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Pozzolanic Materials and Waste Products for Formulation of Geopolymer Cements in Developing Countries: a Review

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ABSTRACT

Potential use of Geopolymers as binders in concrete instead of ordinary Portland cement (OPC) has attracted worldwide attention in recent years, due to its advantages such as environmental benefits, better durability and acceptable mechanical properties. In this paper, it is shown that the large resources of aluminosilicate waste materials in developing countries present a great opportunity for their use to make geopolymer concretes towards building of local physical infrastructure. This paper reviewed research on characteristics and properties of geopolymer binders and concretes. The effects of different raw materials, various activators, mixture formation and curing are discussed.

Keywords: Alkali-activators, Geopolymer Cements, Binders, Pozzolanic Materials, Waste Products.

1. INTRODUCTION

Concrete has become the world's most commonly used building material. Due to its many advantages, ordinary Portland cement (OPC) is used as the binder in concrete, as it provides important qualities such as fire resistance, acceptable compressive strength, chemical attack resistance and long-term durability. However, OPC continues to face high criticism due to its production, which has a significant adverse effect on environment. Cement production industry has been identified as one of the most important users of carbon-based fuels [1], with this production generating 5-8% of the world CO_2 emissions [2]. In South Africa, the CO_2 tax may be implemented in the nearby future[3]. Accordingly, there is need to develop alternative cements with lower CO_2 emission for application in the construction industry. One of the alternatives is to produce more environmentally friendly concrete using geopolymer cements (GPC).

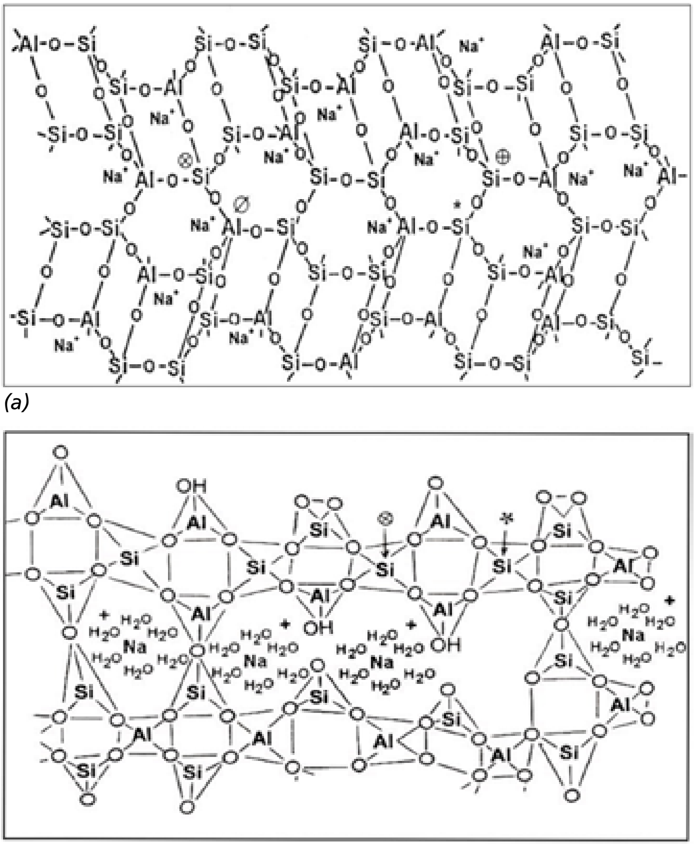
In 1959, Gluchovskij as cited in Skvara [4] demonstrated the possibility of preparing new materials by reaction of alumino-silicate raw materials such as blast-furnace slag, fly ash, clay materials etc. with alkaline compounds typically carbonates, hydroxides, silicates. It is on this basis that the term "Geopolymer" is used [5]. Due to their long-term durability, low energy consumption in production, low CO_2 emission, low production cost, and other special properties, GPC may be considered preferable to other mineral binders, including OPC. Depending on raw material selection and processing condition, GPC can exhibit superior performance compared to OPC essentially in durability aspects such sulphate attack [6,7], acid attack [8], alkali-silica reaction [8-12] and high temperature resistance [13-15]. Large quantities of industrial wastes such as Fly Ash (FA), Palm Oil Fuel Ash (POFA), Ground Granulated Blast furnace Slag (GGBS), are generated every year and these wastes cause environmental concerns in many countries. Since coal is the main source of energy in South Africa, a large amount of FA is being disposed throughout the year. Approximately 36 million tons of coal fly ash are produced annually from electricity generation in South Africa [16]. This quantity is significantly higher than the capacity of South African OPC production industry, which is about 13 million tons per year [17]. FA, POFA, GGBS and similar wastes can potentially be re-used as raw materials in GPC [18]. Results of a study by Albitar et al. [19] showed that GPC have a great potential for utilization in the construction industry as a replacement for OPC-based concrete, since both cementitious systems exhibit comparable structural properties. These valuable characteristics along with environmental considerations make GPC quite desirable for concrete production.

In another study by Duxson et al. [15], the fundamental characteristics of Metakaolin (MK), FA and GGBS-based GPC, and the effects of each raw material on the final product, were reported. Although, most of the GPC mixes now being used in academic researches and industrial activities are based on FA, GGBS or MK, a wider range of aluminosilicate waste materials have potential to be used as precursor for the GPC. Bernal et al. [20] reviewed a number of aluminosilicate wastes. Based on their source and production processes, the waste materials were classified in several groups comprising urban wastes, agriculture industrial wastes, wastes from mining and mineral industries, waste from other industries. In their study, the properties of raw materials and synthesized final products of each waste as well as their availability worldwide were discussed, which indicated great potential for their use as GPC.

Generally, there is presently limited activity associated with GPC in the South African construction industry and most developing countries [21]. Accordingly, comprehensive studies on local materials, demands, and capacities are needed to provide understanding of possibilities. This paper reviews some of these various aspects related to binder materials for GPC.

2. ALKALI-ACTIVATION

Geopolymer binders are prepared through alkali-activation process. Their raw materials are aluminosilicates, characterized by two- to three-dimensional Si-O-Al structure. The reaction of these aluminosilicate materials in a strong alkaline environment takes place in stages. Dissolution of the solid aluminosilicate raw material by alkaline hydrolysis, produces aluminate and silicate species [15]. The first step of dissolution mechanism starts by ion exchange of H^+ for alkali-earth or alkali-metals cations. Water and hydroxide ions also attack the particles and breakdown the network [22]. Dissolution of the solid aluminosilicate source and liberation of aluminates and silicates into the solution, produce a supersaturate aluminosilicate solution [15]. Finally, aluminosilicate gel precipitates from the aluminate and silicate species with release of water that was consumed during the dissolution. In this process, aluminosilicate gels which are zeolite precursors are mostly formed. The composition of these gels is characterized by the formula $Mn[-(Si-O)z-Al-O]n.\ wH_2O$ [5]. C-S-H and C-A-H phases may also form depending on composition of raw materials and condition of the reaction. Secondary H_2O may also be formed during this reaction through poly-condensation. Amorphous, partially amorphous or crystalline substances may be formed depending on characteristics



(a)

(b)

Fig. 1: (a) Davidovits model [5], (b) Barbosa model [23]

of raw materials and the reaction conditions. Concentration of solid matter plays a substantial role in the process of alkali activation [4]. In the empirical formula Mn[-(Si-O)z-Al-O]n. wH_2O, M = K or Na atoms; n = the degree of poly-condensation; z = 1,2,3 or more than 3. Two different three-dimensional network models have been proposed by Davidovits et al. [5] and Barbosa et al. 23] to characterize this formula. It may be noted that these models represent a poly-sialate-silox [5] product type formed by alkali activation of MK. Fig. 1 shows the chemical structures of the models.

Several factors directly influence the degree of reaction observed in a geopolymer paste mixture, which either enhance or hinder the polymerization process and subsequent phases that form binder properties of the hardened cement. Both, the activation reaction and the chemical composition of reaction products depend on several factors including particle size distribution and mineral composition of raw material [24].

3. RAW MATERIALS

3.1 Fly Ash

Fly Ash (FA) is one of the residues generated in combustion of coal. It comprises fine particles that rise with flue gases in coal power stations. In the past, FA was generally released into the atmosphere, but the need for pollution control has mandated a search for its beneficial use in recent decades. Accordingly, FA is captured in coal power stations then stored prior to its use or disposal. Several experimental studies have demonstrated FA as one of the most adequate aluminosilicate raw materials for use in geopolymerization.

McKenzie [25] studied a combination of South African FA and GGBS for preparation of GPC. In the study, FA was used as the predominant binder since it contained the required chemical properties for polymerization to take place, whilst the hydraulic properties of GGBS were used to control strength development. Table 1 shows the typical composition of these materials. The investigation [25] was specifically done on self-compacting concrete. Sodium silicate solution with a solid content of 45% mixed with NaOH at the ratio of 1:1, was used as the activator. The sodium silicate solution was considered to be the main activator while NaOH served to control setting time and early strength. The 28-day compressive strength of the concrete was 48.1 MPa. These results demonstrate the possible production of self compacting geopolymer cement concrete (GPCC) and its potential application thereof in precast industry.

Table 1: Chemical composition of fly ash and slag within South Africa [25]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	K_2O	SiO_2	Na_2O	TiO_2
FA (%)	29.2	7.75	2.5	2.25	0	<1.0	37.95	<1.5	1.75
GGBS (%)	12.45	32.7	0.58	11.2	1.32	0.86	37.95	0.36	0.65

FA-Fly ash, GGBS-Ground Granulate Blast Furnace Slag

In another study, Attwell [21] reported the application of FA/slag-based alkali-activated concrete at City Deep Container Terminal, Johannesburg were GPCC was used in the surface beds without reinforcement. Low calcium (Class F) FA produced at Lethabo power station and GGBS supplied by Slagment pty, were used as raw materials. A combination of sodium silicate and sodium hydroxide solutions were employed as activator to prepare 32 different mixes in the laboratory. The optimal mix which gave good workability of fresh concrete, adequate compressive strength, and low drying shrinkage was chosen and used to cast GPCC at site. Results obtained were 28-day compressive strength of 44.7 MPa while the slump of fresh concrete was 180 mm. Albitar et al. [19] investigated the mechanical properties of Class F FA-based GPCC. In their study, low-calcium FA produced at Port Agusta power station in South Australia was used as raw material. The alkaline solution used consisted of sodium silicate solution with solid content of 38 wt% and SiO_2/Na_2O molar ratio (silicate modulus) of 3.24, premixed with 14M NaOH at a ratio of 1.5. Their results indicated that Class F FA-based GPCC exhibits higher tensile strength than OPC-based concrete. Also, Tho-In et al. [26] found similar results showing the ratio of split tensile to compressive strength of high calcium (Class C) FA-based GPCC, to be slightly higher than for OPC- based concrete. They also reported the density of Class C FA-based GPCC to be approximately 30% lower than that of conventional concrete.

The existing OPC models for elastic moduli and stress-strain relationship were reported to be reasonably accurate for prediction of these characteristics in GPCC as well [19]. Junaid et al. [27] proposed a new empirical model based on Collin's OPC stress-strain model [28] to predict the behaviour of FA-based GPC concretes in ambient temperature. Their models are represented by Eq. 1.

$$\sigma_c = f_c^{1} \frac{\varepsilon_c}{\varepsilon_{cm}} \frac{n}{n-1+\left(\frac{\varepsilon_c}{\varepsilon_{cm}}\right)^{nk}} \qquad \text{(Eq. 1)}$$

Where:

ε_c = Strain at any given stress; ε_{cm} = Strain at peak stress;

σ_c, f_c^{1} = peak compressive stress;

For normal aggregate:

$n = 0.7 + (f_c^{1}/23)$

$k = 0.6 + \left(\frac{f_c^{1}}{86}\right)$, when $\frac{\varepsilon_c}{\varepsilon_{cm}} > 1$

$k = 1.0$, when $\frac{\varepsilon_c}{\varepsilon_{cm}} \leq 1$

for lightweight aggregate:

$$n = 0.72 + (f_c^1/11)$$

$$k = 0.6 + \left(\frac{f_c^1}{70}\right), \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} > 1$$

$$k = 1.0, \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} \leq 1$$

Moreover, they reported that some phenomena, such as further geopolymerization, loss of water and formation of new phases within the geopolymer system, influence stress-strain curves at elevated temperatures. The damage due to escape of water at temperatures between 20 and 200 °C decreased the stiffness of GPC specimens. However, there was recovery in stiffness at temperatures between 200 and 400 °C that may be attributed to further geopolymerization in the GPC matrix. The stiffness of specimens again decreased with increase of temperature from 400 to 800 °C. This reduction in stiffness may be a result of possible disintegration of the geopolymer gel and formation of new phases within the GPC system.

Temuujin et al. [29] suggested a reduction in dissolution rate of FA particles to be a factor that may lead to increase in compressive strength of GPCCs. Most studies have suggested use of heat-curing to obtain better performance in FA-based GPC. However, being able to cure GPCC in ambient temperature is very important in terms of practical application. Results of some studies [30,31] showed that it is possible to alkali-activate FA blended with GGBS and/or $Ca(OH)_2$ under ambient temperature, to approach mechanical performance similar to that of heat-cured FA-based GPCs.

3.2 Ground Granulated Blast Furnace Slag

Generally, slag is an industrial by-product leftover after a desired pure metal has been separated from its ore. Slag is usually a mixture of metal oxide and silicon oxide. However, slag may contain metal sulphides and elemental metals. GGBS and granulated lead smelter slag (GLSS) may exhibit the potential as raw material for use in GPCC due to their silica and alumina constituents. Several studies have been carried out on different types of slag-based GPCCs with or without other aluminosilicate materials.

Albitar et al. [32] studied the use of GLSS in GPC with or without FA, as binders for GPCC. Its influence on mechanical properties was investigated. GLSS was also used as fine aggregate along with river sand. They examined the influence of several parameters including slag to FA ratio, slag to river sand ratio, activator to binder ratio, and curing method. They reported that the particle size of GLSS did not have a major influence on compressive strength. When GLSS was used as fine aggregate in the mixture, there was no effect on 100% FA GPCC. Compressive strength of GPCC reduced with increased replacement of FA by GLSS as binder. Compressive strength reduced with increase in the activator to binder ratio from 0.37 to 0.75. The mechanical properties of the optimum GPCC mix design, contained 25% FA and 75% GLSS and gave similar properties as 100% FA-based GPCC.

3.3 Metakaolin

Metakaolin (MK) is a dehydroxylated form of clay kaolinite. Stone materials that are rich in kaolinite, usually referred to China clay or kaolin, are widely used in the manufacture of paper. Particles of metakaolin are much finer than cement particles. Davidovits [33] studied the molecular framework of MK-based geopolymer. The Magic Angel Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy of the geopolymer products exhibited a chemical shift in the range of 55 ppm, which indicates AlQ4(4Si) type and is tetrahedrally coordinated. Based on these results, he proposed the three-dimensional microstructure model for products of geopolymerization that were discussed in Section 1.0. The reactivity of MK in geopolymerization is related to calcination methods of the raw kaolin clay source due to the intensity of different types of Al species in terms of the coordination number of aluminium in various Al-O compounds [34]. Meinhold et al. [35] reported that at calcination temperature of above 400°C, approximately 8% of Al remained within the undistorted sites, of which about 50 and 25% of these were Al(6) and Al(4) respectively. The other 25% included either Al(4) or Al(5). Intensity of Al(5), which is known as the most reactive Al species, increased when the calcination temperature increased from 450 to 850 °C, and decreased beyond 850°C. The maximum intensity of Al(5) was obtained between 700 to 850°C. Kriven et al. [37] investigated the physical and mechanical properties of fully reacted MK-based GPC. Three different MKs were prepared by calcination of three different clays consisting of Kaolex BN, Hydrite PXN and KaG-1b, at 700°C for 1 hour. Table 2 gives chemical composition of the raw clays. A mix of silica fume and NaOH solution at solid to liquid ratio of 0.5 was used to prepare GPC mix of molar ratios $SiO_2/Al_2O_3 = 3.3$, $Na_2O/SiO_2 = 0.3$ and $H_2O/Na_2O = 11$. Another mix of silica fume and KOH solution was used to prepare GPC samples to achieve the mix molar ratios of $SiO_2/Al_2O3 = 4$, $K_2O/SiO_2 = 0.3$ and $H_2O/K_2O = 11$. Curing of GPC samples was done by one of three methods comprising, pressureless curing (PC) method at 40 or 60°C for 48 hours, warm pressing (WP) method at 80°C and 18 MPa for 2 hours, and high pressure autoclave (HPA) method with isostatical loading at 20 MPa while being heated at 80°C for 24 hours. The results of Mercury Intrusion porosimetry (MIP) for KOH activated samples that were cured by HPA method showed that the intrusion volume mainly occurred between 0.1 and 0.01 μm, where the inherent pore size of the GPC was between 10 and 100 nm. It could be concluded that the HPA method effectively rid the GPC samples of large pores. It was also observed that the microstructure of fully reacted MK GPCs was sponge-like with nanopores and nanoparticulates. Moreover, the results of microchemistry analysis of GPCs frequently showed that the ratio of SiO_2 to Al_2O_3 was 4.0, which corresponds to Polysialate Siloxo (PSS) system with atomic ratio of Si to Al of 2.0 [33]. Although, the MK GPC samples made from Naolex BN where not as fully reacted compared to the others made from Hydrite PXN or KaG-1b, they exhibited superior mechanical performance. These observations could be attributed to the role of unreacted clay sheets in MK GPC samples made from Naolex BN. These unreacted species may have served as filler material in the GPC, which led to lower pore volume and higher compressive strength.

Zhang et al. [38] studied the formation of crystalline phases in MK-based GPC systems. Sodium hydroxide of various concentrations was used as alkali activator in combination with a sodium silicate solution of silicate modulus = 2.0 and 44 % solid content. The Si/Na ratios of alkali solution mix was varied from 0.66 to 3.0. The MK GPC specimens were cured at 40°C for various durations of 2 hours to 10 days.

Table 2: Chemical composition of raw clays [37]

Label of clay	Kaolin	Muscovite	Crystalline SiO_2	FeO	Fe_2O_3	TiO_2
Kaolex BN (%)	65	7	10-13	-	-	2.6
Hydrite PXN (%)	98	-	-	-	0.6	1.4
KaG-1b (%)	98	-	-	0.08	0.1	1.4

Results showed that in MK-GPC samples activated with only NaOH, sodium content of the solution significantly influenced the nature and quantity of the crystalline phase in GPC system. The crystalline zeolite-A ($Na_{96}Al_{96}Si_{96}O_{384}$) was formed in specimens containing Si/Na ratios of 4/4 or less. However, the MK-GPC systems containing Si/Na ratios greater than 4/4 produced nanosize crystals or another zeolite ($Na_6[AlSiO_4]_{6\text{-}4}H_2O$). Moreover, introducing sodium silicate in the system significantly reduced the quantity of crystalline phases.

Pelisser et al. [39] investigated mechanical and micro-nanomechanical properties of MK-based geopolymer cement through evaluation of the effect of sodium silicate to sodium hydroxide molar ratio. They prepared samples by mixing sodium silicate with solid content of 37 wt% and silicate modulus of 2.5 with 98% pure sodium hydroxide as activator solution. Maximum values of 10 GPa elastic modulus and 0.4 GPa hardness were achieved when an intermediate sodium silicate to sodium hydroxide molar ratio of 1.6 was used. The samples made with sodium silicate to sodium hydroxide of 2.2 also showed similar results but use of a lower ratio of 1.0, diminished the mechanical properties. High increase of porosity, as observed by scanning electron microscopy, explained the poor performance of the sodium silicate to sodium hydroxide of 1.0 formulation, suggesting that geopolymerization reactions were not completed. A strong relationship between flexural and compressive strength was found. Good resistance of geopolymer paste to cracking while under stress, was also reported.

Mortars prepared by combining MK of composition Si = 44.0, Al = 20.6, O = 23.4, Na = 12.0 wt%, with distinct proportions of sand were also studied. Using a binder/sand ratio = 1:5 gave a substantial 55.8 MPa compressive strength for samples cured at 80 °C. This strength of MK binder is quite competitive as compared to OPC concrete mixtures, which often use higher binder contents [39].

A study carried out by Muniz-Villarreal et al. [40] investigated the effects of curing conditions on properties of MK-based geopolymer. They used MK of 1.2μm particle size as raw material and a mix of sodium silicate, sodium hydroxide and distilled water was used as activator to prepare specimens that were formulated at molar oxide ratios $SiO_2/Al_2O_3 = 3.3$, $Na_2O/SiO_2 = 0.25$, $Na_2O/Al_2O_3 = 0.488$ and $H_2O/Na_2O = 13.73$. The curing procedure consisted of two steps: Firstly, samples were dried at 40ºC for 2h to prevent cracking due to an abrupt loss of water. The second step was curing at 30, 40, 50, 60, 75 or 90ºC for 24h, to develop mechanical properties. Results showed 60ºC to be the optimum temperature that gave the best geopolymerization process. These results were supported by a leaching study carried out on the geopolymer mixtures.

Kuenzel et al. [41] investigated MK characteristics, to determine their relationship to properties of geopolymer paste. Three types of commercial MK were chosen and characterised using Al-NMR to determine the coordination number of Al (IV, V, VI). Acid/alkali dissolution analysis was done to determine reactive Si and Al content in MK. The mechanical properties of samples made using various MK types were tested. No clear correlation was found between the Al(V) content in MK samples and geopolymer setting time, heat output or strength development. It was reported that dissolution of MK in 8M NaOH may be used to determine reactive Si and Al content. They suggested that this method is preferable to dissolution in 1% hydrofluoric acid (HF), as the latter causes partial dissolution of quartz impurities, leading to overestimation of the reactive Si. The unreactive content in MK may increase the rate of initial heat output and accelerate geopolymer setting, possibly through accelerated nucleation and growth of geopolymer gel.

Although use of MK as a raw material gives a purer GPC system [37] compared to GPCs produced from other aluminosilicate materials, MK-based GPCs also have some relative disadvantages. Due to the low ratio of Si/Al typically in MKs, a high amount of sodium silicate is required to provide an adequate amount of Si. Regarding the high environmental impacts of sodium silicate, MK-GPCs could be considered as less environmental friendly than the other GPCs [42]. In addition, calcination of kaolin clay at high temperatures for MK production process, increases its cost compared to the other raw materials that usually are industrial waste by-products.

3.4 Palm Ash

There are two types of palm ash waste i.e. palm oil fuel ash (POFA) and boiler ash. POFA is a by-product from power electricity generation stations that use palm oil shells and palm oil bunches as burn materials, while boiler ash is a biomass found in form of mesocarp fibre or shell. It consists of clinkers and ash that is already burnt in a boiler [43]. POFA is widely produced in West African developing countries including Benin Republic, Ghana and Nigeria [44]. Several studies [18, 43, 45] have investigated the utilization of POFA as a raw material in GPC due to its richness in SiO_2, being more than 40% [45]. Both, POFA and boiler ash have the potential to be used as geopolymer raw materials. Of the two materials, only POFA has been mostly studied. However, boiler ash also contains SiO_2 but further studies are required to determine the possibility of using it as a raw material for GPC.

In a study carried out by Chub-Uppakarn et al. [46], mechanical properties of geopolymer mortar made with MK and palm ash were investigated. Since palm ash is rich in SiO_2 but lacks Al_2O_3, the two important components necessary to produce geopolymer with good strength, the addition of MK was necessary to compensate for the lack of alumina in palm ash. Results from the study [46] showed improvement of compressive strength produced by adding MK to palm ash.

A blend of Pulverized Fly Ash (PFA) and POFA for use in GPCC was also studied by Zarina et al. [47]. They reported that compressive strength of GPCC made with 100% POFA was lower than that of concrete containing a mixture of POFA and PFA. Moreover, when the ratio of PFA/POFA increased, compressive strength and workability also increased. Increasing the molarity of NaOH and the ratio of alkaline activator to solid also gave similar results. Compressive strength of 25 MPa was obtained for PFA/POFA ratio of 70:30.

Mechanical properties of geopolymer mortars produced from POFA, FA, GGBS were investigated by Azizul-Islam et al. [43]. Different mixtures containing 100% GGBS, 100% FA, 100% POFA, 50% GGBS+50% POFA, 50% FA+50% POFA, 50% GGBS+50% FA were tested. A 100% FA mixture cured at 65ºC for 24-h produced the lowest compressive strength while the corresponding 100% GGBS mixture produced the highest compressive strength. Moreover, a blend of POFA with GGBS achieved a compressive strength of about 56 MPa. It was reported that POFA could be an ideal substitute pozzolanic material than FA since

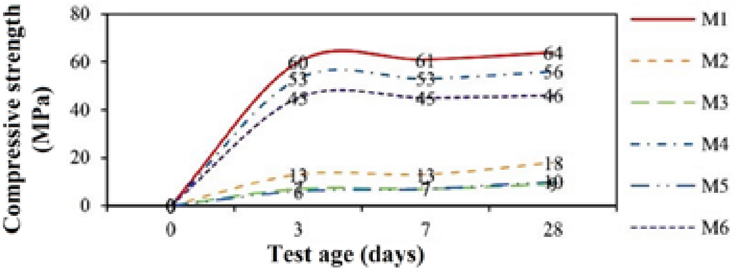


Fig. 2 Development of compressive strength of mortar with varying binder content ratio M1 - 100% GGBS, M2 - 100% FA, M3 - 100% POFA, M4 - 50% GGBS + 50% POFA, M5 - 50% FA + 50% POFA, M6 - 50% GGBS + 50% FA [43].

the compressive strength of the mix prepared using POFA was found to be higher, compared to the mix prepared using FA[43]. Fig. 2 gives the results of compressive strength development in various geopolymer mixes.

3.5 Volcanic Ash

An investigation by Lemougna et al. [48] showed volcanic ash (VA) to be capable of producing GPC. The low energy geopolymerization process can synthesize this natural pozzolan into a viable product with properties suitable for building construction and low-grade refractory applications. The VA used in their study was obtained from Foumbot Petponoun site, Cameroon. NaOH was used as activator to prepare five different mixes. Na_2O/SiO_2 molar ratios of the mixes were varied from 0.15 to 0.35, however the ratio of H_2O/VA was maintained at 0.21 in all mixes. Like other geopolymers, both the Na_2O/SiO_2 molar ratio and curing conditions i.e. temperature, wet or dry exposure etc. influenced the development of compressive strength. Dry curing was reported to give a superior compressive strength of about 50 MPa compared to 42 MPa of the same materials cured under water. An optimum compressive strength of about 55 MPa was obtained for Na_2O/SiO_2 ratio of 0.30, but use of higher Na_2O concentration was found to be detrimental to mechanical properties.

Tchakoute Kouamo et al. [49] used a combination of VA and MK as raw materials for GPC. The VA and MK used in their study were taken from Galim and Mayouom, West Cameroon. They showed that by enhancing the reactivity of VA using alkali fusion, and balancing Na/Al ratio through metakaolin addition, VA could be used as alternative sources for geopolymer synthesis. Table 3 gives the chemical composition of raw materials used in their study.

Fused VA had a higher content of reactive phases compared to raw VA, suggesting alkali fusion to be an effective means of enhancing reactivity of volcanic ashes for geopolymerization. The excess alkali in the fused VA can be consumed by the addition of MK [49]. No significant change in compressive strength was reported upon varying the composition of the alkaline solution. However, KOH promotes thermal stability of materials while NaOH promotes faster reaction rate and higher strength. Compressive strength of 40 MPa and 20 MPa were obtained after 21 days of dry and wet cure respectively.

Tchakoute et al. [50] also investigated the utilization of two types of VA for GPC cured at ambient temperature. The GPC properties were found to depend on certain characteristics of the raw materials. The VA sample with low specific surface area and low content of free CaO led to geopolymers with long setting time. On the other hand, the formation of ettringite caused expansive cracks which in turn led to low compressive strength of 9 to 19 MPa. VA sample with high specific surface area and higher Al_2O_3+SiO_2 of amorphous phase, gave geopolymers possessing compressive strength between 23 and 50 MPa.

3.6 Bottom Ash

Bottom Ash (BA) comprises residue of combustibles formed in coal-burning furnace during its operation. Utilizing bottom ash as a raw material would draw major benefits due to a significant amount of BA that is being disposed-of as waste.

Xie et al. [51] used combinations of FA and BA as raw materials to produce specimens of GPCC. Table 4 shows the chemical composition of these materials. Combinations of sodium hydroxide and sodium silicate with silicate modulus of 3.22 in weight and solid content of 38 wt% were also used as activators. They reported that the mass ratio of FA to BA influences workability of mixture, and mixes with higher FA content exhibited better workability. Also, an increase of the liquid to binder ratio, improved the workability of mixtures. There was an increase in density and homogeneity of GPC as the FA to BA ratio increased. This indicates that FA undergoes a higher degree of geopolymerization compared to BA. Accordingly, compressive strength increases with increase in FA to BA ratio. Both the elastic modulus and flexural strength showed strong correlation with compressive strength. Also, GPC with lower FA to BA ratio developed higher drying shrinkage due to its lower degree of geopolymerization and irregularly shaped unreacted BA particles. Likewise, the GPC made with lower FA to BA ratio exhibited higher water absorption.

Qiao et al. [52], used $Ca(OH)_2$ to activate BA. Setting time and compressive strength of mixes were measured at different curing times. It may be noted that there is considerable difference in CaO content of BA's in Tables 4 and 5. They reported that alkali activation of the BA shown in Table 4, produced macro-porous binder that could rapidly set but it showed low strength property [52].

Table 3: Chemical composition of volcanic ash and sand [49]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	K_2O	SiO_2	Na_2O	TiO_2	LOI*
VA (%)	14.06	10.38	13.22	9.73	0.18	1.53	44.19	3.69	2.74	-0.62
Sand (%)	15.93	3.98	3.22	1.04	0.10	1.33	68.54	4.30	0.27	0.93

*LOI-loss of ignition, VA-volcanic ash

Table 4: Chemical composition of bottom ash [51]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	SiO_2	Na_2O	TiO_2	P_2O_3	LOI*
FA (%)	31	5	3	3	0	1	49	4	2	1	0
BA (%)	25	5	4	2	0	1	54	3	2	1	2

*LOI- loss of ignition, FA-fly ash, BA-bottom ash

Table 5: Chemical composition of bottom ash [52]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	SiO_2	Na_2O	TiO_2	P_2O_3	Cl	ZnO	CuO	PbO	LOI*
BA (%)	8.48	20.20	6.21	1.58	2.34	1.04	36.20	2.93	0.89	1.59	0.89	0.37	0.30	0.24	12.80

*LOI-loss of ignition, BA-bottom ash

Table 6: Chemical composition of CWP [53]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	LOI*
CWP (%)	17.43	1.10	0.88	1.07	0.98	70.79	4.47	1.78

*LOI- loss of ignition

3.7 Ceramic Waste Powder

Ceramic industries produce significant amounts of ceramic waste powder (CWP) which have a high percentage of SiO_2 and Al_2O_3. El-Dieb and Shehab [53] studied the use of CWP as a raw material in GPC while considering different concentrations of sodium hydroxide i.e. 8M, 10M, 12M, 14M, 16M NaOH as alkali-activator. Table 6 shows the chemical composition of the CWP used. Compressive strength, water absorption, electrical resistivity, and microstructure of the produced GPCC were investigated. They reported the GPC to have achieved compressive strength of more than 35 MPa, which satisfies the BS-EN 197-1-2000 requirements for CEM I-32.5N. Also, strength increased from 28 to 38 MPa when the alkalinity of the activation solution was increased from 8M to 12M NaOH but it decreased when alkalinity was increased beyond 12M NaOH. It is thought that exceeding the available OH ion concentration causes aluminosilicate gel precipitation at very early stage, resulting in lower strength. Furthermore, water absorption continued to decrease as the pH value of NaOH increased. Electrical resistivity also increased as molarity of the activator increased.

3.8 Thin-film Transistor Liquid-Crystal Display

It has become apparent that electronic and electrical equipment waste needs to be re-used and recycled to reduce the amount of e-waste deposed to landfills. By the 2013, demand for thin-film transistor liquid-crystal display (TFT-LCD) panels was approximately 9.8 million tonnes per annum [54], which will result in a significant amount of waste TFT-LCD in future. Lin et al. [54] studied the preparation of GPCC from TFT-LCD blended with MK. They investigated the effects of the Solid/Liquid and SiO_2/Na_2O ratios on its properties. In the study, 0 to 40% TFT-LCD was used to replace MK. The samples were hardened in an oven at 30 °C for 24 h, then cured at room temperature. Setting time and compressive strength tests were done on specimens. It was observed that compressive strength of GPCC increased with increase in SiO_2/Na_2O and Solid/Liquid ratios. These results agree with findings of another study reported earlier [48]. Results also showed that incorporation of TFT-LCD into MK-based GPC led to increase in geopolymer paste workability. In addition, the compressive strength of TFT-LCD/MK-based GPCC increased with curing time, which was maintained from 1 to 15 days. Cumulative pore volume of the GPC paste decreased with time, indicating infilling of pores by reaction products [54].

3.9 Rice Husk Ash

Rice Husk Ash (RHA) is a silica-rich agriculture waste material, produced from combusting rice husk, a by-product of rice milling. It typically consists of 88 to 95 wt% amorphous SiO_2[55]. Over 120 million tonnes of rice husk are produced annually, worldwide. The cement and concrete industry can help in the disposal of this solid waste by consuming large quantities of it [56]. Sturm et al. [55] investigated one-part geopolymer using low carbon RHA as solid silica source. One-part geopolymers are made by aluminosilicate materials and solid alkali activators, which can be activated by adding only water. In their study, the solid part of geopolymer was prepared by mixing RHA and solid sodium aluminate. Table 7 shows chemical composition of the solid materials used. Subsequently, water was added at a nominal water/binder ratio of 0.5 by mass, to yield molar ratios $Na_2O{:}Al_2O_3{:}SiO_2{:}H_2O$ of 10.17:16.76:34.46:35.03 wt%. Paste samples were made and cured at 80 °C and 80% relative humidity, for various periods of 24 hours to 7 days.

Results showed that the activation of low carbon RHA produced almost completely amorphous reaction products, which could be considered pure geopolymers. The one day specimens achieved compressive strength of 29.8 MPa on average. It was concluded that curing time longer than 24 hours did not have a significant effect on compressive strength of the GPC specimens. The obtained strength were significantly higher than the strength of one-part GPCs with similar composition but different raw materials.

Hjimohammadi et al. [56] investigated the use of high carbon RHA as a solid silica source in one-part GPC. To prepare the solid part of GPC mix, RHA was mixed with solid sodium aluminate at Si/Al molar ratios of 1.5 and 2.5. Water was added to the mixtures to obtain H_2O/Al molar ratios of 12 and 14, while molar ratio Na/Al = 1.27 was kept constant in all mixes. Results showed that higher content of unburnt carbon in geopolymer system increased the water demand due to the absorption of water by unburnt carbon. Increasing the amount of water generally increased crystallinity, decreased the reaction rate and increased porosity, which is not desirable. However, the GPC specimens made from high carbon RHA gave acceptable compressive strength. Although, using low carbon RHA in GPC gives better mechanical properties compared to using high carbon RHA, heating of the latter at high temperatures of about 500 to 900°C is required to obtain low carbon RHA. This heat treatment can have environmental impact. Generally, low carbon RHA could be considered a suitable solid silica source for one-part GPCs.

Bernal et al. [57] studied the application of RHA as an alkali-activator in combination with NaOH. In their study, combinations of MK and GGBS in various ratios, were used as raw material. Three types of alkali-activator solution produced by mixing silica fume (SF), RHA or commercial sodium silicate, with NaOH solution were used. Results showed that GPC specimens activated with RHA+NaOH gave higher compressive strength than specimens activated using other solutions, when GGBS/MK ratio was between 20 and 6%. In another study, Mejia et al. [58] studied utilizing RHA instead of sodium silicate as a silicate source in FA/GGBS-based GPC. The activators and raw materials were mixed with SiO_2/Na_2O molar ratios of 1.2, 0.49 and 0.19 for 100% GGBS, 100% FA and 50/50 FA/GGBS respectively. Results showed that FA/GGBS-based GPC with FA/GGBS ratio = 0.5, gave slightly lower compressive strength when RHA was used in activator solution instead of sodium silicate. However, the GPCs with 100% FA and 100% GGBS exhibited significantly lower strength when the activators containing RHA were used.

4.0 ALKALINE-ACTIVATORS AND THEIR PROPERTIES

Generally, alkaline solutions that are capable of interacting with aluminosilicates to generate geopolymerization include: alkaline metal or alkaline-earth hydroxides (ROH, $R(OH)_2$), weak acid salts (R_2CO_3, R_2S, RF), strong acid salts (Na_2SO_4, $CaSO_4$-$2H_2O$,) and $R_20(n)SiO_2$-type siliceous salts, where R is an alkaline ion such as N, K or Li [1]. While, common activators include NaOH, Na_2SO_4, $Na_2O.nSiO_2$, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 and cement clinker, the most utilized alkaline activators are a mix of sodium or potassium hydroxide (NaOH, KOH) and sodium waterglass ($Na_2O.nSiO_2$) or potassium waterglass (K_2SiO_3) [26].

Table 7: Chemical composition solid materials [55]

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	TiO_2	SO_3	P_2O_3	LOI*
RHA (%)	0.58	1.0	0.31	0.88	2.91	88.49	0.24	0.03	0.54	1.83	2.48
$NaAlO_2$ (%)	59.74	0.39	0.02	0.01	0.01	<0.01	36.35	<0.01	0.04	n.d.	2.63

n.d.: not determined; LOI: loss on ignition at 1000 C.

4.1 Sodium Hydroxide

NaOH is one of the most commonly used alkaline activators in GPC. The effective parameter of NaOH upon geopolymerization process is its concentration. NaOH concentration has been investigated in several studies [1,53, 59-61] to determine its effect on properties of final products. According to a study carried out by El-Dieb et al.[53], the strength of geopolymer paste increased when NaOH concentration was raised from 8M to 12M. However, when the NaOH concentration increased above 12M, strength decreased. Similar results have been obtained in other studies [1,59] on FA and GGBS geopolymers, where strength decreased when KOH concentration was raised to 15M. An experimental study [60] which investigated FA-based geopolymers, found high NaOH concentration to give better compressive strength of GPCC with no decrease in strength at concentrations higher than 12M, contrary to the results of [53]. Ridtirud et al. [61] also reported an increase in compressive strength of FA-based GPC mortars, in which strength decreased as NaOH concentration was increased from 7.5M to 12.5M NaOH.

4.2 Sodium Silicate

Sodium silicate is essentially a combination of sodium oxide and silicate with some water. The general formula for sodium silicate is $Na_2O.nSiO_2$, where n is the modulus of silicate defining the number of moles of silica (SiO_2) per mole of sodium oxide (NaO_2). There are different manufacturing methods for producing sodium silicate i.e. hydrothermal, alkaline fusion, etc.[62]. Using each method can provide different properties in terms of silicate modulus and solid to water ratio of sodium silicate. The most common sodium silicates that are used as alkali activator in GPC have a silicate modulus of 2 to 3.3 and solid content of 37 to 48 wt% [63].

4.3 Potassium Hydroxide

KOH possesses a high potential for polymeric ionization due to K^+ which is more basic than Na^+ [59]. Compressive strength of GPCC increases with increase in KOH concentration. However, KOH concentrations above 10M have been shown to cause decrease in GPCC strength due to excessive K^+ ions in solution. It has been reported that Si/Al leaching from KOH-activated binders is greater than in binders activated by NaOH. Though KOH possesses high potential for dissolution due to high alkalinity, NaOH actually has greater capacity to form silicate and aluminate monomers[59].

4.4 Combination of Sodium Silicate and NaOH or KOH Solutions

Sodium silicate is rarely used as an independent activating agent, since it does not possess enough activation potential to initiate pozzolanic reaction on its own. Rather, it is commonly mixed with NaOH or KOH as a fortifying agent to enhance alkalinity and increase overall geopolymer strength. The most common alkaline liquid used in alkali-activation is a combination of sodium silicate solution and NaOH. Sodium silicate solution is considered to be the main activator while NaOH controls setting time, improves early strength development, and aids workability [25]. As already indicated, a combination of sodium silicate solution and NaOH increases mechanical properties beyond the ability of a hydroxide activator alone. There are different suggestions in the literature concerning the suitable mixing ratio for the substances. A study by Ridrirud et al. [61] found the $Na_2O.nSiO_2$ to NaOH ratio of 1.5 to give the highest compressive strength of FA-based GPC mortars, where a sodium silicate solution with silicate modulus of 2.33 and solid content of 46 wt% was mixed with 10M NaOH solution. Also, a study[39] carried out by Pelisser et al. [39], suggested 1.6 for the ratio of sodium silicate to sodium hydroxide, where the sodium silicate with solid content of 37.1 wt% and silicate modulus of 2.5 were used. Heah et al. [64] found SiO_2/Na_2O = 0.32 to give best strength results, where 8M NaOH was mixed with sodium silicate solution of 39.5 wt% solid content and silicate modulus of 3.2. SiO_2 to Na_2O ratio is one of the most important properties of alkaline activator solutions, which influences the mechanical and physical properties of GPCs. The percentage of soluble silicate has an important role on the rate of crystallization and the associated reaction kinetics that promote formation of a Si-rich gel [24]. Lin et al. [54] studied the effect of this ratio on compressive strength of TFT-LCD/MK-based geopolymers. They reported increase in compressive strength as SiO_2/Na_2O ratio was raised from 0.8 to 2.0. Skvara et al. [65] suggested a range from 1 to 1.4 for SiO_2/ Na_2O ratio of the activator solution containing sodium hydroxide and sodium silicate. In a study by Tchakoute et al. [50], which investigated VA-based GPC, rise in strength and decrease in setting time was reported when the SiO_2/Na_2O ratio was increased from 0.7 to 1.4. Figs. 3 and 4 show the variation of setting time and compressive strength for the VA-based GPC specimens respectively.

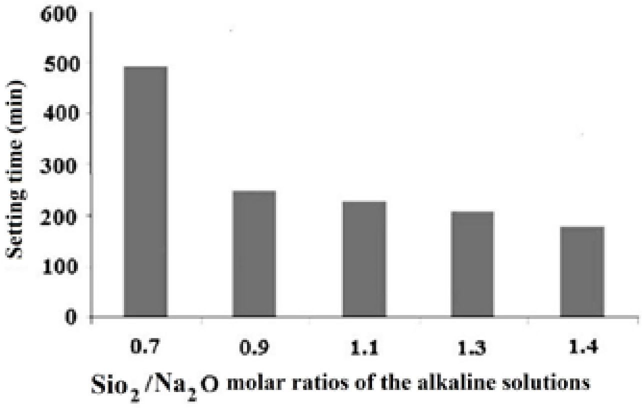


Fig. 3: Setting time of the volcanic ash-based geopolymers [50]

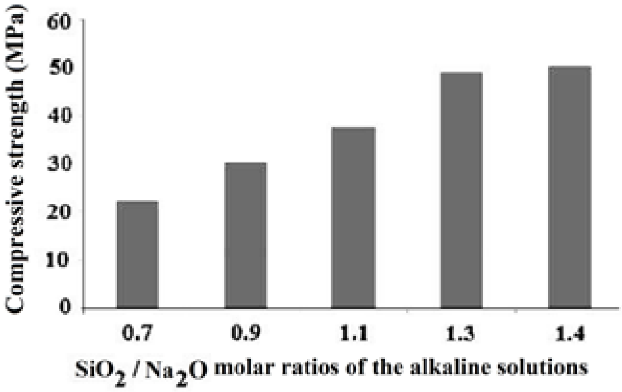


Fig. 4 :Compressive strength of the volcanic ash-based geopolymers [50]

Lemougna et al. [48] reported a decrease in strength beyond SiO_2/Na_2O = 3.33 in VA-based geopolymers, as shown in Fig. 5. Strength reduction at this SiO_2/Na_2O molar ratio is probably related to the formation of significant cracking. These results indicate that a sufficient amount of alkalis must be present for complete dissolution of the starting materials.

4.5 Activator to Pozzolan Ratio

The activator (liquid) to pozzolan (solid) ratio has a significant influence on the properties of geopolymers. Heah et al. [66] investigated the effect of this ratio on MK-based geopolymers and observed that compressive strength increased when the liquid (L) to solid (S) ratio decreased from 1.7 to 0.83. Also, Lin et al. [54] obtained similar results from an investigation on TFT-LCD/MK-based geopolymers. In Ridtirud et al's [61] study on FA-based geopolymer specimens, L/S = 0.4 to 0.8 gave corresponding decrease in compressive strength from 42 to 25 MPa, as shown in Fig. 6. Albitar et al. [32] also obtained similar results for the slag-based GPCC samples, whose L/S was varied from 0.37 to 0.75.

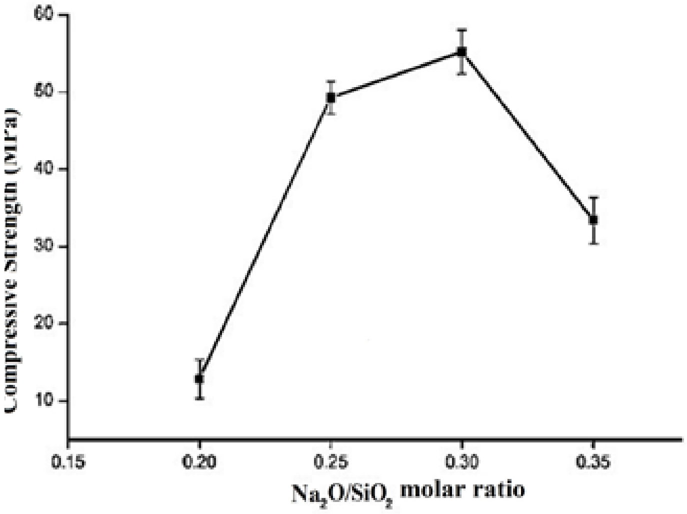


Fig. 5: Compressive strength of the volcanic ash-based geopolymers [48]

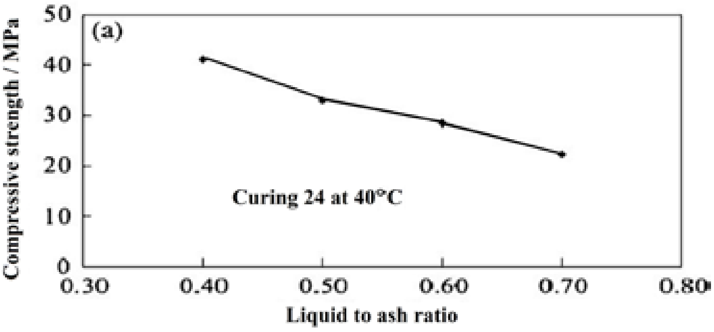


Fig. 6: Compressive strength of mortar with various liquid to solid ratios [61].

5. CONCLUSIONS

This paper has provided a review for geopolymer cements as potential alternative binders to Portland cement, particularly in developing countries, where the cost of cement is quite high and affordable alternative binders are sought. The high interest in geopolymer binders is attributed to their long-term durability, low energy consumption in production, very low CO_2 emission, low production cost, and other special properties. The effects of different factors on physical and mechanical properties of geopolymer binders, including raw material type, alkali activator type, and binder mixtures, have been discussed.

The following specific findings of the review are drawn:

1. Several artificial and natural pozzolans comprising FA, GGBS, VA, POFA, MK, BA, CWP, RHA and TFT-LCD, have been shown to be potentially suitable for use as raw materials for geopolymer cements. A majority of these materials are available in various developing countries.
2. Dry curing gives superior compressive strength in geopolymer binders compared to wet curing. The low compressive strength under wet curing may be attributed to reduction of geopolymerization rate in later ages due to decrease in concentration of OH in pore solutions.
3. While various alkaline activators comprising NaOH, KOH, sodium silicate, etc. may be used, a combination of sodium silicate solution and sodium hydroxide has been shown to be the most effective compound for generating adequate properties in geopolymer cements. In the case of combination of sodium silicate solution and sodium hydroxide as activator, SiO_2/Na_2O of mix is the most effective factor, indicating the ratio of $Na_2O.nSiO_2$ to NaOH. A range of SiO_2/Na_2O from 0.7 to 5 have been used in the literature for making different types of geopolymer cements. Further comprehensive investigations are needed to clarify the effects of this mixing ratio.
4. Setting time decreases and compressive strength increases as SiO_2/Na_2O ratio increases. Values of 0.7 to 2.0 have been used in the literature.
5. Decrease in the Liquid to Solid ratio generally leads to increase in compressive strength and other mechanical properties of geopolymer binders. However, its influence also depends on composition of activator.

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