

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 more environment friendly, 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.

1.0 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 CO₂ emissions [2]. In South Africa, the CO₂ tax is likely to be implemented from 2017 [3]. Accordingly, there is need to develop alternative cements with lower CO₂ emission for application in the construction industry. One of the

30 alternatives is to produce more environmentally friendly concrete using geopolymer cements
31 (GPC).

32 In 1959, Gluchovskij as cited in Skvara [4] demonstrated the possibility of preparing new
33 materials by reaction of alumino-silicate raw materials such as blast-furnace slag, fly ash, clay
34 materials etc. with alkaline compounds typically carbonates, hydroxides, silicates. It is on this
35 basis that the term “Geopolymer” is used [5]. Due to their long-term durability, low energy
36 consumption in production, low CO₂ emission, low production cost, and other special
37 properties, GPC may be considered preferable to other mineral binders, including OPC.
38 Depending on raw material selection and processing condition, GPC can exhibit superior
39 performance compared to OPC essentially in durability aspects such sulphate attack [6,7], acid
40 attack [8], alkali-silica reaction [8-12] and high temperature resistance [13-15]. Large
41 quantities of industrial wastes such as Fly Ash (FA), Palm Oil Fuel Ash (POFA), Ground
42 Granulated Blast furnace Slag (GGBS), are generated every year and these wastes cause
43 environmental concerns in many countries. Since coal is the main source of energy in South
44 Africa, a large amount of FA is being disposed throughout the year. Approximately 36 million
45 tons of coal fly ash are produced annually from electricity generation in South Africa [16]. This
46 quantity is significantly higher than the capacity of South African OPC production industry,
47 which is about 13 million tons per year [17]. FA, POFA, GGBS and similar wastes can
48 potentially be re-used as raw materials in GPCs [18]. Results of a study by Albitar et al. [19]
49 showed that GPCs have a great potential for utilization in the construction industry as a
50 replacement for OPC-based concrete, since both cementitious systems exhibit comparable
51 structural properties. These valuable characteristics along with environmental considerations
52 make GPCs quite desirable for concrete production.

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

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

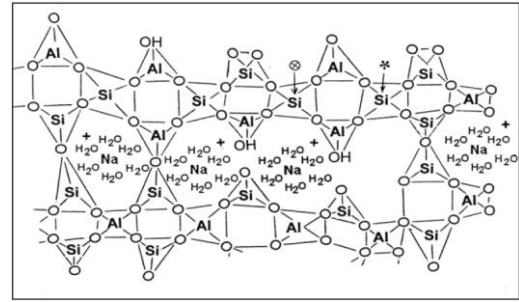
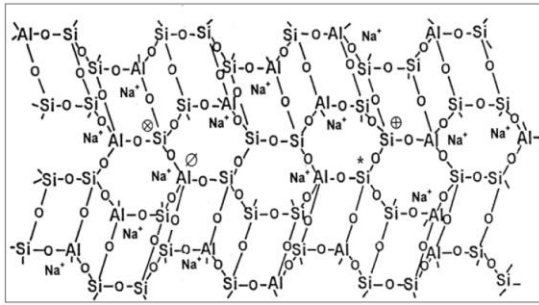
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69 **2. Alkali-Activation**

70 Geopolymer binders are prepared through alkali-activation process. Their raw materials are
71 aluminosilicates, characterized by two-to three-dimensional Si-O-Al structure. The reaction of
72 these aluminosilicate materials in a strong alkaline environment takes place in stages.
73 **Dissolution of the solid aluminosilicate raw material by alkaline hydrolysis, produces**
74 **aluminate and silicate species [15]. The first step of dissolution mechanism starts by ion**
75 **exchange of H⁺ for alkali-earth or alkali-metals cations. Water and hydroxide ions also attack**
76 **the particles and breakdown the network [22]. Dissolution of the solid aluminosilicate source**
77 **and liberation of aluminates and silicates into the solution, produce a supersaturate**
78 **aluminosilicate solution [15]. Finally, aluminosilicate gel precipitates from the aluminate and**
79 **silicate species with release of water that was consumed during the dissolution.** In this process,
80 aluminosilicate gels which are zeolite precursors are mostly formed. The composition of these
81 gels is characterized by the formula $M_n[-(Si-O)_z-Al-O]_n \cdot wH_2O$ [5]. C-S-H and C-A-H phases
82 may also form depending on composition of raw materials and condition of the reaction.
83 Secondary H₂O may also be formed during this reaction through poly-condensation.
84 Amorphous, partially amorphous or crystalline substances may be formed depending on
85 characteristics of raw materials and the reaction conditions. Concentration of solid matter plays
86 a substantial role in the process of alkali activation [4].

87 In the empirical formula $M_n[-(Si-O)_z-Al-O]_n \cdot wH_2O$, where M = K or Na atoms; n = the degree
88 of poly-condensation; z = 1,2,3 or more than 3. Two different three-dimensional network
89 models have been proposed by Davidovits [5] and Barbosa [23] to characterize this formula. It
90 may be noted that these models represent a poly-sialate-silox [5] product type formed by alkali
91 activation of MK. Fig. 1 shows the chemical structures of the models.

92



(a)

(b)

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

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, were 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 development, in addition to improving workability. Test results gave flow of 685 mm, T_{500} slump flow 1.5-2.5 sec, and J-ring of 625 mm. The 28-day

120 compressive strength of the concrete was 48.1 MPa. These results demonstrate the possible
 121 production of self compacting geopolymer cement concrete (GPCC) and its potential
 122 application thereof in precast industry.

123

124 **Table 1.** Chemical composition of fly ash and slag within South Africa [25]

Oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	MnO	K ₂ O	SiO ₂	Na ₂ O	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

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

126

127 In another study, Attwell [21] reported the application of FA/slag-based alkali-activated
 128 concrete at City Deep Container Terminal, Johannesburg where GPCC was used in the surface
 129 beds without reinforcement. Low calcium (Class F) FA produced at Lethabo power station and
 130 GGBS supplied by Slagment pty, were used as raw materials. A combination of **sodium silicate**
 131 and **sodium hydroxide solutions** were employed as activators to prepare 32 different mixes in
 132 the laboratory. The optimal mix which gave good workability of fresh concrete, adequate
 133 compressive strength, and low drying shrinkage was chosen and used to cast GPCC at site.
 134 Results obtained were 28-day compressive strength of 44.7 MPa while the slump of fresh
 135 concrete was 180 mm. Albitar et al. [19] investigated the mechanical properties of Class F FA-
 136 based GPCC. In their study, low-calcium FA produced at Port Augusta power station in South
 137 Australia was used as raw material. The alkaline solution used consisted of **sodium silicate**
 138 **solution with solid content of 38 wt% and SiO₂/Na₂O molar ratio (silicate modulus) of 3.24,**
 139 **premixed with** 14M NaOH at a ratio of 1.5. Their results indicated that Class F FA-based GPCC
 140 exhibits higher tensile strength than OPC-based concrete. Also, Tho-In et al. [26] found similar
 141 results showing the ratio of split tensile to compressive strength of high calcium (Class C) FA-
 142 based GPCC, to be slightly higher than for OPC- based concrete. They also reported the density
 143 of Class C FA-based GPCC to be approximately 30% lower than that of conventional concrete.
 144 The existing OPC models for elastic moduli and stress-strain relationship were reported to be
 145 reasonably accurate for prediction of these characteristics in GPCC as well [19]. **Junaid et al.**
 146 **[27] proposed a new empirical model based on Collin's OPC stress-strain model [28] to predict**

147 the behaviour FA-based GPC concretes in ambient temperature. Their models are represented
148 by Eq. 1.

149

$$150 \quad \sigma_c = f'_c \frac{\varepsilon_c}{\varepsilon_{cm}} \frac{n}{n-1 + \left(\frac{\varepsilon_c}{\varepsilon_{cm}}\right)^{nk}} \quad (\text{Eq. 1})$$

151 Where:

152 ε_c = Strain at any given stress; ε_{cm} = Strain at peak stress; σ_c, f'_c = peak compressive stress;

153 For normal aggregate:

$$154 \quad n = 0.7 + (f'_c / 23)$$

$$155 \quad k = 0.6 + \left(\frac{f'_c}{86}\right) \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} > 1$$

$$156 \quad k = 1.0 \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} \leq 1 ;$$

157 for Flashing/lightweight aggregate:

$$158 \quad n = 0.72 + (f'_c / 11)$$

$$159 \quad k = 0.6 + \left(\frac{f'_c}{70}\right) \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} > 1$$

$$160 \quad k = 1.0 \text{ when } \frac{\varepsilon_c}{\varepsilon_{cm}} \leq 1 ;$$

161 Moreover, they reported that some phenomenon, such as further geopolymerization, loss of
162 water and formation of new phases within the geopolymer system, influence stress-strain
163 curves at elevated temperatures. The damage due to escape of water at temperatures between
164 20 and 200 °C decreased the stiffness of GPC specimens. However, there was recovery in the
165 stiffness at temperatures between 200 and 400 °C that may be attributed to further
166 geopolymerization in the GPC matrix. The stiffness of specimens decreased with decrease of
167 temperature from 400 to 800 °C. This reduction in stiffness may be a result of possible
168 disintegration of the geopolymer gel and formation of new phases within the GPC system.

169 Temuujin et al. [29] suggested a reduction in dissolution rate of FA particles to be a factor that
170 may lead to increase in compressive strength of GPCCs. Most studies have suggested use of
171 heat-curing to obtain better performance in FA-based GPC. However being able to cure in
172 ambient temperature is very important in terms of practical application. Results of some studies
173 [30,31] showed that it is possible to alkali-activate FA blended with GGBS and/or Ca(OH)₂

174 under ambient temperature to approach mechanical performance similar to that of heat-cured
175 FA-based GPCs.

176

177

178 **3.2 Ground Granulated Blast Furnace Slag**

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

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

195

196

197 **3.3 Metakaolin**

198 Metakaolin (MK) is a dehydroxylated form of clay kaolinite. Stone materials that are rich in
199 kaolinite, usually referred to China clay or kaolin, are widely used in the manufacture of paper.
200 Particles of metakaolin are much finer than cement particles. Davidovits [33] studied the
201 molecular framework of MK-based geopolymer. The Magic Angel Spinning Nuclear Magnetic
202 Resonance (MAS-NMR) spectroscopy of the geopolymer products exhibited a chemical shift
203 in the range of 55 ppm, which indicates $AlQ_4(4Si)$ type and is tetrahedrally coordinated. Based
204 on these results, he proposed the three-dimensional microstructure model for products of

205 geopolymerization that were discussed in Section 1.0. The reactivity of MK in
206 geopolymerization is related to calcination methods of the raw kaolin clay source due to the
207 intensity of different types of Al species in terms of the coordination number of aluminium in
208 various Al-O compounds [34]. Meinhold et al. [35] reported that at calcination temperature of
209 above 400 °C, approximately 8% of Al remained within the undistorted sites, of which about
210 50 and 25% of these were Al(6) and Al(4) respectively. The other 25% included either Al(4)
211 or Al(5). Intensity of Al(5), which is known as the most reactive Al species, increased when
212 the calcination temperature increased from 450 to 850 °C, and decreased beyond 850 °C. The
213 maximum intensity of Al(5) was obtained between 700 to 850 °C. Kriven et al. [37]
214 investigated the physical and mechanical properties of fully reacted MK-based GPC. Three
215 different MKs were prepared by calcination of three different clays consisting of Kaolex BN,
216 Hydrite PXN and KaG-1b, at 700 °C for 1 hour. Table 2 gives chemical composition of the
217 raw clays. A mix of silica fume and NaOH solution at solid to liquid ratio of 0.5 was used to
218 prepare GPC mix of molar ratios $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.3$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 11$.
219 Another mix of silica fume and KOH solution was used to prepare GPC samples to achieve the
220 mix molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$, $\text{K}_2\text{O}/\text{SiO}_2 = 0.3$ and $\text{H}_2\text{O}/\text{K}_2\text{O} = 11$. Curing of GPC samples
221 was done by one of three methods comprising, pressureless curing (PC) method at 40 or 60 °C
222 for 48 hours, warm pressing (WP) method at 80 °C and 18 MPa for 2 hour, and high pressure
223 autoclave (HPA) method with isostatical loading at 20 MPa while being heated at 80 °C for 24
224 hours. The results of Mercury Intrusion porosimetry (MIP) for KOH activated samples that
225 were cured by HPA showed that the intrusion volume mainly occurred between 0.1 and 0.01
226 μm , where the inherent pore size of the GPC was between 10 and 100 nm. It could be concluded
227 that the HPA method effectively rid the GPC samples of large pores. It was also observed that
228 the microstructure of fully reacted MK GPCs was sponge-like with nanopores and
229 nanoparticulates. Moreover, the results of microchemistry analysis of GPCs frequently showed
230 that the ratio of SiO_2 to Al_2O_3 was 4.0, which corresponds to Polysialate Siloxo (PSS) system
231 with atomic ratio of Si to Al of 2.0 [33]. Although, the MK GPC samples made from Naolex
232 BN were not as fully reacted as compared to the others made from Hydrite PXN or KaG-1b
233 due to the less purity, they exhibited superior mechanical performance. These observations
234 could be attributed to the role of unreacted clay sheets in MK GPC samples made from Naolex
235 BN. These unreacted species may have served as filler material in the GPC, which led to lower
236 pore volume and higher compressive strength.

237

238

239 **Table 2.** Chemical composition of raw clays [37]

Label of clay	Kaolin	Muscovite	Crystalline SiO₂	FeO	Fe₂O₃	TiO₂
Kaalex BN (%)	65	7	10-13	-	-	2.6
Hydrite PXN (%)	~98	-	-	-	0.6	1.4
KaG-1b (%)	~98	-	-	0.08	0.1	1.4

240

241 Zhang et al. [38] studied the formation of crystalline phase in MK-based GPC systems. Sodium
 242 hydroxide of various concentrations was used as alkali activator in combination with a sodium
 243 silicate solution of silicate modulus = 2.0 and 44 % solid content. The Si/Na ratios of alkali
 244 solution mix was varied from 0.66 to 3.0. The MK GPC specimens were cured at 40 °C for
 245 various durations of 2 hours to 10 days. Results showed that in MK-GPC samples activated
 246 with only NaOH, sodium content of the solution significantly influenced the nature and
 247 quantity of the crystalline phase in GPC system. The crystalline zeolite-A (Na₉₆Al₉₆Si₉₆O₃₈₄)
 248 was formed in specimens containing Si/Na ratios of 4/4 or less. However, the MK-GPC
 249 systems containing Si/Na ratios greater than 4/4 produced nanosize crystals or another zeolite
 250 (Na₆[AlSiO₄]₆-4H₂O). Moreover, introducing sodium silicate in the system significantly
 251 reduced the quantity of crystalline phases.

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

264 Mortars prepared by combining MK of composition Si = 44.0, Al = 20.6, O = 23.4, Na = 12.0
265 wt%, with distinct proportions of sand were also studied. Using a binder/sand ratio = 1:5 gave
266 a substantial 55.8 MPa compressive strength for samples cured at 80 °C. This geopolymer mix,
267 had 295 kg/m³ of MK binder, which is quite competitive as compared to OPC concrete
268 mixtures, which often use higher binder contents [39].

269 A study carried out by Muniz-Villarreal et al. [40] investigated the effects of curing condition
270 on properties of MK-based geopolymer. They used MK of 1.2µm particle size as raw material
271 and a mix of sodium silicate, sodium hydroxide and distilled water was used as activator to
272 prepare specimens that were formulated at molar oxide ratios SiO₂/Al₂O₃ = 3.3, Na₂O/SiO₂ =
273 0.25, Na₂O/Al₂O₃ = 0.488 and H₂O/Na₂O = 13.73 . The curing program consisted of two steps:
274 Firstly, samples were dried at 40 °C for 2h to prevent cracking due to an abrupt loss of water.
275 The second step was curing at 30, 40, 50, 60, 75 and 90 °C for 24h, to develop mechanical
276 properties. Results showed 60 °C to be the optimum temperature that gave the best
277 geopolymerization process. These results were supported by a leaching study carried out on
278 the geopolymer mixtures.

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

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

297 process, increases its cost compared to the other raw materials that usually are industrial waste
298 by-products.

299

300 **3.4 Palm Ash**

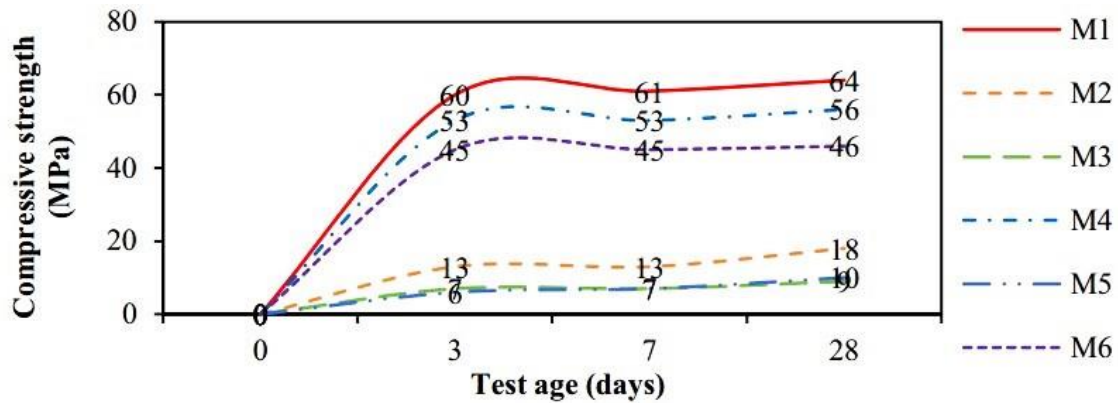
301 There are two types of palm ash waste i.e. palm oil fuel ash (POFA) and boiler ash. POFA is a
302 by-product from power electricity generation stations that use palm oil shells and palm oil
303 bunches as burn materials, while boiler ash is a biomass found in form of mesocarp fibre or
304 shell. It consists of clinkers and ash that is already burnt in a boiler [43]. POFA is widely
305 produced in West African developing countries including Benin Republic, Ghana and Nigeria
306 [44]. Several studies [18, 43, and 45] have investigated the utilization of POFA as a raw
307 material in GPC due to its richness in SiO_2 , being more than 40% [45]. Both, POFA and boiler
308 ash have the potential to be used as a geopolymer raw materials. Of the two materials, only
309 POFA has been mostly studied. However, boiler ash also contains SiO_2 and further studies are
310 required to determine the possibility of using it as raw material for GPC.

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

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

323 Mechanical properties of geopolymer mortars produced from POFA, FA, GGBS were
324 investigated by Azizul Islam et al. [43]. Different mixtures containing 100% GGBS, 100% FA,
325 100% POFA, 50% GGBS+50% POFA, 50% FA+50% POFA, 50% GGBS+50% FA were
326 tested. A 100% FA mixture cured 65°C for 24-h produced the lowest compressive strength
327 while the corresponding 100% GGBS mixture produced the highest compressive strength.
328 Moreover, a blend of POFA with GGBS achieved a compressive strength of about 56 MPa. It

329 was reported that POFA could be an ideal substitute pozzolanic material than FA since the
 330 compressive strength of the mix prepared using POFA was found to be higher, compared to
 331 the mix prepared using FA [43]. Fig. 2 gives the results of compressive strength development
 332 in various geopolymer mixes.



333
 334 **Fig. 2** Development of compressive strength of mortar with varying binder content ratio M1 - 100% GGBS, M2
 335 - 100% FA, M3 - 100% POFA, M4 - 50% GGBS + 50% POFA, M5 - 50% FA + 50% POFA, M6 - 50% GGBS
 336 + 50% FA [43].

337
 338 **3.5 Volcanic Ash**

339 An investigation by Lemougna et al. [48] showed volcanic ash (VA) to be capable of producing
 340 GPC. The low energy geopolymerization process can synthesize this natural pozzolan into a
 341 viable product with properties suitable for building construction and low-grade refractory
 342 applications. The VA used in their study was obtained from Fombot Petponoun site,
 343 Cameroon. NaOH was used as activator to prepare five different mixes. Na₂O/SiO₂ molar
 344 ratios of the mixes were varied from 0.15 to 0.35, however the ratio of H₂O/VA was
 345 maintained at 0.21 in all mixes. Like other geopolymers, both the Na₂O/SiO₂ molar ratio and
 346 curing conditions i.e. temperature, wet or dry exposure etc. influenced the development of
 347 compressive strength. Dry curing was reported to give superior compressive strength of about
 348 50 MPa compared to 42 MPa of the same materials cured under water. An optimum
 349 compressive strength of about 55 MPa was obtained for Na₂O/SiO₂ ratio of 0.30, but use of
 350 higher Na₂O concentration was found to be detrimental to mechanical properties.

351 Tchakoute Kouamo et al. [49] used a combination of VA and MK as raw materials for GPC.
 352 The VA and MK used in their study were taken from Galim and Mayouom, West Cameroon.
 353 They showed that by enhancing the reactivity of VAs using alkali fusion, and balancing Na/Al

354 ratio through metakaolin addition, VAs could be used as alternative sources for geopolymer
 355 synthesis. Table 3 gives the chemical composition of raw materials used in their study.

356

357 **Table 3.** Chemical composition of volcanic ash and sand [49]

Oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	MnO	K ₂ O	SiO ₂	Na ₂ O	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

358 *LOI-loss of ignition, VA-volcanic ash.

359

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

367 Tchakoute et al. [50] also investigated the utilization of two types of VA for GPC cured at
 368 ambient temperature. The GPC properties were found to depend on certain characteristics of
 369 the raw materials. The VA sample with low specific surface area and low content of free CaO
 370 led to geopolymers with long setting time. On the other hand, the formation of ettringite caused
 371 expansive cracks which in turn led to low compressive strength of 9 to 19 MPa. VA sample
 372 with high specific surface area and higher Al₂O₃+SiO₂ of amorphous phase gave geopolymers
 373 possessing compressive strength between 23 and 50 MPa.

374

375 **3.6 Bottom Ash**

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

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

392

393 **Table 4.** Chemical composition of bottom ash [51]

Oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	SiO ₂	Na ₂ O	TiO ₂	P ₂ O 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

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

395

396 Qiao et al. [52], used Ca(OH)₂ to activate BA. Setting time and compressive strength of mixes
 397 were measured at different curing times. It may be noted that there is considerable difference
 398 in CaO content of BAs in Tables 4 and 5. They reported that alkali activation of the BA shown
 399 in Table 4, produced macro-porous binder that could rapidly set but it showed low strength
 400 property [52].

401

402 **Table 5.** Chemical composition of bottom ash [52]

Oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	SiO ₂	Na ₂ O	TiO ₂	P ₂ O 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

403 *LOI-loss of ignition, BA-bottom ash

404

405 **3.7 Ceramic Waste Powder**

406 Ceramic industries produce significant amounts of ceramic waste powder (CWP) which have
407 a high percentage of SiO₂ and Al₂O₃. El-Dieb and Shehab [53] studied the use of CWP as a
408 raw material in GPC while considering different concentrations of sodium hydroxide i.e. 8M,
409 10M, 12M, 14M, 16M NaOH as alkali-activator. Table 6 shows the chemical composition of
410 the CWP used. Compressive strength, water absorption, electrical resistivity, and
411 microstructure of the produced GPCC were investigated.

412

413 **Table 6.** Chemical composition of CWP [53]

Oxides	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	SiO ₂	Na ₂ O	LOI*
CWP (%)	17.43	1.10	0.88	1.07	0.98	70.79	4.47	1.78

414 *LOI-loss of ignition,

415

416 They reported the GPC to have achieved compressive strength of more than 35 MPa, which
417 satisfies the BS-EN 197-1-2000 requirements for CEM I-32.5N. Also, strength increased from
418 28 to 38 MPa when the alkalinity of the activation solution was increased from 8M to 12M
419 NaOH but it decreased when alkalinity was increased beyond 12M NaOH. It is thought that
420 exceeding the available OH ion concentration causes aluminosilicate gel precipitation at very
421 early stage, resulting in lower strength. Furthermore, water absorption continued to decrease
422 as the pH value of NaOH increased. Electrical resistivity also increased as molarity of the
423 activator increased.

424

425 **3.8 Thin-film Transistor Liquid-Crystal Display**

426 It has become apparent that electronic and electrical equipment waste needs to be re-used and
427 recycled to reduce the amount of e-waste deposited to landfills. By the 2013, demand for thin-
428 film transistor liquid-crystal display (TFT-LCD) panels was approximately 9.8 million tonnes
429 per annum [54], which will result in a significant amount of waste TFT-LCD in future. Lin et
430 al. [54] studied the preparation of GPCC from TFT-LCD blended with MK. They investigated
431 the effects of the Solid/Liquid and SiO₂/Na₂O ratios on its properties. In the study, 0 to 40 %
432 TFT-LCD was used to replace MK. The samples were hardened in an oven at 30 °C for 24 h,

433 then cured at room temperature. Setting time and compressive strength tests were done on
 434 specimens. It was observed that compressive strength of GPCC increased with increase in
 435 $\text{SiO}_2/\text{Na}_2\text{O}$ and Solid/Liquid ratios. These results agree with findings of another study reported
 436 earlier [48]. Results also showed that incorporation of TFT-LCD into MK-based GPC led to
 437 increase in geopolymer paste workability. In addition, the compressive strength of TFT-
 438 LCD/MK-based GPCC increased with curing time, which was maintained from 1 to 15 days.
 439 Cumulative pore volume of the GPC paste decreased with time, indicating infilling of pores by
 440 reaction products [54].

441

442 **3.9 Rice Husk Ash**

443 Rice Husk Ash (RHA) is a silica-rich agriculture waste material, produced from combusting
 444 rice husk, a by-product of rice milling. It typically consists of 88 to 95 wt% amorphous SiO_2
 445 [55]. Over 120 million tonnes of rice husk are produced annually, worldwide. The cement and
 446 concrete industry can help in the disposal of this solid waste by consuming large quantities of
 447 it [56]. Sturm et al. [55] investigated one-part geopolymer using low carbon RHA as solid silica
 448 source. One-part geopolymers are made by aluminosilicate materials and solid alkali activators,
 449 which can be activated by adding only water. In their study, the solid part of geopolymer was
 450 prepared by mixing RHA and solid sodium aluminate. Table 7 shows chemical composition of
 451 the solid materials used. Subsequently, water was added at a nominal water/binder ratio of 0.5
 452 by mass, to yield molar ratios $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ of 10.17:16.76:34.46:35.03 wt%. Paste
 453 samples were made and cured at 80 °C and 80% relative humidity, for various periods of 24
 454 hours to 7 days.

455

456 **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_5	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

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

458

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

465 Hjimoammadi et al. [56] investigated the use of high carbon RHA as a solid silica source in
466 one-part GPC. To prepare the solid part of GPC mix, RHA was mixed with solid sodium
467 aluminate at Si/Al molar ratios of 1.5 and 2.5. Water was added to the mixtures to obtain
468 H₂O/Al molar ratios of 12 and 14, while molar ratio Na/Al = 1.27 was kept constant in all
469 mixes. Results showed that higher content of unburnt carbon in geopolymer system increased
470 the water demand due to the absorption of water by unburnt carbon. Increasing the amount of
471 water generally increased crystallinity, decreased the reaction rate and increased porosity,
472 which is not desirable. However, the GPC specimens made from high carbon RHA gave
473 acceptable compressive strength. Although, using low carbon RHA in GPC gives better
474 mechanical properties compared to using high carbon RHA, heating of the latter at high
475 temperatures of about 500 to 900 °C is required to obtain low carbon RHA, which can also
476 have environmental impact. Generally, low carbon RHA could be considered a suitable solid
477 silica source for one-part GPCs.

478 Bernal et al. [57] studied the application of RHA as an alkali activator in combination with
479 NaOH. In their study, combinations of MK and GGBS in various ratios, were used as raw
480 material. Three types of alkali activator solution produced by mixing silica fume (SF), RHA or
481 commercial sodium silicate, with NaOH solution were used. Results showed that GPC
482 specimens activated with RHA+NaOH gave higher compressive strength than specimens
483 activated using other solutions, when GGBS/MK ratio was between 20 and 6%. In another
484 study, Mejia et al. [58] studied utilizing RHA instead of sodium silicate as a silicate source in
485 FA/GGBS-based GPC. The activators and raw materials were mixed with SiO₂/Na₂O molar
486 ratios of 1.2, 0.49 and 0.19 for 100% GGBS, 100% FA and 50/50 FA/GGBS respectively.
487 Results showed that FA/GGBS-based GPC with FA/GGBS ratio = 0.5, gave slightly lower
488 compressive strength when RHA was used in activator solution instead of sodium silicate.
489 However, the GPCs with 100% FA and 100% GGBS exhibited significantly lower strength
490 when the activators containing RHA were used.

491

492 **4.0 Alkaline-Activators and their Properties**

493 Generally, alkaline solutions that are capable of interacting with aluminosilicates to generate
494 geopolymerization include: alkaline metal or alkaline-earth hydroxides (ROH, R(OH)₂), weak
495 acid salts (R₂CO₃, R₂S, RF), strong acid salts (Na₂SO₄, CaSO₄-2H₂O,) and R₂₀(n)SiO₂-type
496 siliceous salts, where R is an alkaline ion such as N, K or Li [1]. While, common activators
497 include NaOH, Na₂SO₄, Na₂O.nSiO₂, Na₂CO₃, K₂CO₃, KOH, K₂SO₄ and cement clinker, the
498 most utilized alkaline activators are a mix of sodium or potassium hydroxide (NaOH, KOH)
499 and sodium waterglass (Na₂O.nSiO₂) or potassium waterglass (K₂SiO₃) [26].

500

501 **4.1 Sodium Hydroxide**

502 NaOH is one of the most commonly used alkaline activators in GPC. The effective parameter
503 of NaOH upon geopolymerization process is its concentration. NaOH concentration has been
504 investigated in several studies [1,53, 59-61] to determine its effect on properties of final
505 products. According to a study carried out by El-Dieb et al. [53], the strength of geopolymer
506 paste increased when NaOH concentration was raised from 8M to 12M. However, when the
507 NaOH concentration increased above 12M, strength decreased. Similar results have been
508 obtained in other studies [1,59] on FA and GGBS geopolymers, where strength decreased when
509 KOH concentration was raised to 15M. An experimental study [60] which investigated FA-
510 based geopolymers, found high NaOH concentration to give better compressive strength of
511 GPCC with no decrease in strength at concentrations higher than 12M, contrary to the results
512 of [53]. Ridtirud et al. [61] also reported an increase in compressive strength of FA-based GPC
513 mortars, in which strength decreased as NaOH concentration was increased from 7.5M to
514 12.5M NaOH.

515

516 **4.2 Sodium Silicate**

517 Sodium silicate is essentially a combination of sodium oxide and silicate with some water. The
518 general formula for sodium silicate is Na₂O.nSiO₂, where *n* is the modulus of silicate defining
519 the number of moles of silica (SiO₂) per mole of sodium oxide (NaO₂). There are different
520 manufacturing methods for producing sodium silicate i.e. hydrothermal, alkaline fusion, etc.
521 [62]. Using each method can provide different properties in terms of silicate modulus and solid
522 to water ratio of sodium silicate. The most common sodium silicates that are used as alkali
523 activator in GPCs have a silicate modulus of 2 to 3.3 and solid content of 37 to 48 wt% [63].

524

525 **4.3 Potassium Hydroxide**

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

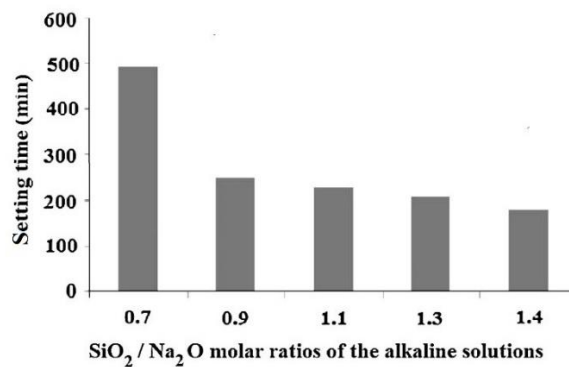
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535 **4.4 Combination of Sodium Silicate and NaOH or KOH Solutions**

536 Sodium silicate is rarely used as an independent activating agent, as it does not possess enough
537 activation potential to initiate pozzolanic reaction on its own. Rather, it is commonly mixed
538 with NaOH or KOH as a fortifying agent to enhance alkalinity and increase overall geopolymer
539 strength. The most common alkaline liquid used in alkali-activation is a combination of **sodium**
540 **silicate solution** and NaOH. **Sodium silicate solution** is considered to be the main activator
541 while NaOH controls setting time, improves early strength development, and aids workability
542 [25]. As already indicated, a combination of **sodium silicate solution** and NaOH increases
543 mechanical properties beyond the ability of a hydroxide activator alone. There are different
544 suggestions in the literature concerning the suitable mixing ratio for the substances. A study by
545 Ridrirud et al. [61] found the $Na_2O.nSiO_2$ to NaOH ratio of 1.5 to give the highest compressive
546 strength of FA-based GPC mortars, **where a sodium silicate solution with silicate modulus of**
547 **2.33 and solid content of 46 wt% was mixed with 10M NaOH solution.** Also, a study [39]
548 carried out by Pelisser et al., suggested 1.6 for the ratio of sodium silicate to sodium hydroxide,
549 **where the sodium silicate with solid content of 37.1 wt% and silicate modulus of 2.5 were used.**
550 Heah et al. [64] found $SiO_2/Na_2O = 0.32$ to give best strength results, **where 8M NaOH was**
551 **mixed with sodium silicate solution of 39.5 wt% solid content and silicate modulus of 3.2.**
552 SiO_2 to Na_2O ratio is one of the most important properties of alkaline activator solutions, which
553 influences the mechanical and physical properties of GPCs. The percentage of soluble silicate
554 has an important role on the rate of crystallization and the associated reaction kinetics that
555 promote formation of a Si-rich gel [24]. Lin et al. [54] studied the effect of this ratio on

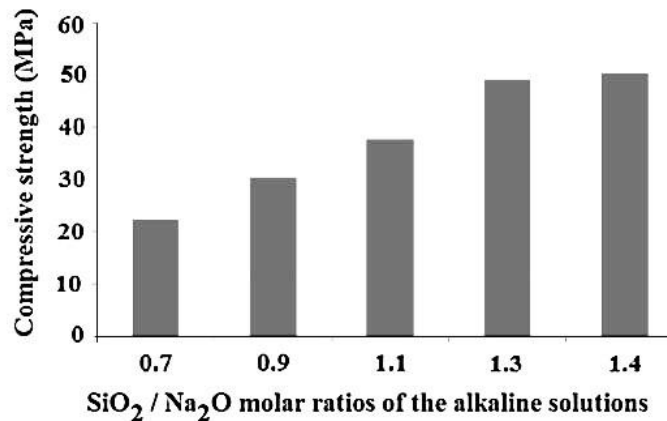
556 compressive strength of TFT-LCD/MK-based geopolymers. They reported increase in
557 compressive strength as $\text{SiO}_2/\text{Na}_2\text{O}$ ratio was raised from 0.8 to 2.0. Skvara et al. [65]
558 suggested a range from 1 to 1.4 for $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the activator solution containing sodium
559 hydroxide and sodium silicate. In a study by Tchakoute et al. [50], which investigated VA-
560 based GPC, rise in strength and decrease in setting time was reported when the $\text{SiO}_2/\text{Na}_2\text{O}$
561 ratio was increased from 0.7 to 1.4. Figs. 3 and 4 show the variation of setting time and
562 compressive strength for the VA-based GPC specimens respectively.



563

564

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



565

566

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

567

568 Lemougna et al. [48] reported a decrease in strength beyond $\text{SiO}_2/\text{Na}_2\text{O} = 3.33$ in VA-based
569 geopolymers, as shown in Fig. 5. Strength reduction at this $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio is probably
570 related to the formation of significant cracking. These results indicate that a sufficient amount
571 of alkalis must be present for complete dissolution of the starting materials.

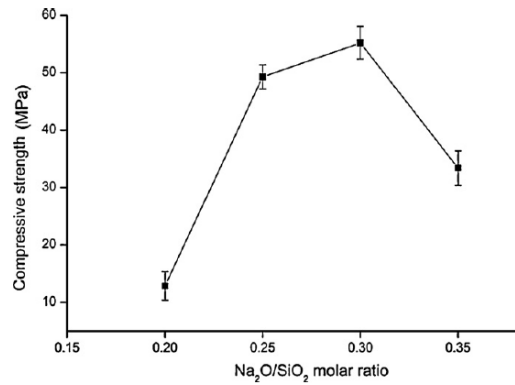


Fig. 5 Compressive strength of the volcanic ash-based geopolymers [48]

4.5 Activator to Pozzolan

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.

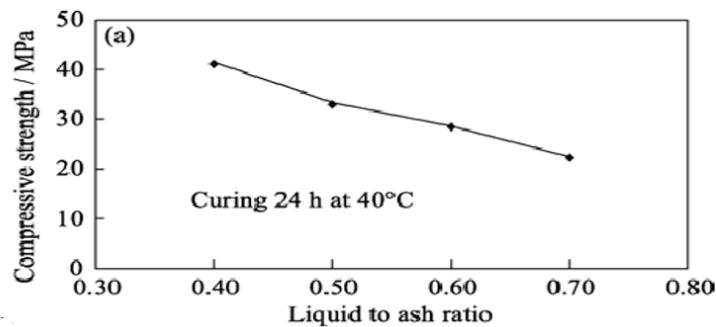


Fig. 6 Compressive strength of mortar with various liquid to solid ratios [61].

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

591 and affordable alternative binders are sought. The high interest in geopolymer binders is
592 attributed to their long-term durability, low energy consumption in production, very low CO₂
593 emission, low production cost, and other special properties. The effects of different factors on
594 physical and mechanical properties of geopolymer binders, including raw material type, alkali
595 activator type, and binder mixtures, have been discussed. The following specific findings of
596 the review are drawn:

- 597 1. Several artificial and natural pozzolans comprising FA, GGBS, VA, POFA, MK, BA, CWP,
598 **RHA** and TFT-LCD, have been shown to be potentially suitable for use as raw materials for
599 geopolymer cements. A majority of these materials are available in various developing
600 countries.
- 601 2. Dry curing gives superior compressive strength in geopolymer binders compared to wet
602 curing. The low compressive strength under wet curing may be attributed to reduction of
603 geopolymerization rate in later ages due to decrease in concentration of OH in pore
604 solutions.
- 605 3. While various alkaline activators comprising NaOH, KOH, **sodium silicate**, etc. may be
606 used, a combination of **sodium silicate solution and sodium hydroxide** has been shown to
607 be the most effective compound for generating adequate properties in geopolymer cements.
608 **In the case of combination of sodium silicate solution and sodium hydroxide as activator,**
609 **SiO₂/Na₂O of mix is the most effective factor, indicating the ratio of Na₂O.nSiO₂ to NaOH.**
610 **A range of SiO₂/Na₂O from 0.7 to 5 have been used in the literature for making different**
611 **types of geopolymer cements. Further comprehensive investigations are needed to clarify**
612 **the effects of this mixing ratio.**
- 613 4. Setting time decreases and compressive strength increases as SiO₂/Na₂O ratio increases.
614 Values of 0.7 to 2.0 have been used in the literature.
- 615 5. Decrease in the Liquid to Solid ratio generally leads to increase in compressive strength and
616 other mechanical properties of geopolymer binders. However, its influence also depends on
617 composition of activator.

618

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623

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