Technical University of Civil Engineering Bucharest

UNIVERSITATEA TEHNICA DE
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DISCIPLINE ELECTIVE REPORT

GEOPOLYMER THEORY

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BY

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1. Introduction

Concrete usage around the world is second only to water and Ordinary Portland Cement (OPC) is conventionally used as the primary binder to produce concrete. The environmental issues associated with the production of OPC are too many. The cement industry is held responsible for some of the CO2 emissions. The amount of the carbon dioxide released during the manufacturing of OPC due to the calcination of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC produced. In addition, the extent of energy required to produce OPC is only next to steel and aluminium [1].

The demand for Portland cement is increasing day by day and hence, efforts are being made in the construction industry to address this by utilising supplementary materials and developing alternative binders in concrete; the application of geo-polymer technology is one such alternative. The abundant availability of fly ash worldwide creates opportunity to utilise this by-product of burning coal, as a substitute for OPC to manufacture concrete. When used as a partial replacement of OPC, in the presence of water and in ambient temperature, fly ash reacts with the calcium hydroxide during the hydration process of OPC to form the calcium silicate hydrate (C - S-H) gel.

In 1978, Davidovits (1999) proposed that binders could be produced by a polymeric reaction of alkaline liquids with the silicon and the aluminium in source materials of geological origin or by-product materials such as fly ash and rice husk ash. He termed these binders as geo-polymers [1].

Palomo et al (1999) suggested that pozzolans such as blast furnace slag might be activated using alkaline liquids to form a binder and hence totally replace the use of OPC in concrete. Hence, in this paper an effort is made to identify and study the effect of salient parameters that affects the properties of low-calcium fly ash-based geo-polymer concrete and the properties of concrete at varied concentrations of alkali solutions and how the change in temperature affects the strength characteristics [1].

The international Energy Agency (IEA) and the World Business Council for Sustainable Development (WBCSD) point out that the current trend in the provision and the using of energy is not sustainable, economic and green for societies and therefore, they have set of course for the replacement of the current energy system with low-carbon energy technologies in order to reduce CO_2 emissions by half in the cement by 2050 [2].

2. Geopolymer theory

Geopolymerization is a geosynthesis –a reaction that chemically integrates minerals [3]. The exposure of aluminusilicate materials such as fly ash,blast furnace slag or thermally activated substances to high alkaline environments (hydroxide,silicates) gives rise to the formation of the Geopolymer.

Geopolymers are characterized a two –to three dimensional Si-O-Al structure [4].These materials represent a new order of cementitious products able to provide ceramic and zeolitic properties not normally present in traditional cement materials.

The term “geopolymer” is generically used to describe the amorphous to crystaline reaction products from the synthesis of alkali aluminosilicates with alkali hydroxide/alkali silicate solution.

Geopolymeric gels and composites are also commonly referred to as low-temperature aluminosilicate glass, alkali- activated cement, geocement, alkali-bonded ceramic, inorganic polymer concrete, and hydroceramic [5]. A geopolymer paste as shown in Figure 1can be used to bind loose aggregates and other non-reacted materials together to form geopolymer concrete shown in Figure 2[4]. Geopolymer binders can provide comparable performance to traditional cementitious binders in a range of applications with the added advantage of significantly reduced greenhouse gas emissions [4].

Figure 1
Fresh Geopolymer Binder Paste [4]

Figure 2
Fresh Geopoymer Concrete [4]

2.2 Geopolymer Development

Geopolymer cements develop through a series of several distinct reaction processes from initial pozzolanic activation to final microstructure development. The benefits of using pozzolans as a matrix binder for agglomeration is that they tend to be economical, environmentally-friendly, more absorbent of liquids and produce a highly durable product [8].

The major processes are dissolution of the aluminosilicate species within a highly basic, alkaline environment, polymerization of the dissolved minerals into short-lived structural gel, precipitation of formed hydration products similar to natural zeolites and final hardening of the matrix by excess water exclusion and the growth of crystalline structures. Figure 3 illustrates the overall polymerization process in alkali-activated geopolymer.

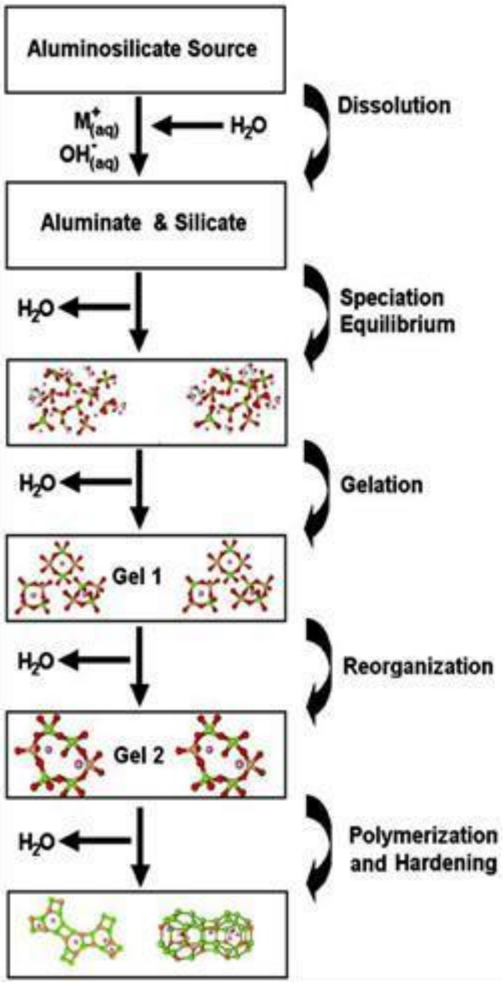


Figure 3. Geopolymer Development Model [5]

2.2.1 Dissolution

Dissolution occurs immediately upon contact between the alkaline solution and the pozzolanic material and allows for ionic interface between species and the breaking of covalent bonds between silicon, aluminum and oxygen atoms. Similarly to PCC, this process generates rapid and intense heat (Fig. 4) and is directly proportional to the pH level of the activating solution. The rate of dissolution is relevant to the amount and composition of the ashes and the pH of the activating solution [9, 10].

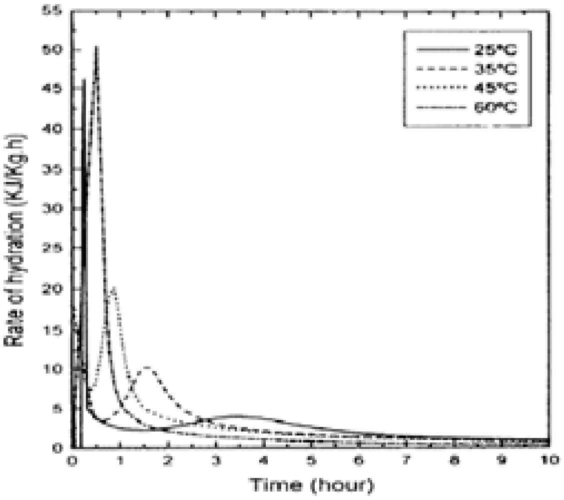


Figure 4. Rate of Slag-Based Geopolymer Hydration Heat vs. Time [11]

2.2.2 Polymerization

The polymerization process involves a substantially fast chemical reaction under alkaline conditions on Si-Al minerals, resulting in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [6]. The formed gel product contains alkaline cations which compensate for the deficit charges associated with the aluminum- for-silicon substitution [10].

An intermediate, aluminum-rich phase is first formed which then gives way to a more stable, silicon- rich three-dimensional gel product of form Q4(nAl), which is dependent upon curing conditions and activator type [9].

2.2.3. Growth

During this process, the slow growth of crystalline structures become evident as the nuclei of the polymerized gel reaches critical size. The matrix crystallinity is relative to the rate by which precipitation occurs: fast reactions between alkali and ash do not allow time for growth of a well-structured crystalline environment (representative of typical zeolites). Therefore, most hardened geopolymer cements are referred to as zeolitic precursors rather than actual zeolites. The final product of geopolymerization is an amorphous, semi-crystalline cementitious material.

2.3 Hydration Reaction Characteristics

Within these process intervals, thermodynamic and kinetic parameters become vital to gel formation and reaction degree. Several factors directly influence the degree of reaction (α) observed in a mixed geopolymer paste and either enhance or detract from the polymerization process and subsequent phases that strictly define the formed cementitious properties of the hardened cement. The activation reaction rate as well as the chemical composition of the reaction products depends on several factors such as the particle size distribution and the mineral composition of the precursor fly ash [9]. A fly ash material used in a study (by Xie and Xi) contained a high fraction of reactive oxides which reacted significantly with a waterglass (Na_2SiO_3) activator, leading to a high strength within a short time and under relatively lower temperatures [12]. Likewise, alkaline activator types, concentration of activators, ratios of solids to liquids and curing temperatures and time are all relevant in the characterization of geopolymer cements and the mechanical properties attained. In practice, no matter which method is used, the selection of proper activators is the most important part of the technology [12].

2.4 Alkaline Activators

The most common activators are hydroxides of sodium and potassium (NaOH and KOH). The highest observed mechanical strengths have resulted from the use KOH in varying concentrations. Since K^+ is more basic, it allows a higher rate of solubilized polymeric ionization and dissolution leading to a dense polycondensation reaction that provides greater overall network formation and an increase in the compressive strength of the matrix [3]. Conversely, a study by Arjunan et al. Revealed that sodium hydroxide in low concentration was the most effective chemical activator for low calcium fly ash [9]. Regardless of type selected, however, higher concentrations of alkaline activators yield greater mechanical strength values. The pH level of the activating solution strongly influences the final cement performance. Khale and Chaudhary reported that the strength measured from samples of pH 14 were five times greater than samples formed from pastes of pH 12; and they concluded that a pH range of 13 –14 was most suitable for the formation of geopolymers with higher mechanical strengths [3].

While the mechanical properties of alkali-activated cement products show satisfactory values, a primary concern of geopolymer production is the ability to attain proper curing without external heating. PCC products are capable of achieving full strength in ambient temperatures but may not perform well in harsh environments. One motivator for adopting geopolymer binder is its ability to resist sulfate and other chemical intrusions and maintain excellent thermal loading capacities. However, the question of curing in field applications is a relevant concern limiting the utility of geopolymer as a practical construction material.

The tests reported by Sumajouw et al. revealed that geopolymer concretes possess high compressive strength, undergo very little drying shrinkage and exhibit moderately low creep. Their data also indicate that geopolymer concretes possess excellent resistance to sulfate attack, resulting in a promising construction material for some harsh environments [1].

3. Geopolymer Binder Constituents

There are two main constituents of geo-polymers, namely the source materials and the alkaline liquids. The source materials for geo-polymers based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, etc. Alternatively, by-product materials such as fly ash, silica fume, slag, rice- husk ash, red mud, etc. could be used as source materials. The choice of the source materials for making geo-polymers depends on factors such as availability, cost, type of application, and specific demand of the end users.

3.1. Pozzolanic Materials

A pozzolan is defined as finely divided siliceous or aluminous and siliceous material that reacts chemically with slaked lime at ordinary temperature and in the presence of moisture to form strong, slow-hardening cement with two disadvantages: they are slower to set and can be intolerant to impurities such as clays, metal ions, sulfides, phosphates, etc. [10]. Materials rich in silicon (such as fly ash or slag) and materials rich in aluminum (kaolin clay) are the primary requirement for geopolymerization to occur [3].

3.1.1 Commercial Fly Ash

According to the American Concrete Institute (ACI) Committee 116R, fly ash is defined as the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system (ACI Committee 232 2004).

Fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere.

Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 µm to no more than 150 µm.

The chemical composition is mainly composed of the oxides of silicon (SiO_2), aluminium (Al_2O_3), iron (Fe_2O_3), and calcium (CaO), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount [12].

Particle size distribution and particle fineness are the physical characteristics of fly ashes (shown in Figure 5) most strongly affecting their reactivity, whereas relative silica content is most influential from a chemical perspective [14]. The presence of highly reactive silica in the ash increases the formation potential of the aluminosilicate gel which provides mechanical strength to

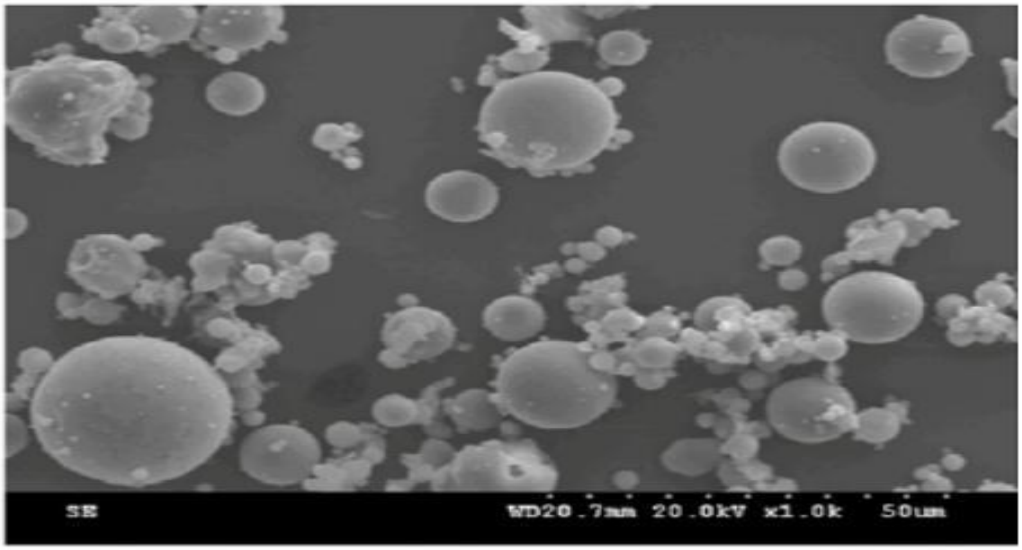


Figure 5. Microscopic Image of Raw Commercial Fly Ash [16]

Geopolymers. Aside from this point, the ability for a specific fly ash material to be alkaline-activated is driven by several other factors: the percentage of unburned material in the ash product act as inert particles causing an increase to the liquid/solid ratio and the content of its vitreous phase, these inert particles are all products of the original coal combustion method [14].

Fernandez-Jimenez et al. found that fly ashes with a highly reactive SiO2 and Al2O3 content and Si/Al ratios below 2.0 perform best under alkaline activation [15]. Table 3 categorizes potential geopolymer uses by their inherent Si/Al ratio value. The final reaction product of alkali-activated fly ash is an amorphous to semi-crystalline structure similar to a zeolite precursor. The activation process and degree of reaction within the geopolymer paste is directly related to the glassy content of the ash material [14].

The key to a fly ash-based geopolymer product with optimum binding properties was stated by Ferndandez-Jimenez to be derived from using a fly ash material with the following properties: less than five percent of unburned material; less than 10 percent Fe2O3; a low content of CaO;40- 50 Percent relative silica; 80–90 percent of particles with diameter equal to or less than 45 µm; and a high vitreous phase [14].

Si:Al Ratio	Applications
1	• Bricks • Ceramics • Fire Protection
2	• Low CO_2 Cements and Concretes • Radioactive and Toxic Waste Encapsulation
3	• Fire Protection Fiberglass Composites • Foundry Equipment • Heat Resistant Composites, 200°C to 1000°C
>3	• Sealants for Industry, 200°C to 600°C • Tooling for Aeronautics SPF Aluminum
20-35	• Fire Resistant and Heat Resistant Fiber Composites

Table 1. Applications of Geopolymer Materials as Related to Atomic Si/Al Ratios [4]

The aluminum content of a fly ash material is critical to the hardening properties of a geopolymer binder. In the presence of alkali aluminosilicate slurries, the aluminum content is believed to be the chemical trigger for irreversible cement hardening [12]. The dissolution of solid Al_2O_3 regions by the activating solution controls the rate, stoichiometry, and extent of solution phase reactions and is dependent upon several variables including pH level, binder temperature, the Si/Al ratio and alkali concentration [12]. For this reason, the composition and mineralogy of raw pozzolans is critical in the formulation of alkali-activated geopolymer materials.The increase in performance relative to the Si/Al ratio can be summarized by Figure 6 and Figure 7 illustrating increasing densities with increasing Si/Al ratios.

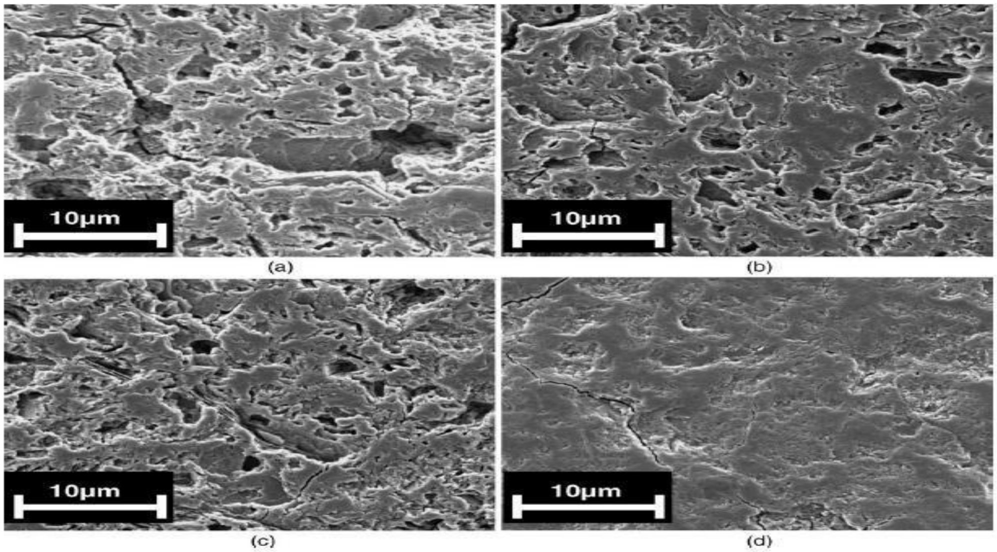


Figure 6. SEM Micrographs of Geopolymers with Si/Al= (a) 1.45, (b) 1.50, (c) 1.55, (d) 1.60 [17]

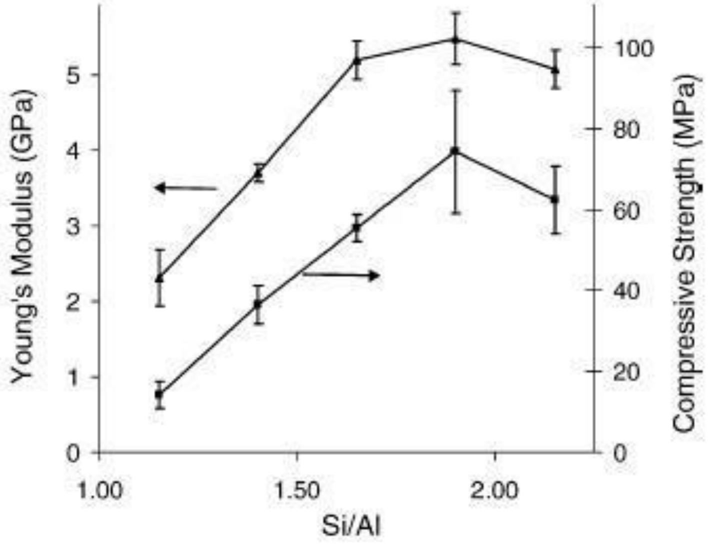


Figure 7. Mechanical Performance of Geopolymers Relative to Si/Al Ratio [17]

3.1.2. Commercial Blast Furnace Slag

Ground granulated blast furnace slag (GGBFS) is another industrial by-product resulting from rapid water cooling of molten steel. It is known to have advantageous properties for the concrete industry as it is relatively inexpensive to obtain, highly resistant to chemical attack and maintains excellent thermal properties.

Major components of the slag product include SiO2, CaO, MgO and Al2O3—commonly found in commercial silicate glasses. Its relative reactivity potential derives from chemical composition, glass phase content, surface morphology and particle size distribution [18]. Typical slag products are ground, granulated and mixed with 3.5–5.5 percent (by mass) sodium hydroxide or waterglass. Alkali-activation yields a low-basic, highly amorphous calcium silicate hydrate (C-S-H) gel product possessing high aluminum content [19]. This product is referred to by some as alkali-activated slag (AAS).

Chemical shrinkage and porosity volumes in saturated GGBFS pastes are significantly higher than in Portland cement pastes and is a legitimate concern during setting [19]. Drying shrinkage is a direct result of hydration heat and increases with increased n modulus and dosage of waterglass activators [20]. Alternatively, the increase in alkaline concentration in the paste mix increases the degree of hydration reaction [19] and reduces pore volumes improving microstructural properties of the C-S-H product. While shrinkage in AAS pastes is more relevant than in Portland cement products, it maintains a much higher ultimate strength by comparison and remains a viable material for commercial use.

3.1.3. Calcined Metakaolin

Metakaolin is a dehydroxylated pozzolanic product derived from the high-temperature firing of raw kaolin. Kaolin, or kaolinite $[Al_2Si_2O_5(OH)_4]$, is a clay mineral containing high amounts of layered tetrahedral silicon atoms connected via oxygen to octrahedral aluminum atoms. It is commonly used in the manufacture of porcelain.

Kaolin contains hydroxyl ions that are strongly bonded to the aluminosilicate framework and can only be altered by temperatures above 550 °C, thus rearranging the atomic structure to form a partly ordered system with great reaction potential to alkaline solutions [21]. The optimum temperature and duration for converting kaolin into metakaolin is 600 °C for two hours [22]. The resulting metakaolin substance is highly reactive and serves as an excellent addition to fly ash for use as a binder in geopolymer cement. Replacement of traditional fly ash material with metakaolin by up to 30 percent (by mass) yielded compressive strength values of 30 –50 MPa for mortar specimens tested by Chareerat et al. [22]. Whereas fly ash material can contain contaminants which affect the final product, metakaolin-based geopolymers can be manufactured consistently with a high level of predictability in hardened characteristics [5]. Figure 8 displays compressive strengths and porosities for both metakaolin geopolymers and metakaolin/fly ash mixtures.

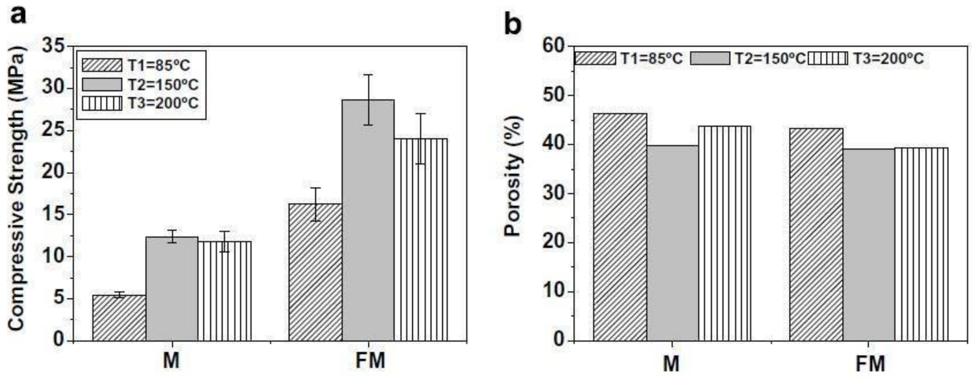


Figure 8. Mechanical Strength and Porosity of Metakaolin Geopolymers [21]

3.2. Alkaline Activators

Activation of the selected pozzolanic material is the most significant factor in producing a mechanically-sound cementitious material via the geopolymerization process. The activators prompt the precipitation and crystallization of the siliceous and aluminous species present in the solution. OH- acts as a catalyst for reactivity, and the metal cation serves to form a structural element and balance the negative framework carried by the tetrahedral aluminum [5]. The initial mechanism of reaction is driven by the ability of the alkaline solution to dissolve the pozzolanic material and release reactive silicon and aluminum into solution.

When fly ash or other pozzolans are mixed with alkaline solutions, their vitreous component is quickly dissolved. There is not sufficient time or space for the resulting gel to grow into a well- crystallized structure. As a result a micro-crystalline, amorphous or semi-amorphous structure is formed [3]. The following is a classification of various groups of activating agents where M represents an alkali ion (Pacheco-Torgal *et al.*):

- Alkalis, MOH
- Weak acid salts, M_2CO_3, M_2SO_3, M_3PO_4, MF
- Silicates, $M_2O * nSiO_3$
- Aluminates, $M_2O * nAlO_3$
- Aluminosilicates, $M_2O * nAl_2SO_3 * (2\text{-}6)SiO_2$
- Strong Salt Acids, M_2SO_4

While common activators include NaOH, Na2SO4, waterglass, Na2CO3, K2CO3, KOH, K2SO4 and cement clinker [3], the most utilized alkaline activators are a mixture of sodium or potassium hydroxides (NaOH, KOH) and sodium waterglass (nSiO2Na2O) or potassium waterglass (nSiO2K2O) [23].

3.2.1. Sodium Hydroxide (NaOH)

NaOH is also commonly used as an alkaline activator in geopolymer production. While it does not maintain the level of activation as a K+ ion, sodium cations are smaller than potassium cations and can migrate throughout the paste network with much less effort promoting better zeolitization [5]. Furthermore, it bears a high charge density which promotes additional zeolitic formation energy.

The concentration and molarity of this activating solution determines the resulting paste properties. While high NaOH additions accelerate chemical dissolution, it depresses ettringite and CH (carbon-hydrogen) formation during binder formation [3]. Furthermore, higher concentrations of NaOH promote higher strengths at early stages of reaction, but the strength of aged materials were compromised due to excessive OH- in solution causing undesirable morphology and non-uniformity of the final products [3]. It is found that geopolymers activated with sodium hydroxide develop greater crystallinity thus improving stability in aggressive environments of sulfates and acids [25].

Additionally, the use of sodium hydroxide as an activator buffers the pH of pore fluids, regulates hydration activity and directly affects the formation of the main C -S-H product in geopolymer pastes [18]. There is a linear relationship between NaOH concentration and the heat generation; however, there exists an inverse relationship between concentration and the time at which maximum hydration heat occurs [18].

3.2.2. Potassium Hydroxide (KOH)

KOH has been found to produce high compressive strengths and improved porosity in geopolymer cements. Since K+ is more basic than other activating ions, it possesses a greater potential for polymeric ionization in solution resulting in high reactivity of the prime pozzolan, a denser final product and a matrix formation capable of achieving increased compressive strength values [3]. However, KOH concentrations above 10 M have been shown to decrease strength due to excessive K+ ions in solution and Si/Al leaching of KOH based cements occurred more than those derived from NaOH activation [3]. While KOH is reasoned to provide a greater extent of dissolution due to its higher level of alkalinity, NaOH actually possesses a greater capacity to liberate silicate and aluminate monomers [5].

3.2.3. Sodium Silicate (Na_2SO_3)

Sodium (or potassium) silicates are manufactured by fusing sand (SiO_2) with sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) at temperatures in excess of 1100 °C and dissolving the product with high pressure steam into a semi-viscous liquid referred to as waterglass [8].

Waterglass is rarely used as an independent activating unit, because it does not possess enough activation potential to initiate pozzolanic reaction alone. Rather, it is commonly mixed with NaOH or KOH as a fortifying agent to enhance alkalinity and increase overall specimen strength. The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide or potassium hydroxide and sodium silicate or potassium silicate [7].

Sodium silicate solution is commercially available in different grades [6], but it should be noted that powdered waterglass leads to lower performance compared to the liquid form [23]. For best results, a silicate solution with a SiO_2 to Na_2O ratio (by mass) of 2.0 mixed with an 8 – 16 M activator 24 hours prior to use is recommended [6].

The most important property of this product is its mass ratio of SiO_2 to Na_2O, which is commercially available in the range of 1.5 to 3.2 (with 3.2 being the best suited for geopolymerization) [8]. Soluble silicates reduce alkali saturation in pore solution and promote greater interparticle bonding with both geopolymer binders and the included aggregate material [26]. Testing has revealed that activating solutions containing little or no soluble silicates produced significantly weaker compressive strengths of mortars and concretes than those activated with high doses of soluble silicates [26]. As well, the presence of such silicate material improves interfacial bonding between rock aggregates and geopolymer mortars [26]. On the contrary, additional research shows that under increasing temperatures, specimens containing waterglass decrease in strength while those containing only a base activator (NaOH, KOH) produce higher strengths. Additional research is still required to accurately determine the specific effects produced through the addition of waterglass into geopolymer binder solutions.

3.3. Binder Constituent Proportioning

Geopolymer binder properties are highly dependent upon the type, ratios and concentrations of mixing constituents. Each constituent and the variables associated with that constituent play a significant role in determining the characteristics of the final product.

3.3.1. Activator Concentration

The alkaline activator concentration is the most critical factor for successful geopolymer formation and the evolution of high compressive strength. Regardless of activator type, an increase of concentration increases the reaction rate and degree leading to a less porous and stronger cement material. The addition of activators and increase in concentration results in an increase in volume of smaller pores and lower total porosity for the fly ash-based systems, thus increasing early strength of the mortars samples [18].

The influence of activator concentration increases with time. The nominal molarity for fly ash and GGBFS mixes range from 2–10 M, but higher strengths are obtained when the concentration approaches the maximum range [27]. While it is generally accepted that a higher concentration will result in higher strength capabilities, there seems to be an optimum limit for each activator type, such that crossing this limit results in the reverse affect. Specimens created using a 10 M KOH solution showed the highest compressive strength of 60 MPa, but the strength decreased as the KOH concentration was raised to 15 M [3].

It is believed that the mixture exceeded its saturation point and the unreacted K^+ ions became deterrent to strength gain rather than a benefit. Consequently, a higher alkaline concentration increases set time and delays polymer formations since excessive ion presence limits their mobility and potential to interact with available reactive species. For this reason, the concentration must be addressed clearly in a geopolymer mix design.

3.3.2. Pozzolan/Activator Ratio

The ratio of pozzolanic material (fly ash, blast furnace slag, calcined clays) to a selected activator affects several critical properties of the geopolymer basis. Overall strength is greatly affected by this variable. The alkaline liquid-to-fly ash ratio (by mass) is recommended to be maintained in the range of 0.30 to 0.45 [6]. Higher compressive strengths were obtained when experimentation was conducted using 5 M activator concentrations and a liquid-to-fly ash ratio of 0.4 [16]. The fly ash-to-activator ratio appeared to be the most critical parameter regarding general strength and fire resistance of the geopolymer paste [28].

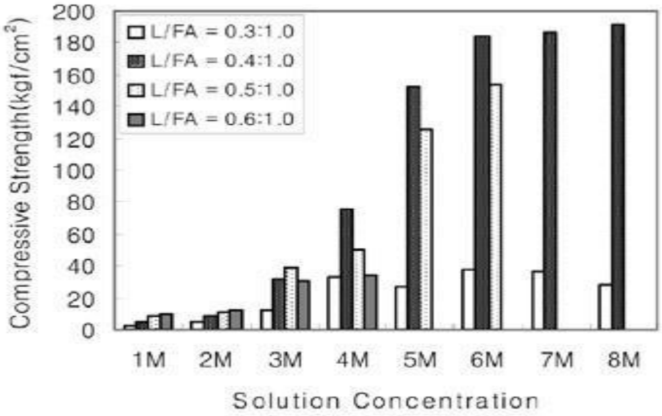


Figure 10. Effect of Liquid Activator Concentration-to-Fly Ash Ratio on Compressive Strength [16]

3.3.3. Sodium Silicate / Hydroxide Activator Ratio

The addition of sodium silicates to the mix design increases mechanical properties beyond the ability of a hydroxide activator alone. However, care must be taken to regulate the ratio between each substance. Laboratory experience suggests that the ratio of sodium silicate-to-sodium hydroxide solution (by mass) be set to an approximate value of 2.5 [6].

3.3.4. SiO2 / Na2O Ratio (Ms Modulus)

The SiO2 / Na2O ratio is a highly important parameter in geopolymer design. It is well known that variations in the SiO2 / Na2O ratio significantly modifies the degree of polymerization of the dissolved species in the alkaline/silicate solution, thus determining the mechanics and overall properties of the synthesized gel product [5]. Higher percentages of soluble silica in geopolymer systems retards dissolution of the ash material due to increased saturation of the ionic silica species and promotes the precipitation of larger molecular species, resulting in a stronger gel with an enhanced density [29]. At intervals of short cure times, an increase in soluble silica favored the development of high mechanical strength, while lower silica content produces the highest strength values at longer cure times [29]. The presence of soluble silica directly affects the reaction kinetics, the rate of crystallization, and promotes a Si-rich gel formation which is responsible for material strength development. A ratio of 2.0 for commercially available SiO2 to Na2O (by mass) is recommended [6]. Figure 11 illustrates the inverse relationship between Na2O and SiO2 on compressive strength characteristics; strength increases with an increased presence of SiO2.

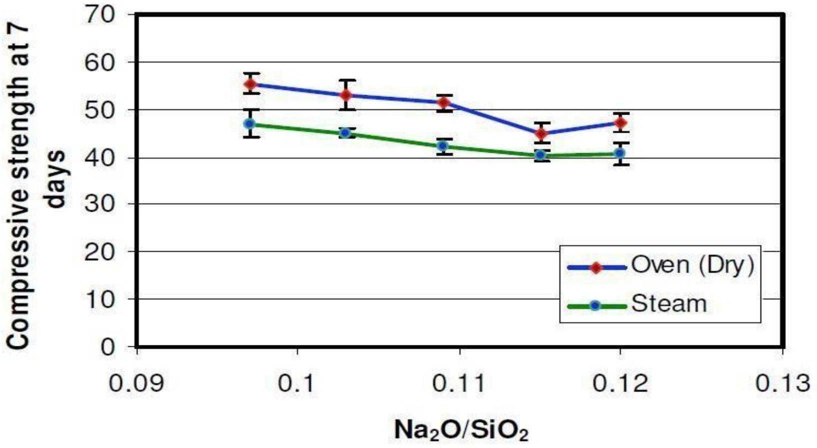


Figure 11. Effect of Molar Na2O/SiO2 Ratio on Compressive Strength [29]

3.3.5. pH Level

The most significant factor affecting compressive strength in geopolymers is pH, with a range of 13–14 being the most suitable for development of good mechanical strength [3]. An increase of the alkaline activator concentration directly raises the pH and consequently enhances the degree of reaction. An increased level of pozzolanic reactivity yields a denser and stronger matrix due to less void space and unreacted particles. The pH also affects the viscosity of the geopolymer mixture: added pH reduces viscosity and the paste becomes more workable, while a lower pH level causes the paste to remain viscous and stiff [3]. With a higher pH, a predominance of smaller chain oligomers and monomeric silicate available to react with soluble aluminum was observed, while lower pH levels produced lower monomer concentration [3].

4. Geopolymer Concrete Production

This section describes the recommended technology for designing, mixing, and curing geopolymer mortars and concretes. Every aspect of the design must be thoroughly investigated and engineered in order to avoid unwanted results and ensure optimum performance for each given service scenario.

4.1. Aggregates

Aggregates in geopolymer concrete serve the same purpose as in Portland cement-based materials, but care must be taken to avoid potential issues from possible aluminosilicate reactivity (ASR) with the alkaline activating solution. Mineral composition including opaline, cryptocrystalline silica, chalcedony and microcrystalline quartz are susceptible to ASR attack which could ultimately lead to aggregate dissolution [31]. Furthermore, the reactions can form crystalline structures of expansive nature, causing internal stress cracking and material spalling. The replacement of calcium- rich Portland cement with pozzolans such as fly ash and blast furnace slag have greatly reduced the potential for ASR to exist; however, this issue must be addressed prior to selection of an applicable aggregate material.

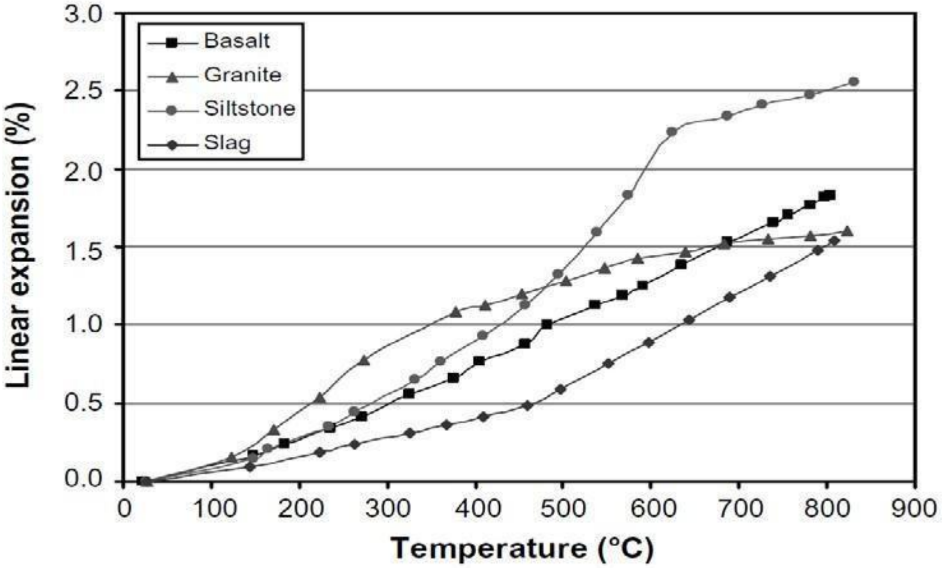


Figure 12. Thermal Expansion Characteristics of Coarse Aggregates Under Extreme Thermal Loading [31]

The recommended mass of combined aggregates for geopolymer mortars and concretes is 75-80 percent of the total geopolymer concrete mass [6]. The fineness modulus of combined aggregate material is best set to 4.5 or 5.0 to allow for maximum interaction and bonding with the geopolymer binder paste solution [6]. The aggregate material is used primarily for filler material to reduce the amount of binder required for production; no added benefit from aggregate inclusion is observed. The geochemical nature of the coarse aggregates (basalt or siltstone) appear to have little effect on the compressive strength of geopolymer concretes; however, basalt yields a slightly stronger interfacial bonding strength than siltstone rock [26].

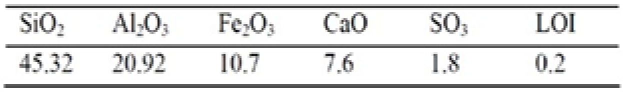
The coarse and fine aggregates in a geopolymer concrete mixtures are assumed to be saturated surface dry (SSD) to prevent either water absorption or addition to the mixture. In reality, this may not be the case and additional water from the aggregate material will inadvertently be introduced to the system. For this reason, it is recommended to allow for slight compensation in the water-to-solids ratio within the geopolymer mix design.

The interfacial bonding between the binder paste and aggregate mix is highly dependent upon the alkaline activator concentration. When the activating solution was low in alkalis and/or soluble silicate, the interfacial bonding strengths between the rock and the geopolymer mortars were also low [26]. While the potential for interfacial bonding is high with the proper alkalinity, additional research shows that thermal loading of geopolymers containing coarse aggregate can be detrimental to the concrete system. The strength of the fly ash-based geopolymer declined with the inclusion of aggregate materials, possibly due to the differential in thermal expansion between the paste and aggregate masses [28]. It is believed that the geopolymer matrix experiences thermally induced contraction, while the aggregates expand upon extreme loading. Additional research is required to successfully identify this phenomenon.

4.2. Mixture Proportioning

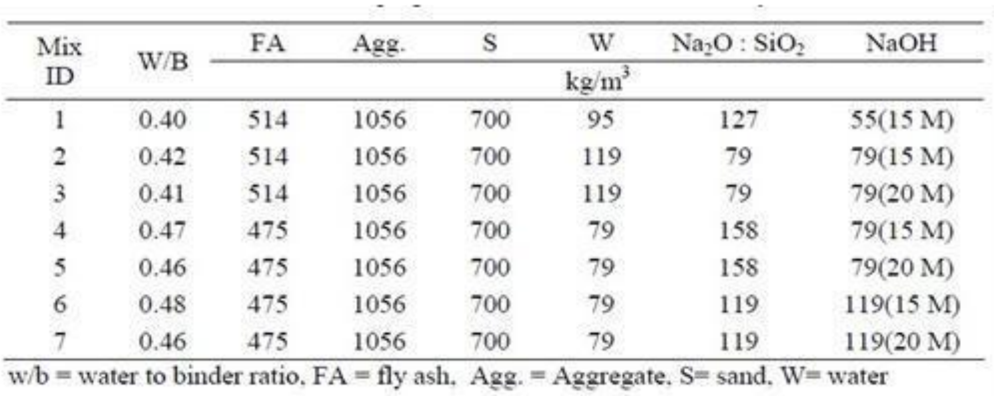
Geopolymer components play an important role in determining final product characteristics. The mechanics of hardened geopolymer mortars and concretes are directly related to factors such as pozzolan composition, activator type and concentration, aggregate size and ratios of added liquids (water, plasticizers). Furthermore, the proportion of each component as related to the whole is critical in the successful development of strength-supporting structures within the geopolymer matrix.

Fly ash composition is generally measured and evaluated by the percentage of existing elements present in the by-product material (Table 2), while other proportioned variables are typically by relative mass, molarity and fluid volume. Table 3 outlines a typical proportion used for a geopolymer mix design. High levels of silicon and aluminum are critical for product development; therefore, the Si/Al ratio in the initial pozzolan bear great significance to the strength potential of a given geopolymer specimen.



SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	LOI
45.32	20.92	10.7	7.6	1.8	0.2

Table 2. Typical Fly Ash Composition (%) [32]

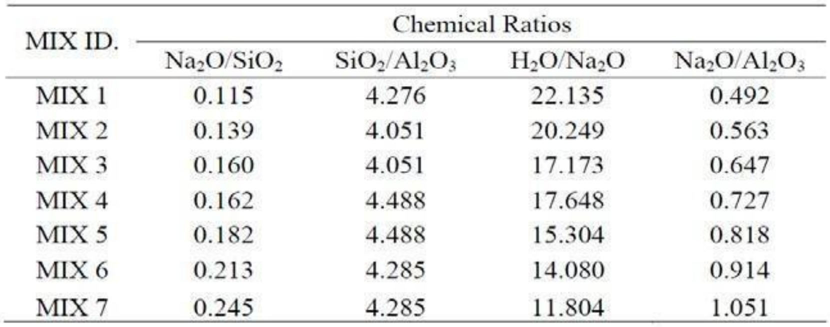


Mix ID	W/B	FA	Agg.	S	W	$Na_2O : SiO_2$	NaOH
		kg/m^3					
1	0.40	514	1056	700	95	127	55(15 M)
2	0.42	514	1056	700	119	79	79(15 M)
3	0.41	514	1056	700	119	79	79(20 M)
4	0.47	475	1056	700	79	158	79(15 M)
5	0.46	475	1056	700	79	158	79(20 M)
6	0.48	475	1056	700	79	119	119(15 M)
7	0.46	475	1056	700	79	119	119(20 M)

w/b = water to binder ratio. FA = fly ash. Agg. = Aggregate. S= sand. W= water

Table 3. Typical Geopolymer Mixture Proportions [32]

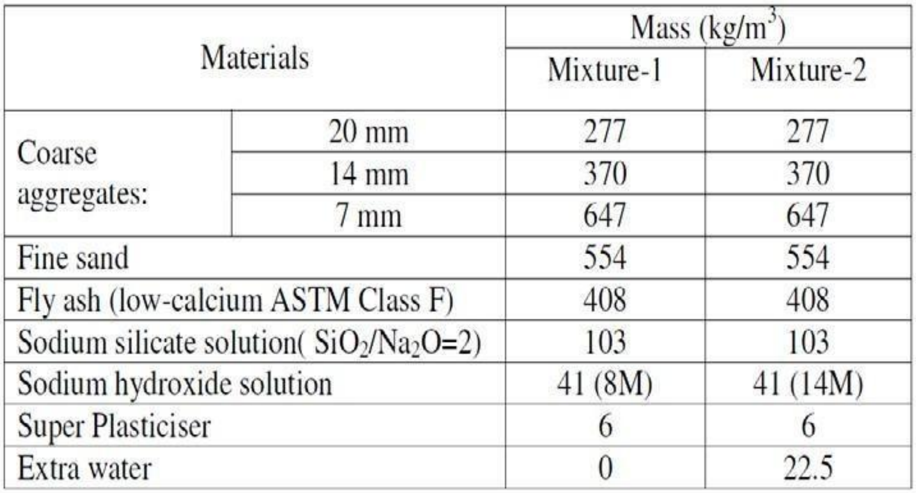
Chemical ratios are also vital in geopolymer creation. Much research has been completed to determine the direct relation between chemical ratios and final strength values, but definitive optimal ratios have yet to be clearly established. Table 4 lists typical ratios for various chemical additives in several geopolymer mixtures.



MIX ID.	Chemical Ratios			
	Na_2O/SiO_2	SiO_2/Al_2O_3	H_2O/Na_2O	Na_2O/Al_2O_3
MIX 1	0.115	4.276	22.135	0.492
MIX 2	0.139	4.051	20.249	0.563
MIX 3	0.160	4.051	17.173	0.647
MIX 4	0.162	4.488	17.648	0.727
MIX 5	0.182	4.488	15.304	0.818
MIX 6	0.213	4.285	14.080	0.914
MIX 7	0.245	4.285	11.804	1.051

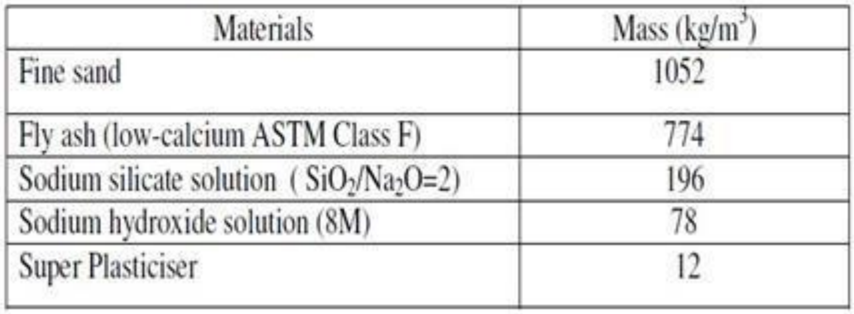
Table 4. Typical Chemical Ratios of Activated Fly Ash Paste [32]

In order to achieve high strength and durability, based on the zeolite chemistry, the use of certain molar ratios is recommended for the alkaline activator: $SiO2/Na_2O$ = 1.85; for the metakaolin: $SiO2/Al_2O_3$ (3.5–4.5), Na_2O/SiO_2 (0.2–0.48), Na_2O/Al_2O_3 (0.8–1.6); between the activator and the metakaolin: $H2O/Na2O$ (10–25) [43]. Tables 5 and 6 represent proportionality values for concrete and mortar mixture designs by Wallah and Rangan [46].



Materials		Mass (kg/m^3)	
		Mixture-1	Mixture-2
Coarse aggregates:	20 mm	277	277
	14 mm	370	370
	7 mm	647	647
Fine sand		554	554
Fly ash (low-calcium ASTM Class F)		408	408
Sodium silicate solution($SiO_2/Na_2O=2$)		103	103
Sodium hydroxide solution		41 (8M)	41 (14M)
Super Plasticiser		6	6
Extra water		0	22.5

Table 5. Typical Geopolymer Concrete of Aggregates and Liquids [4]



Materials	Mass (kg/m^3)
Fine sand	1052
Fly ash (low-calcium ASTM Class F)	774
Sodium silicate solution ($SiO_2/Na_2O=2$)	196
Sodium hydroxide solution (8M)	78
Super Plasticiser	12

Table 6. Typical Geopolymer Mortar Mix [4]

While each component used to formulate the geopolymer bears significance to the final product, it has been determined that the optimum composition resulted from the following chemical ratios: $Na_2O/SiO_2 = 0.25$; $H_2O/Na_2O = 10$; and $SiO_2/Al_2O_3 = 3.3$ [34]. Furthermore, water content was recognized as an important factor to the success of the geopolymer, as testing with H_2O/Na_2O molar ratios equal to 25 produced extremely low mechanical results [34]. It must be stated, however, that while the proportioned values given by specific research publications are deemed as optimum, further investigation is required to fully understand the intrinsic behavior of each component as it relates to the mechanics of the final geopolymer product.

4.3. Consolidation Techniques

The inherent viscosity of fresh geopolymer pastes causes excessive air entrainment during the mixing process. Trapped bubbles have difficulty escaping the thick matrix without mechanical aid. Vibratory plates and ultrasonic technologies are proven methods for helping to reduce air entrainment and improve the hardened porosity.

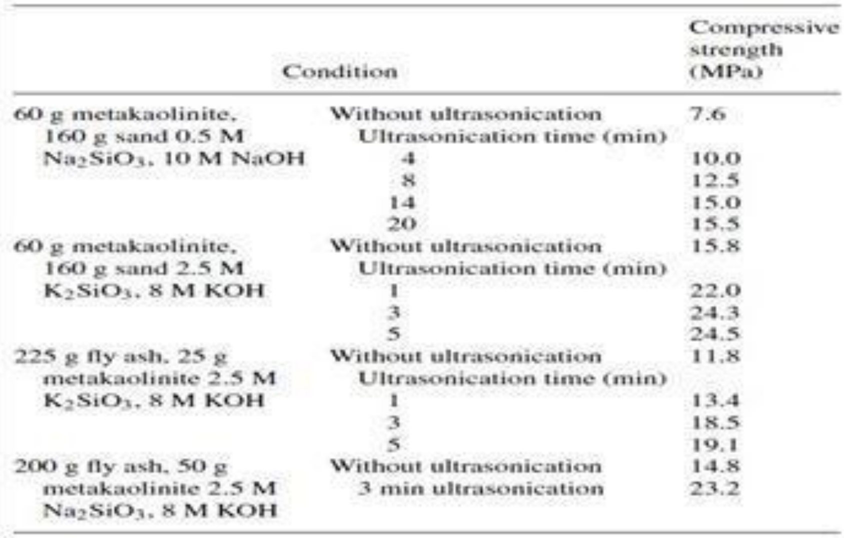
4.3.1. Mechanical Vibration

Mechanical vibration of the fresh geopolymer paste material substantially reduces trapped air pockets and improves the porosity of the final product. The aluminosilicate gel is highly viscous and mixing agitation can easily encapsulate air into the matrix. Vibration of the formed molds serves to reduce this potential and greatly improves the overall strength of the hardened geopolymer concrete.

4.3.2. Ultrasonication

The technique of ultrasonication throughout the fresh paste material was developed to reduce porosity and increase the compressive strength of geopolymer cements. Initial ultrasonication enhanced dissolution, thus promoting the release of additional aluminum and silicon into the gel phase and strengthening the particle surface bonds [35].

It also improved the formation of semi-crystalline to crystalline phases in the hardened cements products. The accelerated dissolution of the Al-Si source materials served to improve the compressive strength and develop thermal stability properties not observed in specimens absent from ultrasonication [35].



Condition		Compressive strength (MPa)
60 g metakaolinite, 160 g sand 0.5 M Na_2SiO_3, 10 M NaOH	Without ultrasonication	7.6
	Ultrasonication time (min)	
	4	10.0
	8	12.5
	14	15.0
	20	15.5
60 g metakaolinite, 160 g sand 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	15.8
	Ultrasonication time (min)	
	1	22.0
	3	24.3
	5	24.5
225 g fly ash, 25 g metakaolinite 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	11.8
	Ultrasonication time (min)	
	1	13.4
	3	18.5
	5	19.1
200 g fly ash, 50 g metakaolinite 2.5 M Na_2SiO_3, 8 M KOH	Without ultrasonication	14.8
	3 min ultrasonication	23.2

Table Compressive Strength of Geopolymers Sythesized with Ultrasonication [35]

4.4. Curing Methodologies

4.4.1. Ambient Temperature Cure

A challenge for successful geopolymer concrete production is obtaining proper mechanics at ambient temperatures. Similar to Portland cement, the geopolymer reaction is more easily achieved with the addition of an external heat source to promote alkaline reactivity of the pozzolanic material. There is a challenge in synthesizing fly ash based geopolymers at ambient temperatures, as others have found that geopolymers did not set at 23 °C [36]. While it may be feasible to expose test specimens to elevated temperatures in a laboratory, a full scale pavement project would be difficult to efficiently heat during cure.

Research has been completed to investigate geopolymer designs with the potential to successfully harden under room temperature environments, yet little understanding has been gained regarding methods of large-scale ambient geopolymer cure. However, it was stated by Rangan (2008) that heat-curing temperatures can be as low as 30 °C, which would be attainable in tropical climate conditions [6].

Figure 13 represents ambient-cure research performed by Wallah and Rangan that shows achieved compressive strength values beyond 50 MPa for specimens cured at temperatures ranging from 8 to 25 °C and relative humidity of 40– 60 percent. While full-scale ambient cure presents logistical difficulties, an option for field implementation would be thermal loading of pre-cast concrete sections prior to field delivery. This method could be a viable solution until a deeper understanding of ambient cured geopolymer is properly developed.

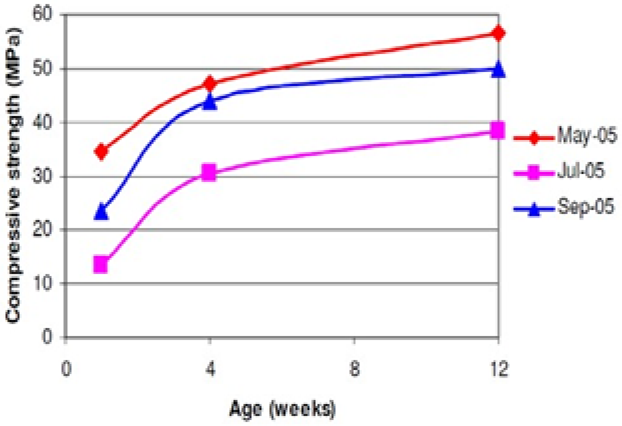


Figure 13. Compressive Strength of Specimens Cured at Ambient Temperatures [4]

4.4.2. Elevated Temperature Cure

As with traditional Portland cements, geopolymers respond better to heated curing methods.Research work has demonstrated that time and temperature greatly affect the mechanical development of geopolymer binders; however, a temperature threshold exists, beyond which the strength gain rate is extremely slow [5]. Temperatures in the range of 50–80 °C are widely accepted values used for successful geopolymer hydration. Both curing temperature and curing time directly influence final compressive strength values of geopolymer specimens. Elevated temperature curing can be achieved through the use of steam or dry-heat methodologies, but test data shows that dry-curing yields a compressive strength increase of 15 percent over the steam curing methods [6].

While it has been noted that an increase of reaction time and temperature positively affect geopolymerization, similar research shows that these factors are only an enhancement to mechanics at an early age. As reaction time increases at later ages, the curing temperature increment has a negative effect, provoking a decrease in final strength values [38]. The basis for explanation lies within the initial heavy formation of the reaction product and a subsequent densification of material immediately upon alkaline introduction. The reaction product becomes exponentially less over time and increased temperatures only serve to degrade previously created aluminosilicate gels within the matrix, thus weakening the overall structure.

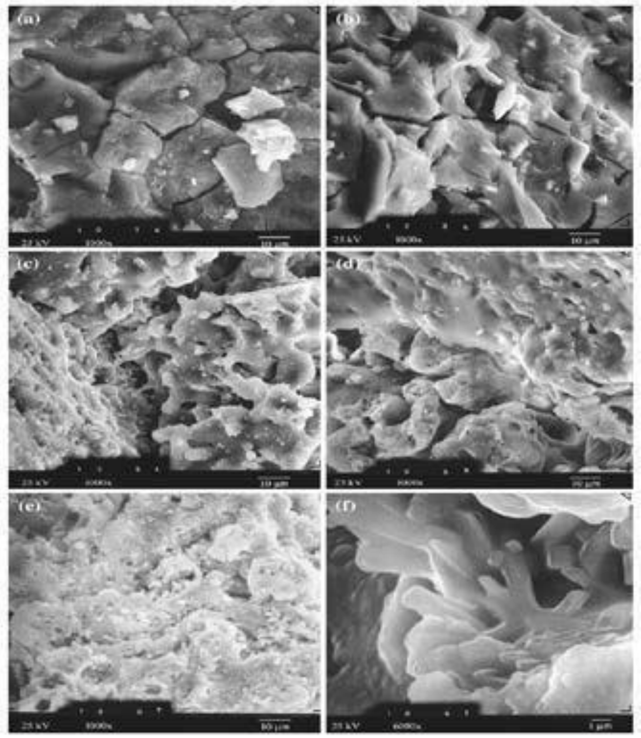


Figure 14. Alkali-activated Aluminosilicate after Thermal Loading to:

(a) 25 °C, (b) 600 °C, (c) 800 °C, (d) 1,000 °C, (e) 1,150 °C, (f) 1,200 °C [36]
(b)

Both compressive and bending strengths reached a minimum value at 800 °C exposure yielding at five times less for compression and 2.5 times less for bending than the control group absent from heat, yet additional loading to 1200 °C had a reverse affect, leading to an increase in both strength characteristics to within 12 percent and 18 percent respectively of the reference control specimens [39]. This is attributed to Akermanite (Ca2MgSi2O7) formations which are observed forming at high temperatures and enhance mechanical strength.

Conductivity decreased under thermal load by approximately 30 percent at 600 °C and by 40 percent at the 800 °C mark; additional loading had no significant affect upon conductivity values [39]. Thermal conductivity reached its minimum value at 1200 °C, while both mechanical strength and porosity were at their respective maximums. Porosity increases with increased thermal load and development of voided pores is thought to be a direct result of product degradation at extreme temperatures [40].

5. Microstructural and mineralogical properties

This section discusses the microstructural and mineralogical characteristics of the hardened geopolymer cement matrix and identifies influential factors contributing to (or detracting from) enhanced mechanical performance. Detailed matrix analysis using XRD (X-ray Diffractometer), Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy (SEM), and ^{29}Si / ^{27}Al Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) technologies allow quantification of minerals and measurement of inherent properties at a micro level.

5.1. Reaction Products

The resulting reaction product formed within alkali- activated geopolymers is defined by the prime materials used, the activating solution and the content of each entity. The main reaction product in fly ash activation under mild curing conditions of 60–90 °C is a three- dimensional aluminosilicate gel of amorphous nature with a predominance of Q4(3Al) and Q4(2Al) units [41]. The controlling mechanism of the reaction which generates this precursor gel is associated with the dissolution process by which the high concentration of OH- in the system breakdown the vitreous phase Si-O- Si, Si-O-Al, and Al-O-Al bonds forming Al-OH and Si- OH groups which condense and give way to the precipitation of the short range zeolitic gel product [43].

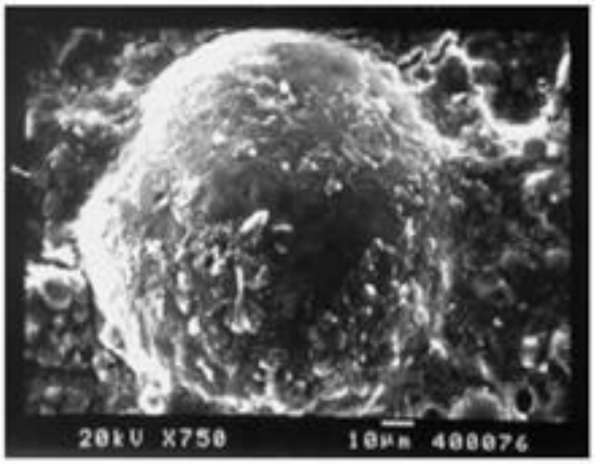


Figure 15. Fly Ash Particle Covered in Reaction Product Crust [41]

5.2. Porosity

The porosity of geopolymer cement is dependent upon several variables of the mix design. It bears direct significance to compressive strength properties of a given cement specimen and is heavily influenced by the activating solution type, concentration and the pozzolan material employed. The alkaline concentration of a given geopolymer binder is inversely proportional to its final porosity; an increase in concentration results in a less porous microstructure of enhanced strength capabilities [18]. Furthermore, GGBFS pastes are observed to possess larger volumes of porosity by comparison to ordinary Portland cement pastes [41]. The pH level of a paste mix also affects the porosity in the same manner by increasing the reaction degree, thus filling available void space with reaction product.

Thermal loading to extreme temperatures has a negative effect on geopolymer porosity. Porosity voids were shown to increase significantly at 600 °C with maximum voids detected at 800 °C [39]. Temperature loading between 800 and 1000 °C did not cause additional porosity changes in the specimens; however, loads to 1200 °C were found to exponentially increase porosity, and yet final compressive strength values did not suffer [39].

Additional testing by Bakharev showed that thermal loading to 1000 °C increased the overall pore volume by 3 percent (increased overall pore volume from 26–29 percent), yet nominal pore size increased from 37.6 nm (pre-loading) to 1835 nm after exposure, which was attributed to material decomposition upon heating [30].

Post-loading analysis revealed the formation of Na-feldspars in the matrix. It was believed that the presence of unreacted sodium in the binder caused crystallization of the Na -feldspars upon firing and contributed to the increase of porosity and the deterioration of strength [40].

Under such conditions, the pore walls experience high stresses due to uncombined water expansion upon heating and the aluminosilicate gels deteriorate quickly. The loss in the strength combined with pore wall stress can cause the collapse of the pore and result in shrinkage cracking throughout the specimen [40].

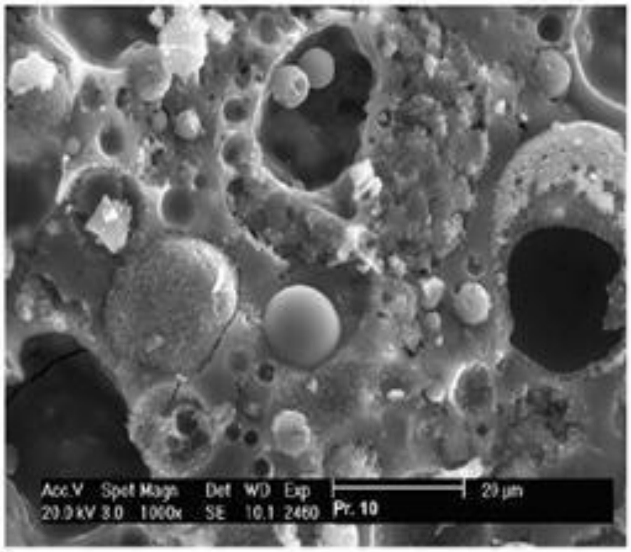


Figure 16. Porous Character of a Geopolymer Matrix at 28-day Hydration [7]

5.3 Durability

Geopolymer cements are inherently resistant to chemical attack and thermal loading due to their reduced porosity and thermal conductivity characteristics. Many of the durability problems associated with PCC arise from its calcium content in the main phases [25]. The C3A reacts with sulfate ions in the presence of Ca(OH)2 to form ettringite and gypsum, which in turn cause expansion and degradation of the cement into a non-cohesive granular mass [25]. It is the low calcium content found within pozzolanic materials that prevents geopolymers from experiencing such negative effects.

While geopolymeric materials possess an enhanced level of durability over Portland -based cements, they are not completely immune to environmental threats. Immersion in seawater slightly affects internal porosity as a result of Na ions being replaced by Mg ions in the gel microstructure. Highly acidic media cause a de-alumination to occur in alkali-activated cements, thus resulting in loss of mass and a decline in mechanical strength. It is noted, however, that the strength loss in comparison to PCC is much less.

5.4 Chemical Durability

Researches shows that geopolymer materials can easily withstand months of immersion in a variety of aggressive elements without experiencing any form of deterioration and/or surface alterations as typically found with Portland cement-based products. High alkalinity boasts a higher degree of reaction and maintains a matrix density that tends to prohibit the permeation of corrosive elements into the internal framework of geopolymer cements.

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