

Properties and Durability of Geopolymer Based Materials and It's Utilizing as a Repair and Strengthening Materials: A Review

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Abstract - The construction industry has been asking for environmentally sustainable repair materials with a lower carbon footprint all around the world. Concrete containing considerable amounts of Portland cement will deteriorate over time and will need to be repaired or replaced. Cementitious mortars, polymer-modified cementitious mortars, resinous mortars, and other restorative materials have all been used to fix the problem. Cement-free geopolymer mortars with a high percentage of silicate aluminium and an alkaline activator solution are gaining popularity as long-term repair materials. Geopolymer binders are preferred because they emit 70–80% less carbon dioxide and significantly less greenhouse gas than ordinary Portland cement. These new binders are in high demand because to their improved durability, sustainability, and environmental friendliness. The review divided into three key sections after introductory section to have a holistic understanding of the using geopolymer based materials as a repair and strengthening materials and to have gaps for future research. The first section presents properties of geopolymer based materials as a repair materials. The second section covers articles on durability of geopolymer based materials against carbonation, sulphate, acids, chlorides and heat effects. The third section reviews studies on the repairs of Portland cement concrete by geopolymer based materials. Finally, conclusions summarise the findings of the review.

Key Words: Geopolymer based materials, Durability, Compressive strength, Bond strength, Repair and Strengthening.

1. INTRODUCTION

In general, reinforced concrete structures are durable and can be used in infrastructure applications as they provide high structural strength and long-term durability. However, if they are exposed to severe environments such as marine environment or exposed directly to dangerous substances, the reinforced concrete structures deteriorate rapidly [1].

Ordinary Portland cement (OPC) has been used for the construction of various infrastructures like road construction, buildings,....etc [2]. However, OPC concrete undergoes deterioration due to the simultaneous action of mechanical and thermal loads [3]. Concrete deterioration is manifested primarily through cracking, spalling [3,4],

surface deterioration, and seepage of concrete [4] and debonding of rebars [3]. Therefore, deteriorated structural elements require efficient and successful repair materials to ensure their continued serviceability [3,5]. The deterioration of OPC-based structures in aging infrastructure are a continuous cause of concern worldwide due to the high costs associated to the protection, repair and rehabilitation of these defects [4,6].

Among the many repair and strengthening techniques, sectional enlargement is the most common one, for which the compatibility between the repair material and the concrete substrate is of great importance [7]. The most direct method for damaged concrete repair is to cover the substrate surface with repair materials, which results in the inevitable formation of adhesive interface between the old concrete substrate and new repair materials. Unfortunately, it was found that the adhesive interface is the weakest section of the repaired structures, and its properties were also relatively weak due to the large number of defects and micro-cracks [8]. In most cases, a layer of interfacial agent is coated on the substrate surface before covering repair materials overlay, and the polymer modified cementitious materials is the most popular [9,10]. It is desirable to improve and investigate the adhesive interface performance for concrete repair, which can guarantee the whole work capability [8, 11].

The commonly-used repair mortars were made from OPC or their derivatives, such as including supplementary cementitious materials-blended OPC mortar, polymer-modified cement mortar, ultra-high-performance concrete, reactive powder concrete, engineered cementitious composite, and magnesium phosphate cement mortar [7,12].

The term of geopolymers was initially proposed as a new material by Davidovits in 1978 [15,16]. The first geopolymer concrete was developed in 1990 (Davidovits 1990). Since then, researchers are continuously improving and developing mix proportions of geopolymer concrete for desired strength, sustainability and energy efficiency for construction [13].

Geopolymer resulting from the reaction of raw material containing high percentages of amorphous silica and alumina (such as kaolin, mining waste, fly ash (FA), ground

granulated blast furnace slag (GGBFS), rice husk ash (RHA), palm oil ash (POA), etc.) with alkaline activators (alkali hydroxide solutions and soluble silicates) [17-19] as a dissolution agent [17] in the room or high temperature environment [18, 19].

Aluminosilicate minerals were dissolved in solutions, then free SiO_4 and AlO_4 tetrahedral units were reacted by sharing oxygen atoms. Polymeric Si-O-Al-O bonds which are similar to amorphous feldspar were formed [20]. Actually, the geopolymerization is influenced by the ability of aluminum ions to induce crystal structure and chemical reaction of SiO_2 skeleton [21]. Previous studies show that geopolymer concrete has excellent mechanical properties, high durability, low shrinkage, and material cost; approximately 10–30% lower than OPC concrete to chemical attacks fascinated the scientific community [22,23]. On the other hand, water mainly acts as the reaction medium in the geopolymerization reaction and promotes the dissolution of aluminosilicate, which reduces the waster requirement [24]. Abbas et al. [26] pointed out that the geopolymer concrete achieved a reduction in global warming potential by 61% and improved the human health category by 9.4%. Thus, geopolymer concrete is considered the better alternatives for OPC concrete across some range of applications due to the high worldwide availability of aluminosilicate materials and excellent workability and mechanical properties, enabling engineering processing using the trained concrete workers [26]. Although the utilization of industrial waste and reduction of carbon dioxides is very much essential, the geopolymer has to look into the hardened properties requirements in terms of quality specified for OPC concrete. With this in mind, the durability of concrete subjected to aggressive environments has become a crucial issue for field applications due to the increasing demand for the maintenance-free and long service life of concrete structures, which is also one of the most momentous properties within geopolymer commercialization [16].

Besides their sustainable nature, geopolymers have several interesting features such as high strength, corrosion resistance, water resistance, enclosed metal ions, high temperature resistance [15], adjustable thermal expansion coefficient, and acid resistance [17]. Geopolymers find broad range of applications in the field of transportation, emergency repairs, metallurgy, coating, membrane materials, and nuclear waste disposal. Despite significant commercial and technological potential geopolymers' easy-brittle character limits their extensive applications where great efforts are made to overcome such shortcomings [15].

Advances in concrete repairs focus on low-carbon alternatives such as the use of geopolymers [13,14] as it is sustainable, environmentally friendly and plays a significant role in waste management. These materials are not only environmentally friendly, but also present comparable bond strengths to conventional repairs [14].

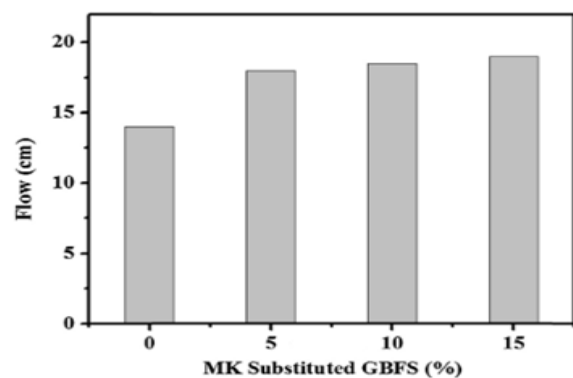
2. Properties of geopolymer based materials as repair materials

2.1 Fresh Properties

The workability of geopolymer mortar as a repair material was recently investigated. Husein et al. [27] investigated the influence of metakaolin (MK) on the workability and setting time of geopolymer mortars based on GGBFS. Increased MK concentration in the matrix improved the workability and setting time of the prepared geopolymer mortars significantly as shown in (Fig.1).

Moreover, Tanakorn et al. [28] investigated the influence of sodium hydroxide and the calcium oxide to silicate ratio on geopolymer mortar workability. An increase in the molarity of sodium hydroxide could increase the initial and final setting time of geopolymer mortar when the percentage of OPC replaced by FA was increased. FA (class C) was substituted by OPC with 0%, 5%, 10%, and 15% to evaluate the impact of calcium oxide to silicate ratio. Besides, the addition of steel slag could accelerate the setting time [29].

Moura et al. [30] studied the effects of different superplasticizer ratios (1%, 2%, and 3%) on the flow of geopolymer mortar. The flow of the alkali activated mortars without superplasticizer was less than 50%. On the other hand, the mortars with more superplasticizer content displayed an enhanced flow as indicated in (Fig.2). The mortars with a high calcium hydroxide content and a low MK content flowed better. For better solubility, MK's high Blaine fineness necessitated a high liquid phase. Meanwhile, at high sodium hydroxide concentrations, flow was similarly reduced. Mortars with a sodium hydroxide concentration of 10M and a calcium hydroxide content of 10% had the maximum flow. The mortar was improved by combining a 3% superplasticizer component with a 10% calcium hydroxide content increased mortar flow from less than 50% to over 90% [31].



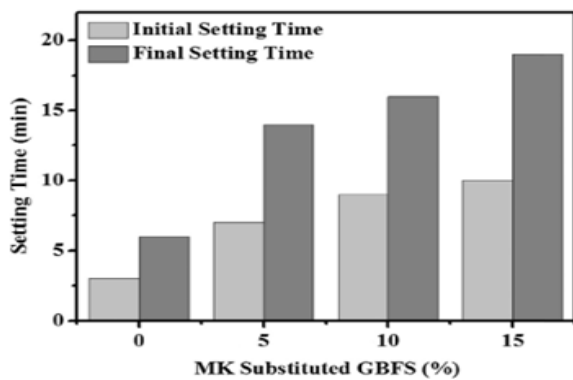


Fig. 1. Impact of MK substituted GGBFS on flow geopolymer mortars, a) Flow, b) Setting time [27]

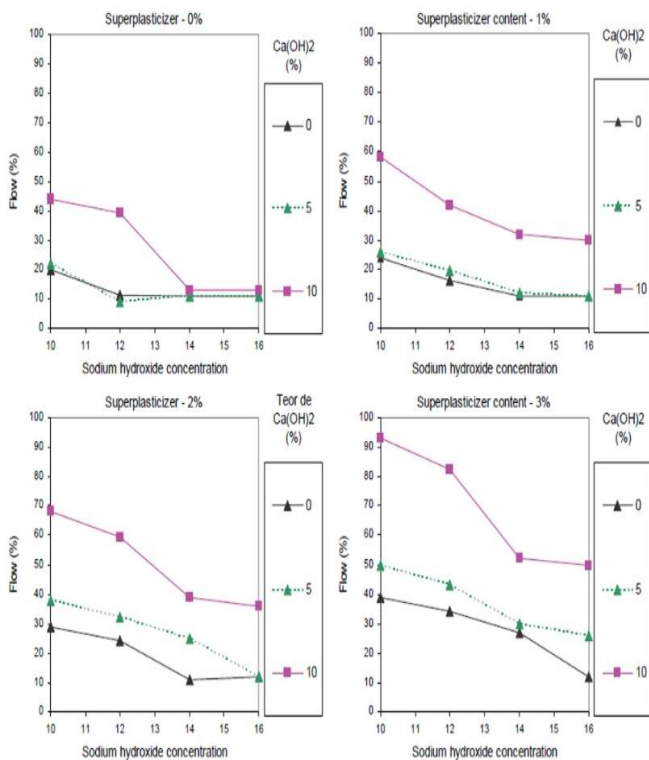


Fig. 2. Sodium hydroxide concentration dependent flow variation of super-plasticizer for different calcium hydroxide contents [30]

2.2 Hardened Properties

2.2.1 Compressive strength

The most valuable physical property of concrete is its compressive strength, and high early strength is required for repair materials. Compressive strength influences other properties such as tensile strength, flexural strength, and modulus of elasticity. The ASTM C109/C109M standard is commonly used to determine the compressive strength of geopolymer mortars. Binder to aggregate ratio, molarity of sodium hydroxide, sodium silicate to sodium hydroxide ratio,

solution to binder ratio, silicate to aluminium ratio, silicate to sodium oxide, and calcium content are all factors that influence geopolymer mortar strength. The impact of some of these factors on the strength of geopolymer mortars (GPMs) is discussed in the following sections [15].

2.2.1.1 Effect of calcium content

Husein et al. [27] created GPMs in which GGBFS was replaced by MK at 0%, 5%, 10%, and 15% levels. After 28 days of curing, the compressive strength of the resultant GPMs was found to have increased from 42 MPa to 63.1 MPa, with an increase in MK content of 10 to 15%, respectively. The effect of MK replaced GGBFS on the early compressive strength of GPMs is seen in (Fig.3) [27]. On the other hand, using MK improved the compressive strength with the best enhancement recorded at 20% MK [32]. The strength reduced with decrease in calcium content and curing temperatures. With a 1.08 calcium to silicate ratio and a 90 °C oven curing temperature, low strength was observed [33].

Tanakon et al. [28] employed FA class C and OPC to investigate the effect of calcium ratio on the binding feature of geopolymer mortar. FA was used in place of OPC, with percentages of 0%, 5%, 10%, and 15% respectively, increasing the calcium level from increased the compressive strength. Furthermore, increasing the calcium level to high alkali (14M) increased compressive strength for the first 10% and thereafter decreased it.

Phoongernkham et al. [34] investigated the effect of high calcium content when FA was replaced with GGBFS at 0%, 50%, and 100%. The compressive strength of all NH and NS series was observed to rise as the GGBFS concentration increased. The readily available free calcium ions that reacted with silica and alumina to generate C-(A)-S-H gels and coexisted with geopolymer gels were credited with this improvement [35,36]. Furthermore, because the reaction of GGBFS with alkali solutions is an exothermic process, heat was generated to aid the geopolymerization process. As a result, an increase in GGBFS content increased geopolymer paste (GPP) compressive strength [34].

As shown in (Fig.4), Hawa et al. [37] employed para-wood ash (PWA) class C to test its effect on the compressive strength of MK-based GPM. The compressive strength was found to be high in the first two hours. This was partly due to the fact that the GPMs were made as a hot mixture and then cured in an oven. Furthermore, particle size effects (6.31 m of MK vs. 25.13 m of PWA) were blamed for a decrease in compressive strength as PWA content increased. Active polymerization was caused by the increased surface to volume ratio of finer particles [38,39]. Another element contributing to the decrease could be the reduction of Si and Al when MK was replaced with PWA. In fact, the CaO in PWA did not participate in geopolymerization and was slowly hydrated.

Winnefeld et al. [40] discovered that high calcium content resulted in lower strength due to poor reactivity with alkaline activators in FA-based geopolymers. It was confirmed that compressive strength might be lowered by adding CaO to raw materials. Despite this, encouraging results [41] were discovered at a curing temperature of 70 °C. Moura et al. [30] investigated the effects of CaO₂ replacement in MK-based geopolymers with 0%, 5%, and 10% CaO₂. It was discovered that replacing MK with CaO₂ resulted in a 10% increase in compressive strength. GGBFS and FA municipal solid waste incinerator (MSWI). FA were used as waste binder in Dai et al. [42] 's study of the effect of high content calcium on geopolymer mortar.

Shuguang et al. [29] studied the effects of GGBFS replacement on MK-based geopolymer mortars with 0% and 20% GGBFS replacement. The compressive strength of cement repair material was found to be lower than the compressive strength of geopolymeric repair material with or without steel slag. The higher early compressive strength achieved for geopolymeric repair materials with steel slag.

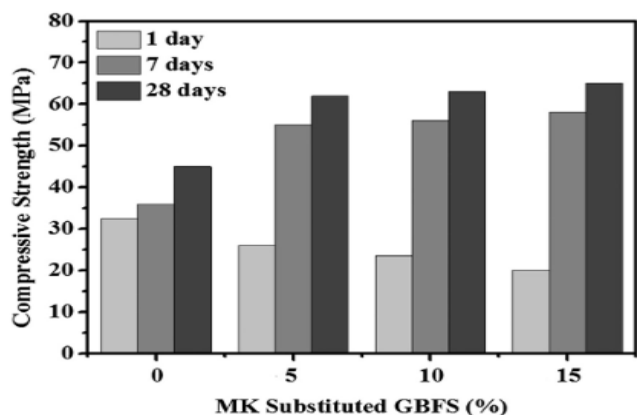


Fig. 3. Impact of MK substituted GGBFS on the early compressive strength of GPMs [27]

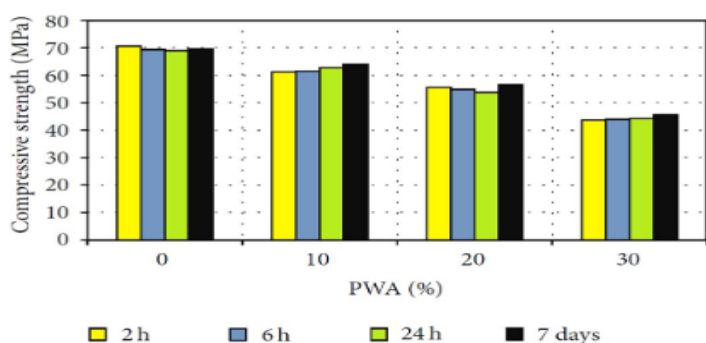


Fig. 4. PWA dependent% compressive strengths for different mixtures with curing age of 4h in an oven [37]

2.2.1.2 Effect of sodium hydroxide molarity

Tanakon et al. [28] investigated the effects of different NaOH molarities (6M, 10M, and 14 M) on the development of compressive strength in geopolymer mortar. The study showed that as molarity increased, compressive strength increased as well. On the other hand, the effect of concentration of NH solution in terms of molarity (8M, 10M, 12M, 14M) the results show that the compressive strength of the geopolymer mortar mixes increased with increase of concentration in terms of molarities of NaOH. The highest compressive strength achieved at 14M as 50.3 MPa at 28 day as presented in (Fig.5) [43].

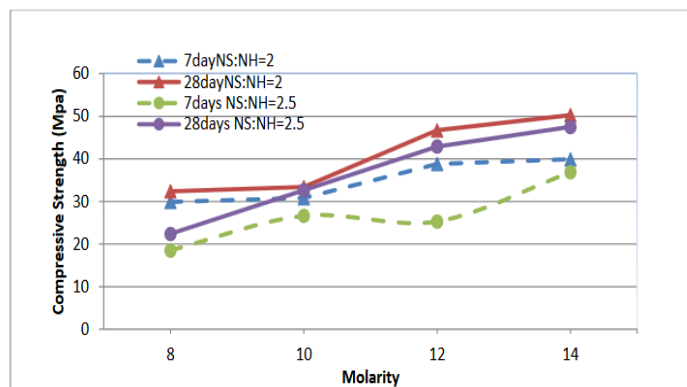


Fig. 5. Effect of concentration of sodium hydroxide solution [43]

2.2.1.3 Effect of solution types

Phoongernkham et al. [34] reported the effect of different solution types on the activation process of waste materials with a high silicate aluminate content. 3 types of solution sodium hydroxide (NH), sodium silicate (NS), and sodium hydroxide sodium silicate (NHNS) were used. (Fig.6). clearly shows that a 100% FA mix produced low early strengths for All NH, NHNS, and NS series. The NH solution was crucial in dissolution the Si⁴⁺ and Al³⁺ ions from raw materials and in the subsequent geopolymerization process[45]. However, at ambient temperature, the strength growth of FA paste activated by either NH or NS was shown to be relatively low [45-47].

At later ages, the use of NHNS showed a considerable improvement in strength development. The 7-day compressive strength of FA paste with NHNS was very low, but the compressive strengths of 28-day and 60-day old specimens were substantially higher, with 45.0 and 52.9 MPa, respectively. The slower reaction rate at ambient temperature was attributed for the lesser strength of FA paste early on. FA paste, on the other hand, developed strength in a similar way to OPC concrete over time [47]. The paste with NH and the paste with increased GGBFS component (FA + GGBFS paste) produced lower strength than the pastes with NHNS and NS. The leaching of silica and alumina required NaOH, as

previously stated. Nonetheless, at ambient temperature (23 °C), the leaching and subsequent reaction were decreased [48]. When NS was used alone or in combination with NH, the system produced more silicate. This aided the geopolymerization process, leading to higher compressive strength. Furthermore, at all curing ages, the FA + GGBFS paste with NHNS outperformed the NH and NS pastes. The FA + GGBFS blend with NHNS was considered the most effective alkali activated binder in combination with a high strength mix. Sodium sulphate was also used to make high-strength GBFS geopolymer mixtures [49]. After using four different alkaline solutions, the solutions were a mixture of sodium silicate (NS), sodium hydroxide (NH), potassium silicate (KS) and potassium hydroxide (KH) as NS + NH, NS + KH, KS + NH and KS + KH it is noticed that the values of the compressive strength of sodium silicate-based GP mortar (NN+NH) mixes were higher than potassium silicate-based GP mortar (KN, KK) at 7 and 28 days as shown in (fig.7) [50]. Because of the reaction between CaO from GGBFS and SiO₂ with subsequent formation of CSH, the paste with NS had the highest compressive strength at 28 and 60 days [51].

According to Ismail et al. [51], alkali activation of GGBFS resulted in the dissolution of Ca and the participation of Si and Al in the formation of CSH and CASH gel, resulting in high mechanical strength. Furthermore, the compressive strength of geopolymer was predominantly determined by the molar ratio of SiO₂ to Al₂O₃ [52]. The ratio of SiO₂ to Al₂O₃ of roughly 3.50 was found to form a high strength high calcium geopolymer [39]. The ratio of SiO₂/Al₂O₃ in GGBFS paste with NS was found to be 3.49. The compressive strength of this paste after 28 days of curing at ambient temperature was found to be extremely high (171.7 MPa).

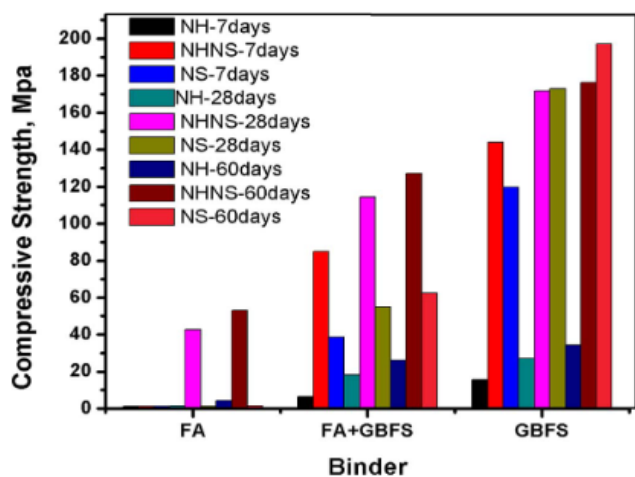


Fig. 6. Binder nature dependent compressive strength of geopolymer pasts [34]

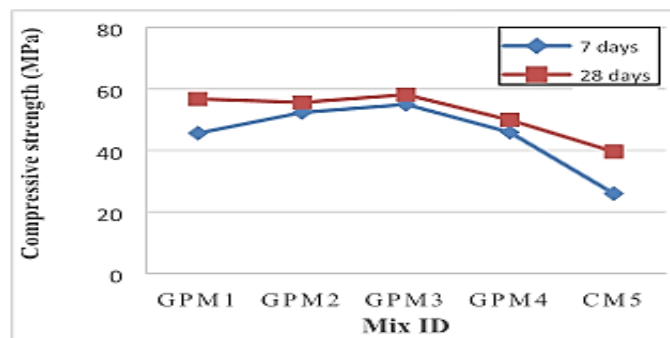


Fig. 7. Compressive strength of mortar mixes [50]

2.2.1.4 Effect of sodium silicate to sodium hydroxide ratio

Most researches have previously dealt with GPM as repair materials, with sodium silicate to sodium hydroxide molar ratios of 2.5 [30,37,44,53] and 2.0 [28,34] kept constant. However, the effect ratios of sodium silicate to sodium hydroxide solution by mass (1:1, 1.5:1, 2:1 and 2.5:1) was studied, and the results were as shown in (Fig.8) [43]. The impact of the sodium silicate to sodium hydroxide concentration ratio on the strength development of geopolymer as a repair material. Besides, sodium silicate solution is characterized by its SiO₂ to Na₂O weight ratio which affects on strength as shown in Table 1.

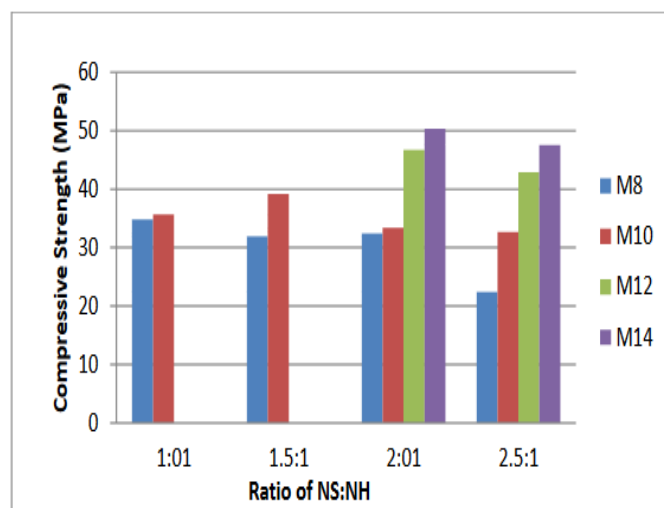


Fig. 8. Effect of varying ratio of Sodium Silicate to sodium hydroxide solution [43]

Table 1: Test results on effect of SiO₂ to Na₂O ratio

Reference s	SiO ₂ to Na ₂ O ratio	Results
Huseien et al. [27]	1.16	The geopolymer mortar with a solution molarity of 14M showed high early strength compared to geopolymer mortars with other

		molarities (10M and 12M).	
Mirza et al. [33]	2.0	An increase in the ratio (more than 2.0) can decrease the strength at room temperature. Furthermore, when geopolymer mortars were cured at oven temperature (60 °C), the strength of the mortars was increased at higher ratios. The strength of geopolymer mortars was somewhat reduced as the curing temperature was increased from 60 to 90 °C.	
Dai et al. [42]	(0.96, 1.28, and 1.91)	For a ratio of 0.96, compressive strength of up to 47.1 MPa was achieved. When the SiO ₂ to Na ₂ O molar ratio was raised, the compressive strength was also reduced. The participation of excessive Si ions in the geopolymerization process cause this reduction in the compressive strength. At a ratio of 1.91, the lowest compressive strength (40.8 MPa) was found.	

compressive strength of the full-height 200 mm AAC specimens ranged from 26.7 MPa to 40.3 MPa [64].

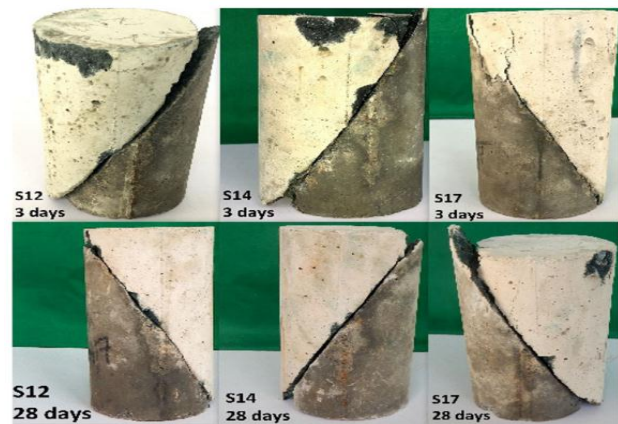


Fig. 9. Slant shear test specimens with failure plane along GPC-PCC interface [38]

2.2.2 Bond Strength

A good bond strength and compatibility between the existing and repair materials are two of the most important characteristics for a repair material [54]. The friction and adhesion between two surfaces determine the bond strength between them [55-59]. It is therefore necessary to take into account the level of surface roughness [60]. The bond strength is determined from the combination of compressive stress and shear stress [61,62].

According to Momayez et al. [61], the measured adhesion strength was found to decrease with the testing process in the order of slant shear, bi-surface shear, splitting, and pull-off. Similarly, Laskar and Talukdar [63] studied bond strength between GPC and PCC with slant angle 30° as shown in (Fig.9) after the test, it was discovered that the bond between the GPC and PCC interface was weaker than the bond within the GPC or PCC matrix in mixes with low bond strength. The failure surface was along the GPC and PCC interface (see Fig.9). The failure surface for GPC with higher bond strength, on the other hand, was not only along the interface but also in the matrix of GPC or PCC. as shown in (Fig.10).



Fig.10 .Slant shear test specimens with cracks in GPC and PCC region [38]

On the other hand, Goma et al.[64] Used different slant angles 45°, 33.75°, and 22.5° respectively and different heights of cylinders (200 and 337.5 mm) as shown in (Fig.11). The results were, repaired at 45° and 22.5° exhibited an excellent bond where the shear demand on the repair was less than the bond between the substrate and repaired material. Repairs at 33.75° displayed a combination of sliding and damage to either the substrate, repaired, or both. The

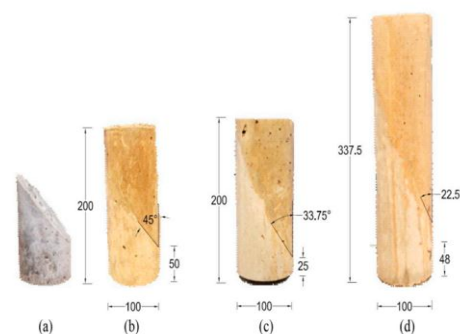


Fig. 11. Cement Concrete specimens (a) before repair with an inclination angle of 45°, and after repair with inclination angles of: (b) 45°, (c) 33.75°, and (d) 22.5° before and after repair [64]

Cement concrete (CC) and alkali-activated concrete (AAC) beams with no cold joints were prepared for comparison purposes as well as those with cold joints and full-depth CC and AAC specimens. A layer of CC having a height of 75 mm was placed in each; then, either no surface treatment (Fig.12,13), a concrete bonding adhesive or sandblasting was applied to each CC surface. Thereafter, a layer of AAC mixture was placed against the CC surface of each specimen and the repaired speckled specimens were cured as described in the slant shear test [65].

The failure of the interface between the aluminium disc and the repair materials showed a weak epoxy, and the test was considered a failed test (Fig.14a).The surface treatment had an effect on the failure mode of the repaired beams for the remaining beams.The interface surface between the repair and substrate materials failed in around 90% of the repaired beams with no surface treatment and 100% of those coated with the adhesive (Fig. 14b), indicating weak bond strength.In the repair material, the remaining 10% of the no-surface-treatment specimens failed (Fig.14c).Furthermore, within the CC substrate material, 100% of the sandblasted beams failed (Fig.14d), suggesting a good binding strength.[64].

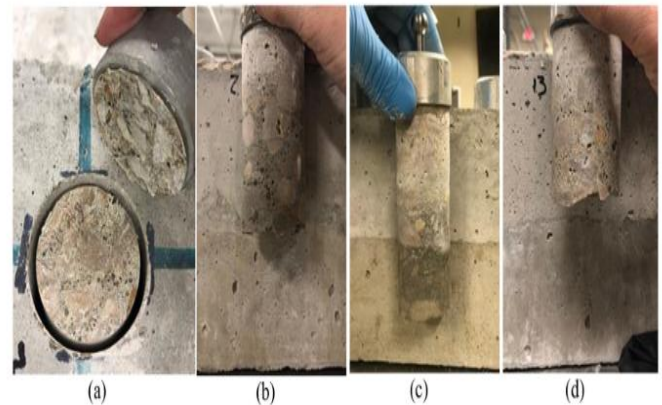


Figure 14 . Failure of the pull-off specimens in: (a) top surface of the repair material, (b) bond surface area, (c) repair material, and (d) substrate material [64]

3. Durability of geopolymer based materials

Durability of geopolymer concrete refers to the ability to maintain properties for its service period of exposure to aggressive environments which related to the safety of construction engineering [66].

According to Xie et al. [67], the durability of geopolymer concrete is regulated by a number of parameters that require more laboratory and field research. Table 2 also shows some of the most current studies, as well as aluminosilicate precursors and alkali activator solutions.

Table 2: Some current studies on durability of geopolymer concrete

Reference	Activator	Precursors	Durability properties
Bondar et al. [68]	KOH + Na ₂ SiO ₃	NP	Sulfate resistance
Bernal et al. [69]	NaOH + Na ₂ SiO ₃	FA+GGBFS	Carbonation resistance
Ghazy et al. [50]	NaOH + Na ₂ SiO ₃ , KOH + Na ₂ SiO ₃ , NaOH + K ₂ SiO ₃ , KOH + K ₂ SiO ₃	FA	Sulphate, sulphuric acid resistance and water absorption
Ariffin et al. [70]	NaOH + Na ₂ SiO ₃	FA+POFA	Acid corrosion resistance
El-Sayed et al.[71]	NaOH + Na ₂ SiO ₃	GGBFS	Sulfate resistance
Fernandez-Jimenez et al.[72]	Na ₂ SiO ₃	FA	Heat resistance

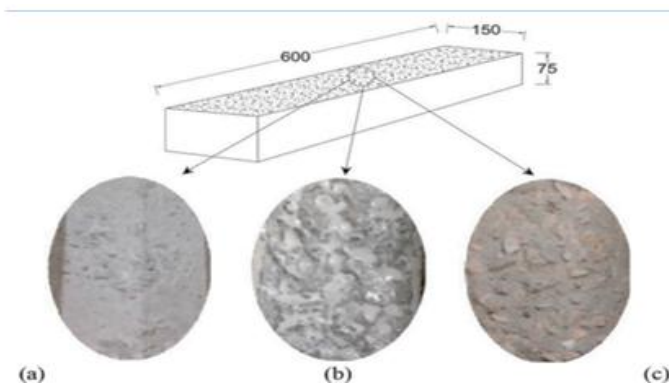


Fig. 12. CC substrate surface before placing the AAC,(a) no treatment,(b) concrete bonding adhesive,and (c) sandblasting [65]

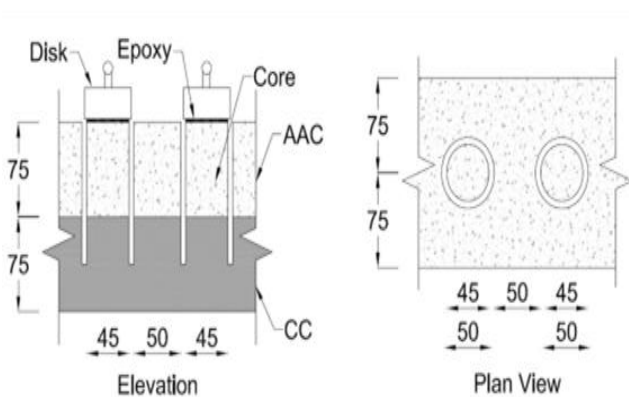


Fig.13 .Geometry of the pull-off test beams (dimensions are in mm) [65]

Bernal et al. [73]	NaOH + Na ₂ SiO ₃	MK+GGBFS	Chloride resistance
Prabu et al. [74]	NaOH + K ₂ SiO ₃ , KOH + Na ₂ SiO ₃	FA+RHA	Acid and sulfate resistance
Khan et al. [75]	NaOH + Na ₂ SiO ₃	FA+GGBFS	Carbonation resistance
Nkwaju et al. [76]	NaOH + Na ₂ SiO ₃	LS	Wet-dry cycles and heat resistance
Park et al. [77]	Ca(OH) ₂	GGBFS	Chloride resistance
K.Ramesh [36]	NaOH + Na ₂ SiO ₃	GGBFS+FA	Sulphuric acid, sodium chloride resistance

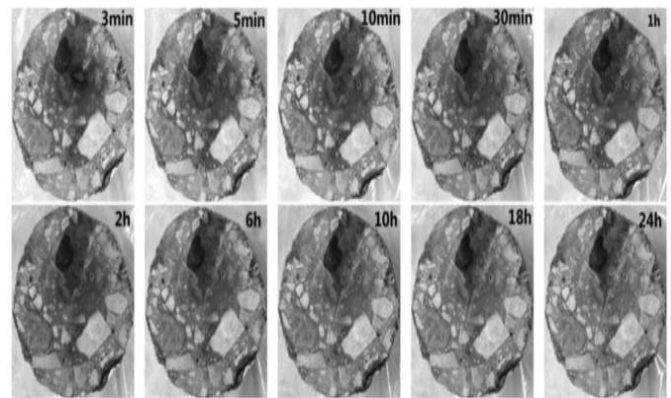


Fig. 15. Color change for GPC after a carbonation test with 5% CO₂ [81]

Where FA is fly ash, GGBFS is granulated blast furnace slag, NP is natural pozzolan, LS is lateritic soil, POFA is palm oil fuel ash.

3.1 Carbonation Resistance

Carbonation damages concrete structures by decreasing the alkalinity of the pore solution, destroying the surface oxide film on steel bars, and eventually leading to structural failure due to internal expansion stress [79].

In OPC, the pH is mostly controlled by the hydration product calcium hydroxide, but in geopolymer concrete, the pH is solely controlled by the pore solution. Due to the creation of hydrogen carbonate and carbonates, the pH of geopolymer concrete decreases noticeably during carbonization [66]. Khan et al. [75] classified the degree of carbonation according to the change of phenolphthalein color (include uncarbonated area, partially carbonated area, and carbonated area), however, the border between colored and colorless areas is unstable, which is quite different from OPC concrete carbonization area as shown in (Fig.15) [80,81].

Bernal et al. [69] observed that the compressive strength of fly ash/slag based geopolymer decreases linearly after carbonization, which results in the formation of N-A-S-H gel. It is also reported that geopolymer concretes after carbonation have lower extent of reaction and lower mechanical properties [75–78].

Many researchers have also improved the pore structure and reactant composition of geopolymer concrete by adding calcium hydroxide [85], Portland cement [85], nano- TiO₂ [86], micro silica [87], and slag content [82]. Li et al. [83] discovered that the slag activated with NaOH were more resistant (about 13.6 strength loss) to carbonation than NaOH/Na₂SiO₃ (26%). The addition of nano-TiO₂ refines the microstructure and improves carbonation resistance of fluidized bed fly ash based-geopolymer concrete. Duan et al. [86] reported that the carbonation depth decreased with the increase of nano-TiO₂, and the carbonation depths at 180 days are only 42% to the reference specimens with 5 wt% addition. Behfarnia et al. [87] investigated carbonation depth of slag-based geopolymer concrete produced via partially replacing slag by micro silica in proportion of 5, 10, and 15 wt%. Carbonation depth of concrete being controlled at 4% accelerated carbonation in two cycle of 14 and 28 days. The results show that the replacement slag with micro silica had a positive effect on the properties of geopolymer with 32% and 34% decreases in carbonation depth after 14 and 28 days accelerated carbonation cycles, respectively. However, increasing the content of MK in the binder will lead to the formation of secondary aluminosilicate phases and increasing the susceptibility to carbonization [84].

3.2 Sulphate Resistance

Geopolymer erosion in a sulphate environment has different mechanisms depending on calcium concentration. Due to the similarities of hydration products, high-calcium alkali-activated systems have similar erosion mechanisms to OPC.

In comparison to MgSO₄ solution, high-calcium systems have better resistance in Na₂SO₄, unlike low-calcium systems. Exposure to Na₂SO₄ appears to encourage geopolymer gel structural evolution, while Mg²⁺ in solution promotes high-calcium system decalcification and M-S-H type phase decay [89]. Saavedra et al. [89] discovered that when fly ash/slag geopolymer concrete was subjected to MgSO₄ for 360 days, it lost 33 percent of its mechanical resistance, which was higher than the value in Na₂SO₄ solution. Low-

calcium alkali-activated systems, on the other hand, allow for ion exchange between the sulphate solution and the network structure, potentially making it more resistant to sulphate attack [88,90,91]. Douglas et al. [92] found that after 90 and 120 days of exposure to a 5 percent Na_2SO_4 solution, the visual appearance, mass, strength, expansion, and dynamic modulus of elasticity of slag-based geopolymer concrete change little, outperforming OPC concrete. However, after 270 days, the fly ash/ slag geopolymer concrete had a larger deposition of salts and cracks, and the physical deterioration of the OPC concrete was much greater for the same exposure periods as shown in (Fig.16) [89]. El-Sayed et al. [71] found that a slag-based geopolymer activated with 6 wt% NaOH lost 49% of its strength after 6 months of exposure to 5% MgSO_4 , compared to 21% activated NaOH and Na_2SiO_3 (3:3), which could be due to excess hydroxide ions forming excess ettringite. Furthermore, the strength of concrete activated by two different types of activators is remarkably similar to the strength of concrete cured at room temperature.

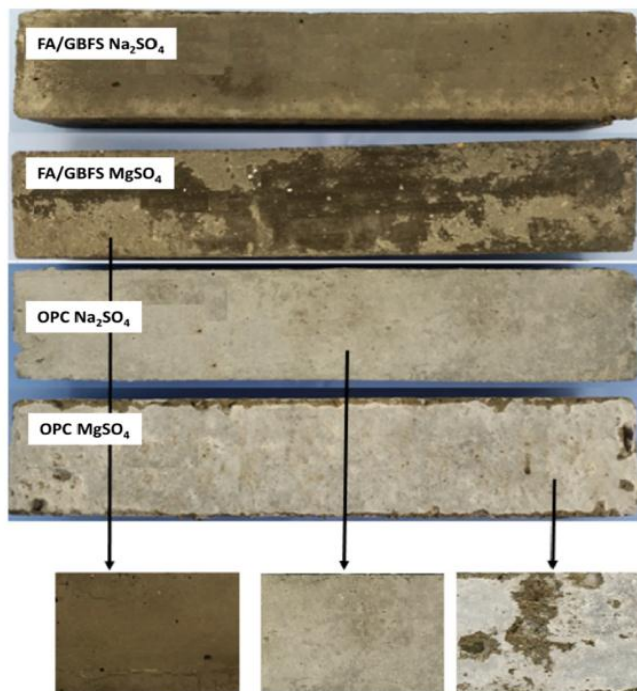


Fig.16 Visual appearance of geopolymer concretes exposed to 5% Na_2SO_4 and 5% MgSO_4 solutions for 270 days [89]

3.3 Acid Resistance

The depolymerisation of aluminosilicate polymers and the liberation of silicic acid influence acid corrosion resistance in geopolymer concrete [70,93]. Visual appearance, physical qualities, weight loss, and corrosion depth of geopolymer/cement concrete can all be used to determine the degree of acid corrosion [94,95]. According to reports, geopolymer concrete is more resistant to acid damage than OPC concrete. Depolymerisation of aluminosilicate polymers and liberation of silicic acid in acid solution break the Si-O-Si

and Si-O-Al bonds, resulting in fissures or crystallisation of zeolites [70,94].

Bakharev et al. [94] soaked slag-based geopolymer concrete in a pH 4 HAc solution for a year and found that the geopolymer lost 33% of its strength compared to 47% for OPC concrete. In comparison to cement paste, Fernandez-Jimenez et al. [95] found that fly ash-based geopolymer outperformed cement paste in terms of corrosion behaviour and residual strength. When immersed in 5% H_2SO_4 , the mechanical properties of fly ash-based geopolymer degraded somewhat after 28 days, according to Zheng et al. [64,99], but the corroded concretes still met the acid soaking safety index of the standard GB 50212-2002 [100].

The visual appearance of specimens subjected to 5% H_2SO_4 for 30 days is shown in Fig. 17a [96]. Due to the decreased CaO content, the OPC concrete displayed severe erosion with soft white depositions on the surface, meanwhile the fly ash-based geopolymer remained comparatively intact. The addition of nano-silica has a good effect on durability, but the effect is not apparent under short-term acid erosion, as shown in Fig.17. (b). According to Rajak et al. [98], geopolymer concretes with polypropylene fibre addition have higher durability than control, which they ascribe to polypropylene's high resistance to alcohol, organic acids, esters, and ketones, as well as its decreased capillary porosity. Under sulfuric acid attack, Thokchom et al. [97] discovered that specimens with higher Na_2O concentration lost alkalinity faster than those with lower Na_2O content, which had higher residual compressive strength.

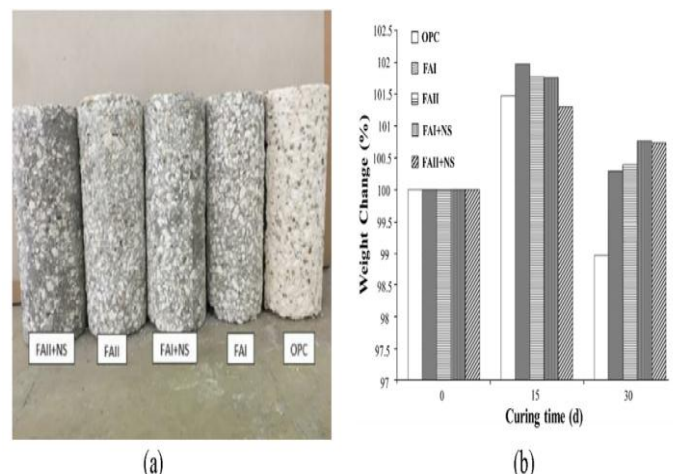


Fig.17 .Visual appearance (a) and weight loss (b) of specimens in 5% H_2SO_4 after 30 days [96]

3.4 Chloride Resistance

Chloride binding mechanisms for alkali-activated materials are linked in a variety of ways. Ismail et al. [101] and Zhang et al. [102] believed that the chloride binding of fly ash-slag based geopolymers was primarily due to physical adsorption, but Ke et al. [103] discovered two forms of Friedel's salt in a

Na_2CO_3 -activated slag containing CaCl_2 solution. Because of the differences in chemical characteristics of pore fluids, the rapid chloride penetration test (RCPT) utilised for OPC is thought to be unsuitable for geopolymer [104].

Previously, studies on the chloride resistance of geopolymer concrete were conducted using several methodologies, including (a) ASTM C1202 or AASH-TO T277, (b) NT Build 492, and (c) NT Build 443 [105]. The rapid chloride permeability test, for example, is based on the ASTM C1202 measurement of electrical conductivity, with the findings influenced by changing solution chemistry on current flow. As illustrated in (Fig.18), silver nitrate (AgNO_3) solution may precipitate the chloride ion and is commonly used to measure chloride penetration depths, and the binding gel mix proportion has a significant impact on chloride resistance [101]. Ravikumar et al. [105] employed total charge passed to measure NaOH and Na_2SiO_3 activated slag-based geopolymer transport coefficients, which is more accurate. According to earlier studies, the correlation between the electric accelerated chloride test and long-term chloride diffusion, as well as the testing method for chloride binding, should be established and improved [101,106,107]. Tennakoon et al. [108] discovered that the corrosion current of steel bars made of fly ash/slag-based geopolymer concrete subjected to 0.6 M NaCl solution was lower than that of OPC concrete (Fig.19).

Furthermore, the authors [108] discovered that OPC concrete had a higher apparent chloride diffusion coefficient solution than geopolymer concrete. Kayyali et al. [109] found that replacing cement with proportions of slag up to 70% improved the chloride resistance of slag-based geopolymer concrete over OPC concrete. Furthermore, in 30 percent CaCl_2 solutions, there was reduced swelling and cracking of geopolymer concrete, and in 5% MgCl_2 solutions, there was higher strength [110–111]. Figure 20(d) further demonstrates that OPC concrete has the deepest chloride penetration depth of 25 mm, while geopolymer concretes have depths of 1 to 10 mm. The reaction products, hydrotalcite, were discovered to absorb chloride ions by Kayyali et al. [109] and Shi et al. [112].

Ismail et al. [101] discovered that the trend of chloride migration coefficients is similar to the results of ponding experiments, and that chloride resistance is linked to structural compactness and pore structure. Park et al. [77] investigated the chloride resistance of slag concrete activated by various activators in a 3.0% NaCl solution for 6 hours at 60 V constant voltage. $\text{Ca}(\text{OH})_2$ activated the lowest levels of degradation, owing to the creation of $\text{Ca}(\text{ClO})_2$ to eliminate free chlorides. Ravikumar et al. [105] also note that chloride penetration of slag-based geopolymer concrete activated by KOH and NaOH is similar to that of OPC concrete, although Na_2SiO_3 activated geopolymer has good resistance. The chloride resistance of geopolymer concrete made with extra additions was likewise strong. Zhang et al. [113] substituted

the slag with 30 wt% lithium slag particles, which resulted in a significant reduction in chloride ion penetration.

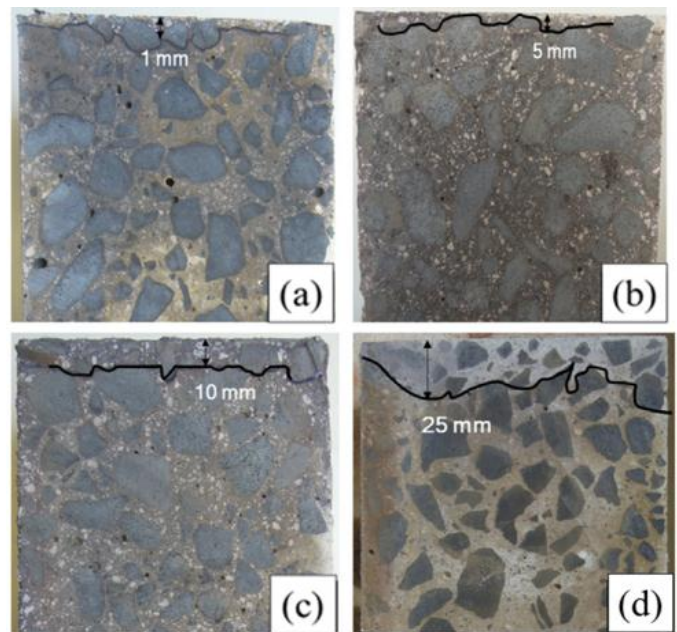


Fig. 18 .Visual appearance the (a) slag, (b) slag: fly ash = 3: 1, (c) slag: fly ash = 1: 1 based geopolymer concrete, and (d) OPC concrete at the end of the ponding test 3.5% NaCl for 28 days [101]

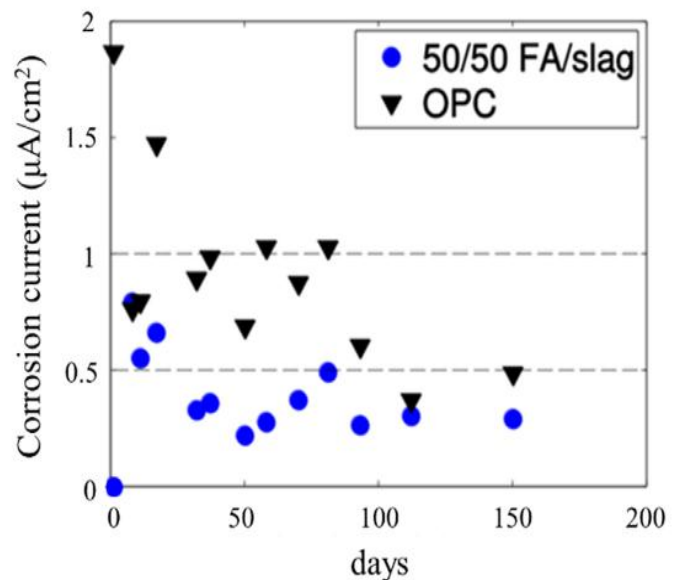


Fig.19. Corrosion current of steel bar of geopolymer compared to OPC concrete in 0.6 M NaCl solution [108].

3.5 Heat Resistance

Because building fires cause large economic losses and casualties, it is critical to improve the heat resistance of concrete in order to ensure the protection of people and property [116]. The hydration product of OPC paste is degraded and dehydrated at temperatures of around 300-

400°C, after which water and entrained air break the internal walls of the micropores, causing a rapid loss of strength [114,115]. When compared to OPC concrete, geopolymer concretes have a higher heat resistance. When Gourley et al. [117] evaluated the heat resistance of geopolymer and cement, they discovered that the former is essentially a type of glass, unlike cement is a hydrate. Heat resistance of geopolymer is measured using visual appearance, residual strength, and thermal conductivity [115,118]. Duan et al. [94] looked into it. Temperature profile, compressive strength, and stability were used to measure thermal durability. (Fig.20a) illustrates this. Also reported Instability and shrinkage are additional signs of geopolymer concrete's heat resistance. After 600°C exposure, geopolymer concrete loses less mass than OPC concrete due to Ca (OH)² decomposition of OPC (Fig.20b). Metakaolin-based geopolymers have an amorphous structure and no phase shift at 1000°C, according to Temuujin et al. [119]. Perera et al. [120] discovered that at 1200°C curing, phase was not much melted, primarily in the form of leucite. According to Ye et al. [121], a tailing/slag-based geopolymer's strength reduces by more than 40 MPa after a 1000°C fire, but increases after a 1200°C fire, which could be due to sintering and densification. The fly ash-based geopolymer contracted by around 1% between 200 and 300°C, and another 0.6 percent between 700 and 800°C, according to Kong et al. [122].

Furthermore, it was discovered that the geopolymer mortar coating was corrosion resistant and produced strong bonding to the reinforcing steel [127].

Geopolymer concrete has recently been used as a pipeline coating material. Biogenic corrosion of wastewater pipelines was studied using three different coating materials [128]. Geopolymer, OPC, and numerous composite coatings made of geopolymer magnesium phosphate were used to produce these coating materials in wastewater pipelines. materials were investigated for accelerated biocorrosion after six months of corrosion, the coating materials' flexural strength was measured. In comparison to the other coatings, the multiple phase coating showed good corrosion resistance and bond strength, according to the test results. Furthermore, repairs with new concrete may result in macro-cell corrosion [129].

This was not looked into in the research. Al-Majidi et al. (2019) [130] used fibre-reinforced geopolymer concrete to strengthen beams and then exposed them to accelerated corrosion. GGBFS, silica fume, polyvinylalcohol, and steel fibres were combined to make a fibre-reinforced geopolymer. When compared to standard steel-concrete beams, the test results after applying a fibre reinforced geopolymer jacket demonstrated higher corrosion resistance, reduced crack propagation, and higher flexural capabilities. In comparison to OPC, some researchers [131] produced a new type of geopolymer-based composite piles with geogrid, polyvinyl chloride, and fibre reinforced polymer that were corrosion resistant and very ductile. Shear strengthening of reinforced concrete beams was achieved using textile geopolymer concrete [132]. Laskar and Talukdar (2017) [133] presented a geopolymer repair method containing ultrafine GGBFS, FA and alkali activator with a suitable amount of superplasticizer. The geopolymer concrete's compact microstructure produced good bond strength and compressive strength. Similarly, Zanotti et al. (2017) [134] proposed using metakaolin geopolymer mortar to repair Portland cement concrete structures. OPC substrate and metakaolin geopolymer mortar with and without polyvinyl alcohol fibres were used. Early-age cracking was apparent in the specimens with metakaolin geopolymer mortars cured in an ambient environment, both in general and at the interface between OPC substrate concrete and geopolymer repair mortar. However cohesion was found to be improved when polyvinyl alcohol fibres were added, as previously reported [135]. There are a few other important research on the flexural strength of geopolymer concrete beams [136], structural retrofitting [129,136-139], and geopolymer concrete bond-slip [137]. Steel fibre reinforced geopolymer matrix composites were used by Carabba et al. 2017 [140] to strengthen reinforced structures. The results show that reducing the molar content of the NaOH activating solution improves the interfacial bond behaviour between matrix and fibres, which improves the effectiveness of the strengthening system's composite action.

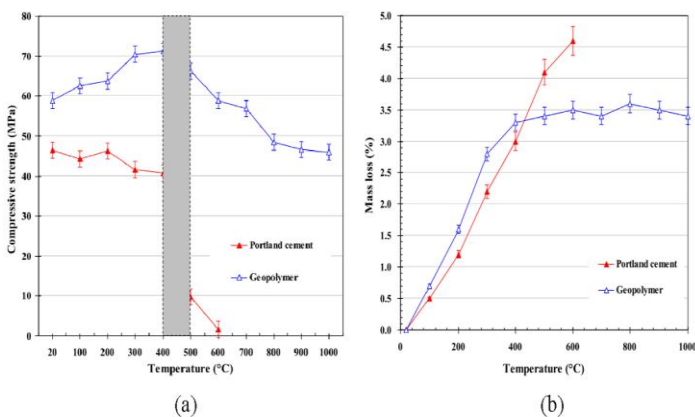


Fig. 20. Compressive strength change (a) and weight loss (b) of specimens curing at various temperatures for 28 days [114]

4. Geopolymer based materials as a repair and strengthening materials for Portland cement concrete

Alkali-activated geopolymer concretes have been reported for their fire and chloride resistance, as well as a corrosion-resistant coating material [122-125].

McAlorum et al. (2021) [126] created an automated sensing coating of geopolymer for structural repairs. Curing aluminosilicate with an alkaline activator solution at 40°C for 1-3 days produced a binder with high adhesive properties.

Researchers have also used geopolymer concretes made of MK and F and C classes of FA for buried infrastructure repairs and compared them to OPC [141]. Among all the other types of concrete, geopolymer concrete with class F FA was determined to be the most durable, while the other geopolymer concretes were almost as comparable as OPC.

Laskar et al. 2019 [142] repaired doubly reinforced beams of 2-meter length of OPC with GGBFS and class F FA geopolymer. Reinforced concrete beams were subjected to flexural failure after 28 days of curing. After the beams have been loaded, cracks appear in various ratios as shown in (Fig.21) and then repaired by geopolymer and Portland cement mortar as shown in (Fig.22) for further flexural testing.

The performance of the PCM repaired fully damaged RC beam at 28 days was lower than that of the GPM repaired fully damaged RC beam at 3 days. The repaired beam's stiffness was found to be higher than that of the PCM repaired beam. Due to the use of GPM as a repairing agent versus PCM as a repairing agent, the appearance of the first crack was delayed compared to the PCM repaired beam. The early compressive and bond strength increase of GPM was critical in arresting the cracks and, as a result, the crack development and propagation in the GPM repaired beam. In comparison to the PCM repaired fully damaged RC beam, the PCM repaired partially damaged RC beam had a higher stiffness. The values exhibited by GPM repaired partially damaged RC beams were much higher than those exhibited by GPM and PCM fixed fully damaged RC beams. The flexural capacity of the repaired beam with geopolymer mortar was found to be better than that with Portland cement mortar.

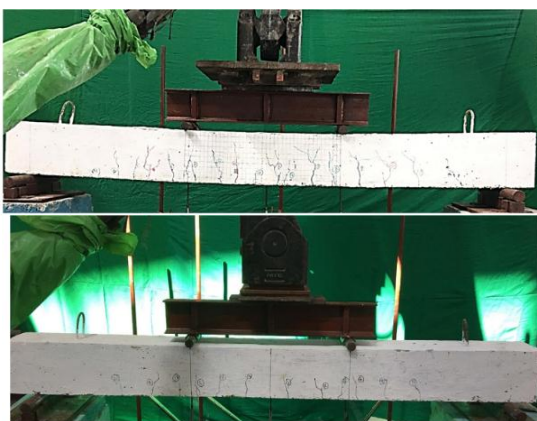


Fig. 21. (a) Cracks in a fully damaged RC beam, (b). Cracks in a partially damaged RC beam [142]

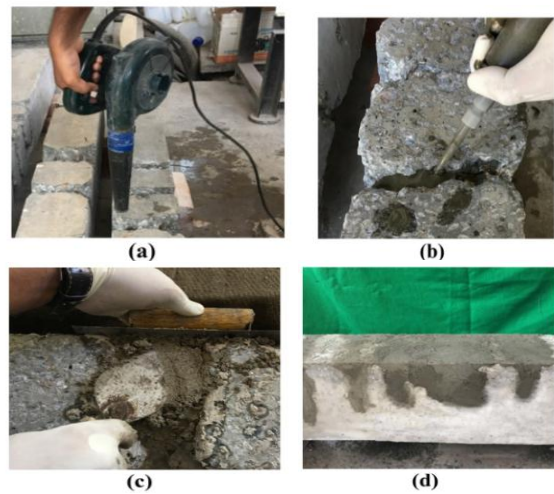


Fig. 22. (a) Air blower, (b) applying paste using syringe, (c) applying mortar using trowel (d) RC beam after repair [142]

Ghazy et al. 2021 [143] used the cement base bonded overlay technique to increase the flexural capacity of concrete slabs by applying overlay layer of geopolymer concrete on an existing slab. At first, the effect of different types of roughness on bond strength between substrate RC and GPC overlay was studied. For this the substrate concrete surfaces were roughened by different techniques shown in (Fig. 23) and left at ambient temperature for 7 days then casted the overlay.

All slabs tested after 3 months the measured deflection at mid span, cracks pattern and failure mode of tested slabs are shown in (Fig. 24, 25). According to results, the type of interface roughness determines the slab's ductile performance, not just the addition of GPC to the topping and a stiff brush was used to roughen the surface in the transverse directions, which reduced the cracks width and changed the failure mode to one that was more ductile.



a) Dowels with diameters 8 mm and Z shape section (Dowels-Z)



b) Carving and drilling 20 mm wide and 10 mm depth (Carv-20 mm)



c) Painting the surface with epoxy resin (Epoxy-R)



d) Surface prepared with steel brush in the transverse direction (Brush-TD)



e) Surface prepared with steel brush in both the



f) Smooth f) Smooth as cast (Smooth and Control)

Fig. 23. Substrate specimens with different surface preparations [143]

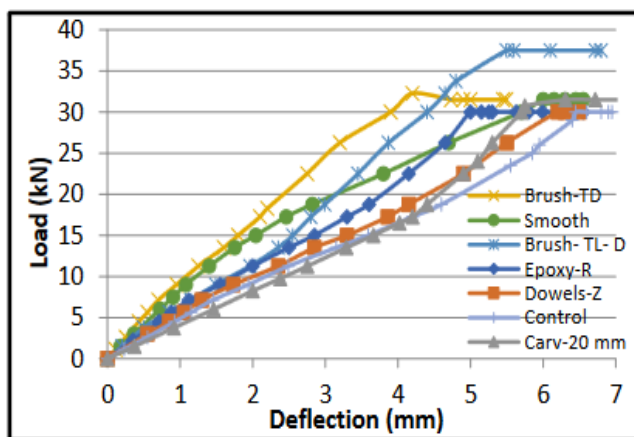


Fig. 24. Load-deflection relationships for the tested slabs

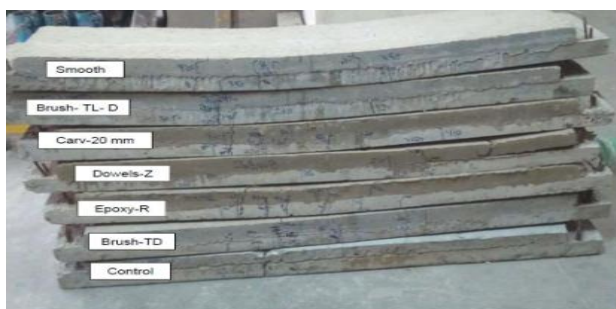


Fig. 25. Crack pattern and failure mode of the tested slabs [143]

5. Conclusions

The current review summarizes previous studies that were concerned with using geopolymer based materials as a repair and strengthening materials that can be summarized in the following:

1. Geopolymer mortars workability can be reduced by increasing sodium hydroxide concentration and also with a high replacement of MK and calcium hydroxide.

2. The compressive strength is increased with elevated sodium hydroxide concentration. However, The chemical compositions of the FA used resulted in changes in the compressive strength of geopolymer concrete. The compressive strength based FA increased when the calcium concentration was increased.

3. Alkaline activation of aluminosilicate wastes in the presence of silica fume and metakaolin using sodium hydroxide and sodium silicate in the ratio of 3:3 wt.% leads to the formation of a geopolymer that possess an enhancement in both mechanical and microstructural properties. The process can help in an ideal utilization of demolition wastes in disposal landfills all over the world and produce valuable sustainable materials.

4. The durability of fly-based geopolymer concrete is greatly governed by the internal configuration of aluminosilicate gel components in extreme environments. The GPCs made with a sodium silicate activator are less crystalline than those made with sodium hydroxide.

5. The durability of geopolymer concrete is better than OPC concrete. It displays as geopolymer concrete has lower strength loss and slight erosion in acid, sulfate, and chloride solution, and minor surface cracklings occurred after high-temperature exposure. However, geopolymer concrete after carbonation has a lower extent of reaction and lower mechanical properties mainly due to a higher Ca/Si ratio of C-S-H gel of OPC concrete.

6. There is no significant changes in the mass and the compressive strength of test specimens after exposure to acid up to one month. Exposure to sulphuric acid causes damage to the surface of heat-cured geopolymer concrete test specimens and causes a mass loss after the exposure. The severity of the damage depends on the acid's concentration and the period of exposure.

7. The geopolymeric repair materials possess better repair characteristics than cement-based repair materials.

8. Geopolymer mortar on using as concrete repairing agent show better performance than Portland cement mortar. A GGBFS-based geopolymer mortar can be used to successfully repair reinforced concrete structural members.

This review can assist researchers in their future studies on the use of geopolymer based materials in the repair work of deteriorated concrete and can also assist in the development of decision tools and strategies for maintenance and repairs for asset managers and owners to reduce this significant cost.

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