

ALKALINE ACTIVATION OF AMBIENT CURED GEOPOLYMER
MORTAR AND CONCRETE BASED ON CLASS C FLY ASH

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ALKALINE ACTIVATION OF AMBIENT CURED GEOPOLYMER
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ABSTRACT

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The critical element for sustainable growth in the construction industry is the development of alternative cements. A new technological process called geopolymerization provides an innovative solution, and the presence of aluminum and silicon oxides in fly ash has encouraged its use as a source material. To promote the employment of geopolymers for practical concrete applications, the present study investigated the material's properties, practices and applications. An experimental program was also executed to establish a relationship between the alkaline activator composition and the properties of geopolymer mortar and concrete in fresh and hardened states. Concentrations of sodium hydroxide and sodium silicate were ascertained that are advantageous for constructability and physical properties. Test results indicate that there is potential for the concrete industry to utilize alkaline activated fly ash as an alternative to portland cement in structural building applications.

CHAPTER I

INTRODUCTION

1.1 Background

Concrete is the most widely used construction material in the world. With hundreds of millions of tons used annually, it is second only to water as the most consumed resource (Seal et al., 2011). The principal component and binder in concrete is portland cement (PC). To supply the material on such a large scale, the PC industry in the United States consumes 500 trillion btu of energy per year (Worrell & Galitsky, 2008). The production of PC is consequently one of the largest global sources of combustion and chemical process-related carbon dioxide (CO₂) emissions (Hanle et al., 2011). The emissions are created by burning fossil fuels to heat limestone to 2640°F and by the conversion of calcium carbonate (CaCO₃) to calcium oxide (CaO). The production of 1 ton of PC directly generates 0.6 tons of chemical CO₂, and the required combustion of carbon-based fuel generates an additional 0.4 tons. This process results in the emission of approximately 1 ton of CO₂ for every ton of PC produced, accounting for 5% of global CO₂ production or approximately 1.7 trillion tons per year (Pearce, 1997; PCA, 2012).

The current trend in the construction industry is leaning more towards sustainable practices every year, making research valuable by providing a means to limit waste and recycle material. The use of recycled materials and byproducts has ecological effects that benefit the environment by lowering energy consumption and saving valuable landfill

space while also accrediting new buildings in accordance with Leadership in Energy and Environmental Design standards (USGBC, 2005). The use of recycled materials in concrete research has been limited to recycled admixtures, recycled reinforcement fibers and recycled aggregates. The critical element for sustainable growth, however, is the development of alternative cements to replace PC (Davidovits, 1989).

Fly ash (FA) is a term used to describe the fine particulate material precipitated from the stack gases of industrial furnaces that burn solid fuels. Hundreds of millions of tons of this byproduct are produced worldwide every year in coal burning power plants (Seal et al., 2011). FA was initially used in concrete as an admixture to enhance rheological properties and reduce the alkali-aggregate reaction (Mindess & Young, 1981). As a pozzolan, FA also exhibits cementitious properties when combined with calcium hydroxide ($\text{Ca}(\text{OH})_2$). However, FA from different sources may have varying effects due to chemical composition or the type of PC being used. Thus, only a small percentage of the FA produced annually is actually used as a concrete admixture (Popovics, 1982).

An alternative method of reducing the use of PC is by incorporating FA into a new technological process called geopolymerization (Silverstrim et al., 1999). Geopolymers are formed when aluminum and silicon oxides (Al_2SiO_5) dissolve in a strong alkaline solution, reorganize and polycondense into a hardened state. Due to its similarity to natural sources of Al_2SiO_5 , FA can be combined with an alkaline solution to produce new geopolymer binders (Jiang & Roy, 1992). Consequently, geopolymer mortar (GPM) and geopolymer concrete (GPC) have the potential to become low-cost and low-emission structural building materials (Seal et al., 2011). By applying this new

technology, byproducts can be transformed into useful construction materials, and the CO₂ from PC production can be reduced by as much as 90% (Davidovits, 1994). Like many innovative materials, however, the appropriate practices, properties and applications of geopolymers have not yet been fully determined.

1.2 Statement of the Problem

The problem of the present study was to experimentally analyze the effect of the alkaline activator composition on the fresh and hardened properties of GPM and GPC based on Class C FA from the Calaveras Power Station in San Antonio, Texas.

1.3 Statement of the Purpose

The purpose of the present study was to develop information, specifically concerning GPM and GPC composition, that will enable the concrete industry to utilize alkaline activated FA as an alternative to PC in structural building applications.

1.4 Statement of the Objective

The objective of the present study was to ascertain what concentrations of sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) are advantageous for the constructability and physical properties of GPM and GPC. The following factors were investigated:

- Temperature
- Flow / Slump
- Density
- Air Content
- Setting Time
- Pulse Velocity
- Splitting Tensile Strength
- Compressive Strength
- Drying Shrinkage

CHAPTER II

REVIEW OF THE LITERATURE

2.1 Geopolymer

Geopolymers are inorganic materials that polycondense similar to organic polymers. The reaction of Al_2SiO_5 with alkali polysilicates produces an amorphous to semi-crystalline three-dimensional structure of polymeric sialate (Si-O-Al-O) bonds (Davidovits, 1991). The tetrahedral configuration of sialate, an abbreviation for alkali silicon-oxo-aluminate, is illustrated in Figure 1 with potassium, sodium, calcium or lithium being the alkali (Davidovits, 1976).

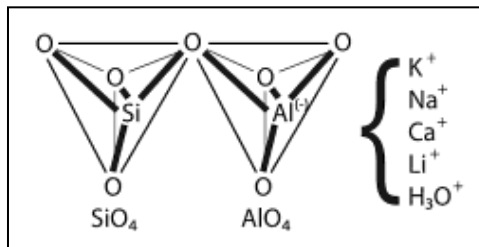


Figure 1. Tetrahedral Configuration of Sialate (Davidovits, 1976).

Through the action of hydroxide (OH^-) ions, the Al_2SiO_5 dissolves from the source material. Precursor ions then organize into monomers and polycondense to form polymeric structures (Hardjito & Rangan, 2005). Poly(sialates) have the following empirical formula (Davidovits, 2011):

$$\text{M}_n [-(\text{SiO}_2)_z - \text{AlO}_2]_n, w\text{H}_2\text{O}$$

H_2O is released during the formation and curing of the geopolymer matrix, leaving behind discontinuous nano-pores that influence performance. Contrasting the

hydration required for PC, H_2O is not necessary for the chemical reaction to occur. The role of H_2O is to simply produce a mixture that is adequately workable (Hardjito & Rangan, 2005).

Natural sources of Al_2SiO_5 include kaolinite, clays, micas, andalusite and spinel. However, source materials can also be byproducts of industrial processes, such as silica fume, slag and FA. The geopolymerization of the source materials is generally accomplished through the use of an aqueous colloidal alkali polysilicate solution based on sodium that contains diverse forms of silica (Brykov, 2004; Leelathawornsuk, 2009).

In contrast to geopolymer, the production of PC results from the calcination (thermal decomposition) of CaCO_3 and silico-aluminous materials, such as clay, shale or silica sand (Davidovits, 2011). Hydration of the resulting calcium silicate and calcium aluminate forms calcium silicate hydrate (C-S-H), calcium aluminate hydrate (C-A-H) and $\text{Ca}(\text{OH})_2$. Formation of these compounds generates heat, causing thermal expansion and strength development (Taylor et al., 2007).

2.2 Fly Ash

FA is a byproduct of coal combustion power plants. The siliceous and aluminous material is classified as a pozzolan due to its ability to chemically react with $\text{Ca}(\text{OH})_2$ to form cementitious compounds. FA produced from anthracite and bituminous coals are Class F, while sub-bituminous and lignite coals produce Class C FA. Class F FA contains large amounts of Al_2O_3 and SiO_2 but less than 10% CaO . Alternatively, Class C FA has a CaO content greater than 10%, giving it unique self-hardening characteristics (Headwaters, 2005; ASTM C618, 2012).

The presence of Al_2SiO_5 in FA has encouraged its use as a source material for the geopolymerization of alternative cements (Zeobond, 2007). Due to the existence of larger amounts of CaO impurities in Class C FA, the geopolymer precursors react to form C-S-H and C-A-H parallel to the formation Si-O-Al-O bonds. During hydration of the compounds, the alkalinity of the mixture rises and promotes faster dissolution and polycondensation. The presence of CaO can, therefore, improve the chemical reaction and increase the strength of the hardened matrix (Diaz-Loya et al., 2011). The reactivity of the FA, however, is also dependent upon the nature and proportion of the SiO_2 (Hemmings & Berry, 1988).

2.3 Alkaline Activator

The alkali polysilicate solution is most commonly composed of NaOH and Na_2SiO_3 for geopolymers based on FA. It is also recommended for the NaOH component to be 25-100% NaOH with up to 75% H_2O and for the Na_2SiO_3 component to be 38-55% Na_2SiO_3 with 45-62% H_2O by mass and a $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of approximately 2:1 to 3.22:1 (Silverstrim et al., 1997). The addition of Na_2SiO_3 allows the quantity of the mineral component to be reduced, and including it in the mixture is also advantageous for faster hardening of the binder. The benefit of incorporating NaOH into geopolymer mixtures is its exothermic capacity as a strong chemical base to increase dissolution and polycondensation of the source material (Davidovits, 1975).

2.4 Applications

The oldest geopolymer artifact is the Venus from Dolni Vestonice, a 27000 year old ceramic figurine. Clay was used as a natural source of Al_2SiO_5 and alkaline soluble salts, generating a chemical reaction when heated over a fire (Davidovits, 2011). An

investigation of the origin of geopolymer binders has also provided evidence indicating that the Great Pyramids of Giza were built using similar technology. The theory speculates that Egyptian workers mixed crushed limestone with H_2O from the Nile River for the required Al_2O_3 and SiO_2 . Locally available salts were then used to make the mixture alkaline. Opposing traditional engineering theories, the chemistry theory claims that the mixture was cast into wooden molds and cured in the desert heat to form pyramid stones (Farkas, 1985). Similar conjectures have been made concerning antiquated structures in Italy and Germany (Davidovits, 1994).

Due to its modern rediscovery, there is potential for the new binder to be used for a wide variety of applications (Davidovits, 2011). Geopolymers are being investigated in many scientific and industrial disciplines, including modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology and other engineering process technologies. Bricks, ceramics and fire protection materials can be made from geopolymers with a Si : Al atomic ratio of 1, corresponding to a three-dimensional network of poly(sialate). A binder consisting of sialate-siloxo (Si-O-Al-O-Si-O) bonds, however, corresponds with a Si : Al atomic ratio of 2 and can be used for radioactive and toxic waste encapsulation or for cement, mortar and concrete (Davidovits, 2002).

2.5 Foundational Research

Foundational research established four stages for the synthesis of geopolymers. However, the stages that form the structure of geopolymeric materials proceed in parallel and are indistinguishable. As per Table 1, the first stage is the dissolution of the Al_2SiO_5 from the source material in a strong alkaline solution. The dissolution is followed by the formation of geopolymer precursors consisting of covalent bonds of Si-O-Al-O type. By

alternately linking via common oxygen ions, the oligomers polycondense to form a three-dimensional framework of AlO_4 and SiO_4 tetrahedra. This mechanism also involves the simultaneous removal of H_2O . Finally, the solid particles bond and harden to form the polymeric structure (Giannopoulou & Panias, 2007).

Table 1. Geopolymerization Mechanism.

Dissolution	$(\text{SiO}_2, \text{Al}_2\text{O}_3) + 2\text{MOH} + 5\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + 2\text{Al}(\text{OH})_4^- + 2\text{M}^+$
Formation	$\text{Si}(\text{OH})_4 + \text{Al}(\text{OH})_4^- \Leftrightarrow (\text{OH})_3\text{Si-O-Al}(-)(\text{OH})_3 + \text{H}_2\text{O}$
Polycondensation	$n[(\text{OH})_3\text{Si-O-Al}^{(-)}(\text{OH})_3] \rightarrow \begin{array}{c} \quad \\ (-\text{Si-O-Al}^{(-)}\text{-O-})_n \\ \quad \\ \text{O} \quad \text{O} \end{array} + 3n\text{H}_2\text{O}$
Hardening	$>\text{T-OH} + \text{HO-} \begin{array}{c} \quad \\ (-\text{Si-O-Al-O-})_n \\ \quad \\ \text{O} \quad \text{O} \end{array} \rightarrow >\text{T-O-} \begin{array}{c} \quad \\ (-\text{Si-O-Al-O-})_n \\ \quad \\ \text{O} \quad \text{O} \end{array} + \text{H}_2\text{O}$

M denotes the alkali (Na, K, Ca, Li) and $>T$ denotes surface Si or Al sites.

In recent years, there has been exponential growth in the body of literature regarding geopolymer science (Geopolymer Institute, 2010). The worldwide increase in geopolymer research has provided a substantial amount of insight concerning the methods and materials required for the alkaline activation of FA. However, due to a lack of standard geopolymer preparation and testing procedures, there is large variation in research methodologies.

The variation in practices parallels deviations found in the chemical composition of the source materials. Even though there are classifications of FA, inconsistencies in composition are found between FA from different power plants and even between batches of FA from the same source. For this reason, many investigations have focused solely on optimizing the quantity, constituents and concentration of the alkaline activator.

Other studies have investigated the effect of curing geopolymer specimens at elevated temperatures to accelerate polycondensation and hardening. In search of optimal source materials, some investigations have also examined differences between geopolymers based on Class C and Class F FA, while others have compared coarse and fine FA. However, limited research has been conducted with regards to the rheological behavior of geopolymers.

2.5.1 Alkaline Activation

Hardjito & Rangan (2005) presented the findings of an experimental program regarding the development of GPC based on Class F FA from the Collie Power Station in Western Australia. Commercial grade NaOH pellets (97% purity) and Na_2SiO_3 solution (14.7% Na_2O , 29.4% SiO_2 , 55.9% H_2O) were utilized as the alkaline activator. NaOH pellets were dissolved in H_2O to prepare the NaOH solution. Similar to concrete based on PC, aggregates occupied 75-80% of the GPC mass. Saturated surface dry (SSD) coarse and fine aggregates were prepared in accordance with AS 1141.5-2000 and AS 1141.6.1-2000. Three different aggregate combinations were investigated. In the primary experimental design, the ratio of Na_2SiO_3 : NaOH was manipulated from levels of 0.4 to 2.5, and the molarity of the NaOH solution varied from 8M to 16M. Most mixtures also contained naphthalene suphonate super plasticizer in the range of 0% to 2% to improve workability.

Compressive strength was selected as the benchmark parameter due to its importance in the design of concrete structures, but other parameters were also considered. The preliminary lab work revealed that higher H_2O content created segregation, resulting in lower strength. However, if the Na_2SiO_3 and NaOH solutions

were mixed together 1 day before adding them to the solid constituents, then segregation ceased. Specimens did not immediately harden at room temperature, having a handling time of at least 24 hours.

The FA and aggregates were mixed in an 80L pan mixer for 3 minutes, and then the H₂O, super plasticizer and alkaline activator were added and mixed for an additional 4 minutes. A conventional slump test was conducted to measure the workability of the fresh concrete. Specimens were cast in steel molds and compacted by 60 manual strokes per layer in 3 equal layers followed by 10 seconds on a vibration table. 4"×8" cylindrical concrete specimens were cast for determination of compressive strength, and 6"×12" specimens were cast for determination of splitting tensile strength. After being wrapped with vacuum bagging film and twist tie wire, specimens were either cured in an oven or steam chamber.

The experimental study indicated that a higher concentration of NaOH and a higher ratio of Na₂SiO₃ : NaOH resulted in stronger specimens. Additional mixtures were designed with a 2.5 Na₂SiO₃ : NaOH ratio, as the test results for this parameter were considered to be consistent and more economical. Strength also increased as an effect of raising the curing temperature. Additional specimens were prepared and cured at 140°F for periods ranging from 4 to 96 hours, and longer curing time resulted in higher strength.

The initial setting time of the GPC could not be measured due to the lack of a suitable method; however, it was determined that the fresh mixture could remain in ambient conditions for up to 2 hours without losing workability or compressive strength. Super plasticizer volumes up to 2% improved workability without lowering compressive strength. Strength increased if specimens were left in ambient conditions for up to 3 days

before curing at elevated temperatures. Similar to concrete based on PC, increasing the $\text{H}_2\text{O} : \text{Na}_2\text{O}$ molar ratio decreased strength but increased workability of the GPC. Results of the study also indicate that strength increased with longer mixing times.

Determined in accordance with AS 1012.17, the elastic modulus of the GPC increased with higher compressive strength. Modulus of elasticity measurements were between 3336 ksi and 4467 ksi. Poisson's ratio was determined to be 0.13 to 0.16 for the mix designs, and the average density was 147 lb/ft^3 . Compressive testing also indicated that the geopolymer matrix was stronger than the crushed granite. An analysis of the stress-strain relationship of the GPC revealed that it conformed to the prediction model. The strains at peak stress were 0.0024 to 0.0026, which are similar to concrete based on PC. The splitting tensile strength was determined to only be a fraction of the compressive strength, although it was higher than the values recommended by the prediction model.

Mustafa et al. (2011) studied geopolymer based on Class F FA from Sultan Abdul Aziz Power Station in Kapar, Malaysia, to determine the effect of oxide molar ratios of $\text{SiO}_2 : \text{Al}_2\text{O}_3$, H_2O content of the alkaline activator and the Na_2SiO_3 content for each activator : FA ratio. NaOH pellets (97-99% purity) were dissolved in H_2O to make a 15M NaOH solution. One day prior to adding the activator to the solid constituent, technical grade Na_2SiO_3 solution (9.4% Na_2O , 30.1% SiO_2 , 60.5% H_2O) was mixed with the NaOH solution.

The alkaline activator : FA ratio was manipulated from levels of 0.3 to 0.4 during the experiment. Prior to casting the geopolymer into 2" cube specimens, FA was mixed with the alkaline activator and 17% H_2O by mass for 15 minutes. Specimens were cured

for 24 hours at room temperature then for 24 hours at 158°F in a furnace. The specimens were demolded after curing at elevated temperatures and aged for 7 days at room temperature. To prevent H₂O evaporation, the molds were sealed with plastic during storage, curing and aging.

Test results indicated that the compressive strength of the geopolymer was highest, up to 1204 psi, when the Na₂SiO₃ : NaOH ratio was 1.0. This value corresponded with a SiO₂ : Al₂O₃ ratio of 4.12 and a H₂O : Na₂O ratio of 11. Decreased strength resulted from varying the constituents less or more than the suitable value.

Guo et al. (2010) investigated the use of Class C FA from First Energy Corporation in Ohio for a geopolymer binder. NaOH pellets (99.2% purity) and Na₂SiO₃ solution (9.1% Na₂O, 29.2% SiO₂, 61.7% H₂O) were acquired from Fisher Scientific Company. In the experimental design, the molar ratio of SiO₂ : Na₂O in the mixed alkali activator was manipulated at levels of 1.0, 1.5 and 2.0. For each molar ratio, the content of the activator varied from 6% to 15% by the mass proportion of Na₂O : FA. The mass ratio of H₂O : FA remained at a constant level of 0.40, including the H₂O in the mixed alkaline activator.

The geopolymer binder was mixed at approximately 73°F; however, the procedure for mixing was not described. The fresh paste was then poured into 1" cube molds and covered with a vinyl sheet to prevent moisture loss and carbonation of the surface. Half of the specimens were cured at 73°F for 3, 7 and 28 days, and the other half were cured at elevated temperatures of 140°F to 194°F for 4, 8 and 24 hours.

The optimum molar ratio of SiO₂ : Na₂O for improving compressive strength was 1.5, and the proper content of the activator was 10% by the mass proportion of Na₂O :

FA. Compressive strengths of 3278 psi, 5004 psi and 8601 psi were measured for specimens cured at 73°F for 3, 7 and 28 days, respectively. The elevated curing temperature of 167°F produced the strongest specimens, and higher compressive strengths were measured as specimen age increased. Compressive strengths of 4438 psi, 5163 psi and 5627 psi were measured for specimens at 4, 8 and 24 hours, respectively, when the molar ratio and activator content were at the optimum levels.

2.5.2 Ambient Curing vs. Heat Curing

Vijai et al. (2010) studied the effect of curing conditions on the compressive strength of GPC based on Class F FA from Mettur Thermal Power Station in Tamil Nadu, India. NaOH flakes (98% purity) and Na₂SiO₃ solution (14.7% Na₂O, 29.4% SiO₂, 55.9% H₂O) were used as the alkaline activator. The NaOH flakes were dissolved in H₂O to make an 8M NaOH solution, and the ratio of Na₂SiO₃ solution : NaOH solution was fixed at 2.5. A 0.4 ratio of activator : FA was also maintained. Aggregates composed 77% of the GPC mass, and 30% of the aggregate was river sand. Extra H₂O and super plasticizer were also added to the mixture to achieve adequate workability.

The NaOH and Na₂SiO₃ solutions were mixed 1 day prior to combining them with the solid constituents. Aggregates and FA were mixed in a pan mixer for 3 minutes, and then the alkaline activator was added and mixed for an additional 4 minutes. 6" cube specimens were cast and subjected to mechanical vibration. After 5 days, the specimens were demolded and cured in different conditions. Half of the specimens were left in ambient conditions, and the other half were cured at 140°F in an oven for 24 hours.

The density of the hardened GPC specimens was found to be similar to concrete based on PC, ranging from 141 lb/ft³ to 150 lb/ft³. Only slight variations in density were

measured due to the effect of age and curing type. Specimens that were cured in ambient conditions obtained a compressive strength of 564 psi after 7 days and 2566 psi after 28 days. However, specimens cured in the oven reached strengths of 4106 psi after 7 days and 4818 psi after 28 days.

Skvara et al. (2007) examined the properties of GPC based on FA from Czech power plants. Concrete was prepared by mixing fine and coarse aggregate with FA and an alkaline activator. The aggregate gradation was in accordance with DIN/ISO 3310-1 standards. The SiO_2 : Na_2O molar ratio of the alkaline activator was manipulated by combining NaOH with soluble glass, and molar ratios ranging from 1 to 1.6 were considered. The ratio of the activator Na_2O : FA by mass varied in the range of 6% to 10%, and H_2O : FA ratios ranging from 0.30 to 0.40 were also used in the experiment. Ground slag, gypsum and limestone were added to the concrete in some cases. The effect of steel, glass and synthetic fiber reinforcement was also studied.

Some specimens were cured, demolded and maintained at room temperature with 40% relative humidity for 28 days. Specimens were also submersed in solutions of Na_2SO_4 , MgSO_4 and NaCl in accordance with CSN EN 206-1 standards. GPC was subjected to freeze-thaw cycling tests in accordance with CSN 72-4252 standards. Other specimens were subjected to heat treatment ranging from 104°F to 194°F for 6 to 24 hours then aged for 2, 7, 28, 90 and 360 days at room temperature before measuring their compressive strength.

Results of the study indicated that concrete containing higher amounts of FA have increased levels of static and dynamic viscosity and, therefore, require longer compaction treatments. However, higher levels of H_2O content led to segregation of the aggregate

and cement, regardless of whether vibration treatment occurred. The inclusion of ground slag, gypsum and limestone decreased segregation. Faster mixing of the fresh GPC led to an increased air content, which remained enclosed in the fresh concrete due to its low mobility.

The compressive strength of the specimens increased with age, and the highest strength was measured from GPC containing FA and slag. Measured values of compressive strength ranged from 2176 psi to 23206 psi. No shrinkage due to hydration was measured for the specimens. The ratio of compressive : splitting tensile strength varied in the range of 10:5.5, compared to 10:1 for concrete based on PC.

Original FA particles were present in some specimens, and the effect of gradual dissolution was evident. The specimens also exhibited a higher porosity, which was influenced by the H_2O : FA ratio, the SiO_2 : Na_2O molar ratio and the Na_2O content. Specimens containing FA with slag or gypsum had decreased porosity and higher compressive strength.

The mass and form of the specimens did not change during the freeze-thaw cycling tests, but their compressive strength was lower than specimens kept in ambient conditions. Specimens exposed to NaCl solution resisted corrosion, and their compressive strength still consistently increased over time. The mass of the specimens increased by approximately 3% after one year then stabilized.

The effect of elevated temperatures ranging from 302°F to 2012°F on mechanical properties was also considered. Specimens were subjected to three-point loading to determine tensile strength, and the lowest strengths were measured in the temperature range of 1112°F to 1292°F. The strength of the specimens exposed to high temperatures

was 40% less than those kept at ambient conditions. Plastic deformation led to the gradual rupture of the GPC specimens.

Nano-pores are similar in GPC regardless of the preparation process. However, macro-pores are produced by air introduced during the mixing procedure, causing a substantial decrease in strength. Additives that contain CaO were shown to reduce porosity as the geopolymer phase coexisted with the C-S-H matrix.

Manjunath et al. (2011) investigated the mechanical behavior of ambient cured GPM containing the following industrial byproducts: quarry dust, silica fume, ground granulated blast furnace slag and Class F FA from Raichur Thermal Power Station in Karnataka, India. Commercial grade NaOH pellets (97-98% purity) and Na_2SiO_3 liquid were utilized as the alkaline activator.

Variables manipulated for GPM composition included the binder : fine aggregate ratio (1:2, 1:2.5), FA : slag : silica fume ratio (60:40:0, 60:35:5, 50:50:0, 50:45:5, 40:60:0, 40:55:5), activator molarity (12M, 14M) and activator : binder ratio (0.4, 0.45). A constant ratio of 1:2 was maintained for NaOH : Na_2SiO_3 . For each set of parameters, the binder components were first combined with the quarry dust, and then the activator solution was added and mixed until a homogeneous mortar resulted. 3" cube specimens were cast and compacted with a vibrator. Specimens were demolded after 2 hours of curing in ambient conditions and left at room temperature until tested.

The compressive strength of the ambient cured GPM increased with age due to the continuous formation of Si-O-Al-O and C-S-H gel. The strength of the specimens was comparable to mortar containing PC, sufficient enough for handling and transport after 1 day and early masonry work after 7 days. The silica fume marginally reduced the

compressive strength but improved the flowability. An activator : binder ratio of 0.45 also produced GPM with adequate workability, fewer voids and higher strength; however, a ratio of 0.4 produced a dryer mixture that required additional compaction effort. The researchers recommend for further study to be undertaken with regards to the effect of the activator : binder ratio on the workability of fresh geopolymers. An alkaline activator with a higher molarity will increase the formation of geopolymeric gel; therefore, the 14M alkaline activator solution corresponded to higher compressive strength when compared to the 12M solution. Improved strength was also related to a higher binder : fine aggregate ratio.

2.5.3 Class C Fly Ash vs. Class F Fly Ash

Diaz-Loya et al. (2011) performed an experimental study on the mechanical properties of GPC based on FA from 25 sources in the United States, consisting of 12 Class C and 13 Class F sources. Na_2SiO_3 (45% by mass with a SiO_2 : Na_2O ratio of 2) and 14M NaOH solution were mixed at a 1:1 ratio by mass. To obtain adequate workability, the activator : FA ratio was adjusted. Sand and gravel served as the fine and coarse aggregate.

The constituents were mixed in a vertical mixer with planetary action. First, the FA and NaOH solution were mixed for 30 seconds, and then the Na_2SiO_3 solution was added and mixed for 30 seconds. Sand was mixed in for 60 seconds, and then gravel was added and mixed for 120 seconds. A high-range water reducer was also put in the mixture 60 seconds prior to ending the mixing cycle. 6"×12" cylindrical concrete specimens were cast to determine compressive strength, static elastic modulus and Poisson's ratio. 4"×4"×16" rectangular prism specimens were also cast to determine

flexural strength. The setting time of the GPC was measured with a Vicat needle.

Specimens were demolded after 24 hours, cured at 140°F for 72 hours and aged 1 day at room temperature before testing.

The density of the hardened GPC varied from 118 lb/ft³ to 148 lb/ft³, and 1.5 to 600 minutes were measured for the setting times. The compressive strength ranged from 1500 psi to 11657 psi, and the flexural strength ranged from 397 psi to 929 psi. On average, when compared to Class F, the Class C FA specimens had higher density, compressive strength, flexural strength and faster setting time. Based on the results of the study, it was determined that the fineness, crystallographic distribution and chemical composition of the FA as well as the mix design parameters dictate the mechanical behavior of GPC.

Leelathawornsuk (2009) studied the role of NaOH concentration in geopolymer based on Class C and Class F FA from the Mae Moh Lignite Power Plant in Lampang, Thailand. NaOH flakes (98% purity) and Na₂SiO₃ solution (14.7% Na₂O, 29.4% SiO₂, 55.9% H₂O) were utilized as the alkaline activator. The NaOH was dissolved in H₂O to prepare NaOH solutions varying from 2M to 10M, and the NaOH : FA ratio was also manipulated, ranging from 0.21 to 1.17 by mass. The amount of Na₂SiO₃ solution utilized for each mix design was equal to the mass of NaOH.

Before casting the geopolymer into 1.5"×3" cylindrical molds, the FA and NaOH solution were mixed for 5 minutes. This was followed by the addition of the Na₂SiO₃ solution and another 5 minutes of mixing. Specimens were demolded after 24 hours of curing at room temperature, and then they were wrapped with plastic film and kept in zip lock bags to prevent evaporation of H₂O. Compressive testing of specimens was

conducted at ages of 1, 3, 7, 14 and 28 days. An investigation of the geopolymer microstructure was also performed as part of the experimental study.

An increase in the age of the geopolymer specimens resulted in higher compressive strength, up to 5076 psi, and most strength was gained during the first 14 days. Specimens based on Class C FA were slightly stronger than their Class F counterparts, and higher NaOH content also increased strength due to improved dissolution of Al_2SiO_5 . The higher CaO content of the Class C FA was found to have a positive effect on the compressive strength of the geopolymer binder. Formation of amorphous Ca-Al-Si gel decreased microstructural porosity and, thereby, increased strength.

Setting times ranged from 30 to 2035 minutes, and geopolymer based on Class C FA had a shorter setting time than the Class F. Scanning electron microscopy revealed pores, microcracks and non-reacted FA. A ratio of NaOH : FA over 0.50 produced larger pores and lower strength compared to a NaOH : FA ratio less than 0.50. The density ranged from 90 lb/ft³ to 139 lb/ft³, with the Class C fly ash specimens having higher density. Recommendation was made for a study investigating the inclusion of a CaO admixture, as it is expected to create a binding phase of Ca-Al-Si.

2.5.4 Coarse Fly Ash vs. Fine Fly Ash

Chindaprasirt et al. (2007) performed an empirical study that investigated the variables affecting the workability and strength of GPM based on coarse Class C FA from the Mae Moh Power Station in northern Thailand. Knowledge of geopolymers will benefit this region due to the large annual output of coarse FA from the power station. The experiment employed NaOH and Na_2SiO_3 (15.32% Na_2O , 32.87% SiO_2 , 51.81%

H₂O) as the alkaline activator and river sand as the fine aggregate. A constant fine aggregate : FA ratio of 2.75 was maintained. H₂O and super plasticizer were also added to sustain workability of the mixture. Three different concentrations of NaOH (10M, 15M, 20M) were made to test mix designs at four different ratios of Na₂SiO₃ : NaOH (0.67, 1.00, 1.50, 3.00). A minimum H₂O content of 5% by mass of the geopolymer paste was used for all mixes.

The procedure began with the NaOH solution, H₂O and FA being mixed in a pan mixer for 5 minutes. This was followed by the addition of the fine aggregate and 5 more minutes of mixing. Finally, the Na₂SiO₃ solution was added and mixed for another 5 minutes. After the mortar was cast into molds, specimens were subjected to different methods of curing, including variations in the duration, time delay and temperature.

Results of the study indicated that GPM specimens prepared with 10M NaOH solution and Na₂SiO₃ : NaOH ratios of 0.67, 1.00 and 1.50 had flows of 135%, 125% and 110%, respectively. The mixtures made with 15M NaOH solution were thicker and required the addition of 3.4% H₂O by mass of FA. The 20M NaOH solution produced the thickest mix and required the addition of 6.8% H₂O by mass of FA. Average compressive strengths of 7020 psi, 7121 psi and 7281 psi were measured for mixtures based on 10M, 15M and 20M NaOH solutions, respectively. The effect of NaOH concentration on compression strength was not apparent, possibly due to the variation in H₂O content between the mixtures. However, it was evident that Na₂SiO₃ : NaOH ratios of 0.67 and 1.00 produced GPM with higher strength compared to ratios of 1.5 and 3.0.

The study concluded that increases in NaOH and Na₂SiO₃ content reduced the flow of fresh GPM. Workability could be improved, however, with the addition of H₂O

but not super plasticizer. The most suitable method for obtaining high strength GPM was to subject the samples to heat after a time delay of 1 hour by curing them in the oven at 167°F for not less than 2 days.

Sulc & Svoboda (2009) also examined the effect of alkaline activation on the mechanical behavior of ground FA from the Opatovice Coal Power & Heating Plant in the Czech Republic. The FA was ground in a Los Angeles type grinding mill to produce eight samples of that varied by a grinding time from 0 to 270 minutes. Some specimens were cured at an ambient temperature of 68°F, and others were cured at an elevated temperature of 176°F for 24 hours. After 14, 28 and 90 days, respectively, the geopolymer based on the finest FA obtained compressive strengths of approximately 1740 psi, 5511 psi and 10442 psi.

Chindaprasirt et al. (2011) performed a more recent study that focuses on the effect of FA fineness on the properties of fresh and hardened GPM. The experimental design included the following variables: original coarse FA (Class C FA from source), medium FA (finest 40% from source) and fine FA (finest 10% from source). Locally available river sand was mixed with the fly ash, 10M NaOH solution and Na_2SiO_3 solution (15.32% Na_2O , 32.87% SiO_2 , 51.81% H_2O). The GPM was prepared with a 1:1 mass ratio of NaOH solution : Na_2SiO_3 solution and a fine aggregate : FA ratio of 2.75. The procedure started with mixing FA, NaOH and H_2O in a pan mixer for 5 minutes, and then the fine aggregate was added and mixed for another 5 minutes. Finally, the Na_2SiO_3 solution was added and mixed for a final 5 minutes. After compacting the GPM into 2" cube molds, the specimens were wrapped with vinyl sheets.

The curing process was manipulated to determine its effect on the geopolymerization of the source materials. Time delay was varied from 0 to 24 hours, curing temperature was set from 86°F to 194°F, and curing period was investigated from 1 to 5 days. Following the curing period, the compressive strength of the specimens was measured at ages of 7, 28 and 90 days. The workability, setting time and drying shrinkage were also considered.

Results of the study indicated that the most effective scenario for producing high strength GPM was with a 1 hour time delay and curing temperature of 167°F for 3 days. Compressive strength of the specimens also increased with age. The highest strengths achieved from the coarse FA after 7, 28 and 90 days were 6237 psi, 7687 psi and 7977 psi, respectively. At the same ages, however, the highest strengths for fine FA specimens were 10878 psi, 12183 psi and 12618 psi.

With respect to the order, initial setting times of 315, 280 and 165 minutes and final setting times of 390, 305 and 240 minutes were measured for coarse, medium and fine FA specimens. Hence, finer FA decreases setting time. Also, the flow of the fresh GPM was 125%, 150% and 175%, increasing as FA particle size decreases. The small spherical particles with smooth surfaces that characterize finer FA contribute to its enhanced workability.

The study concluded that finer FA is much more effective for synthesizing high strength geopolymers, providing high workability and excellent volumetric stability. The drying shrinkage tests also indicated minimal strain of the specimens. While the experiment found fine Class C FA to be superior in many ways, the specimens began to

slightly expand after 14 days rather than shrink. Further investigations into the microstructural changes that occur during drying were recommended.

Somna et al. (2011) also studied the effect of NaOH concentration on the strength of ambient cured geopolymer based on ground Class C FA from Mae Moh Power Plant in Thailand. 32% of the original FA could be retained on a #325 sieve. To decrease the median particle size, the FA was ground utilizing a ball mill until 2% could be retained on a #325 sieve. NaOH solution was the source of the alkaline activator, and concentrations varied from 4.5M to 16.5M. FA was mixed with the activator for 5 minutes, and then the geopolymer was cast into 1"×2" cylinders. The specimens were stored in a controlled chamber at 77°F to 82°F. Compressive testing was performed in accordance with ASTM D1633 at 7, 14, 28, 42 and 60 days, and a microstructural analysis was also conducted.

The strength of the specimens increased over time due to the reaction of Al_2SiO_5 in the presence of alkaline ions, and higher compressive strength was measured for geopolymer based on ground FA compared to original FA. Increasing the fineness and, therefore, the surface area of the FA was favorable for geopolymer formation. Through the leaching of Al_2O_3 and SiO_2 , the compressive strength of the specimens also increased for concentrations of NaOH up to 14M. The specimens obtained compressive strengths of 2901 psi to 3336 psi when NaOH concentration ranged from 9.5M to 14M.

Excessive OH^- ions accelerated dissolution but decreased polycondensation, causing the binder to precipitate early and lose strength. Based on the results of the study, NaOH concentrations of 9.5M to 14M were recommended for ground FA with a median particle size of 10.5 μm ; however, coarser FA needs higher concentrations and

may require curing at elevated temperatures. Results of the microstructural analysis indicated that geopolymerization occurred in ambient conditions.

2.5.5 Rheological Behavior

Rheology is the study of the flow of materials. Bhattacharjee & Laskar (2010) presented the results of a study on the rheological behavior of GPC based on Class F FA. Commercial grade NaOH (97% purity) and Na₂SiO₃ solution (18.2% Na₂O, 36.7% SiO₂, 45.1% H₂O) were used to prepare the alkaline solution. The molarity of the NaOH solution was manipulated for the experimental program. The FA and aggregates were mixed for 2 minutes, and then the alkaline solution was added and mixed for another 2 minutes.

Rheological measurements were taken 15 minutes after mixing with a rate controlled concrete rheometer, which consisted of a servo motor driving an impeller through a gearbox. The GPC behaved accurately in accordance with the Bingham model. Yield stress and plastic viscosity could be estimated from the torque-speed plot.

2.6 Review Summary

Based on the conclusions found within the scientific literature regarding the synthesis of geopolymers, the following claims can be made:

1. Increasing the NaOH and Na₂SiO₃ content reduces the flow of fresh geopolymer.

Workability can be improved, however, with the addition of extra H₂O.

2. Excessive OH⁻ ions accelerate dissolution but decrease polycondensation, causing the binder to precipitate early and lose strength.
3. Excessive H₂O content creates segregation between the constituents and lowers the strength of the final structure.

4. Nano-pores are similar in GPC regardless of the preparation process. However, a higher rate of mixing leads to an increased amount of air content, which remains enclosed in the fresh concrete due to its low mobility. Additives that contain CaO reduce porosity as the geopolymer phase coexists with the C-S-H matrix.
5. GPC containing high amounts of FA has increased levels of static and dynamic viscosity and, therefore, requires higher compaction energy.
6. Decreased strength results from varying the constituents of the alkaline activator less or more than the suitable value.
7. Strength increases as an effect of age, longer mixing time and raising the curing temperature.
8. The density of GPC is similar to concrete based on PC, varying only slightly due to the effect of age and curing type.
9. Fine FA is much more effective for synthesizing high strength geopolymers, providing increased surface area, high workability and excellent volumetric stability.
10. The mix design parameters as well as the fineness, crystallographic distribution and chemical composition of the FA dictate the mechanical behavior of geopolymers.
11. On average, when compared to Class F, geopolymer based on Class C FA has higher density, compressive strength, flexural strength and faster setting time. The presence of CaO improves the chemical reaction through formation of amorphous Ca-Al-Si gel that decreases microstructural porosity and increases strength of the hardened matrix.

2.7 Recommendations for the Present Study

The following recommendations have been made for the present study based on the findings of previous investigations:

1. Further research is needed to develop ambient cured geopolymers for practical applications in the concrete industry (Davidovits, 2011).
2. FA from different sources should be considered for use in geopolymer binders due to variations in particulate size, surface area and mineral content (Leelathawornsuk, 2009).
3. Further study should be undertaken with regards to the effect of the alkaline activator on the workability and strength of geopolymers (Manjunath et al., 2011).
4. Additional investigation is needed to determine the microstructural changes that occur during the drying of geopolymers (Chindaprasirt et al., 2011).
5. The rheological behavior of GPC based on FA should be considered, as limited investigation has been made concerning its flow characteristics (Bhattacharjee & Laskar, 2010).

CHAPTER III

METHODOLOGY

3.1 Geopolymer Mortar

3.1.1 Specimen

To determine the effect of the alkaline activator composition on constructability and physical properties, GPM was mixed and cast into 2" cube specimens. Table 2 presents the composition of the mix designs.

Table 2. Geopolymer Mortar Mix Designs.

#	NaOH : FA Ratio	Na ₂ SiO ₃ : FA Ratio	Fly Ash (lb/yd ³)	Limestone Sand (lb/yd ³)	H ₂ O (lb/yd ³)	NaOH Pellets (lb/yd ³)	Na ₂ SiO ₃ Solution (lb/yd ³)
1	0.050	0.025	1213	1213	567	61	69
2	0.050	0.050	1213	1213	529	61	138
3	0.050	0.075	1213	1213	491	61	206
4	0.050	0.100	1213	1213	452	61	275
5	0.075	0.025	1213	1213	567	91	69
6	0.075	0.050	1213	1213	529	91	138
7	0.075	0.075	1213	1213	491	91	206
8	0.075	0.100	1213	1213	452	91	275
9	0.100	0.025	1213	1213	567	121	69
10	0.100	0.050	1213	1213	529	121	138
11	0.100	0.075	1213	1213	491	121	206
12	0.100	0.100	1213	1213	452	121	275
13	0.125	0.025	1213	1213	567	152	69
14	0.125	0.050	1213	1213	529	152	138
15	0.125	0.075	1213	1213	491	152	206
16	0.125	0.100	1213	1213	452	152	275

The fine aggregate : FA ratio of 1.0 and H₂O : FA ratio of 0.5 remained constant for all GPM mixes. H₂O content of the Na₂SiO₃ solution was included in the ratio and accounted for during mix design calculations. As per the experimental design, the specimens varied only by their NaOH : FA ratio and Na₂SiO₃ : FA ratio by mass.

Additional 2" cube specimens were cast as required to determine the effect of age on the compressive strength of the strongest GPM mix design. GPM was also cast into 1"×1"×11.25" prism specimens to determine the effect of age on drying shrinkage. The specimens are shown in Figure 2.

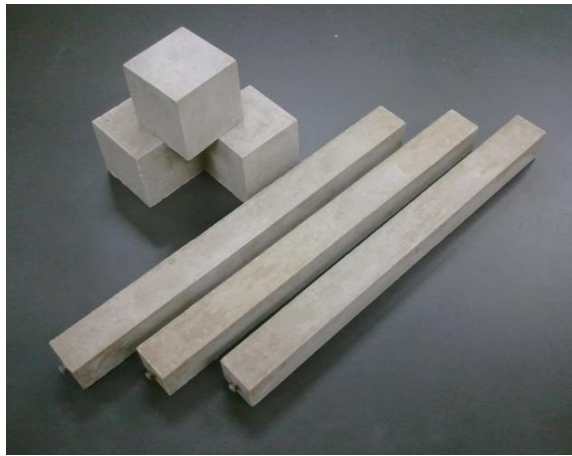


Figure 2. Geopolymer Mortar Specimens.

3.1.2 Materials

FA from the Calaveras Power Station in San Antonio, Texas, was utilized as the primary component of the GPM. Limestone sand was the source of fine aggregate, and the alkaline activator was composed of NaOH and Na₂SiO₃. Table 3 presents the physical properties of the geopolymer components.

Table 3. Physical Properties of Geopolymer Components.

Material	Source	Chemical Composition	Specific Gravity	Retained on #325 Sieve
Class C Fly Ash	Boral Material Technologies	> 80% CaAl ₂ Si ₂ O ₈ < 15% Fe ₂ MgO ₄ < 5% Na ₂ K ₂ SO ₅	2.65	11%
NaOH Pellets	Fisher Scientific	> 95% NaOH < 3% Na ₂ CO ₃	2.13	-
Na ₂ SiO ₃ Solution	PQ Corporation	14.7% Na ₂ O 29.4% SiO ₂ 55.9% H ₂ O	1.53	-
Water	Tap	H ₂ O	1.00	-

The specific gravity, density and absorption of the limestone sand were calculated, and a sieve analysis was also performed (ASTM C136, 2006; ASTM C33, 2011; ASTM C128, 2012). Table 4 presents the physical properties of the limestone sand, and Figure 3 illustrates the results of the sieve analysis.

Table 4. Physical Properties of Limestone Sand.

Material	OD SG	SSD SG	Apparent Specific Gravity	OD Density (lb/ft ³)	SSD Density (lb/ft ³)	Apparent Density (lb/ft ³)	Absorption (%)	Fineness Modulus
Limestone Sand	2.46	2.57	2.77	153	160	172	4.6	2.91

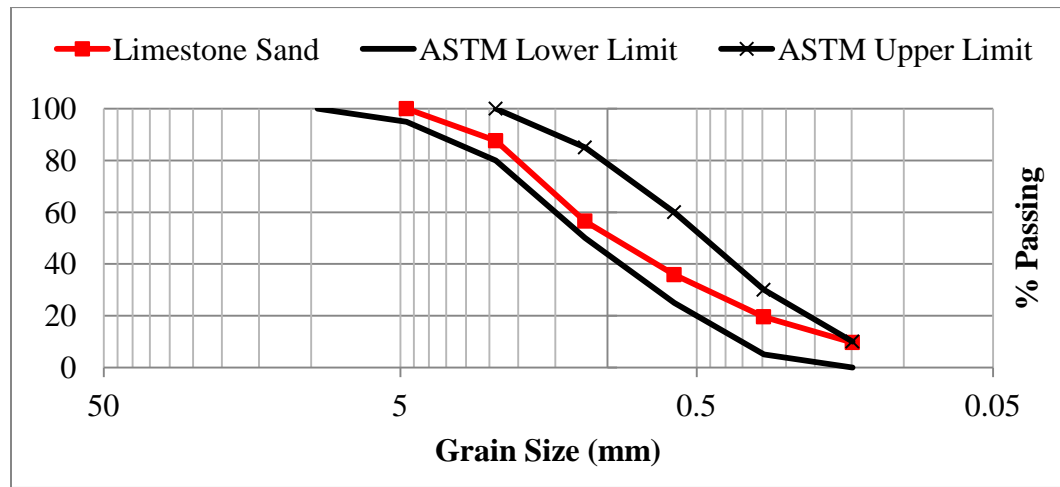


Figure 3. Sieve Analysis of Limestone Sand.

3.1.3 Procedures

3.1.3.1 Mixing

Components of the GPM were stored in sealed containers in a laboratory setting at approximately 75°F. Prior to beginning the mixing procedure, each component was measured as per the mix design specification. Due to the tendency of geopolymer based on Class C FA to flash set in unfavorable conditions, the GPM was mixed by hand to prevent unnecessary damage to laboratory equipment. First, the FA and limestone sand were dry mixed for 1 minute, and then the H₂O and Na₂SiO₃ solution were added and

mixed for 2 minutes. Finally, the NaOH pellets were incorporated, and the GPM was mixed for an additional 10 minutes. This mixing procedure was based on previous investigations.

3.1.3.2 *Temperature*

The temperature of the fresh GPM was measured with a digital stem type thermometer in accordance with ASTM C1064 (2011).

3.1.3.3 *Flow*

A flow table was utilized to measure the flow of the fresh GPM in accordance with ASTM C1437 (2007).

3.1.3.4 *Casting*

The fresh GPM was cast into 2" cube specimens and then subjected to external vibration for 1 minute if required in accordance with ASTM C109 (2011). Molds were stored in ambient conditions and sealed with plastic wrap to prevent H₂O evaporation. Specimens were demolded immediately before measuring hardened physical properties.

3.1.3.5 *Density*

Digital scales and calipers were utilized to measure mass and dimensions in order to determine the density of fresh and hardened GPM specimens.

3.1.3.6 *Compressive Strength*

The compressive strength of the specimens in the factorial design was determined 7 days after the mixing procedure. Additional 2" cube specimens were cast as required to determine the effect of age on the compressive strength of the strongest GPM mix design. Measurements were recorded at 1, 3, 7 and 28 days. Compressive testing was performed with a Test Mark CM400 Compressive Machine in accordance with ASTM C109 (2011).

3.1.3.7 Drying Shrinkage

1"×1"×11.25" prism specimens were cast as required to determine the effect of age on the drying shrinkage of the strongest GPM mix design. A length comparator was utilized to measure drying shrinkage in accordance with ASTM C596 (2009). Prism specimens were cured in ambient conditions rather than curing in lime saturated water, and measurements were recorded at 1, 7, 14, 21 and 28 days.

3.1.4 Analytical Techniques

The data was subjected to an analysis of variance (ANOVA) utilizing SPSS statistical software. This method establishes the magnitude of the total variation in the results and distinguishes the random variation from the contribution of each variable. A conventional level of significance ($p < 0.05$) was used for the statistical analysis.

3.2 Geopolymer Concrete

3.2.1 Specimen

To determine the effect of the alkaline activator composition on constructability and physical properties, GPC was mixed and cast into 3"×6" cylindrical specimens.

Table 5 presents the composition of the mix designs.

Table 5. Geopolymer Concrete Mix Designs.

#	NaOH : FA Ratio	Na ₂ SiO ₃ : FA Ratio	Fly Ash (lb/yd ³)	Limestone Sand (lb/yd ³)	River Gravel (lb/yd ³)	H ₂ O (lb/yd ³)	NaOH Pellets (lb/yd ³)	Na ₂ SiO ₃ Solution (lb/yd ³)
1	0.09	0.09	674	674	1831	260	61	138
2	0.09	0.10	674	674	1831	251	61	153
3	0.09	0.11	674	674	1831	243	61	168
4	0.10	0.09	674	674	1831	260	67	138
5	0.10	0.10	674	674	1831	251	67	153
6	0.10	0.11	674	674	1831	243	67	168
7	0.11	0.09	674	674	1831	260	74	138
8	0.11	0.10	674	674	1831	251	74	153
9	0.11	0.11	674	674	1831	243	74	168
10	0.12	0.09	674	674	1831	260	81	138
11	0.12	0.10	674	674	1831	251	81	153
12	0.12	0.11	674	674	1831	243	81	168

The H_2O : FA ratio of 0.5 remained constant for all GPC mixes. H_2O content of the Na_2SiO_3 solution was included in the ratio and accounted for during mix design calculations. Constant ratios of fine and coarse aggregate were also maintained. As per the experimental design, the specimens varied only by their NaOH : FA ratio and Na_2SiO_3 : FA ratio by mass.

Additional 3"×6" cylindrical specimens were cast as required to determine the effect of age on the pulse velocity, splitting tensile strength and compressive strength of the strongest GPC mix design that was adequately workable. GPC was also cast into 3"×3"×11.25" prism specimens to determine the effect of age on drying shrinkage. The specimens are shown in Figure 4.



Figure 4. Geopolymer Concrete Specimens.

3.2.2 Materials

River gravel was the source of coarse aggregate. The specific gravity, density and absorption of the aggregate were calculated, and a sieve analysis was also performed (ASTM C136, 2006; ASTM C127, 2007; ASTM C33, 2011). Table 6 presents the physical properties of the river gravel, and Figure 5 illustrates the results of the sieve analysis.

Table 6. Physical Properties of River Gravel.

Material	OD SG	SSD SG	Apparent Specific Gravity	OD Density (lb/ft ³)	SSD Density (lb/ft ³)	Apparent Density (lb/ft ³)	Absorption (%)	Fineness Modulus
River Gravel	2.52	2.55	2.59	157	159	161	1.1	5.88

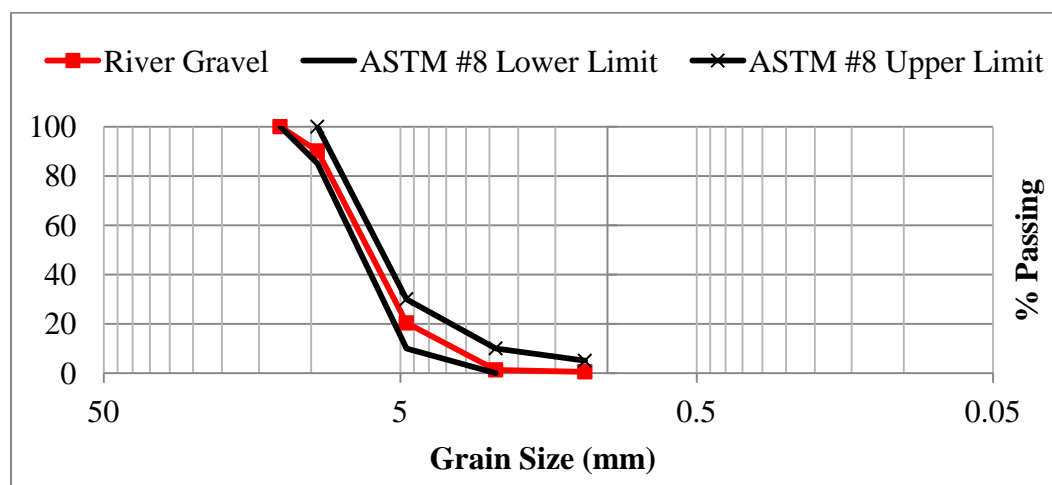


Figure 5. Sieve Analysis of River Gravel.

3.2.3 Procedures

3.2.3.1 Mixing

Components of the GPC were stored in sealed containers in a laboratory setting at approximately 75°F. Prior to beginning the mixing procedure, each component was measured as per the mix design specification, and the coarse aggregate was prepared in a SSD condition. Mixing was performed with a 20 quart planetary mixer. First, the FA, limestone sand and river gravel were dry mixed for 1 minute, and then the H₂O and Na₂SiO₃ solution were added and mixed for 1 minute. Finally, the NaOH pellets were incorporated, and the GPC was mixed for an additional 5 minutes. This mixing procedure was based on previous investigations.

3.2.3.2 Temperature

The temperature of the fresh GPC was measured with a digital stem type thermometer in accordance with ASTM C1064 (2011).

3.2.3.3 Slump

A slump cone was utilized to measure the slump of the fresh GPC in accordance with ASTM C143 (2010).

3.2.3.4 Air Content

An air meter was utilized to measure the air content of freshly mixed GPC in accordance with ASTM C173 (2010).

3.2.3.5 Casting

The fresh GPC was cast into 3"×6" cylindrical specimens and then subjected to external vibration for 1 minute if required in accordance with ASTM C192 (2007).

Molds were stored in ambient conditions and sealed to prevent H₂O evaporation.

Specimens were demolded immediately before measuring hardened physical properties.

3.2.3.6 Setting Time

A penetration resistance apparatus was utilized to measure the setting time in accordance with ASTM C403 (2008).

3.2.3.7 Density

Digital scales and calipers were utilized to measure mass and dimensions in order to determine the density of fresh and hardened GPC specimens.

3.2.3.8 Pulse Velocity

The pulse velocity of the specimens in the factorial design was determined 7 days after the mixing procedure. Additional 3"×6" cylindrical specimens were cast as required

to determine the effect of age on the pulse velocity of the strongest GPC mix design that was adequately workable. A James Instruments V-Meter MK III pulse generator with transmitting transducer was utilized to measure the pulse velocity of hardened GPC specimens in accordance with ASTM C597 (2009).

3.2.3.9 *Splitting Tensile Strength*

The splitting tensile strength of the specimens in the factorial design was determined 7 days after the mixing procedure. Additional 3"×6" cylindrical specimens were cast as required to determine the effect of age on the splitting tensile strength of the strongest GPC mix design that was adequately workable. Measurements were recorded at 1, 3, 7 and 28 days. Testing was performed with a Test Mark CM400 Compressive Machine in accordance with ASTM C496 (2011).

3.2.3.10 *Compressive Strength*

The compressive strength of the specimens in the factorial design was determined 7 days after the mixing procedure. Additional 3"×6" cylindrical specimens were cast as required to determine the effect of age on the compressive strength of the strongest GPC mix design that was adequately workable. Measurements were recorded at 1, 3, 7 and 28 days. Testing was performed with a Test Mark CM400 Compressive Machine in accordance with ASTM C39 (2009).

3.2.3.11 *Drying Shrinkage*

3"×3"×11.25" prism specimens were cast as required to determine the effect of age on the drying shrinkage of the strongest GPC mix design that was adequately workable. A length comparator was utilized to measure drying shrinkage in accordance with ASTM C596 (2009). Prism specimens were cured in ambient conditions rather than

curing in lime saturated water, and measurements were recorded at 1, 7, 14, 21 and 28 days.

CHAPTER IV

RESULTS

4.1 Geopolymer Mortar

4.1.1 Temperature

The properties of fresh GPM are considered to be important due to the relation they have with the material's workability. Table 7 and Figure 6 show the test results for temperature, which ranged from 89.4°F to 129.0°F. The temperature increased with higher levels of NaOH and Na_2SiO_3 due to the caustic nature of the strong chemical base.

Table 7. Effect of Sodium Silicate and Sodium Hydroxide on Temperature.

Temperature (°F)		NaOH : FA Ratio by Mass			
		0.050	0.075	0.100	0.125
Na ₂ SiO ₃ : FA Ratio by Mass	0.025	89.4	94.8	109.6	126.5
	0.050	91.4	97.7	108.3	129.0
	0.075	93.6	102.9	111.2	120.7
	0.100	99.1	105.3	115.3	125.5

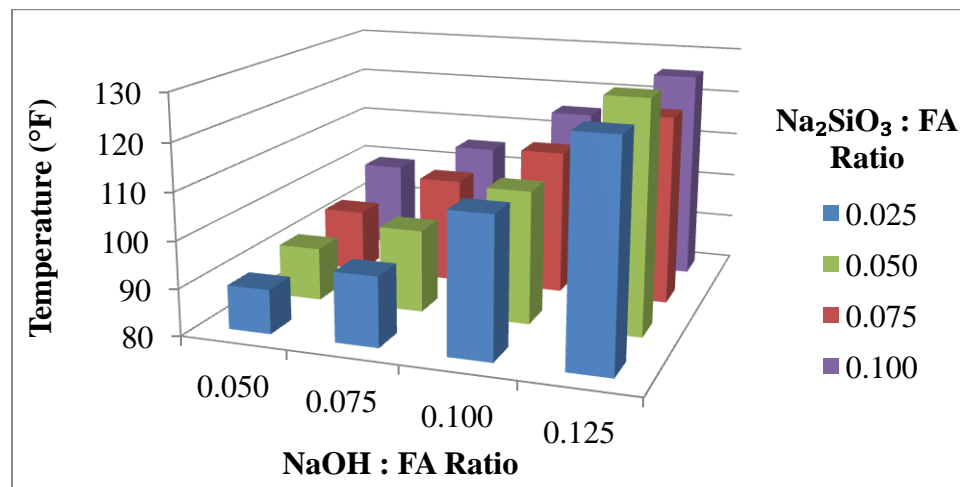


Figure 6. Effect of Sodium Silicate and Sodium Hydroxide on Temperature.

4.1.2 Flow

Flow was measured as the resulting percentage increase in average base diameter of the fresh GPM. The test results for flow are shown in Table 8 and Figure 7. Lower levels of NaOH and Na₂SiO₃ produced mixtures with flow greater than 150%. However, the flow decreased as a result of increasing the NaOH component. Additional OH⁻ ions accelerated dissolution, causing the binder to precipitate earlier. Higher viscosity and rapid formation of the binder also resulted from increasing the Na₂SiO₃ component.

Table 8. Effect of Sodium Silicate and Sodium Hydroxide on Flow.

Flow (%)		NaOH : FA Ratio by Mass			
		0.050	0.075	0.100	0.125
Na ₂ SiO ₃ : FA Ratio by Mass	0.025	> 150	> 150	> 150	134
	0.050	> 150	> 150	> 150	128
	0.075	> 150	> 150	> 150	112
	0.100	> 150	132	120	94

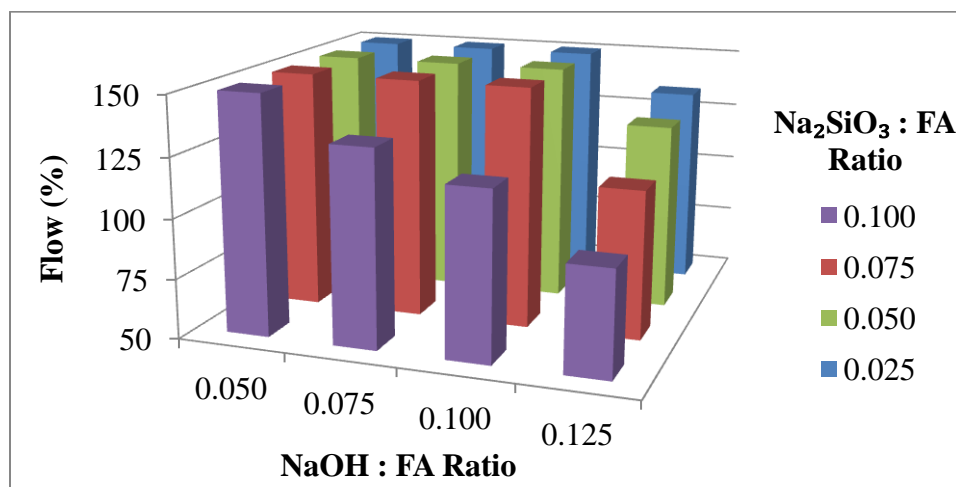


Figure 7. Effect of Sodium Silicate and Sodium Hydroxide on Flow.

4.1.3 Density

Density should also be considered when investigating mechanical behavior, because it affects the material's elastic modulus. Table 9 and Table 10 present the density of the fresh and hardened GPM. The average fresh density was 136 lb/ft³,

ranging from 133 lb/ft³ to 139 lb/ft³. The average hardened density was 134 lb/ft³, ranging from 132 lb/ft³ to 137 lb/ft³. No substantial variation in density was measured due to the manipulation of the alkaline activator components.

Table 9. Effect of Sodium Silicate and Sodium Hydroxide on Fresh Density.

Density (lb/ft ³)		NaOH : FA Ratio by Mass			
		0.050	0.075	0.100	0.125
Na ₂ SiO ₃ : FA Ratio by Mass	0.025	138	136	136	134
	0.050	134	136	139	133
	0.075	134	136	137	135
	0.100	134	134	137	135

Table 10. Effect of Sodium Silicate and Sodium Hydroxide on Hardened Density.

Density (lb/ft ³)		NaOH : FA Ratio by Mass			
		0.050	0.075	0.100	0.125
Na ₂ SiO ₃ : FA Ratio by Mass	0.025	132	135	136	132
	0.050	132	135	135	133
	0.075	132	135	137	134
	0.100	133	133	136	133

The effect of age on hardened density is presented in Table 11. The hardened density ranged from 134 lb/ft³ to 136 lb/ft³. No substantial variation in density was measured due to the manipulation of the specimen age.

Table 11. Effect of Age on Hardened Density.

Age (days)	1	3	7	28
Density (lb/ft ³)	134	135	136	135
Na ₂ SiO ₃ : FA Ratio = 0.10 NaOH : FA Ratio = 0.10				

4.1.4 Compressive Strength

The compressive strength of GPM is commonly considered to be its most important characteristic, although in some cases, the bond strength or flexural strength may be more critical. Table 12 and Figure 8 illustrate the test results. The average compressive strength was 3535 psi, ranging from 713 psi to 5821 psi. Strength increased

gradually as a result of incorporating additional NaOH and Na₂SiO₃. However, increasing the NaOH : FA ratio only resulted in higher compressive strength up to the 0.10 level. Excessive OH⁻ ions accelerated dissolution but decreased polycondensation, causing the binder to precipitate early and lose strength.

Table 12. Effect of Sodium Silicate and Sodium Hydroxide on Compressive Strength.

Compressive Strength (psi)		NaOH : FA Ratio by Mass			
		0.050	0.075	0.100	0.125
Na₂SiO₃ : FA Ratio by Mass	0.025	713	2249	3797	3302
	0.050	1212	3775	4610	3592
	0.075	1443	4645	5108	3877
	0.100	2945	4671	5821	4793

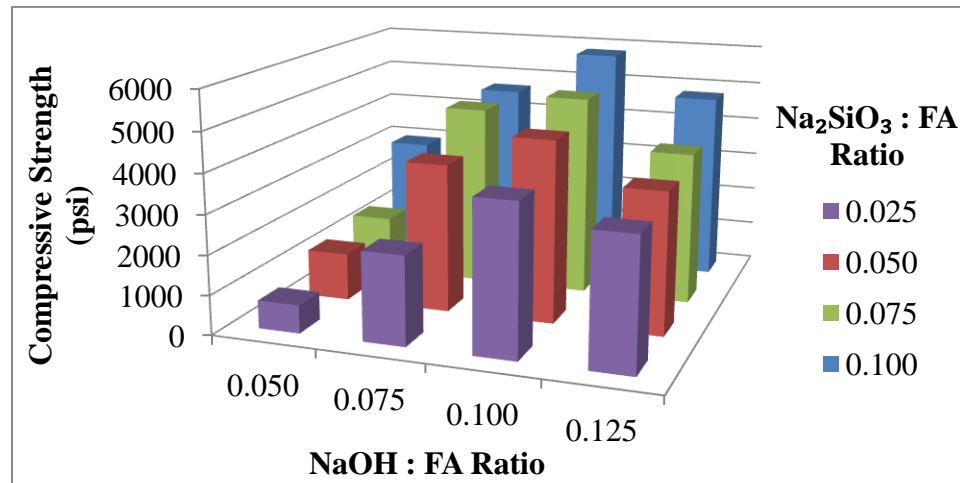


Figure 8. Effect of Sodium Silicate and Sodium Hydroxide on Compressive Strength.

The mix design with the highest compressive strength was chosen for additional investigation, because it is also important to consider specimen age to determine the mechanical behavior of GPM over time. The test results are shown in Table 13 and Figure 9. After aging 28 days, the compressive strength was 6196 psi. The majority of the strength was acquired gradually during the first 7 days of geopolymer formation. Only a slight increase in compressive strength was measured from 7 to 28 days.

Table 13. Effect of Age on Compressive Strength.

Age (days)	1	3	7	28
Compressive Strength (psi)	1558	3529	5821	6196
Na ₂ SiO ₃ : FA Ratio = 0.10				
NaOH : FA Ratio = 0.10				

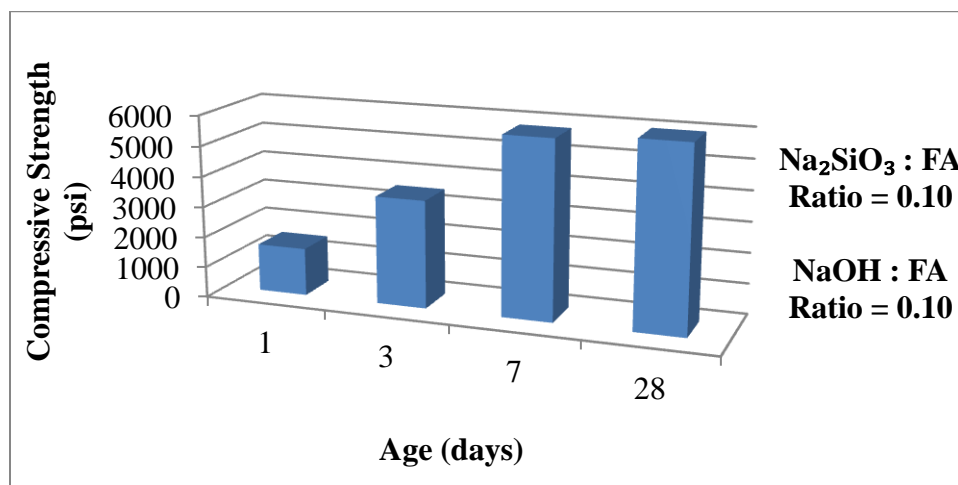


Figure 9. Effect of Age on Compressive Strength.

The ANOVA for compressive strength is presented in Table 14. Results indicate that the main effects of NaOH : FA ratio and Na₂SiO₃ : FA ratio on compressive strength were statistically significant ($p < 0.01$), signifying that the alkaline activator components improved dissolution and polycondensation of the source material.

Table 14. Analysis of Variance for Compressive Strength.

Source	Sum of Squares	Degrees of Freedom	Mean Squares	F Ratio	p (significance)
NaOH : FA Ratio	68807764	3	22935921	75.26	< 0.01
Na ₂ SiO ₃ : FA Ratio	26354810	3	8784937	196.49	< 0.01
NaOH \times Na ₂ SiO ₃	3848052	9	427561	3.66	< 0.01
Error	3735389	32	116731	-	-
Total	102746015	47	-	-	-

Manipulated variables interact if the effect of one of the variables differs depending on the level of the other variable. An interaction effect between the variation sources on compressive strength was also found to be significant ($p < 0.01$), meaning that

for each level of NaOH, varying degrees of strength augmentation were measured for every increment of the Na_2SiO_3 component.

4.1.5 Drying Shrinkage

The drying shrinkage of GPM is a phenomenon that can cause decreases in length as a consequence of influential factors, such as temperature, humidity or evaporation rate. Table 15 and Figure 10 show the test results for drying shrinkage. After aging 28 days, the drying shrinkage was 1.5%. The majority of the shrinkage occurred during the first 7 days of geopolymer formation. Only a slight increase in drying shrinkage was measured from 7 to 28 days.

Table 15. Effect of Age on Drying Shrinkage.

Age (days)	1	7	14	21	28
Drying Shrinkage (%)	0.52	1.31	1.43	1.48	1.50
Na_2SiO_3 : FA Ratio = 0.10 NaOH : FA Ratio = 0.10					

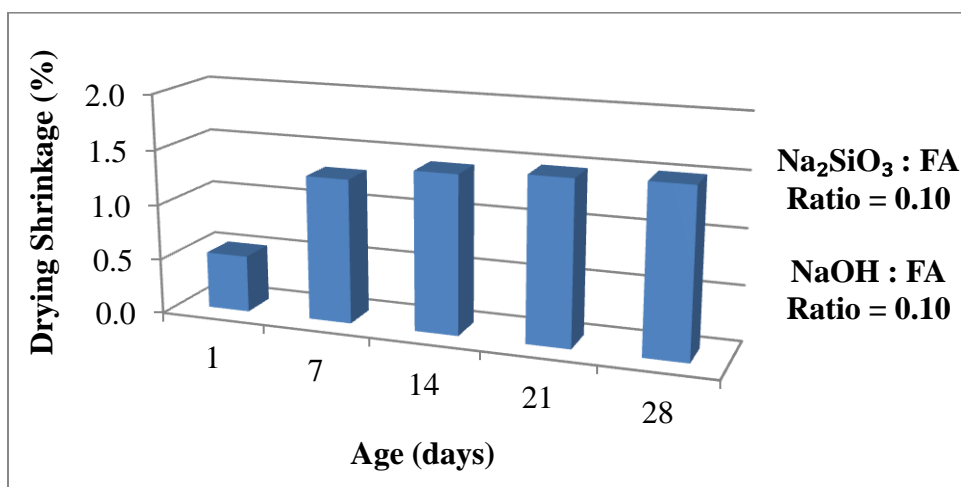


Figure 10. Effect of Age on Drying Shrinkage.

4.2 Geopolymer Concrete

4.2.1 Temperature

The properties of fresh GPC are considered to be important due to the relation they have with the material's workability. Table 16 and Figure 11 show the test results for temperature, which ranged from 104.2°F to 115.0°F. The temperature increased with higher levels of NaOH and Na₂SiO₃ due to the caustic nature of the strong chemical base.

Table 16. Effect of Sodium Silicate and Sodium Hydroxide on Temperature.

Temperature (°F)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	104.2	107.6	109.8	111.9
	0.10	105.6	108.1	110.8	113.0
	0.11	107.2	108.7	112.3	115.0

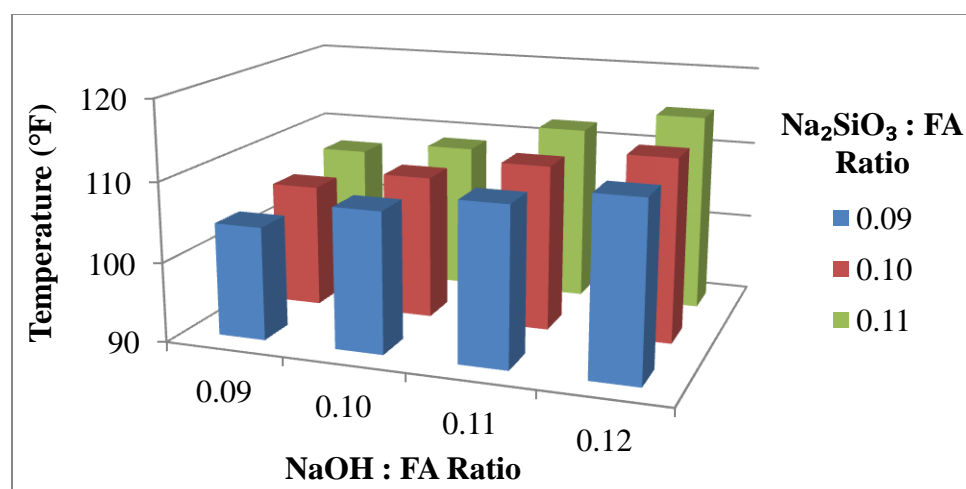


Figure 11. Effect of Sodium Silicate and Sodium Hydroxide on Temperature.

The effect of time on temperature is presented in Table 17 and Figure 12. The initial temperature measurement of 111.4°F decreased gradually over the 20 minute time period. A final measurement of 96.1°F was taken when the mixture lost workability.

Table 17. Effect of Time on Temperature.

Time (min)	0	10	20
Temperature (°F)	111.4	102.4	96.1
Na ₂ SiO ₃ : FA Ratio = 0.09 NaOH : FA Ratio = 0.12			

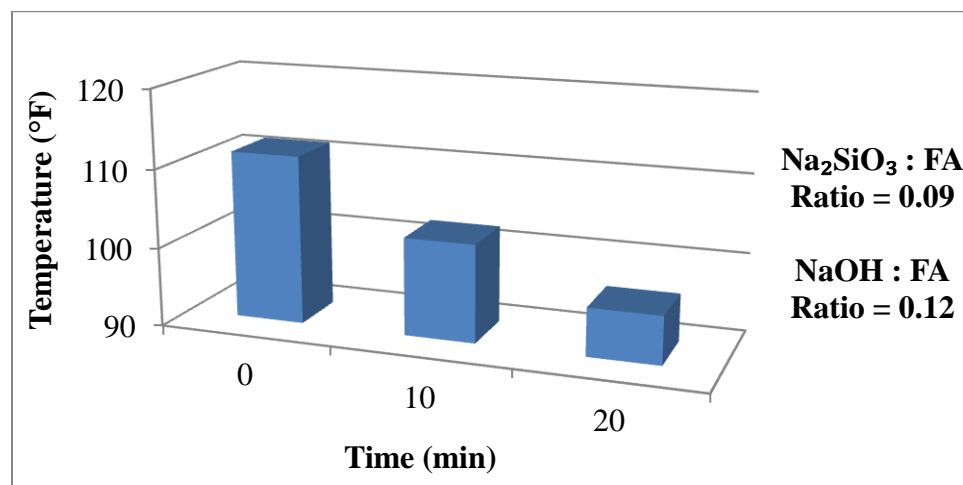


Figure 12. Effect of Time on Temperature.

4.2.2 Slump

Slump was measured as the subsidence of fresh GPC during the test. The results for slump are shown in Table 18 and Figure 13. The slump decreased as a result of increasing the NaOH component. Additional OH⁻ ions accelerated dissolution, causing the binder to precipitate earlier. Higher viscosity and rapid formation of the binder also resulted from increasing the Na₂SiO₃ component.

Table 18. Effect of Sodium Silicate and Sodium Hydroxide on Slump.

Slump (in)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	9.0	8.5	8.5	7.5
	0.10	8.0	7.0	6.0	3.0
	0.11	3.5	3.0	2.5	1.0

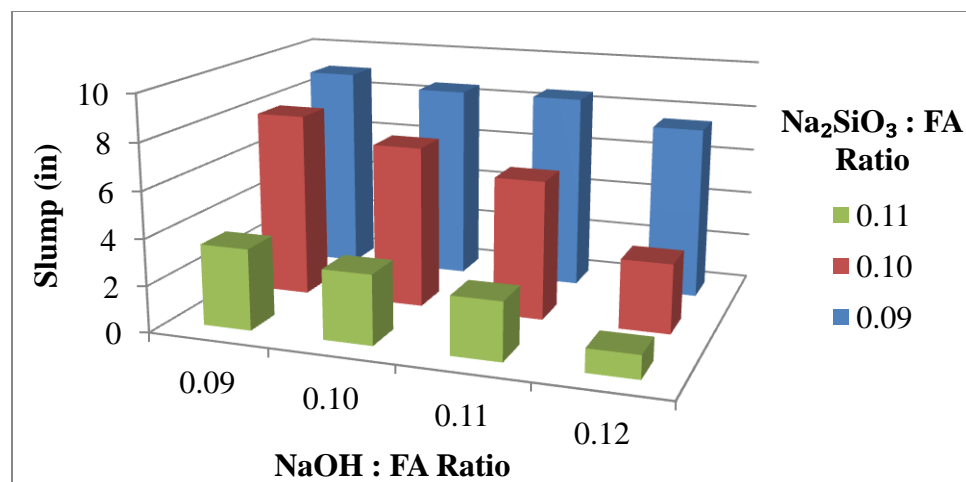


Figure 13. Effect of Sodium Silicate and Sodium Hydroxide on Slump.

The effect of time on slump is presented in Table 19 and Figure 14. The initial slump measurement of 7.0" decreased rapidly over the 20 minute time period. A final measurement of 0.5" was taken when the mixture lost workability.

Table 19. Effect of Time on Slump.

Time (min)	0	10	20
Slump (in)	7.0	2.5	0.5
Na ₂ SiO ₃ : FA Ratio = 0.09 NaOH : FA Ratio = 0.12			

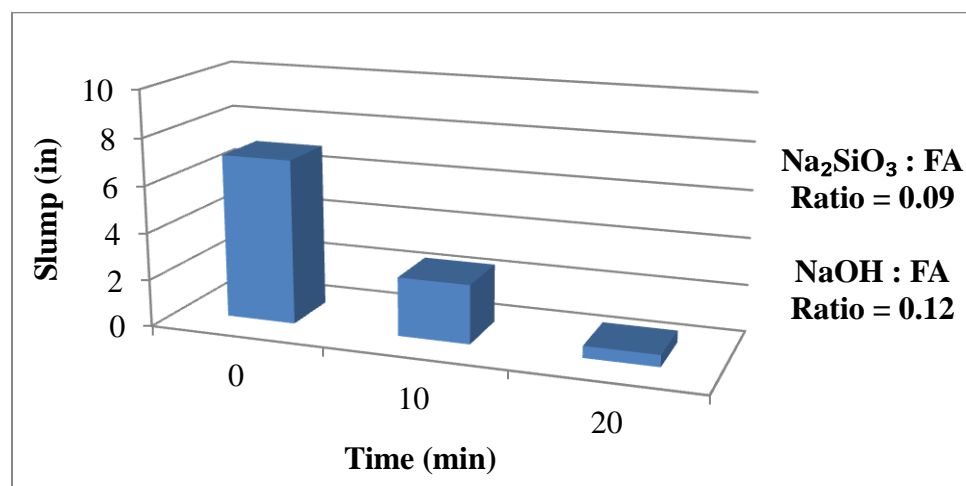


Figure 14. Effect of Time on Slump.

4.2.3 Air Content

When investigating the density and porosity of concrete, the air content is of critical importance. Air content of 2.5% was measured for the GPC mixture with a 0.09 Na_2SiO_3 : FA ratio and 0.12 NaOH : FA ratio. The air content of hardened GPC may be either higher or lower than that determined by the test method for freshly mixed GPC.

4.2.4 Setting Time

Initial and final setting times are specified as the times when the penetration resistance equals 500 psi and 4000 psi, respectively. Table 20 shows the effect of time on penetration resistance. The initial setting time of the GPC mixture was less than 30 minutes, and the final setting time was less than 60 minutes.

Table 20. Effect of Time on Penetration Resistance.

Time (min)	30	60
Penetration Resistance (psi)	1750	> 8000
Na_2SiO_3 : FA Ratio = 0.09 NaOH : FA Ratio = 0.12		

4.2.5 Density

Density should also be considered when investigating mechanical behavior, because it affects the material's elastic modulus. Table 21 and Table 22 present the density of the fresh and hardened GPC. The average fresh density was 152 lb/ft^3 , ranging from 151 lb/ft^3 to 153 lb/ft^3 . The average hardened density was 144 lb/ft^3 , ranging from 143 lb/ft^3 to 144 lb/ft^3 . No substantial variation in density was measured due to the manipulation of the alkaline activator components.

The effect of age on hardened density is presented in Table 23. The hardened density ranged from 143 lb/ft^3 to 144 lb/ft^3 . No substantial variation in density was measured due to the manipulation of the specimen age.

Table 21. Effect of Sodium Silicate and Sodium Hydroxide on Fresh Density.

Density (lb/ft ³)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	151	152	153	152
	0.10	152	152	152	153
	0.11	152	152	152	152

Table 22. Effect of Sodium Silicate and Sodium Hydroxide on Hardened Density.

Density (lb/ft ³)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	144	144	144	144
	0.10	144	144	143	144
	0.11	143	143	143	143

Table 23. Effect of Age on Hardened Density.

Age (days)	1	3	7	28
Density (lb/ft ³)	143	144	144	144
Na ₂ SiO ₃ : FA Ratio = 0.09 NaOH : FA Ratio = 0.12				

4.2.6 Pulse Velocity

Pulse velocity is a measurement used to assess the uniformity of GPC and to indicate the presence of voids or cracks. Table 24 and Figure 15 illustrate the test results for pulse velocity. The average pulse velocity was 12604 ft/s, ranging from 11893 ft/s to 13442 ft/s. Increasing the NaOH component resulted in higher pulse velocity measurements. Dissolution of the source material in stronger alkaline conditions enhanced polycondensation, thereby improving uniformity and reducing the presence of voids or cracks.

Table 24. Effect of Sodium Silicate and Sodium Hydroxide on Pulse Velocity.

Pulse Velocity (ft/s)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	12466	12370	12827	13410
	0.10	12060	11893	12318	13316
	0.11	12308	12430	12405	13442

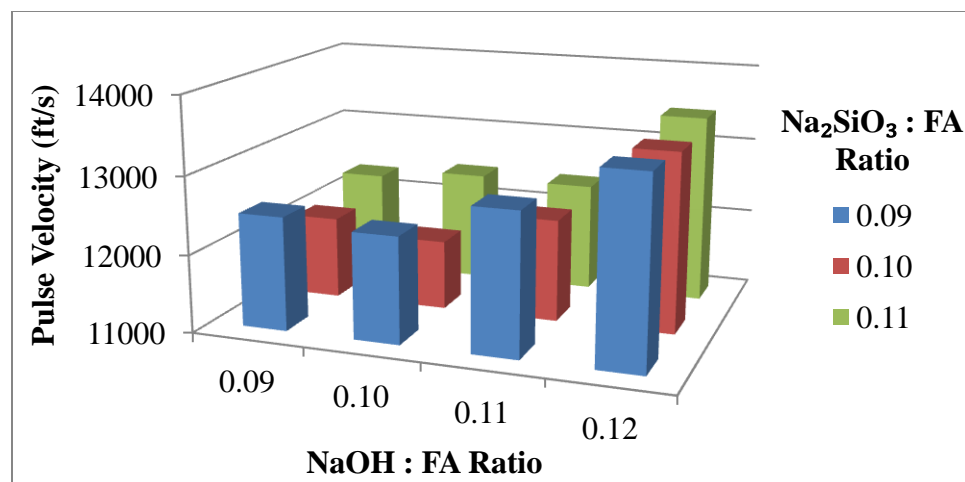


Figure 15. Effect of Sodium Silicate and Sodium Hydroxide on Pulse Velocity.

The effect of age on pulse velocity is presented in Table 25 and Figure 16. After aging 28 days, the pulse velocity was 13622 ft/s. The majority of the uniformity was acquired gradually during the first 7 days of geopolymer formation. Only a slight increase in pulse velocity was measured from 7 to 28 days.

Table 25. Effect of Age on Pulse Velocity.

Age (days)	1	3	7	28
Pulse Velocity (ft/s)	11737	12736	13410	13622
Na ₂ SiO ₃ : FA Ratio = 0.09 NaOH : FA Ratio = 0.12				

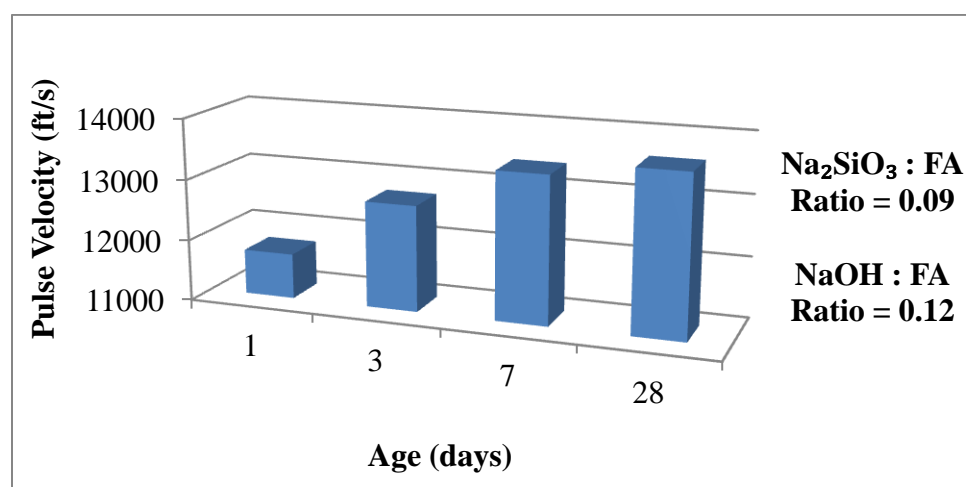


Figure 16. Effect of Age on Pulse Velocity.

4.2.7 Splitting Tensile Strength

Splitting tensile strength is generally lower than flexural strength and greater than direct tensile strength for conventional concrete. The test results are presented in Table 26 and Figure 17. The average splitting tensile strength was 478 psi, ranging from 420 psi to 573 psi. Limited differentiation in strength was observed, however, due to the range of the manipulated variables.

Table 26. Effect of Sodium Silicate and Sodium Hydroxide on Splitting Tensile Strength.

Splitting Tensile Strength (psi)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	557	573	461	514
	0.10	433	447	485	453
	0.11	420	483	461	450

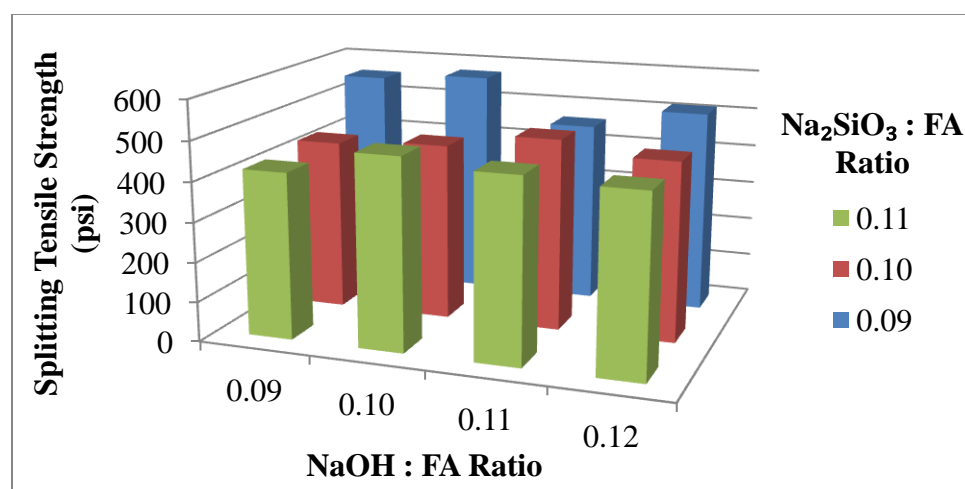


Figure 17. Effect of Sodium Silicate and Sodium Hydroxide on Splitting Tensile Strength.

The effect of age on splitting tensile strength is presented in Table 27 and Figure 18. After aging 28 days, the splitting tensile strength was 766 psi. The strength increased gradually during geopolymer formation.

Table 27. Effect of Age on Splitting Tensile Strength.

Age (days)	1	3	7	28
Splitting Tensile Strength (psi)	273	413	514	766
Na_2SiO_3 : FA Ratio = 0.09 NaOH : FA Ratio = 0.12				

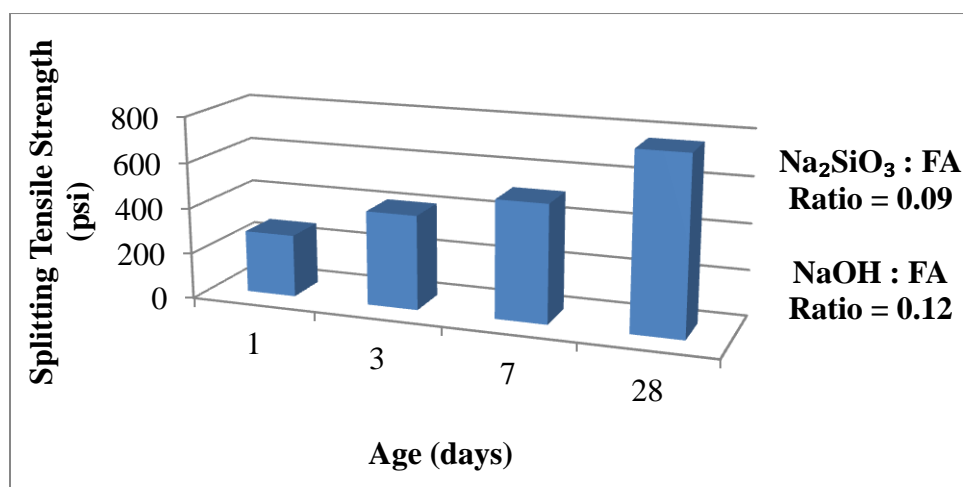


Figure 18. Effect of Age on Splitting Tensile Strength.

4.2.8 Compressive Strength

The compressive strength of GPC is commonly considered to be its most important characteristic, although in some cases, the durability or impermeability may be more critical. Table 28 and Figure 19 illustrate the test results. The average compressive strength was 2948 psi, ranging from 2295 psi to 3853 psi. Strength increased as a result of incorporating additional NaOH and Na_2SiO_3 . Supplementary OH^- ions improved the geopolymerization mechanism, promoting the binder to precipitate and gain strength. Rapid formation and strength augmentation of the binder also resulted from increasing the Na_2SiO_3 component.

Table 28. Effect of Sodium Silicate and Sodium Hydroxide on Compressive Strength.

Compressive Strength (psi)		NaOH : FA Ratio by Mass			
		0.09	0.10	0.11	0.12
Na ₂ SiO ₃ : FA Ratio by Mass	0.09	2320	2748	3050	3576
	0.10	2295	2437	2911	3617
	0.11	2639	2511	3415	3853

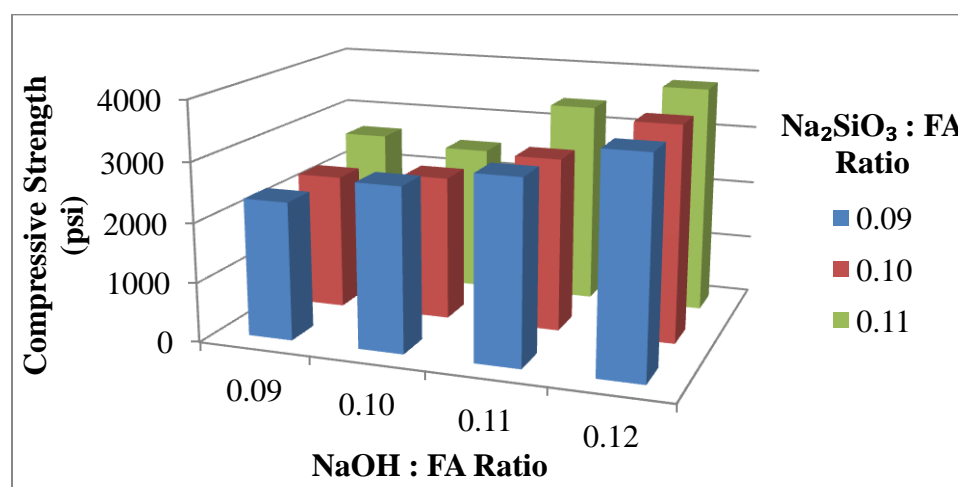


Figure 19. Effect of Sodium Silicate and Sodium Hydroxide on Compressive Strength.

A mix design with adequate workability and relatively high compressive strength was chosen for additional investigation, because it is also important to consider specimen age to determine the mechanical behavior of GPC over time. The test results are shown in Table 29 and Figure 20. After aging 28 days, the compressive strength was 4585 psi. The strength increased gradually during geopolymer formation.

Table 29. Effect of Age on Compressive Strength.

Age (days)	1	3	7	28
Compressive Strength (psi)	1667	2753	3576	4585
Na ₂ SiO ₃ : FA Ratio = 0.09 NaOH : FA Ratio = 0.12				

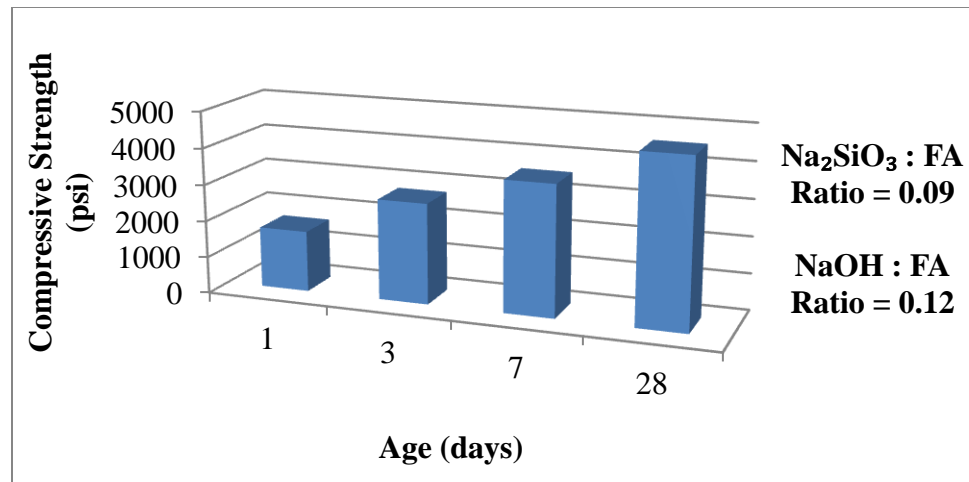


Figure 20. Effect of Age on Compressive Strength.

Physical properties of materials are related if variation sources influence them in a similar manner, thereby providing a means to predict mechanical behavior. Figure 21 illustrates the correlation between pulse velocity and compressive strength, and Figure 22 illustrates the correlation between splitting tensile strength and compressive strength. Compressive strength increased gradually in relation to higher pulse velocity and splitting tensile strength measurements.

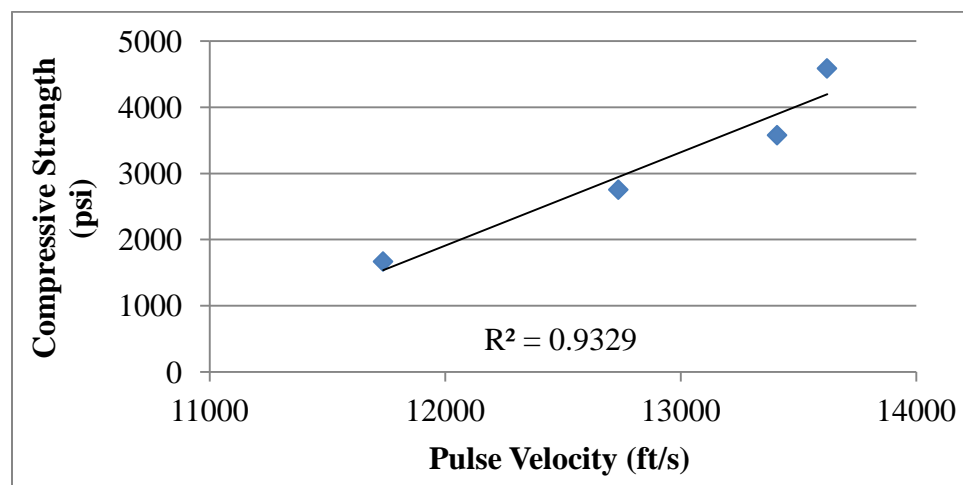


Figure 21. Correlation of Pulse Velocity and Compressive Strength.

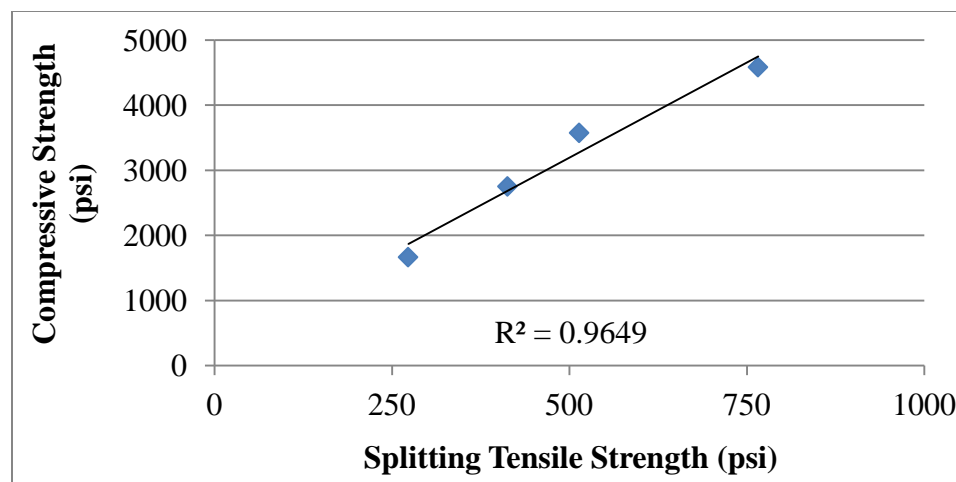


Figure 22. Correlation of Splitting Tensile Strength and Compressive Strength.

4.2.9 Drying Shrinkage

The drying shrinkage of GPC is a phenomenon that can cause decreases in length as a consequence of influential factors, such as temperature, humidity or evaporation rate. Table 30 and Figure 23 show the test results for drying shrinkage. After aging 28 days, the drying shrinkage was 0.18%. The majority of the shrinkage occurred gradually during the first 7 days of geopolymer formation. Only a slight increase in drying shrinkage was measured from 7 to 28 days.

Table 30. Effect of Age on Drying Shrinkage.

Age (days)	1	7	14	21	28
Drying Shrinkage (%)	0.09	0.15	0.17	0.18	0.18
Na ₂ SiO ₃ : FA Ratio = 0.10					
NaOH : FA Ratio = 0.10					

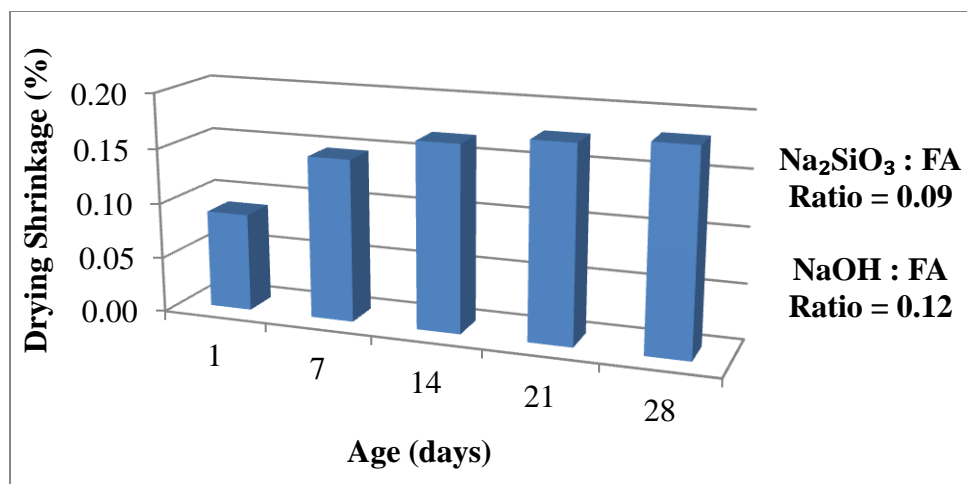


Figure 23. Effect of Age on Drying Shrinkage.

CHAPTER V

CONCLUSIONS

An experimental program was executed to evaluate the effect of the alkaline activator composition on the fresh and hardened properties of GPM and GPC. Test results indicate that there is potential for the concrete industry to utilize alkaline activated FA as an alternative to PC in structural building applications. Based on the mix design parameters established within the study, concentrations of NaOH and Na₂SiO₃ were ascertained that are advantageous for constructability and physical properties. The following conclusions can be drawn from the results of the study:

1. Temperature of freshly mixed GPM and GPC ranged from 89.4°F to 129.0°F, increasing with higher levels of NaOH and Na₂SiO₃ due to the caustic nature of the strong chemical base.
2. Flow and slump decreased as a result of increasing the NaOH component. Additional OH⁻ ions accelerated dissolution, causing the binder to precipitate earlier. Higher viscosity and rapid formation of the binder also resulted from increasing the Na₂SiO₃ component.
3. Strength of hardened GPM and GPC increased as a result of incorporating additional NaOH and Na₂SiO₃. However, excessive OH⁻ ions accelerated dissolution but decreased polycondensation, causing the binder to precipitate early and lose strength.

4. Dissolution of the source material in optimum alkaline conditions enhanced polycondensation, thereby increasing pulse velocity measurements and improving uniformity.
5. Based on the parameters of the GPM mix design, the optimum NaOH : FA ratio was 0.10 and Na₂SiO₃ : FA ratio was 0.10.
6. The flow of the optimum GPM mixture was 120%. After aging 28 days, the compressive strength of the specimens was 6196 psi, and during that time period, the drying shrinkage increased to 1.5%.
7. Based on the parameters of the GPC mix design, the optimum NaOH : FA ratio was 0.12 and Na₂SiO₃ : FA ratio was 0.09.
8. The slump of the optimum GPC mixture was 7.5", and the initial setting time was less than 30 minutes. After aging 28 days, the compressive strength of the specimens was 4585 psi. During that time period, the splitting tensile strength increased to 766 psi, and the drying shrinkage was 0.18%.

Based on these conclusions, there is a need for further research in the following areas:

1. A microstructural analysis should be performed in order to further optimize the composition of the alkaline activator.
2. The long term properties must be investigated to determine if GPC can be applied in permanent structural building applications.
3. An experimental study should be executed to evaluate the application of GPC for structural and architectural precast panels.

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VITA

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