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Review

Impact of Pernicious Chemicals on Geopolymer and Alkali-Activated Composites Incorporated with Different Fiber Types: A Review

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Abstract

Over the past decade, developing geopolymer mixes to replace ordinary Portland Cement (OPC) composites has yielded positive results, leading to extensive research. The incorporation of fibers in geopolymers, besides impacting the mechanical properties, has also significantly impacted durability, mainly when dealing with the most pernicious forms of deterioration resulting from chloride attack, water penetration, sulfate attack, acid attack, as well as freeze-thaw, which occurred through chemical transgression. This study presents a systematic approach to thoroughly review the durability properties of fibrous geopolymer composites exposed to harmful chemicals and extreme environmental conditions. The multi-parameters and factors critically influencing fibrous geopolymers' physical and chemical stability are examined. The study is further aimed at providing an update on the research work undertaken to assess the impact of fiber incorporation on the durability of geopolymer and alkali-activated composites thus far. Furthermore, this review hopes to promote and facilitate research on durability for the long-term, large-scale adoption, and commercialization of advanced fibrous, non-OPC-based materials.

Keywords
Alkali activated composites; geopolymers; durability; sulfate attack; freeze-thaw; chloride attack; acid attack

1. Introduction

Despite numerous advantages, ordinary Portland Cement (OPC)-based composites are associated with high embodied carbon emissions due to cement production [1-3]. For example, producing one ton of OPC results in one ton of CO_2 being released into the environment [4-8]. Due to overloading or deterioration under extreme conditions, the durability issues in OPC-based composites further undermine the objective of a sustainable built environment [9, 10]. The composite penetrability, porosity, and available calcium hydroxide play a vital role in deciding the extent of longevity it possesses in hostile environments. The high carbon footprints emanating from cement production and the limitations in the durability of OPC-based composites [11, 12] propel the need to develop an advanced, durable, and sustainable building material with minimal environmental impact. Over the last decade, the development of geopolymer composites as a replacement for OPC-based materials has shown encouraging results, leading to extensive research in this regard (Figure 1).

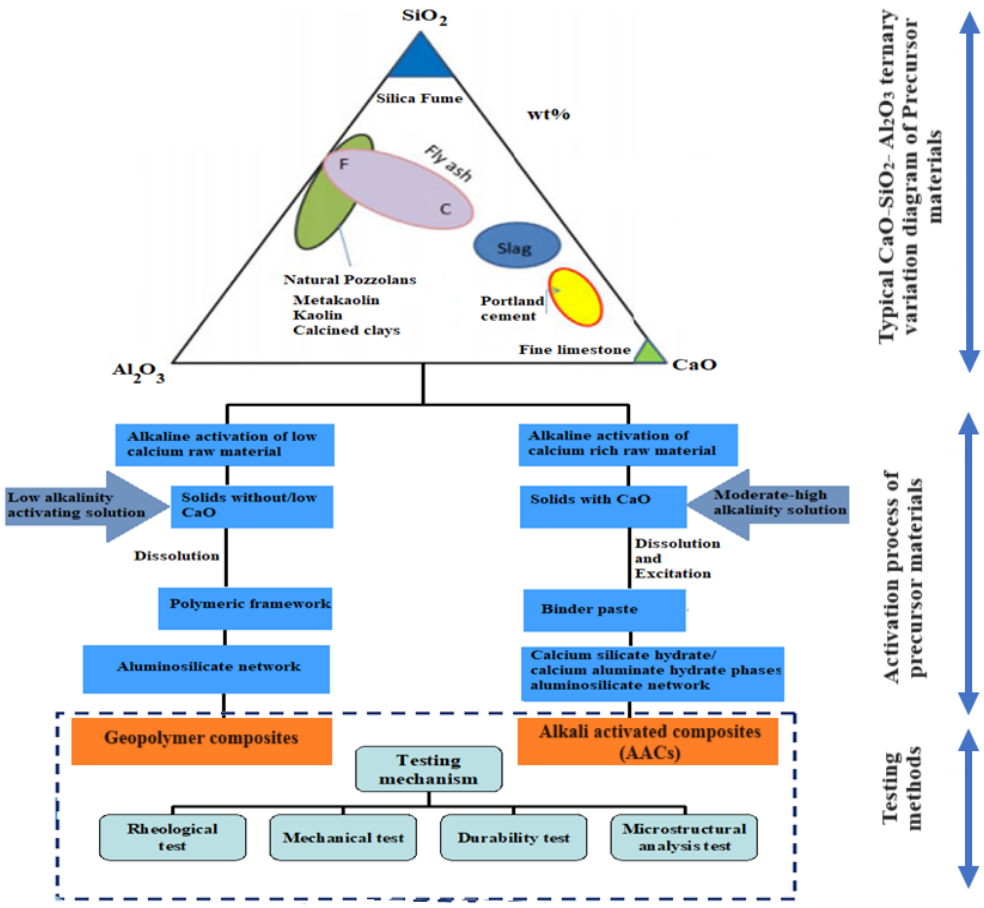

Figure 1 Process flow involved in synthesis and testing AAC/geopolymer composites.

Geopolymerization technology is an appealing and innovative product that creates environmentally friendly concrete. Geopolymers are significant substitute materials that can be utilized to promote sustainability and recycling [13]. The geopolymerization of aluminosilicates differs significantly from the chemistry of Portland cement, which is based on calcium silicate hydrates [14]. Geopolymer concrete's binder is geopolymer cement, made from alkaline activated aluminosilicates found in natural clays or industry byproducts. Alkaline activation involves a precursor and an alkaline activator [15]. Aluminosilicate precursors such as metakaolin, fly ash, ground granulated blast furnace slag (GGBFS), silica fume, and rice husk ash are typically used as precursors for geopolymer cement. At the same time, sodium silicate, potassium silicate, and sodium hydroxide are the commonly used alkaline activators [16].

In contrast to OPC, the synthesis of geopolymer cement requires reduced energy consumption of raw materials. Energy consumption to produce geopolymer concrete can be attributed to preparing the activating solution, producing sodium hydroxide, and, if applicable, external heat for curing [17]. However, sodium silicate activator production requires less thermal energy, producing small CO_2 emissions [18]. The durability of geopolymer is attributed to the production of sodium aluminosilicate hydrate (N-A-S-H) gel. The geopolymerization mechanism involves destruction, coagulation, and crystallization [19]. The breakdown of the aluminosilicate structure by hydroxide ions from an alkaline activator initiates the polymerization process. The degree of dissolution of silicate and aluminate species controls this process. Aluminosilicate oligomers are created due to interactions between the tiny dissolved species and any silicate that the activating solution initially supplied [20].

The durability of geopolymer concrete exposed to an aggressive environment has been reviewed critically by Chen et al. [21]. Still, there is a lack of comprehensive literature on fibrous geopolymer and the mix design that can maximize the construction material's long-term robustness. Similar to OPC-based materials, the utilization of geopolymer composites is constrained under higher flexural and tensile stresses due to its inherent quasi-brittle nature. The brittleness in composites increases their susceptibility to crack formation, eventually impacting their mechanical and durability performances. As a remedial measure, incorporating fibers into geopolymer composites has been found to enhance their flexibility, shrinkage resistance, and flexural and tensile capacity [22-25]. The addition of steel fibers to the geopolymer concrete beam-column joints was found to improve their flexibility, energy absorptivity, and toughness. Steel-fiber-reinforced alkali-activated geopolymer concrete is a viable building material option for buried tunnels that could explode from gas because it can achieve extraordinary mechanical performance and emit fewer carbon emissions than conventional concrete [26]. In a different study, Alrshoudi et al. [27] improved high-strength geopolymer concrete's compressive strength and flexibility by adding glass and carbon-fiber-reinforced polymers. In addition, fiber-reinforced concrete has fair durability in terms of water permeability, impact resistance, abrasion resistance, drying shrinkage, and penetration of chloride ions [28].

The incorporation of fibers such as Polyvinyl Alcohol (PVA), Polyvinyl Chloride (PVC), polypropylene, steel, etc., in geopolymers, despite having high embodied energy and carbon, results in composites with much lower global warming impact compared to materials made from OPC [29]. The reinforcement of fibers, besides impacting the mechanical properties [30], has a significant impact on durability [31], particularly while dealing with the most pernicious forms of deterioration such as chloride attack, freeze-thaw, water absorption, sulfate attack, and acid attack [32].

However, understanding the performance of fibrous geopolymer composites at the microstructural level and the physical/chemical processes causing deterioration due to extreme environmental conditions needs further research and articulation. Another detailed study by Ganesh et al. [33] investigated the influence of plastic waste in PET bottles ground into a powdered form. There was an increase in the compressive and split tensile strengths of geopolymer concrete, which increased by 5.8% and 24%, respectively, when 10% plastic powder was used as a partial replacement for sand. Table 1 details the influence of different fiber types on geopolymers and alkali-activated composite mixes.

Table 1 Influence of different fiber types on geopolymers and alkali-activated composite mixes.

Fiber type	Key properties	Performance in Geopolymer/AAC
Steel	Porosity, toughness, absorptivity, and sulfate resistance	Improve mechanical properties, suitable for use in buried tunnels that could explode from gas and emit fewer carbon emissions [26]. Densification of the overall mixes and improving the fiber-matrix interface [24]. Reduced water absorption. Increased weight gain after exposure to 90 cycles of freeze-thaw. It is durable against the dual impact of sulfate corrosion and the drying-wetting cycle [34]. Improved performance in the acidic medium [35].
Plastic waste	Porosity, absorption	Reduces the absorption rate in composite mixes.
Bamboo fiber	Acid resistance	Bamboo fiber has a negative influence on geopolymer composites exposed to sulfuric acid. In addition, a decrease in compressive strength and mass loss were observed [36].
Glass and carbon fiber	Compressive strength, resistance against leaching	Improved compressive strength and ductility of high-strength geopolymer concrete means it has fair durability in terms of water permeability [27]. It showed enhancement against hydrochloric acid due to micro-crack reduction [37]. Improved performance in the acidic medium [38].
Polyvinyl alcohol Fiber	Impact strength and stiffness, freeze-thaw resistance, sulfuric acid resistance, chloride penetration.	Improvement of freeze-thaw resistance and sulfate attack [39-41]. Enhance stiffness and no noticeable decrease in impact strength [39]. Reduction in chloride penetration [42].
Cotton and polypropylene fiber	Porosity, freeze-thaw, electrical resistivity, rapid chloride migration	Increase porosity of the mix, resulting in a loose fiber-matrix interfacial bondage. Enhanced freeze-thaw resistance. There is no improvement in the mechanical properties of composites when exposed to freeze-thaw [43, 44]. Mixes showed improved mechanical properties as well as durability [45].
Polyethylene terephthalate	Tensile strength, resistance to chemicals	Increase absorption and give rise to the porous surface [46].

Curaua fiber	Compactness	Improves the durability and reduces the absorption of the composites.

The present review aims to apprehend the durability study undertaken in fiber-reinforced geopolymer and alkali-activated composites (AACs). To facilitate that, VOS viewer software was used for scientific mapping and quantitative assessment of listed keywords in CSV files obtained from the Scopus database. Figure 2 depicts the visualization of keywords concerning co-occurrence and density of occurrence in 529 manuscripts received from the Scopus database. The 529 manuscripts were aggregated from the Scopus database based on a title search of “fiber-reinforced geopolymer concrete”, “fiber-reinforced geopolymer composite”, “fiber-reinforced alkali-activated concrete” and “fiber-reinforced AACs”. As evident from the figure, the historical data reveal a lack of research into the durability aspect of the fibrous geopolymer and AACs compared to the mechanical properties.

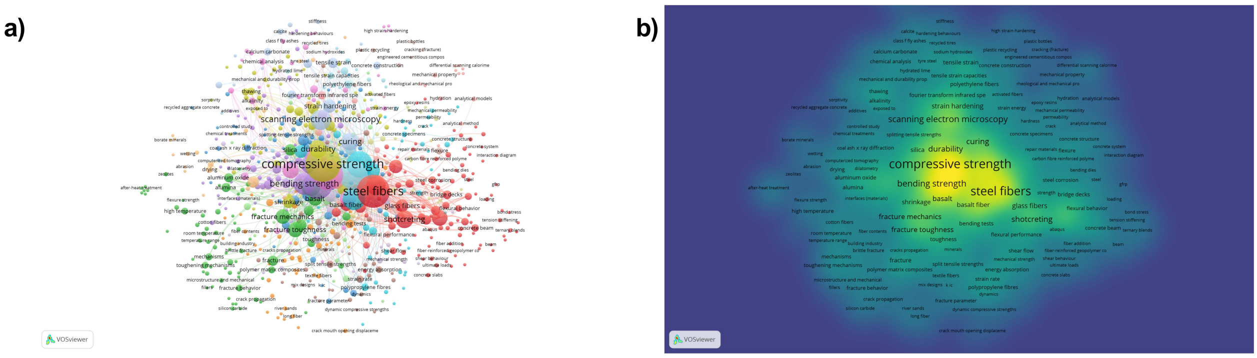

Figure 2 Mapping the keywords in geopolymer and alkali-activated composites a) Network mapping b) Density mapping.

For sustainable construction and the deliverance of intended performance over the service lifetime, the durability aspect of the cementitious materials needs equal consideration, if not more. This manuscript presents a thorough and updated review of the research work undertaken to assess the effect of chemical transgression on the durability of fibrous geopolymer and AACs. The multi-parameters and factors that critically influence the durability of fibrous geopolymers are studied and summarized in this paper. This review focused on six sectional topics: porosity, water absorption, and sorptivity; freezing and thawing resistance; sulfate resistance; acid resistance; and chloride permeability.

2. Porosity

The state of permeability, number, and size of voids in the composite provides transgressional access for the movement of water and other harmful materials into the composite. The susceptibility of the composite to deteriorating attacks from extreme environmental conditions increases with the increase in permeable voids, i.e., porosity. Studies have reported a reduction of the average effective porosity from 7.1% to 6.7% and 10.8% to 9.9% for AACs incorporated with steel fibers, in the range of 0.5–1 vol.% [47] and at 120 kg/m^3 [48], respectively. This is evident from the 14-day and 28-day evaluations of the composites. F80/G20NS means the composite mix contains 80% fly ash and 20% GGBFS with natural sand as fine aggregate. Also, LSS and WGS represent ladle slag sand and waste glass sand, respectively. Ahmad et al. [49] also assert that the porosity and absorption for all mortar mixes evaluated at 28 days decreased when plastic waste replaced the sand proportion. The flow of the matrix around the fibers and the fiber bridging across the micro-cracks reduced the void interconnection and densified the matrix in both studies (Figure 3). Similarly, the disposition of extra hydration products on and around fibers due to an increase in ground granulated blast furnace slag (GGBFS) content in steel fiber reinforced ternary binder mix geopolymer concrete with fly ash, silica fume and GGBFS resulted in overall densification and reduction in porosity [24]. The steel fibers in all these cases have acted as matrix "holding sites" rendering enhanced fiber-matrix interface.

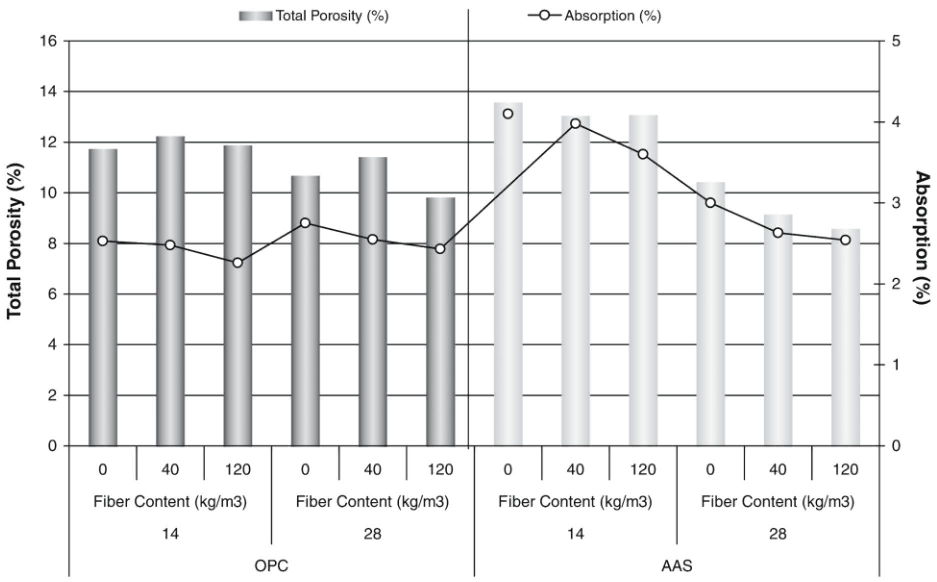

Figure 3 Influence of steel fiber content on total porosity/absorption in OPC and alkali-activated concrete [48].

Contrarily, the inclusion of 1 wt.% of cotton fiber content has increased porosity from 20 to 30% in AACs due to the voids induced into the matrix by fibers, resulting in weak fiber-matrix interfacial bondage. The higher porosity of composites may also be associated with the accumulation, decomposition, and dehydration of cotton fibers at higher dosages [50]. Similarly, incorporating polypropylene fiber at 0.05, 0.10, and 0.20 vol.% increased porosity by 11, 14, and 18%, respectively [51].

3. Water Absorption and Sorptivity

Water absorption and sorptivity indicate the relative ease with which deleterious ions and chemicals transgress into the composites and change their performance in terms of strength and durability. The incorporation of sisal fibers up to 2 wt.% and pulp and polypropylene fibers between 0.5 – 2 wt.% has shown a moderate reduction in water absorption due to the synergetic interaction between fiber and matrix that enhanced the packing density of composites [52]. Using polyethylene terephthalate (PET) to replace varying volumes of sand fractions at 10%, 20%, and 50% increases water absorption in that order [46]. Albano et al. [53] evaluated the influence of various PET aggregate sizes and the rate of replacement obtained from shredded bottles. The depth of water penetration was investigated, and the results revealed that gradually increasing the size and number of polymer aggregate fibers decreased the water permeability of concrete by a substantial amount (17-42%). Choi et al. [54] investigated the replacement of natural aggregates with PET fine aggregate in mortar mixes and reported a higher sorptivity coefficient. The inclusion of NaOH-treated Curaua fiber at a dosage of 2% in mortar has also been reported to have shown improvement in durability, in terms of water absorption, due to enhancement in composite compactness [55]. Ganesan et al. 2015 [47] reported reduced water penetration into concrete pores by capillary action due to the use of steel fibers. The sorptivity of the composite reduced from 2.85 × 10^{-3} cm/$min^{1/2}$ for non-fibrous concrete to 2.11 × 10^{-3} cm/$min^{1/2}$ for concrete with 1% vol. fraction of steel fiber content. The improvement in durability due to fiber addition, in lower content, was due to the flow of concrete around the fibers and fiber bridging that led to minimal interconnecting voids. Similar results of reduced water absorption were reported for AACs incorporated with 40 and 120 kg/m^3 of steel fibers (Figure 3). A maximum reduction of 20% in water absorption was recorded for a maximum steel fiber dosage of 120 kg/m^3, probably due to reduced total porosity and fiber bridging effect [48]. Incorporating 2% nano-silica and 1% polypropylene fiber showed lesser water absorption of 7.6% in fly ash GGBFS-based AACs, compared to 8.9% in the control non-fibrous mix. The authors attributed the results to the enhancement of matrix compactness due to the interaction of synthetic fibers and silica fume [56].

On the Contrary, an enhancement in water absorption due to the addition of polypropylene fiber [57], as well as hybrid glass and polypropylene fibers [47], was reported due to the hydrophobicity of the synthetic fiber and accumulation that resulted in the creation of additional pores within the matrix. The increased number and size of pores eventually resulted in higher transgression of water into the concrete. Similarly, compared to non-fibrous composites with lead smelter slag/waste glass sand, water absorption increased due to the incorporation of natural fibers due to fibers' porous nature and moisture absorption ability. The geopolymer composite with ramie fibers showed 17% and 29% higher water absorption than non-fibrous composites in 80% fly ash/20% GGBFS and 50% fly ash/50% GGBFS series, respectively. F80/G20NS means the mix contains 80% fly ash and 20% GGBFS with Natural sand as fine aggregate. Also, LSS and WGS represent ladle slag sand and waste glass sand, respectively. The composite with hemp fibers showed water absorption, which was 3% higher than the non-fibrous composites. An increase in ramie fiber dosage from 1% to 2% resulted in a rise of 3% in water absorption of geopolymer composite for a given binder proportion and sand type (Figure 4) [58].

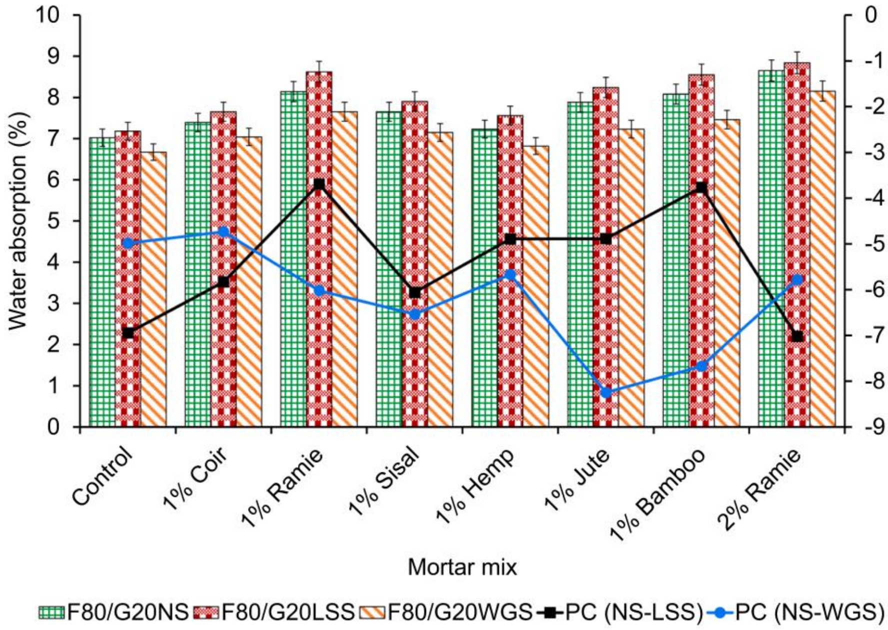

Figure 4 Influence of various natural fiber types and content on water absorption of geopolymer composites [58].

4. Freezing and Thawing

The water freezes and expands to about 9 vol.% under the influence of freezing-thawing cycles, leading to the development of hydraulic pressure within the micro and mesopores of previous composites [59]. The solution concentration in the pores increases during the freezing cycle, which causes a vapor pressure difference, leading to the diffusion of water from the gel pores into adjoining pores and voids, thereby causing drainage and osmotic pressure on the composite microstructure. Furthermore, the wide gap between the thermal expansion coefficient of the composite material and the coarse aggregate (especially in higher strength/performance concretes) induces thermal stresses, leading to microstructural degeneration of the composite during cyclic temperature alternation. The frost action and the difference in thermal expansion eventually develop pressure in adjacent areas, resulting in micro and macroscopic cracks and subsequent reduction in strength and durability [60, 61].

Crystal, gel, and free water are the three forms of water in cementitious composites. While the crystal and gel water don't freeze due to the smaller pore sizes of the gel pores and the inability of the bubble hole to retain water, the free water in the capillary pores freezes at minus temperatures. During the freezing, the chemical composition of the water inside the composite remains unchanged, while as the physical state changes, that eventually impacts the density of the previous microstructure. Therefore, the resistance against freezing-thawing in composites can be effectively enhanced by decreasing the composite structure's pores and strengthening the microstructure's compactness [24]. Even though, compared to conventional cementitious composites, geopolymers are expected to withstand higher pressures caused by the freeze-thaw environment [62], the incorporation of fibers not only improves the toughness of materials but also enhances the ability to reduce the crack proliferation and coalescence further.

An increase in weight and compressive strength was observed in a GGBFS-based geopolymer composite incorporated with steel fibers after exposure to 90 cycles of freeze-thaw. The weight gain was attributed to the deposition of gypsum and ettringite in the voids, which formed due to the accumulation of penetrated sulfate particles. The increase in compressive strength was attributed to the densification caused by the crystallization of reaction calcium silicate products and the exertion of internal confinement due to pressure from expanded elements. The improved performance in fibrous composites was attributed to steel fibers' fiber-bridging and confining effects. The composites with 6 mm long steel fiber, 12 mm long steel fiber (12 mm), and non-fibrous composites recorded an average compressive strength increase of 10.50, 10.60, and 6.70%, respectively. Baring minor micro-cracking with slight surface abrasion, no significant changes in the external appearance of the specimens were reported [63].

Substantially higher freeze-thaw resistance was reported in metakaolin/fly ash-geopolymer composites reinforced with PVA short fibers and manufactured by extrusion technique, with marginal enhancement in impact strength and stiffness, under exposure to 20 freeze-thaw cycles. The authors reasoned the enhancement to the counterbalancing ability of fibers against the internal stresses developed by cyclic water freezing. The study further reported similar improvement of impact strength in PVA-reinforced metakaolin-based composite (without fly ash), post-freeze-thaw, due to the densifying and compacting ability of fibers that resulted in minimum void space for water transgression and therefore negligible freeze-thaw deterioration. The authors also attributed the continued polymerization under the humid conditions of the extended freeze-thaw test as a contributory factor for strength increase [39]. Similar results of enhanced freeze-thaw resistance under the coupled attack of sulfate and 150 cycles of freeze-thaw [40] and 300 cycles of freeze-thaw [41] were reported due to PVA fiber incorporation. The composites incorporated with polypropylene fibers [64] and basalt fiber [65] also showed similar results of enhanced freeze-thaw resistance.

Contrary to the above, Kuranlı et al. 2022 [43], while investigating the influence of incorporating three different fiber types of polypropylenes, steel, and polyamide on the freeze-thaw resistance of slag-fly ash-based geopolymer concrete, observed no improvement in residual compressive strength or general freeze-thaw resistance properties of concrete, due to fiber addition. Compared to the non-fibrous control mix, the fibrous series showed lesser or equivalent compressive strength after exposure to freeze-thaw. Even though concrete with 0.4 vol.% of steel fiber showed an improvement of 7.87% in residual compressive strength, this improvement turned negative as the steel fiber content was increased to 0.8%. Further, while the study attributed the improvement in the residual flexural strengths in non-fibrous mixes to the continued polymerization process during freeze-thaw, the addition of fibers showed no improvement in the flexural strength under the freeze-thaw effect compared to the control mixes (Figure 5). Similarly, Puertas et al. 2003 [44] reported higher stability of activated slag mortars than fly ash or cement mortar against 50 cycles of freeze-thaw test. Furthermore, incorporating polypropylene fibers was reported to have no significant effect on the freeze-thaw resistance of different composite types. The incorporation of 0.5% polypropylene fiber in fly ash showed the highest enhancement (even though marginal) of 0.6 MPa in flexural strength and 6.3 MPa in compressive strength.

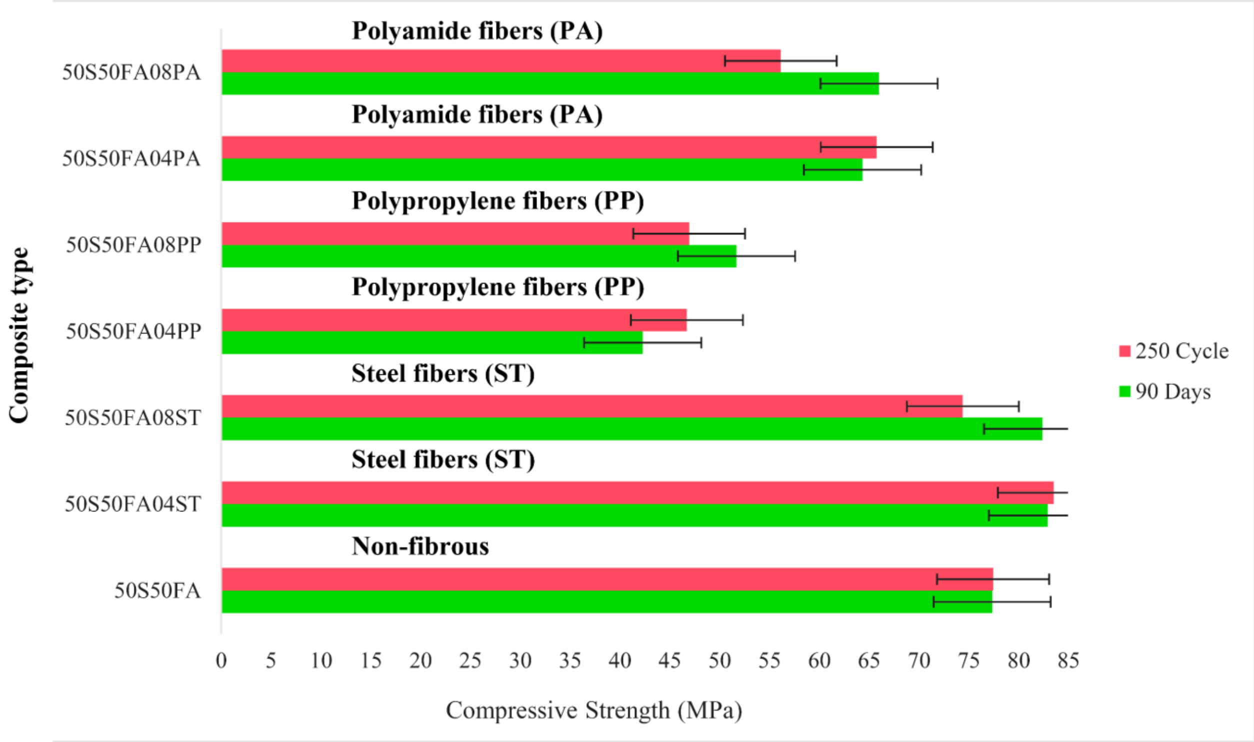

Figure 5 Influence of various fiber types and content on freeze-thaw resistance of composite [43].

5. Sulfate Resistance

The inadequacy of a composite to resist continued sulfate solution exposure results in considerable changes in its weight and compressive strength. While the weight of the composite primarily depends on the dissolution of the paste into the solution and/or the absorption of the solution into the geopolymeric micro-structure [66], the compressive strength is primarily governed by continued geopolymerization process impacting porosity [34, 67] and/or the dissolution/leaching status of alkali and Si from the geopolymer matrix into the sulfate solution [34, 67, 68]. Stability and enhancement in compressive and flexural strength of fly ash and steel slag-based geopolymer composite specimens exposed to the dual impact of sulfate corrosion and drying-wetting cycle processes were reported due to the incorporation of polypropylene, basalt, and steel fibers. After 15 cycles, the composite with 0.4 vol.% steel fiber recorded the highest compressive strength of 67.9 MPa, and the composite with 0.3 vol.% basalt fiber recorded the highest compressive strength growth rate of 96.6%. In terms of mass loss, after 15 cycles, the composite with 0.2% polypropylene fibers showed a minimal mass loss of 3.5%.

In contrast, the mass loss of samples with other fibers was lower than 5.0%, indicating moderate mass loss and minimal deterioration of sample microstructure due to cyclic drying-wetting and the corrosive effect of sodium sulfate solution (Figure 6). The authors attributed the enhanced performance to the crack-reducing ability of fibers through fiber bridging and compactness that eventually restricted the ion transgression into the composite microstructure [69]. Similarly, due to the addition of short basalt fibers, substantial enhancement in sulfate and chloride attack resistance was observed in metakaolin-based geopolymer composite incorporated with wollastonite/tremolite. Under the exposure of Na_2SO_4 and NaCl solutions, the mix with 2% basalt fiber and 5% wollastonite and tremolite recorded the highest compressive strength. The enhancement was attributed to the intense basalt fibers-matrix bondage and the compact composite microstructure [70].

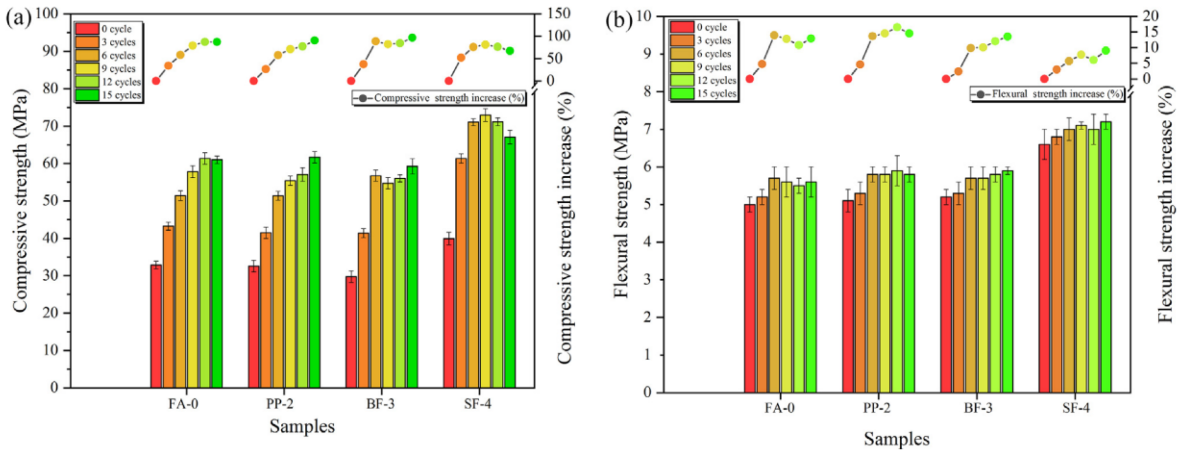

Figure 6 Influence of fly ash (FA), polypropylene (PP) basalt (BF), and steel (SF) fiber types and content on the a) compressive and b) flexural strength of the composite after sulfate solution exposure [69].

Guo et al. 2020 [71] investigated the sulfate resistance of metakaolin-based geopolymer composites reinforced with polypropylene fiber, PVA fiber, and wollastonite. The study concluded that incorporating polypropylene and PVA fiber in hybrid form and wollastonite, inorganic mineral microfiber, in geopolymer composite effectively resisted sulfate attack. The multipronged effect of two different types of fibers enhanced the residual compressive strength of the composites (Figure 7). While polypropylene fibers with a lower elastic modulus may have weaker bonding with the matrix, their uniform distribution and large number of filaments) In the matrix, crack initiation is delayed during the initial loading period.

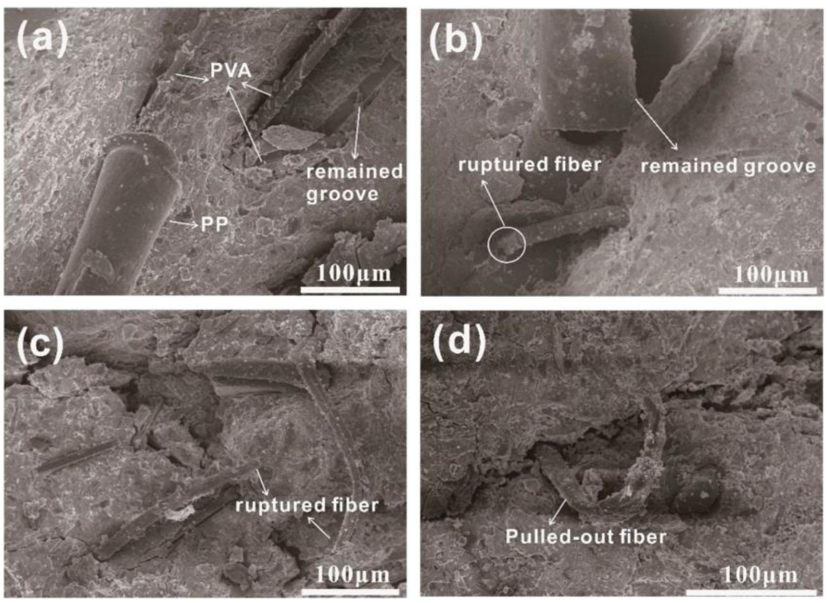

Figure 7 Fractured image of samples with PVA and polypropylene fibers, post-sulfate exposure [71].

In contrast, PVA fibers with a higher elastic modulus inhibit the coalescence of cracks from micro to macro, limiting damage in specimens to elastic deformation [72]. Steel fiber-reinforced GGBFS-based geopolymer composites exposed to seawater and different sulfate concentrations for 180 days showed increased compressive strength and weight gain, with Na_2SO_4 solution resulting in the highest weight gain and seawater being the least. The fibrous composites showed a maximum weight gain of 2.42%, which was quite reasonable. The enhancement in compressive strength was attributed to the densification of the microstructure due to the crystallization of hydration and pozzolanic reaction products of calcium silicates in the pores. An average compressive strength gain of 31%, 26%, and 15.3% was attained for composites exposure to Na_2SO_4, $MgSO_4$ solutions, and seawater. Incorporation of 6 mm long steel fiber exhibited better results than composites with 12 mm long steel fibers due to their uniform distribution and relatively lesser accumulation [63]. Similar results of enhanced durability were reported by [40] for concrete structures under marine conditions of sulfate erosion and freeze-thaw cycles due to PVA fiber reinforcement.

Rashidian-Dezfouli & Rangaraju, 2017 [66], while comparing the sodium sulfate resistance of geopolymers made from three different source materials, fly ash, ground glass fiber, and glass powder, observed significantly better performance of ground glass fibers (GGF) and fly ash-based geopolymers, compared to the glass powder based geopolymer. The study further attributed the superior sulfate resistance to multi-factors that include the micro-filler effect of aluminosilicate-rich GGF that enhanced the delicate aggregate-paste bondage due to finer particle sizes, the role of unreacted cylindrical-shaped GGF particles of more complex nature that act as a reinforcement that enforces circumvention of initiated cracks, and the pozzolanic reactivity that resulted in lower calcium hydroxide content compared to mixes based on other source materials.

6. Acid Resistance

The extent of acid transgression within the composite and the acid type, its concentration, and pH have an enormous impact on the overall loss of alkalinity, weight, and compressive/flexural strengths of the material. The corrosion in metallic fibers or reinforcements is mitigated by the passive state developed by the presence of soluble silicates in the highly alkaline pore solution with a pH nearing 13.5 [38, 73, 74]. For low calcium fly ash-based geopolymer concrete exposed to 3% sulfuric acid solution for 180 days, the addition of steel fibers improved the microstructural durability of both geopolymer and conventional cement concrete. Compared to the average compressive strength deficit of 20.01% in plain geopolymer concrete, the strength deficit in steel fiber reinforced geopolymer concrete was relatively lower at 19.10%, even though the average weight loss in plain geopolymer composites was lower (1.82%) than the steel fiber reinforced geopolymer concrete (2.19%). The authors attributed the enhancement to the concrete flow around the fibers and the fibers bridging across the micro-cracks that led to the depreciation of the void's ratio. Also, due to the lower calcium content in the fly ash, the formation of calcium sulfate was lesser in quantity, which enhanced its resistance to H_2SO_4 attack [47]. Similarly, the stability and acid resistance of metakaolin-based geopolymer incorporated with glass fiber in 5.0 and 2.5 wt.% against leaching in 0.2% HCl showed enhancement due to the micro-crack reduction by fiber bridging. Despite decomposition due to increased macro-porosity, post-leaching, the optimal glass fiber content withstood leaching, improved mechanical properties, and reduced open porosity [37].

Yunsheng et al. 2008 [39] investigated the impact of fly ash and PVA fiber content on the sulfuric acid resistance of metakaolin-based geopolymer composite manufactured by extrusion technique, exposed to H_2SO_4 of pH = 1 for 30 days. After 30 days of the H_2SO_4 solution attack, no noticeable decrease in impact strength and stiffness was observed for various PVA-reinforced composites. In some cases, some enhancement was also observed, attributed to micro-crack reduction by fiber bridging. Similarly, a positive effect of the carbon fiber waste on the open porosity and acid attack resistance of GGBFS-based geopolymer composite was observed mainly because of the porosity created due to the generation of the voids between geopolymer gel and the carbon fiber waste particles, which behaved as an inert material and generated spaces to calcium-sulfate products precipitation. The composites with 20% carbon fiber waste showed the maximum compressive strength, post-acid attack, due to the penetration of sulfate ions into the pore structure and its reaction with calcium ions, resulting in the formation of calcium-sulfate products, which eventually precipitate into the open pores. Depending on porosity, pore size distribution, and content of calcium-sulfate formation, the voids get filled and densified, thereby making the microstructure more compacted and stronger [75]. Similar results of improved performance due to enhanced fiber-matrix interface and fiber bridging under acidic conditions due to basalt and carbon fibers [38] and steel fiber [35] were reported in the literature.

Contrarily, the sulfuric and hydrochloric acids resistance of metakaolin-based geopolymer composite incorporated with bamboo fiber, exposed for 112 days in varied acid concentrations of 0 to 15 wt.%, showed a negative influence. Compared to an average mass loss of 14 and 11% in sulfuric and hydrochloric acid, after 112 days of immersion, the composite with bamboo fibers showed a mass loss of 18%. Both fibrous and plain geopolymer composites showed no mass loss in 0 wt.% acid (100% water) solutions. Exposure to sulfuric acid with a concentration of 15 wt.% resulted in minor visible cracks on the surface sample and the darkened appearance of bamboo fibers due to the dissolution of biological matter of the bamboo fibers. The compressive strength of bamboo fiber-reinforced composites was reduced with the increase in immersion time of 7 to 28 days in both solutions, from 8.1 to 7.7 MPa and 9.3 to 7.1 MPa, while as the mass loss increased from 2.26 to 2.42% and 1.04 to 2.38%, respectively. The relatively higher loss of compressive strength in bamboo fibers reinforced geopolymer composites was attributed to lower fiber modulus and voids created by the agglomerated fibers in the matrix [36].

7. Chloride Permeability

Chloride attack is a prominent cause of degradation of marine structures, especially the reinforced concrete, and worsens with the increase in permeability of the composite [76]. Mousavinejad & Sammak. 2021 [45] experimentally investigated the chloride ion penetration resistance of steel and polypropylene fibers incorporated in GGBFS-based geopolymer concrete. Electrical resistivity, rapid chloride migration test, and rapid chloride penetration tests were conducted to assess the chloride ion penetration resistance of the concrete. The results showed that incorporating polypropylene fibers into steel fiber samples improved its mechanical and durability properties. Further increase in the replacement of steel fiber content with polypropylene fiber reduced the passing flow through the concrete, even though it reduced the mechanical strength of the concrete. Ren et al. 2017 [70] evaluated the durability performance of short basalt fiber reinforced metakaolin-based geopolymer incorporated with wollastonite and tremolite by exposing it to the sodium chloride (NaCl) solution with a concentration of 5–20%. The highest compressive strength was shown by composite mixes with 5% wollastonite, 5% tremolite, and 2% basalt fibers. The loss in compressive strength after exposure to chloride attack is due to micro-cracking and increased porosity/void ratio. The residual compressive strength of geopolymer composites decreased with the increased retention time or concentration of NaCl solutions. The study concluded that incorporating mineral particles and basalt fibers is an effective way to enhance the resistance to chloride attack and the compressive strength of geopolymer composite (Figure 8).

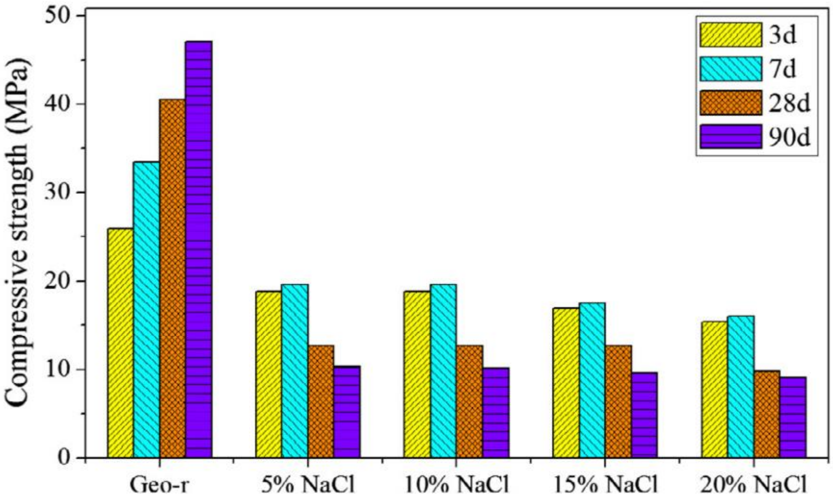

Figure 8 Residual compressive strengths after exposure to chloride solution for 3, 7, 28, and 90 days [70].

Rani et al. 2022 [77] studied the influence of polypropylene fiber incorporation on the properties of geopolymer composite subjected to different durability tests. The rapid chloride penetration test revealed inhibition in chloride penetration due to polypropylene fiber incorporation. After 8 weeks of exposure to chloride attack, the samples showed a significantly lower mass loss, with the highest loss within 1.67%, indicating minimal leaching and penetrability in the fibrous geopolymer concrete. Fibrous concrete's reduced compressive strength deficit was due to enhanced resistance to chloride solution penetration and fiber bridging instilled by incorporated PVA fibers. Compared to conventional plain geopolymer or OPC concrete, Mohseni et al. 2019 [78] reported relatively higher chloride penetration resistance of polypropylene fiber-reinforced rice husk ash and nano-Al_2O_3 lightweight geopolymer. The study, however, attributed the enhancement in chloride penetration resistance to the close rice husk ash-nano-Al_2O_3 rather than including polypropylene fiber. Similar results of enhancement in chloride penetration resistance and water permeability of composites incorporated with 0.25 to 1% of 0.5 mm diameter and 30 mm long steel fibers hooked end steel fibers were reported by Ganesan et al. 2015 [47]. Contrarily, Deng et al. 2022 [42] reported a reduction in chloride penetration resistance due to an increase in PVA fiber content in alkali-activated GGBFS and fly ash geopolymer composite, owing to increased porosity, the increased number of connected pores and the hydrophilicity of the PVA fibers. Even though the chloride resistance decreased with the increase in PVA fiber content, the total charges passed were within the range of 1000–2000 C, which was well within the permissible limits prescribed by ASTM C1202-19 (Figure 9).

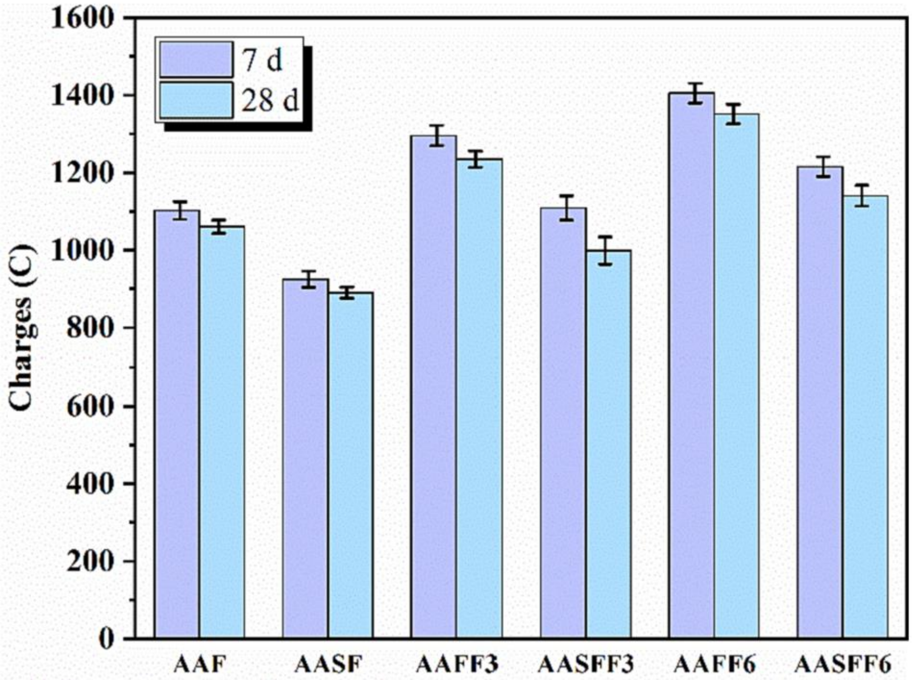

Figure 9 Depicting charge passage through AAF (alkali-activated fly ash) and AASF (alkali-activated slag fly ash) with 0, 0.3, and 0.6%vol, fraction PVA fiber [42].

8. Conclusion

This paper has explored the influence of fiber reinforcement on the durability performance of geopolymer composites. Based on the discussions made in this paper, the following conclusions are drawn:

- The incorporation of steel fibers in the lower range (approximately around 1%vol. fraction) has resulted in a slight reduction in the porosity of the composite due to the flow of matrix around the fibers, providing deposition sites for reaction products and the fiber bridging across the micro-cracks, that reduces the voids inter-connection and densifies the matrix.
- The margin of reduction in water absorption and sorptivity due to the synergetic interaction between fiber and matrix, which enhanced the packing density of composites, is delicately poised on the fiber type, fiber content, and the type of source material in use.
- The inclusion of celluloid fibers like cotton fibers and low-modulus fibers like polypropylene has shown an increase in porosity due to voids induced into the matrix from weak fiber-matrix interfacial bondage and workability deficit.
- Overall, substantial enhancement in freeze-thaw resistance has been observed due to the fiber incorporation, resulting from fiber bridging and confining effect, that counterbalances the internal stresses caused by water freezing.
- Fiber incorporation has shown substantial enhancement in sulfate, acid, and chloride attack resistance due to the crack-reducing ability of fibers through fiber bridging and compactness that eventually restricted the ion transgression into the composite microstructure.
- Since the impact of fiber inclusion on the durability properties of geopolymer composites varies vastly, it is imperative to optimize different geometrical and quantitative properties like aspect ratio, fiber density, etc., for each fiber type, and a comprehensive database needs to be developed before it is used on a large scale.

- The synergetic behavior of different fibers with different precursors and alkali-activating solutions needs to be studied in detail regarding sustainability and mechanical strength. A comprehensive database in this regard shall go a long way to enhance its viability as a commercial product.
- The use of polypropylene and natural fibers is found to be detrimental to the freshness and durability properties. Therefore, it is recommended to investigate using fibers in hybrid form.

A study needs to be undertaken to assess the environmental and economic impact of eliminating heat curing requirements and the longevity provided by fiber reinforcement for different source materials.

Author Contributions

KZF made contribution in conceptualizing, analysis and drafting of the manuscript. ASS made contribution in revision of the manuscript and analysis of data. ABA made contribution in the accumulation of historical data and general literature review. All authors read and approved the final manuscript.

Competing Interests

The authors have declared that no competing interests exist.

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