appears that sodium activation often had the best bond strengths for all fly ash samples at 28 days except DLFA. The magnitudes of these formulations were always either comparable to OPC or greater in some cases. This trend may have existed with DLFA as well if significant expansion had not occurred with the sodium-activated mixes.

The results at elevated temperatures and pressures showed that significant bond strengths were developed much more rapidly. At 135°C (275°F), the liquid silicates

demonstrated the greatest bond strength gain while all formulations had greater bond strengths than OPC. Increasing the temperature further to 204.44°C (400°F) showed that the LPH and SPS formulations had more desirable bond strengths than at lower temperatures. Thus, LPH was studied further, to see if the results would be similar across fly ash samples. What was observed is that fly ash samples with low amounts of CaO and high amounts of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> > 90%) generated the greatest bond strength as in the case of NBFA and GTFA.

### 4.5.5 SUMMARY AND DISCUSSION

The bond strengths of the geopolymer formulations compared very favorably with that of OPC, because most formulations had bond strengths greater than OPC. At elevated temperatures and pressures, the geopolymer formulations outperformed OPC entirely. The fact that geopolymers can provide such significant bond strengths provides a benefit to the petroleum industry that is not currently found within OPC. This could eliminate the issue of micro-annuli existing between the casing and cement and causing loss of zonal isolation because of the cement debonding from casing and / or formation. The potential for use in precast operations also exists where the development length of steel reinforcement could be reduced due to the increased cement-to-steel bonding compared to OPC.

# **CHAPTER 5.** CONCLUSIONS AND FUTURE WORK

### **5.1** CONCLUSIONS

As the world transitions to a more sustainable and environmentally friendly approach to industrial operations, OPC production emissions and performance remain significant concerns. OPC has shown to have durability issues in aging infrastructure across the United States and has also been linked to failures in well cementing operations within petroleum engineering (Thomas, 2007; Nelson and Guillot, 2006). The use of AAMs in the form of Class F fly ash-based geopolymers provides alternatives to OPC that have reduced environmental footprints and desirable properties. The main testing results for the geopolymer formulations studied in this research are listed below:

- Geopolymer slurries can be formulated with suitable rheological properties for well cementing purposes. Potassium-activated formulations were typically less viscous and more appropriate for well cementing applications, while sodium-activated formulations were more viscous and potentially useful in precast concrete operations.
- The set times for geopolymer formulations were found to be highly variable at 76.67°C (170°F) and atmospheric pressure. Sodium-activated formulations had consistently lower set times, around 1 to 2 hours, which were comparable to OPC. Potassium-activated formulations, however, had set times ranging from 0.5 hours to never setting within a 24 hour period. At 51.67°C (125°F) and 20.68 MPa (3000 psi), only LSS and SSS set within 18 hours and 13 hours, respectively. However, at 100°C (212°F) and 20.68 MPa (3000 psi), all formulations set, where sodium-activated formulations had set times around 1.5 hours, and potassium-activated formulations had set times around 1.5 hours. At 135°C (275°F), all

potassium-activated formulations had set times ranging between 2 to 3 hours, with the exception of KIFA having a set time of 45 minutes. This variability between activator type provides the opportunity for many different applications to be undertaken with the same fly ash sample without the addition of any admixtures.

- Compressive strengths for the geopolymers at 76.67°C (170°F) were comparable to OPC for sodium-activated geopolymers, while most potassium-activated formulations had consistently lower strength than OPC. However, some formulations utilizing either sodium silicate or potassium silicate, liquid or solid, had greater compressive strengths than OPC. At elevated temperatures, geopolymers exhibited significant strength gain with time, while neat OPC experienced strength retrogression.
- Tensile strengths of most geopolymer formulations across all fly ash samples were within the range of 1 MPa (145 psi) to 2 MPa (290 psi) when cured at 76.67°C (170°F) which was comparable to OPC. Several formulations also exhibited a substantial increase in tensile strength evolution over time when compared to OPC. At elevated temperatures, all geopolymer formulations had greater tensile strengths than OPC.
- Bond strength values of each geopolymer formulation when cured at 76.67°C (170°F) had similar values of bond strengths compared to values of tensile strengths. Values were generally between 1 MPa (145 psi) to 3 MPa (435 psi) and in most cases equivalent to or greater than the bond strength of OPC. At elevated temperatures, geopolymers demonstrated significantly higher bond strengths 13.5 times higher than OPC. Increasing the temperature further to 204.44°C (400°F), geopolymers still had a bond strength 13 times OPC with certain fly ash samples.
- The amount of CaO in each fly ash sample only affected the compressive strength and bond strength significantly at elevated temperature and pressure conditions. Fly ash samples with high amounts of CaO generally had higher compressive strengths while showing lower bond strengths. Fly ash samples with low CaO and SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+ Fe<sub>2</sub>O<sub>3</sub> > 90% showed low compressive strengths but substantial bond strengths.
- The silicate activators tended to provide minor increases in strength at 28 days for most formulations. However, liquid silicates did prove to provide strength more rapidly early in the curing process, which was evident by observing LSS combined with NBFA, CUFA, and SMFA at 76.67°C (170°F) and atmospheric pressure. Solid silicates and hydroxide activators exhibited slower strength evolution, but eventually produced similar strengths by 28 days. Furthermore, when subjected to 135°C (275°C) and 20.68 MPa (3000 psi), all activators had similar strength gain. However, at 204.44°C (400°F), sodium activation, both hydroxide and silicate, proved to be undesirable.

In this investigation, Class F fly ash-based geopolymers were shown to have the potential to replace OPC systems in oil and gas well cementing and precast concrete applications across a wide range of operating conditions. The latter cover most of the conventional pressure and temperature ranges for oil and gas well cementing operations. Several formulations were found to exhibit equivalent or even better rheological properties, set times, and strength behaviors when compared to OPC. Different fly ashes were shown to behave quite differently, with little predictability based on the mineralogical content at present, but the availability of different activators provides considerable options to tailor formulations to specific field applications.

## **5.2 FUTURE WORK**

While a great amount of work has been done to fully understand what the rheological and mechanical properties of the geopolymers are, there remains a considerable amount of work to be completed. Further work should consist of additional lab testing, but also be focused on the implementation of these materials into the field.

Several properties that need to be the focus of additional lab testing are thermal coefficients of expansion and thermal insulation values. Due to the geopolymer's high thermal stability observed and the spherical shape of fly ash particles, the potential to be utilized in steam injection and geothermal wells is a real possibility. However, not enough is known about these specific properties.

Further studies should also be conducted to determine the unpredictable behavior observed in the results of this research. In order to implement geopolymers into industry, it would be advantageous to reliably predict the properties of a specific geopolymer on the basis of fly ash type and activator used.

As to field implementation, for oil and gas well purposes, geopolymers need to be put to the test in the actual downhole environments, with appropriate verification of their properties. For civil engineering purposes, large structural members need to be created and tested. The present study provides crucial information to justify such larger-scale yard and field testing.

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