



Review

Recent Advances in Geopolymer Technology. A Potential Eco-Friendly Solution in the Construction Materials Industry: A Review

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Abstract: In the last ten years, the Portland cement industry has received wide criticism due to its related high embodied energy and carbon dioxide footprint. Recently, numerous “clean” strategies and solutions were developed. Among these, geopolymer technology is gaining growing interest as a functional way to design more eco-friendly construction materials and for waste management issues suffered by various industries. Previous research has highlighted the attractive engineering properties of geopolymeric materials, especially in terms of mechanical properties and durability, resulting in even higher performance than ordinary concrete. This review provides a comprehensive analysis of current state-of-the-art and implementations on geopolymer concrete materials, investigating how the key process factors (such as raw materials, synthesis regime, alkali concentration, water dosage, and reinforcement fillers) affect the rheological, microstructural, durability, and mechanical properties. Finally, the paper elucidates some noteworthy aspects for future research development: innovative geopolymer-based formulations (including alkali-activated blends for additive manufacturing and thermo-acoustic insulating cellular compounds), concrete applications successfully scaled in the civil-architectural fields, and the perspective directions of geopolymer technology in terms of commercialization and large-scale diffusion.

Keywords: geopolymer technology; carbon dioxide emission; alumino-silicate sources; rheology; mechanical properties; durability; microstructure; thermo-acoustic properties; additive manufacturing; civil applications



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1. Introduction

If the cement industry were a country, it would be the third-largest carbon dioxide (CO₂) emitter in the world, preceded by China and U.S.A. Portland cement (PC) production is responsible for 5–8% of all man-made carbon-based greenhouse emissions across the globe, corresponding to 0.6–0.8 kg of CO₂ generated for every kg manufactured [1,2]. The entire cement production chain (Figure 1), including the extraction of raw materials from the mine and their preparation, the calcination process in the clinker furnaces, and the thermal emission related to the process selectively contributes to the release of CO₂.

Almost half of the CO₂ production is associated with the production of clinker, one of the main components of PC, by high-temperature pyro-processing (about 1500 °C) of raw materials. The remaining emissions are mainly due to the combustion of fossil fuels for calcination and the pre-treatment and preparation of mineral precursors (quarrying, grinding, and transportation) [3]. Due to the rapid urbanization and economic development, the market for cementitious products is constantly growing. It has been estimated that in the next 40 years, the use of concrete materials for civil and architectural works will double, requiring PC production to increase by a quarter by 2030 [1]. In this regard, the research and

design on cement and concrete products with eco-sustainable peculiarities have increased in recent years. For instance, the World Green Building Council (WGBC) has recently published guidelines and strategies for the “green” design of buildings and infrastructures capable of reaching 40% less embodied carbon emissions by 2030 and achieve 100% net zero emissions buildings by 2050 [4]. These actions mainly involve the use of alternative fuels (i.e., processed waste materials) for the clinkering, the adoption of carbon capture and storage systems, the improvement of energy-efficiency of the cement plants, and the development of novel low-impact cement and binding technologies [1].

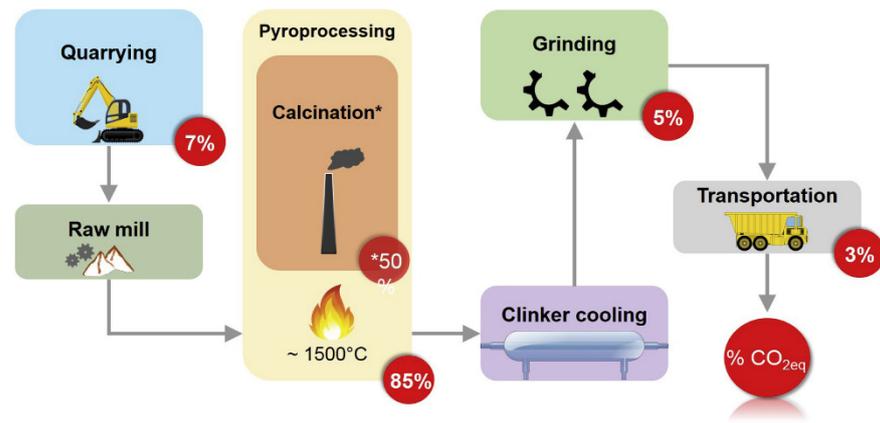


Figure 1. Diagram on PC manufacturing chain and the CO₂ emission rate (in percentage) associated with each stage (reproduced with permission from Maddalena, R. et al., *Journal of Cleaner Production*; Elsevier, 2018).

According to the last point, this review focuses on recent investigations of geopolymer cements (GCs) as promising alternative candidates to ordinary PC for developing various sustainable products in building, industrial, and architectural fields. Geopolymer materials are zero-PC binders formed through a polycondensation reaction of aluminosilicate sources, derived from waste by-products, in alkaline solutions. The process, commonly defined as “geopolymerization”, produces a three-dimensional (3D) inorganic network with an amorphous/semi-crystalline microstructure. Unlike the ordinary PC, in which calcium silicate hydrates (C-S-H) gel is the main binding compound, GC utilizes the polycondensation of Silica (SiO₂) and alumina (Al₂O₃) sources and a high-alkali environment to obtain structural strength [5,6]. Recent studies confirm the remarkable functionality of geopolymer technology in terms of eco-sustainability and engineering properties. Compared with conventional PC, the superior eco-efficiency of GCs is mainly attributable to the reduced CO₂ footprint, the employment of low-temperature processing, and the use of by-product materials as precursors, which prevents the accumulation of wastes in landfills [7]. Bibliographic analysis performed by Ji and Pei [8] highlights the technological peculiarities of geopolymer binders, including excellent mechanical properties, long-term durability performance in aggressive environments, fire resistance, high thermal insulation, fast curing speed, and heavy metal immobilization, which confer notable versatility in several engineering fields. These properties are not necessarily inherent to all geopolymer-based formulations. The nature of aluminosilicate precursors, process parameters (raw material selection, curing regimes, alkaline molarity), and the mix design are crucial aspects to modulate the performance for a given application.

The current progress of GC technology concerning their application for building materials (concrete and mortars) is reviewed in this paper. Recent research about the effect of raw materials selection, curing thermal regime, and chemical activators on the fresh properties, durability, microstructure, mechanical behavior, and thermo-acoustic performances of GC-based compounds are investigated. Future sustainable developments

and applications are also addressed, with particular attention to the design of geopolymeric mixes for 3D printing fabrication technologies.

2. Geopolymer Cements (GCs): Chemistry, Raw Materials, and Products

GCs, or geocements, refer to a class of alumino-silicate cementitious materials resulting from an inorganic polycondensation reaction (named “geopolymerization”) between solid alumino-silicate precursors and highly concentrated aqueous alkali hydroxide or silicate solution such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na₂SiO₃), or potassium silicate (K₂SiO₃). Davidovits [9] provided the main contribution to the discovery and scientific research of geopolymer materials. In the 1980s, he developed the first inorganic polymer by geopolymerization of natural minerals containing silicon (Si) and aluminum (Al), such as clay, slag, fly ash, pozzolan, and alkaline activator below 160 °C [10].

The chemistry of geopolymerization mechanism involves the following steps:

- (1) *Alkali activation.* An alkaline activator is necessary for the dissolution of Si and Al from the inorganic precursor as well as for the catalysis of the condensation reaction. The reaction of alumino-silicate oxides (Si₂O₅, Al₂O₂) in strongly alkaline solution results in a breakdown of Si-O-Si bonds with the subsequent penetration of Al atoms in the original Si-O-Si structure. The resulting alumino-silicate oxide gels, based on Si-O-Al block, are the geopolymer precursor of the polycondensation reaction. The dissolution/hydrolysis reaction is reported in Figure 3.
- (2) *Polycondensation in Geopolymer network.* The alumino-silicate gel phase is a highly reactive product. Under alkaline condition, substantially fast chemical reactions occur, forming a rigid 3D polymeric and ring framework of Si-O-Al bonds (Figure 2). The proper completion of the geopolymerization process and the conferment of adequate mechanical strength properties to the material require heat curing treatment at a thermal range between 25 and 90 °C [11]. The water released by polycondensation is normally consumed during the dissolution process.

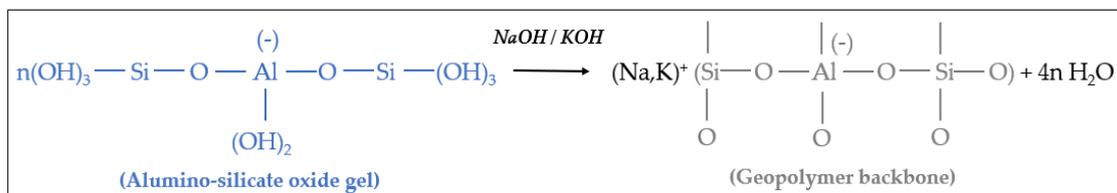


Figure 2. Polycondensation of hydrolyzed aluminate and silicate species and formation of 3D geopolymer network.

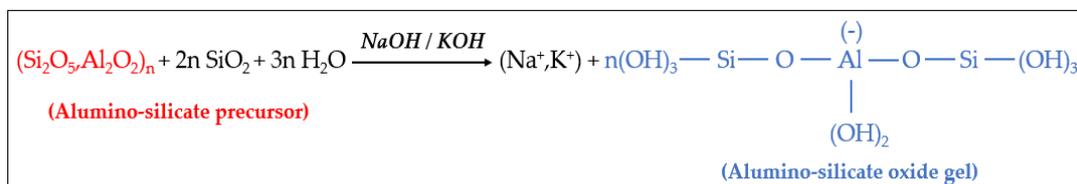


Figure 3. Dissolution and hydrolysis reaction of the alumino-silicate precursor.

Geopolymer networks are polysialate structures, where sialate indicates a Si-O-Al building unit. The Si/Al atomic ratio significantly determines the final reticular structure and degree of crystallinity of the resulted geopolymer binders. Depending on the Si/Al molar proportion, three silicon-oxo-aluminate tetrahedral structures develop (Figure 4): (Si-O-Al-O)-type polysialate, (Si-O-Al-O-Si-O)-type polysialate-siloxo, and (Si-O-Al-O-Si-O-Si-O)-type polysialate disiloxo [10].

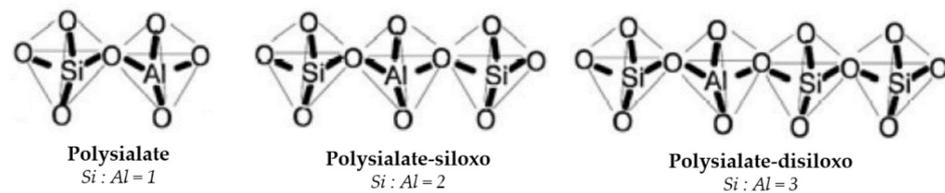


Figure 4. Chemical structures of polysialates.

In this context, Ozer and Soyer-Uzun [12] studied the microstructural properties of metakaolin-based geocement samples at different Si/Al ratios (1.12, 1.77, and 2.20 respectively). An Si/Al ratio of 1.12 results in a highly crystalline nature due to the presence of crystalline components (zeolite and sodalite). However, brittle mechanical behavior and low compressive strength (about 1 MPa) occurs. Conversely, 1.77 and 2.20 molar ratios revealed amorphous patterns and glassy microstructure but mechanical strengths up to 20 times higher, which is attributable to the formation of alumino-silicate network structures. Some alkali metal cations, including Na^+ , K^+ , and Ca^+ , are integrated in the geopolymer network by combined chemical–physical interactions. Its function is to balance the negative charge of Al in 4-fold coordination [10,13].

In agreement with Duxson et al. [14], together with processing conditions, the selection of raw materials is critical in determining the rheological, chemical, physical, and mechanical properties of geopolymer products. GCs can be classified according to the type of alumino-silicate precursor in metakaolin-based geopolymer cements (MGCs), fly ash-based geopolymer cements (FGCs), natural minerals-based geopolymer cements (NGCs), and hybrid geopolymer cements (HGCs).

2.1. Metakaolin-Based Geopolymer Cements (MGCs)

Metakaolin (MK), or calcinated kaolin, is a ceramic powder based on calcined clay that is formed during the calcination process at temperatures between 500 and 800 °C. Thanks to its pozzolanic properties and the reduced thermal energy requirements for its production (80–90% less CO_2 emission than PC), it is generally used to replace traditional cementitious binders to obtain more eco-sustainable building materials. Compared to other alternative binders applied in cement manufacturing (fly ash or blast furnace slags), MK is not a by-product resulting from an industrial process but is obtained in specific calcination conditions [15]. The size, purity degree, and crystallinity of MK sources used in geopolymer technology are strongly related to the kaolinite mineral from which they were extracted. However, the average particle size is smaller than 5 μm [16]. The high specific surface area and plate-shaped texture negatively affect the workability of geopolymer compounds, increasing the processing complexity and the water demand [17]. The last aspect promotes the strong tendency to a large degree of drying shrinkage and cracking. Although MK is a non-renewable resource, the higher concentration of reactive material and purity than other alumino-silicate precursors is beneficial aspects to obtain high-strength and low permeability properties in geopolymer compounds [18].

2.2. Fly Ash-Based Geopolymer Cements (FGCs)

Fly ash (FA) is fine particulate material obtained by separation from the flue gas of power stations or petrochemical industries burning anthracite or bituminous coal. The chemical composition depends on the characteristics of starting coal-based minerals and combustion conditions. The large demand for industrial and domestic energy results in the production of a high amount of FA. In the last 10 years, more than 1 billion tonnes of FA are produced per year [19]. Considering the high disposal costs, a valuable eco-friendly strategy to treat these industrial by-products concerns their use in the cement industry. Low-calcium FA (designated as “F” class) possess pozzolanic properties and was extensively used as a supplementary cementitious material in the PC manufacturing process to minimize the greenhouse emissions, which occur using traditional pozzolanic

aggregates. As reported by Vargas and Halog [20], the employment of industrial waste or by-products for clinker replacement can reduce CO₂ emissions up to 12% when 10% of these secondary raw materials is incorporated in the cementitious mix. Reduction in heat of hydration, increase in workability, and improvement of durability to chemical attacks are other engineering benefits obtainable by using FA in blended cements [21,22]. The typical chemical compositions of some FA products used in cement applications and related source plants are reported in Table 1.

Table 1. Chemical compositions of some FA, deriving from international power plants, used in cement-based applications.

Oxides (%)	Yangzi Power Plant (China) [18]	Secunda Power Plant (South Africa) [19]	Mae Mao Power Plant (Thailand) [22]
SiO ₂	55.86	46.28	39.82
Al ₂ O ₃	31.74	21.27	21.52
Fe ₂ O ₃	3.28	4.29	13.68
CaO	1.67	9.82	15.24
MgO	0.39	2.62	2.78
other	7.06	15.72	6.96

As shown in Table 2, the high percentage of SiO₂ and Al₂O₃, makes fly ashes suitable for GCs manufacturing. Variations in the compositional proportion are mainly attributable to the type of raw coal-based materials (anthracite coal or lignite) involved in the process. Compared to the MK precursor, FA-based geopolymer does not require high-temperature processing and a high level of energy consumption [23]. The lower specific area of fly ash particles than MK ones (0.86 m²/g in FA and 1.84 m²/g in MK, based on [18]) optimize the workability and water demand of GC. Although FGCs exhibit good mechanical strength and durability, the limiting factor in the use of FA as geopolymer precursors is the low reactivity. The incomplete dissolution of FA leads to slowing the setting and strength development [24]. To complete the discussion about the influence of MK and FA precursors on GC properties, it is interesting to present a microstructural comparison between MGC and FGC. Scanning electron microscopy (SEM) images from the research work of Kong et al. [23] are reported in Figure 5.

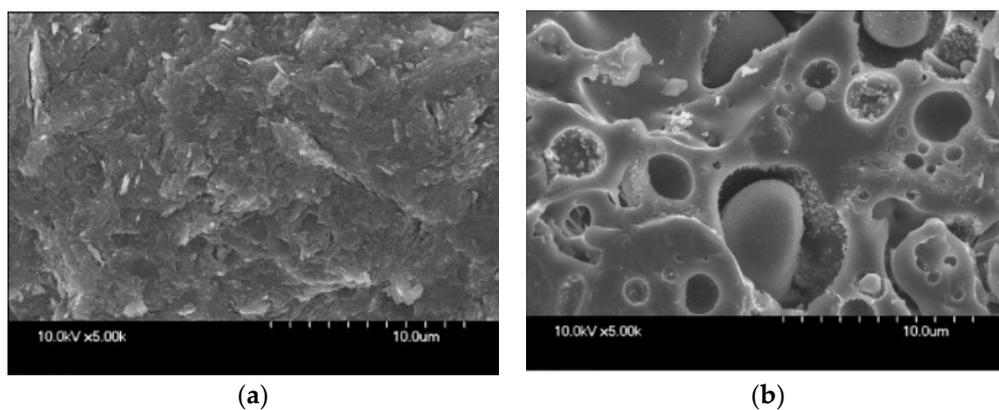


Figure 5. SEM micrographs of MGC (a) and FGC (b) microstructures (reproduced with permission from Kong et al., *Cement and Concrete Research*; Elsevier, 2007).

The micromorphology difference between MGC and FGC is evident. MGC shows a uniform layer-like structure, overall free of voids or cracks (Figure 5a). Comparatively, heterogeneous structure and hollow cavities can be observed in FGC (Figure 5b). Porous microstructure results from the partial alkaline dissolution of FAs, which releases spherical pore in the matrix. Unreacted particles can be located inside these cavities.

2.3. Natural Minerals-Based Geopolymer Cements (NCs)

The synthesis of NGCs includes a variety of natural virgin raw materials such as aluminosilicate precursors. Pumice-type natural pozzolana, natural zeolite, volcanic ash, and mining waste are the main examples of natural materials used as a pozzolanic source for geopolymer preparation.

Pumice is a foam-like aluminosilicate pyroclastic material formed by separating the eruption gases from the magma during cooling. Worldwide, around 18 billion tonnes of pumice are detected in mineralogical deposits and the countries with the highest number of pumice sources are the United States, Turkey, and Italy, respectively [25]. Chemically, higher SiO_2 content (up to 75%) than FA and MK can be revealed due to the presence of minerals with high Si content, such as feldspar, quartz, and biotite [26]. In the geopolymer technology context, several studies have revealed the influence of pumice precursors in enhancing the lightweight and absorption resistance of the material [25,26]. As is well known, a lot of functional properties such as self-weight reduction, heat insulation, and fire resistance derive from the lightweight characteristic. Concerning the absorption properties, Binici et al. [26] revealed that small-grained pumice crystals form a glassy microstructure, which hinders the liquid permeation.

Zeolites are crystalline hydrated aluminosilicates, composed of SiO_4 and AlO_4 tetrahedral structures connected by one O atom (Figure 6).

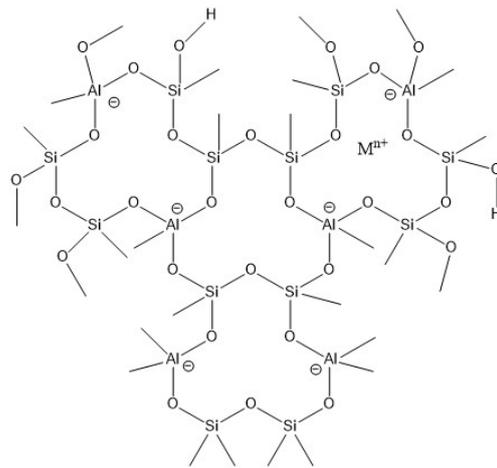


Figure 6. Zeolite skeletal structure.

An attractive contribution to the application of zeolitic addition in GCs manufacturing is presented by Papa et al. [27]. The authors discussed the potential influence of zeolite powder on the properties of a new class of geopolymer-based composites. The typical micro-porous morphology of zeolite can extend the functionality of geopolymer materials in terms of purification of contaminated water, encapsulation of waste material, CO_2 adsorption, and stabilization of heavy metals. Nikolov et al. [28] examined the influence of different types of activator solutions on natural zeolite (clinoptilolite) to produce geopolymer material with practical use. The research reveals low mechanical strength and a high tendency to shrinkage, due to the partial dissolution of main aluminosilicate components and the considerable water demand of the fresh mixes (resulting from a high specific surface of zeolitic particles), respectively. Despite the inapplicability in practical uses as building materials, interesting adhesion properties were verified, making geopolymer–zeolite composites suitable for plasters or concrete coatings.

Volcanic ashes consist of pulverized rocks resulting from volcanic eruptions, whose physical, chemical, and mineralogical properties are strictly related to the composition of the source magma. Extensive studies on the suitability of volcanic ash as a feedstock for GC synthesis were conducted by Djobo et al. [29,30]. The improved durability performances (wet–dry conditions and sulfuric attack) are the most attractive effect highlighted by the

results. High acid resistance is attributable to the formation of sodium (Na)-rich gel after geopolymerization, which neutralizes sulfuric acid mitigating its destructive effects on the geopolymer structure. However, volcanic ash application is restricted by the poor reactivity with alkali activators. This required complex and energy-intensive activation treatments (mechanical activation or alkali fusion process), complicating the GCs manufacturing.

Pacheco-Torgal et al. [31] focused their studies on the use of tungsten mine waste mud (TMWM) as an SiO₂-rich precursor to the development of geopolymeric binders. The mineralogical composition of TMWM, based on muscovite and quartz, induces the formation of a new crystalline phase, named phlogopite, with general formula $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, which contributes to the mechanical behavior of the compound. Although a high Si/Al ratio was detected (5.5 higher than the usual value in other precursors), a low reactivity rate in TMWM was highlighted, requiring strongly alkaline activating solutions (16 M and 24 M) and with an extra Si-supply to start the geopolymerization and achieve proper strength properties (~45 MPa at 60-days curing). This kind of precursor requires high-temperature pre-treatments (950 °C) to reach the dehydroxylated state, which significantly impacts the costs and energy expenditure of the production process.

2.4. Hybrid Geopolymer Cements (HGCs)

“Hybrids” refers to geopolymer binders obtained from a blend of pozzolanic precursors having complementary properties. The scientific literature provides numerous examples of GCs based on alkali silicate-activated blends. Bernal et al. [32] investigated the influence of including granulated blast furnace slags (GBFSs) in MK-based geopolymers in terms of physical–mechanical performances. GBFS, a by-product of the steel manufacturing industry, essentially consists of SiO₂, Al₂O₃, calcium oxide (CaO), and magnesium oxide (MgO). The alkaline activation leads to the dissolution of Ca²⁺ ions, which implies the development of a microstructure rich in stable and high-density hydrate Ca-silicate (C-S-H) phases, resulting in higher mechanical strength than the unblended system (about 60% increase). Under alkaline conditions, the C-S-H gel changes in Na-Ca-silicate hydrate gel (C-N-S-H phase), which confers high durability to GC when exposed to CO₂-rich environments. Highly condensed binder gel and the low content of chemically bonded water in the alkali-activated products promote high stability under high-temperature expositions, providing an attractive technological alternative to traditional cementitious materials in building applications where high thermal conditions occur. Kumar et al. [24] studied the geopolymerization behavior of FA by adding growing amounts of GBFS. In this framework, the effect of GBFS inclusion is to optimize the low reactivity of FA during the alkali-activation. C-S-H gel products from the alkaline dissolution of GBFS sharply change the microstructure of the geopolymer system in terms of compactness and morphological features. The gel phase acts as a coating for fly ash and unreacted particles, promoting the material densification. Consequently, improvement in setting time and compressive strength occur.

Nuaklong et al. [6] researched the use of rice husk ash (RHA) as a functional filler in FGCs. RHA is a by-product obtained by the thermal processing of cereals in agri-food plants. The considerable content of reactive amorphous SiO₂ phase (over 80%) makes it a clean resource for improving the performance of geopolymer composites. As previously discussed, the Si:Al ratio governs mechanical properties, durability in aggressive environments, and corrosiveness of geopolymer-based product [12]. As revealed by the results, when RHA is added in the geopolymer mixture, with optimum dosage, improvement in strength and permeability takes place. The superior performances are related to an increase in density of Si-O-Si bonds of the hydrated product and the development of an amorphous glassy phase that maximizes the strength properties. In terms of eco-efficiency, RHA exhibits physicomechanical functionality comparable to other SiO₂-rich fillers commonly used in the production of cementitious materials (such as nano-SiO₂), which required expensive and high thermal energy processes. Therefore, agricultural wastes represent a

valid and environmental-friendly alternative for reducing the nano-SiO₂ synthesis and the consumption of natural resource.

3. Recent Research Findings of Geopolymer-Based Concrete Properties

Similarly to ordinary Portland-based mixes, geopolymer concrete/mortars consist of the proper combination between mineral aggregates (sand, gravel, stone), chemical admixtures, and geo-cementitious binders (Figure 7).

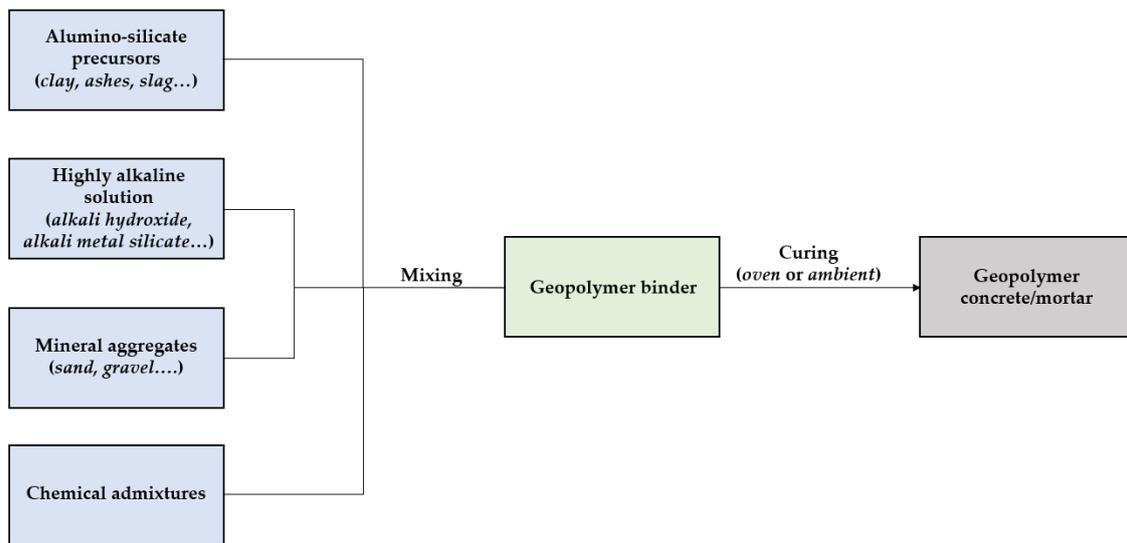


Figure 7. Production of geopolymer concrete. A descriptive model.

This section reviews the recent advances of geopolymer composites (mortar and concrete), including rheology, physical–mechanical properties, durability, and thermo-acoustic performance, investigating the influence of the process factors (such as curing and alkaline conditions) on the material features.

3.1. Rheological Properties

Rheology is a fundamental tool to characterize the fresh properties of cementitious materials (cement paste, mortar, or concrete), in terms of workability, flowability, placement, and cohesion. Numerous researchers have successfully used the Bingham model to describe the rheological behavior. Bingham’s model is based on two constitutive parameters: yield stress (YS) and plastic viscosity (PV). YS, measured in Pa, is related to material slump and more generally to whether or not concrete will flow or stop flowing under applied stress. In practice, this parameter is crucial for formwork or mold filling. In concrete pumping operations, if the material viscosity is low, pumping pressure can increase when YS increase (decreasing in slump properties). Excessive pressure can be reduced by optimizing the material rheology. PV, measured in Pa*s, is related to the flow properties of the cementitious compound. Increasing concrete flowability, resulting from low PV level, facilitates material placing and finishing but promotes segregation phenomena. The segregation of mineral aggregates or water (bleeding) into the cement paste leads to a non-homogeneous compound and may negatively affect the mechanical properties and the service life of the concrete material. To minimize segregation, high-PV or low-YS (or high slump) formulations must be designed. In this regard, the use of chemical admixtures or modulating the particle size distribution of the aggregates are common approaches. YS and PV are also crucial in surface finish quality. The proper balance between the Bingham parameters can minimize the effect of segregation (uneven distribution of the cement paste) and the stabilization of air bubbles in the cement matrix [33,34]. The following diagram (Figure 8) illustrates the influence of rheological parameters (YS and PV) on the performance and quality of fresh cementitious conglomerate.

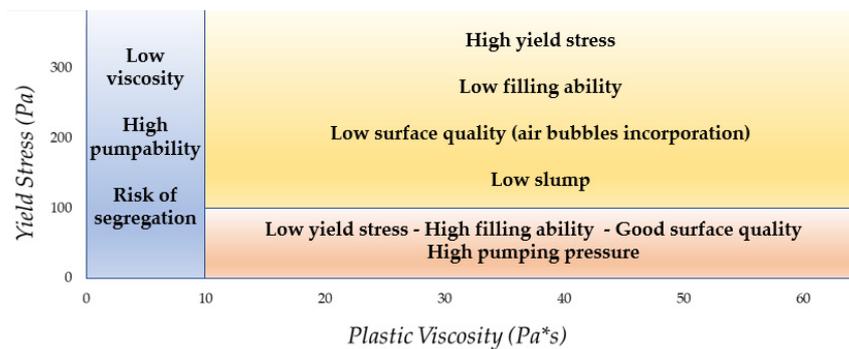


Figure 8. Summary of the impact of rheological parameters on concrete performance (adapted from [33]).

Rifaai et al. [35] examined the effect of alkaline solution (NaOH) molarity on the rheological properties of FA-based geopolymer paste. Six NaOH concentrations (2, 3.5, 8, 11, and 14 M) were investigated, and the influence on setting time, PV, and YS was evaluated. The setting time (t_s) varies considerably for high alkaline conditions. Alkali-activation with 14 M solution involves a setting time of about one week, while the less concentrated solutions promote a faster hardening (3–5 h). Concerning the YS index, 8 M concentration can be considered a threshold value. Up to this concentration, an increase in YS occurs (29 Pa as a maximum value) due to the formation of a rigid network as a result of polycondensation mechanism. For alkaline levels (11 M and 14 M) above threshold concentration, an opposite trend is observed. The reduction in YS to a minimum value of 4 Pa reflects the lower rigidity of the geopolymer matrix. PV does not exhibit a well-defined behavior. However, it can be inferred that the high viscosity of the NaOH solution at higher concentration results in a gradual increase in PV (0.32 Pa*s as a maximum value).

Table 2. Geopolymer concrete samples investigated by Kashani et al.: precursors proportions, particle size, and dry packing density (adapted from [36]).

Formulation	FA(%)	GBFS (%)	Micro-FA (%)	d (μm)	Dry Packing Density (0–1)
M 1	5	25	10	33.1	0.483
M 2	10	20	10	37.7	0.505
M 3	15	15	10	42.8	0.517
M 4	15	20	5	43.5	0.515
M 5	20	15	5	48.6	0.528

Kashani et al. [36] studied the influence of five different combinations of aluminosilicate precursors (FA, GBFS, and micro FA) on the rheology of geopolymer mortar and concrete, keeping the amount of mineral aggregates and the type of chemical activator (Na_2SiO_3) fixed. The research purpose was to evaluate how the particle size distribution (d) and the chemical composition of the precursors affected the workability and the initial t_s of the geopolymer-based compounds, avoiding the use of chemical superplasticizers commonly used in PC-based compounds and considered less effective in GC concrete [37]. Table 2 summarizes the characteristics of the investigated samples.

Concerning the t_s , the influence of the granulometry distribution and chemical composition of precursors is remarkable. High FA contents imply a wider particle size distribution resulting in a greater d-value, resulting in t_s increases (2.9, 4.5, 5.6, 6.5, and 7.1 h in M1, M2, M3, M4, and M5, respectively). The lower specific surface area of larger precursor particles results in a lower reactivity of aluminosilicate sites, increasing t_s . Regardless of d-values, and t_s decrease with increasing GBFS dosage. Higher GBFS content increases the CaO load in the mixtures, acting as an accelerating additive for the setting process. Wider and higher packing density result in greater workability and lower YS and PV values. This evidence

affects the flowability properties of the geopolymer paste: higher packing density means more free water to increase the material fluidity. Hence, the flow and self-compaction behaviors of the compounds are optimized. Therefore, the study demonstrated the possibility of obtaining geopolymer–concrete mixtures with rheological–mechanical properties suitable in self-compacting applications, modulating the design of the mixture proportions, based on the particle size distribution and packing density of the binder.

Unlike the previous research, Alrefaei et al. [38] investigated the effect of using different chemical admixtures, naphthalene-based superplasticizer (NS), melamine-based superplasticizer (MS), and polycarboxylate-based superplasticizer (PS), on the rheological–mechanical behaviors of FA-GBFS Geopolymer compounds. In all mix, 1% (by weight) of superplasticizer was used, and its influence by varying the water/binder (w/b) ratio was also evaluated. Considering the w/b ratio of 0.4, the addition of chemical admixtures extends the t_s by approximately twofold with respect to the reference sample (no admixtures). This delay could be related to the adsorption properties of superplasticizers on the precursor particles in high alkali media. By using admixtures, improving in relative slump occurs. The lump increase rate is comparable for each type of superplasticizer (about 250% increase), but PS was the most effective. This depends on the chemical structure of polycarboxylate molecules, which improves the plasticizing effect. The reduction in w/b ratio is accompanied by a decrease in the fluidity (and slump) of the mixtures, by an increase in YS and PV. By decreasing the use of water (w/b ratio = 0.38), an increase in the alkaline level of the activating solution occurs. This improves the effectiveness and stability of NS, which exhibits a better effect on the GC fluidity (Figure 9a). In terms of mechanical properties, no significant effect occurs in the compressive strength depending on the admixture type and water dosage (Figure 9b). This evidence counteracts the influence of water content in ordinary PC compounds, where reducing the water amount improves the material strength. Two hypotheses were considered by the authors to explain this trend in the geopolymer system: (a) partial dissolution of the solid activator and (b) alteration of the chemical structure of the admixtures due to the increase in the alkaline level, when the w/b ratio is reduced.

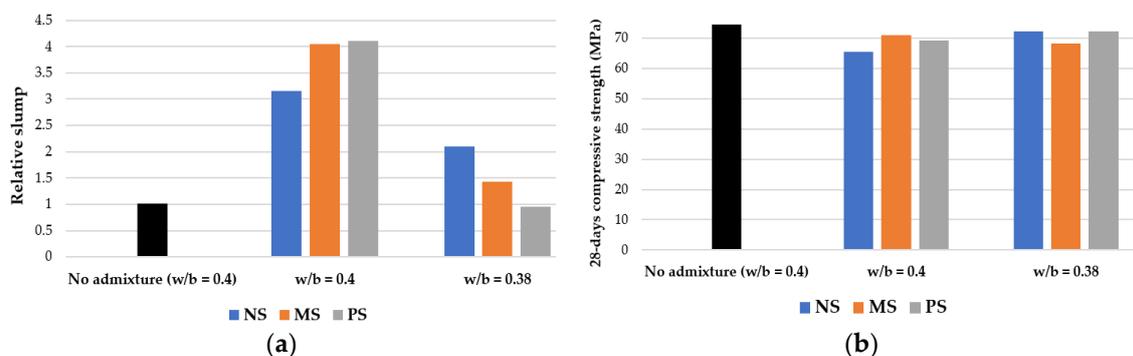


Figure 9. Influence of admixture type and w/b ratio on slump (a) and mechanical strength (b) (adapted from [38]).

3.2. Microstructural Properties

The pore architecture of hardened geopolymeric compounds derives from the complex interaction of intertwined factors, such as size gradation of alumino-silicate precursors, geopolymerization reaction rate, solvent type, mixing proportions, and curing conditions. Generally, in GC matrices, it is possible to detect the coexistence of different void systems [39]: macro-porosity (>50 nm), meso-porosity (from 2 nm to 50 nm), and micro-porosity (<2 nm). Macropores are more interconnected than meso and micropores. This air-void structure mainly arises from three factors: (a) air bubbles that remain entrapped into the paste during the dissolution and polycondensation reaction; (b) empty microstructural spaces generated by the evaporation of water after the drying process; (c) gaps between partially reacted or non-reacted precursor particles. Mesopores represent the typical pores between geopolymer phases. Micropores represent the voids structure of

the geopolymer gel network. The microstructure of the GCs is highly sensitive to process parameters and the chemical–physical characteristics of the raw materials; therefore, the pore size distribution can shift from macro-porosity to meso or micro-porosity as a function of process variables.

- *Particle size distribution of alumino-silicate precursors.* Assi et al. [40] investigated the influence of three different FA particle grades (38.8, 17.9, and 4.78 μm) on the microstructural properties of geopolymer concrete. The finer the average FA particle size distribution, the denser and stronger the geopolymer matrix. In this regard, the increase in surface area is crucial in terms of high reactivity to alkaline dissolution, the preferential formation of geopolymer products, the high ability to fill structural micro-voids, and less free water that evaporates during the curing, causing a decrease in the formation of microcracks.
- *Type of mineral precursor and Si/Al ratio.* Cherki El Idrissi et al. [41] proved how the Si/Al ratio, brought by several mineral precursors, is intimately linked with the porosity distribution in GCs. In this research, three different precursors were analyzed: MK (Si/Al ratio: 2.5), GBFS (Si/Al ratio: 3.5), and FA (Si/Al ratio: 5.9). Experimental pore volume distribution, conducted by mercury intrusion porosimetry (MIP), revealed that the pore distribution of geopolymer medium shifted into smaller voids as the Si/Al ratio increases. This result is consistent with the work of Wan et al. [42]. Geopolymer compounds synthesized at a low Si/Al ratio (Si/Al ratio of 1:1) present a high content of undispersed crystalline zeolitic nuclei into a little geopolymeric binder and macropores. At a Si/Al ratio of 2:1, a proper concentration of aluminate and silicate monomers is involved in a homogeneous geopolymer binder. At a Si/Al ratio of 4:1, many micropores or mesopores are formed due to an insufficient amount of dissolved aluminosilicate monomers. SEM micrographs of GCs synthesized at various Si/Al ratios are reported in Figure 10.
- *Molarity of alkali-activator.* Huseien et al. [43] researched the influence of NaOH molarity (from 2 to 16M) on the water absorption tendency of GBFS-FA-based geopolymer mortars. High NaOH molarity improves the microstructure of samples in terms of density increasing and air voids reduction. The increased concentration of alkali-activator enhances the geopolymerization mechanism in terms of precursors solubility, resulting in a high compactness of the network structure and good interfacial adhesion between the geopolymer paste and mineral aggregates. However, very high alkaline solutions (generally $> 16\text{ M}$) can be deleterious on the microstructural and mechanical properties of geopolymer concrete. Higher NaOH concentrations hinder the polycondensation process due to the accelerated dissolution of the alumino-silicate raw materials. The excess of hydroxyls anion (OH^-) in the alkali-activated matrix results in premature precipitation of geopolymeric gels, deteriorating the mechanical properties of the geopolymer produced.
- *Curing time and temperature.* Recent findings of the effect of curing treatment on the pore system of FGC-based materials are reported in the research of Zhang et al. [44]. The authors investigated the relationship of microstructural properties development of FGCs and its dependence on curing conditions (room temperature, 50 $^\circ\text{C}$ and 80 $^\circ\text{C}$ for 7, 28, and 49 days). For each curing temperature, the porosity rate of the samples decreased with the heat curing period. Macro-pores (50–100 μm) constituted the geopolymer matrix under 7 days curing time. As the heat treatment increased, the percentage of large pores tended to decrease, but a more significant contribution of microcracks due to the material's drying occurred. In this regard, the greater the temporal extension of the thermal treatment, the higher the geopolymer reaction degree, increasing the inorganic gel formation that constructed a more compact microstructure [39]. Curing temperature is crucial to the overall pore volume. Similar pore content was observed at room and middle curing temperatures (about 5% and 4.5%, respectively), while a higher pore fraction (about 8%) was detected in the samples cured at 80 $^\circ\text{C}$. Faster water evaporation and hardening process at higher curing tem-

perature results in a less ordered medium of poorer quality having larger pores and defects. On the other hand, lower curing temperatures help the material densification, as the geopolymer gel tends to saturate the microstructural voids [45].

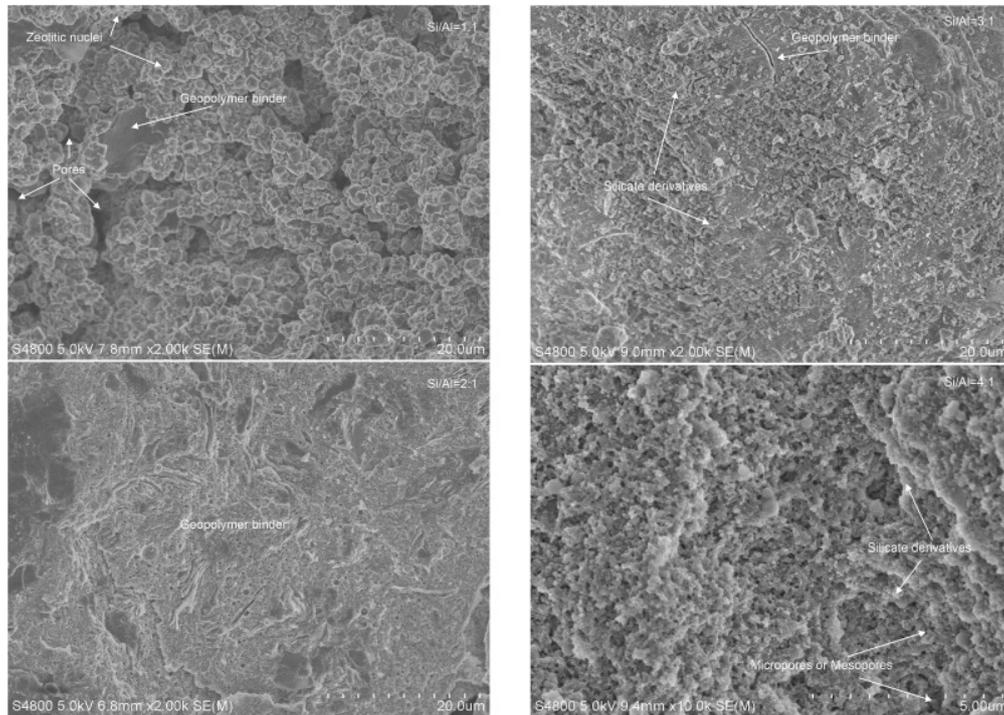


Figure 10. SEM images of MGCs synthesized at different Si/Al ratios (reproduced with permission from Wan, Q. et al., *Cement and Concrete Research*; Elsevier, 2017).

Effects of Mineral Aggregates: Interfacial Transition Zone (ITZ) Porosity

The porosity in the ITZ between mineral aggregates and cementitious matrices is recognized as a key factor with regard to the properties of mortar and concrete in terms of mechanical performances and permeability. Poor interfacial compaction results in low compressive strength and high oxygen permeability and water conductivity. Generally, ITZ voids are larger than the porosity of the bulk paste [46].

Chuan et al. [47] studied the influence of two types of fine mineral aggregates, river sand (RS) and dune sand (DS), on the microstructure of FA-based geopolymer mortars. Regardless of the sand characteristics, elemental analysis by Energy Dispersive X-ray Spectrometry (EDS) revealed the formation of a Si-rich interface, resulting from the dissolution of SiO_2 from sand particles in a highly alkaline “activating” solution. This phenomenon ensures a homogeneous bond between the geopolymeric gel and the fine aggregates. However, dune sand has a much higher fineness ($<150 \mu\text{m}$) than river one. Its incorporation increased the void rate in the geocement matrix, which is due to the higher tendency to the air retention by the aggregates having a larger specific surface. The greater porosity negatively affected the mechanical and water sorptivity properties of mortars. Zhu et al. [48] performed ITZ analysis of geopolymer mortars prepared with recycled geopolymer fine aggregates (RGA), which were obtained from the milling process, as a replacement of traditional RS. GC-RGA ITZs were much thicker and more compact than the GC-RS interface (Figure 11). The unreacted precursor in RGAs was activated by the alkali solution again and enhanced the new geopolymerization, which generated more aluminosilicate gels at the same time, causing a higher interface bond. On the other hand, the incorporation of geopolymer-based inert decreased the strength performances due to the weaker properties of RGA than RS.

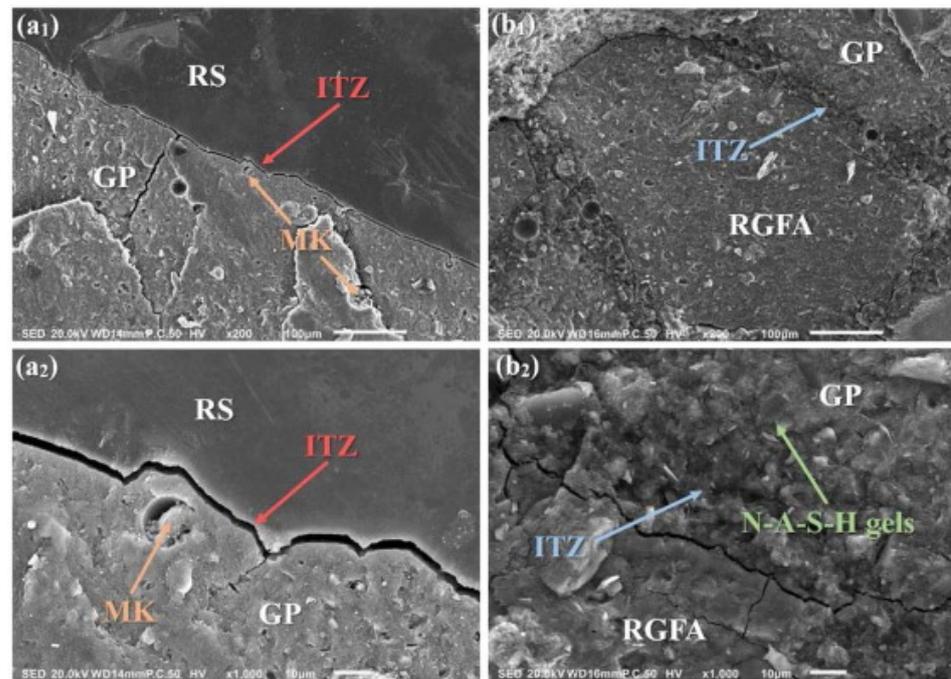


Figure 11. SEM investigation of different ITZs: Microstructural effects of RS and RGA (reproduced with permission from Zhu et al., *Construction and Building Materials*; Elsevier, 2020).

3.3. Mechanical Properties

The complex relationship between the mechanical behavior of geopolymer composites and synthesis parameters, including the reactivity of aluminosilicate precursors, Si/Al ratio, the concentration of alkali activator solution, curing regime, water-to-geopolymer binder ratio (amount of water present in solution and extra water added in the mix + solid precursor and mass of alkali reagents), and type of mineral aggregates is well presented in most research studies [25,36,49–52]. The influence of these factors on the strength optimization of geocement-based concrete/mortars is summarized in Figure 12.

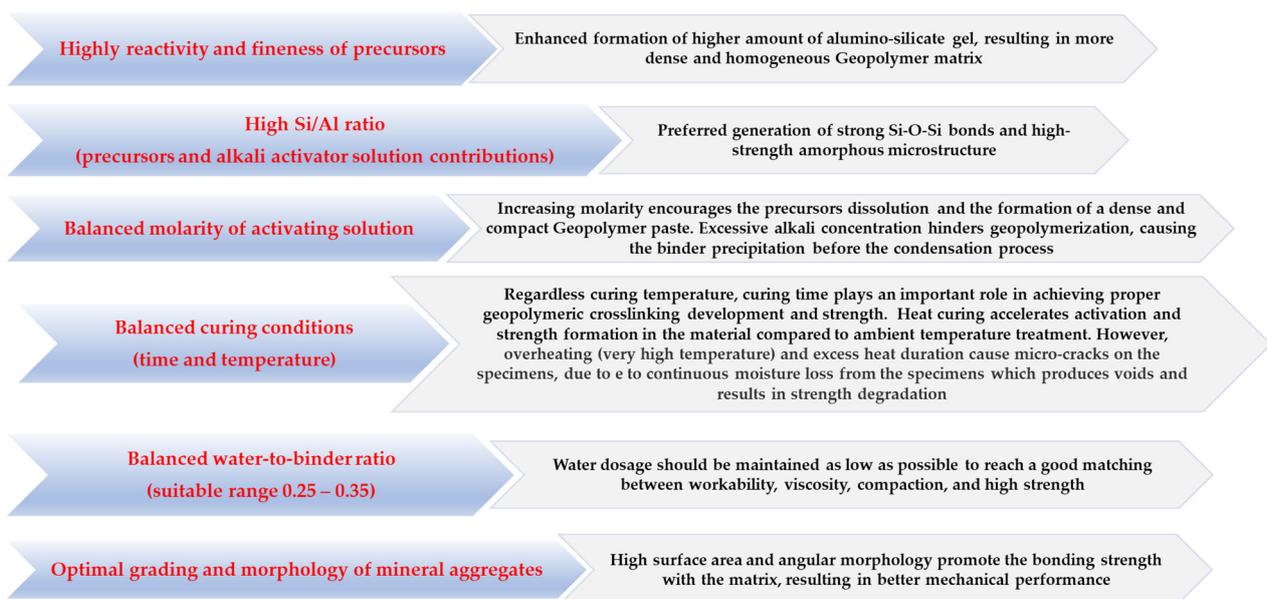


Figure 12. How the synthesis parameters optimize the strength properties of GC composites.

Considering the strong interdependence between the process variables and properties of the final material, the research on the mechanical behavior of geopolymer concrete/mortars was mainly conducted by investigating one or more of these parameters to obtain a mix design suitable for the desired application. Table 3 reports some recent studies on the strength performance of different types of GC formulations, highlighting the main synthesis factor monitored in the experimental study.

Table 3. Effect of process variables on the mechanical properties of geopolymer concrete/mortars.

Type	Variable	Investigated Range	Compressive Strength (MPa)	Flexural Strength (MPa)	Density (g/cm ³)	Primary Findings
FA-based lightweight mortar [25]	Activator molarity	10–14 M	19–30	3–4	1.88–1.92	14 M optimal
FA-GBFS-based concrete [36]	Precursors size distribution	33.1–48.6 μm	48–67	/	/	Finest size gradation optimal
FA-GBFS-based mortar [50]	Heat curing	Ambient–100 °C	40–53	/	1.88–1.96	Ambient (28 days) and 90 °C (1 h) curing similar improvement effect
FA-GBFS-based concrete [51]	FA-GBFS replacement	0–30% by weight of GBFS	26–52	3.5–5	2.38–2.43	30% GBFS replacement optimal
FA-based mortar [52]	Mineral aggregates grading (limestone sand)	0–4 mm; 2–4 mm; 1–2 mm; 0–1 mm	42–49	6.7–6.9	2.03–2.07	2–4 mm gradation optimal

As know, the elastic modulus is a vital structural property of cementitious compounds, indicating the stiffness and the resistance against elastic deformation when a load is applied. In terms of technological applicability, the knowledge of this parameter is crucial to evaluate the stress and deformation distributions of a concrete element under a spatial stress state. High compressive strength and stiffness are the fundamental conditions for a civil structure to support high loads and avoid failure of serviceability [53,54]. On the other hand, high mechanical deformability results in a better impact on vibro-acoustic damping and sound insulation performance against impact noise [55]. In analogy with the mechanical behavior observed in ordinary PC concrete, the elastic modulus varies with the compressive strength. Specifically, as the compressive strength increases, the modulus of elasticity increases [53,54]. Hardjito and Diaz-Loya predictive models, shown in Equations (1) and (2) respectively, are the main correlation relationships between elastic modulus and mechanical strength developed in the context of geopolymer concrete made of FA [56]:

$$E = 2707 \times \sqrt{\sigma_c} + 5300 \quad (1)$$

$$E = 0.037 \times \sqrt{\sigma_c} \times \rho^{1.5} \quad (2)$$

where E is the modulus of elasticity (MPa), σ_c is the compressive strength (MPa), and ρ is the unit weight (kg/m³). Hence, as previously noted for mechanical strength, the stiffness properties of geocement-based compounds also depend on the composition (nature of raw materials and mixture), synthesis process, curing regime, and aggregate-GC ITZ [53]. Aboulayt et al. [57] reported from their studies that adding FA in MK geopolymer grout reduces the reactivity of the mixtures, increases the packing density of the precursor powders, and promotes the retention of air bubbles in the matrix. These factors involve unreacted sites inside the geopolymer matrix and a relevant hygrometric shrinkage, which results in a less rigid and porous alumino-silicate gel. The elastic modulus dropped from 5.14 to 2.24 GPa for the 0 wt % and 60 wt % FA amounts, respectively. Wang et al. [58] investigated the influence of Ca-rich additives, i.e., calcium aluminate (CA) binders, on the mechanical and fracture properties of FA-based geopolymer concrete cured at 75 °C for

16 h. The elastic modulus of plain concrete (0% of CA binder) was 11.84 GPa, corresponding to the compressive strength of 33.45 MPa. The values of modulus were up to 14.79 GPa and 15.44 GPa with CA content of 2.5% and 5% reference to 36.79 MPa and 38.53 MPa, respectively. The highest elastic modulus achieved up to 16.93 GPa with the CA content of 7.5% for compressive strength of 41.02 MPa. Wang et al. [59] determined the optimum precursor proportion and curing regime for FA-GBFS geopolymer concrete. The most relevant results of the study are shown in Figure 13.

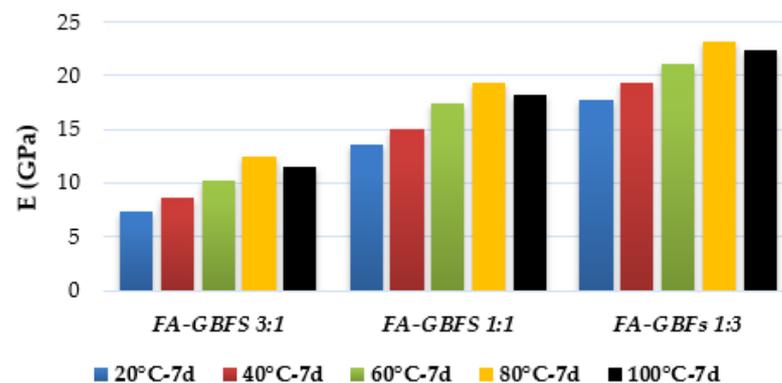


Figure 13. Effect of curing temperature and FA-GBFS ratio on 7-days elastic modulus (adapted from [59]).

Regardless of the curing conditions, the elastic modulus increases with the increasing GBFS/FA ratio. Growing GBFS content promotes denser and more compact geopolymer gel, resulting in better strength development and stiffness. This evidence is consistent with a similar investigation [60]: high CaO concentration in GBFS precursors led to the formation of additional C-S-H gel from the alkali activation. Additional C-S-H amorphous products enhanced the microstructure and strength of geopolymer paste. An increase in GBFS/FA ratio reduced the impact of microstructural defect deriving from unreacted FA particles. For the influence of curing regime, it can be seen that the 7-days elastic modulus gradually increases from 20 to 80 °C (optimum curing temperature) where a peak value occurs (12.42, 19.42, and 23.14 GPa in FA-GBFS 3:1, FA-GBFS 1:1, and FA-GBFS 1:3 samples, respectively). Increasing the temperature accelerates the hydration and dissolution of aluminosilicate precursors, forming a stronger gel that also promoted binding with the aggregates. Over 80 °C, the mechanical properties of geopolymer concrete decrease due to structural defects and residual porosity resulting from the evaporation of free and bonded water, leaving more pores and developing more microcracks in the matrix. At 28 days, the modulus of elasticity of the 80 °C-cured test samples slightly increased by 0.9%, 1.3%, and 1.4% compared to that at 7 days, in FA-GBFS 3:1, FA-GBFS 1:1, and FA-GBFS 1:3 mixes, respectively.

Mechanical Strength Properties Optimization of GC-Based Concrete: Recent Developments

Currently, some research on geopolymer technology focused on the mechanical functionalization of GC-based compounds by the incorporation of reinforcement additives, including nanostructured materials or reinforcing additives.

Gulsan et al. [61] investigated the synergistic effect of nano-SiO₂ and steel fibers (SFs) on the hardened properties of self-compacting FA/GBFS geopolymer concrete. The addition of SF reinforcements in self-compacting cementitious compounds aimed to improve the cracking resistance and the structure's ductile behavior by possibly increasing the post-failure energy absorption [62]. Nano-SiO₂ fillers contribute to higher strength performances due to two factors [63]: (a) nanostructured fillers with high surface area represent highly reactive siliceous media in alkaline ambient, promoting the formation of aluminosilicate gel; (b) Nano-SiO₂ can act as a filler material inside the geopolymer matrix, filling the voids

and increasing the compactness. According to [61] results, the inclusion of 0.5% and 1% of SFs improves the compressive strength by 5% and 7%, respectively. SF-nano-SiO₂ synergy is remarkable with regard to the fracture energy. The simultaneous use of both additives exhibited superior fracture performance. SFs provide crack bridging ability, preventing the cracks propagation and enabling further deformation of the specimens. Nano-SiO₂ enhances the adhesion between the reinforcement fiber and the geopolymer matrix. At 1% of SFs, the fracture energy went from 3100 to more than 4000 N/m, adding 2% of nano-SiO₂.

Bellum et al. [64] studied the influence of graphene oxide (GO) on the durability and mechanical strength properties of FA/GBFS geopolymer concrete. By considering five different addition levels of the carbonaceous load (0%, 1%, 2%, 3%, and 4%), an overall increase of the compressive strength and elastic modulus was observed. Maximum increase rates were found for 3% addition of GO: major compressive strength and elastic modulus values were 66.41 MPa (60 days curing) and 35.57 GPa (28 days curing) respectively, almost 48.26 MPa and 29.60 GPa values in control formulation (0% graphene oxide). The higher strengths were obtained due to the greater surface area and rough morphology of GO nanofillers. Thanks to this morphology, the interlocking mechanism within the geopolymer matrixes has been enhanced. GO addition provided a better effect on the protection of chloride (Cl) ion permeability. In agreement with [65], the layered and cross-linked morphological characteristics of graphene involve a sponge-like structure, which captures Cl-ions, reduces the penetration depth, and improves the material anti-permeability.

Pham [66] examined the mechanical strength enhancement in RHA-based geopolymer concrete by functionalization with short basalt fibers (SBFs) at various RHA-basalt replacement ratios (0%, 10%, 20%, 30, and 100%). A relevant improvement was achieved in strength properties as a result of increasing in SBF content. The maximum obtained compressive strength was 94.12 MPa for 100% fiber content and 90 days curing age. By comparing the control mix (0% SBF) with hybrid ones, a gradual growth in flexural strength was obtained with a maximum increase rate of 58% in 100% basalt content-based compound (corresponding to 10.82 MPa). Basalt is a Ca-rich component and, by participating in the alkaline activation, it promotes the formation of the geopolymeric gel (specifically C-N-A-S-H gel), which improves the compaction of the matrix and saturates the residual porosity in the paste.

3.4. Durability Properties

The durability of building materials strongly affects the service life of structural components. High durability means protecting the structural reinforcements (e.g., steel armor) from corrosion and reducing the deterioration of the material under hostile chemical attacks or fires. Recent research works on durability performances demonstrate that geopolymer concrete can be considered a possible alternative material to ordinary Portland aggregate.

Gunasekara et al. [67] stated in their research project that FA-based geopolymer concrete displayed lower water and air permeability than PC concrete. Water sorptivity investigations indicated a range from $0.291 \times 10^{-7} \text{ m}^3 / \sqrt{\text{min}}$ at 7 days to $0.184 \times 10^{-7} \text{ m}^3 / \sqrt{\text{min}}$ at 90 days, reporting results below the standard index, which is $1.3 \times 10^{-7} \text{ m}^3 / \sqrt{\text{min}}$ (low water permeability behavior). Air permeability evaluation showed a decrease in its values, ranging from 0.054 mbar/min at 7 days to 0.034 mbar/min at 90 days. Such values were below the standard index for ordinary concrete which is 0.1 mbar/min, indicating the high quality of the geopolymeric blends in terms of permeability. Low fluid permeability could prevent ions from crossing its structure; therefore, it has good resistance to Cl and sulfate (S) attacks, as well as good microstructural characteristics against shrinkage deformation, which help in reducing material cracking.

Morla et al. [68] compared the corrosion inertia of geopolymer concrete made of FA and bottom ash and PC concrete. By the linear polarization resistance test method, the geopolymer concrete corrosion rate ranged between 10 and 20 $\mu\text{m}/\text{year}$ (moderate

corrosion condition), while the corrosion rate of ordinary concrete ranged between 57 and 58 $\mu\text{m}/\text{year}$ (very high-risk corrosion condition). The authors hypothesized that this trend was related to the compact and less porous microstructure of the geopolymeric samples, resulting from the alkali-activated polycondensation process. The aluminosilicate gel acts as a filler, further reducing the material porosity and limiting the migration of Cl ions in the matrix.

Cao et al. [69] conducted a research work investigating fire resistance performance in the comparison between FA-based geopolymer mortar blended with calcium aluminate cement (CAC) and ordinary concrete in the temperature range between 23 and 800 °C. As the results in Figure 14 show, geopolymer concrete showed higher fire endurance and hot-strength behavior than that of ordinary concrete at all temperatures ranging between 200 and 800 °C. PC-based samples were found to be much more sensitive to chemical decomposition induced by high temperatures. On the contrary, geopolymer mortars were much more stable and durable also due to the addition of CAC, which improves the fire resistance of the mix.

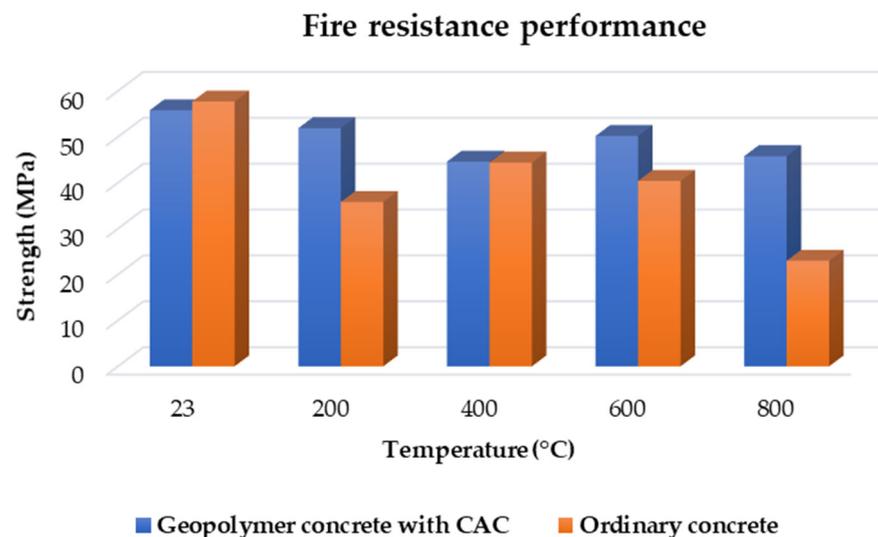


Figure 14. Comparative study on the fire resistance of geopolymer and ordinary concretes (adapted from [69]).

3.5. Thermal and Acoustic Properties

The research for building materials offering high thermo-acoustic performances has increasingly become a goal of the modern construction industry. The need to optimize the energy behavior of buildings is mainly related to two aspects: (a) improving the quality of the urban and domestic environment, in terms of acoustic and thermal comfort; (b) reducing energy consumption and thus minimizing ambient pollution and the excessive exploitation of fossil fuels [70]. Recently, many studies have been conducted on the optimization of the thermal and acoustic properties of geopolymer compounds.

Foamed geopolymer concretes (FGCs) have been extensively investigated as high-performance heat-insulating systems. Generally, there are two usual methods for inducing cellular microstructure to the cementitious medium: mechanical foaming and chemical foaming methods. In the mechanical method, foaming agents (surfactants or premade foam) are added to the mixture to generate bubbles during the mixing process. In the chemical approach, chemicals, including metallic powders, react with the alkaline environment of the cement mix and develop gas voids in the matrix [71]. Pasupathy et al. [72] developed an ultra-lightweight FA-GGBS geopolymer foamed concrete ($<600 \text{ kg}/\text{m}^3$) using porous lightweight aggregates, i.e., expanded perlite (EP), and premade foam activator (Nadodecyl sulfate solution). The addition of EP increased fine air voids in the geopolymer matrix (Figure 15), resulting in an advantageous improvement in mechanical and thermal

properties. In the formulations containing 10% and 20% of lightweight aggregate, an increase in the 28-days compressive strength was observed of 65% and 188% compared with the control sample (0% EP), respectively. The porous nature of EP particles resulted in a thermal conductivity reduction until 12% (0.25 W/m·K in the geopolymer mix containing 20% of EP). Senff et al. [73] studied the effect of aluminum (Al) powder (AP) and glass fibers waste (GFW) as foaming and reinforcement agents to produce low thermal conductivity FA-MK geopolymer mortars. The addition of 2 wt % of GFW enhanced the mortar's flexural and compressive strength by 23% and 30%, respectively. The fibers stabilize the cellular microstructure of the geopolymeric foam, assuring a bridging for the thin layers between adjacent pores. In terms of heat insulation characteristics, AP was the major influential additive. Thermal conductivity dropped from 0.69 W/m·K in control sample (0% AP and 0% GFW) to 0.31 W/m·K and 0.22 W/m·K when 0.1 wt % and 0.2 wt % AP were incorporated to the compositions, respectively. The addition of GFW did not significantly alters the thermal properties. In this regard, the higher GFW content promoted a 5% increase in thermal conductivity value (0.23 W/m·K).

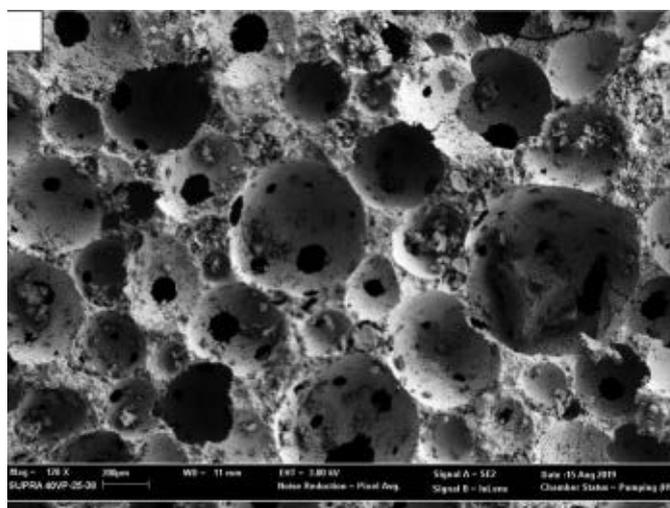


Figure 15. Examples of geopolymer compounds with improved thermal functionality: FGC microstructure (reproduced with permission from Pasupathy et al., *Construction and Building Materials*; Elsevier, 2020).

An alternative approach to FGCs is the functionalization of geopolymer compounds with highly thermo-insulating waste products. Ahmed et al. [74] investigated the effect of different additions of clay brick waste powder (CBP) and aggregates (CBAs) on the thermal conductivity of MK-based geopolymer concrete. The heat conductivity of the reference mix (1.53 W/m·K) declined up to 46% and 54% for mixes with 30% of CBP and CBAs, respectively. This can be attributed to two effects: (a) the incorporation of waste fillers induced a certain porosity degree in the matrix, resulting in high thermal resistance behavior; (b) the porous nature and insulation characteristics of clay minimized the thermal conductivity. Tekin et al. [75] researched novel geopolymer concretes using zeolitic tuff and marble powder as aluminosilicate precursors and waste natural fibers (cotton and viscose fibers) as functional fillers. According to the results, the incorporation of natural fibers leads to a dropped in heat conductivity. Regardless of the type of fibers, the lowest value was around 0.396–0.398 W/m·K for 2% fiber volume fraction compared to 0.910 W/m·K in reference sample (0% fibers). The higher air void and capillary microcracks contents in the fiber-reinforced geopolymer composites are the main reasons for this evidence.

In terms of acoustic performance, some research studies demonstrated the high sound absorption efficiency of FGCs. The cellular microstructure promotes the friction-energy loss and the dissipation into the heat of the acoustic waves during the continuous collision with the micro holes. Regarding pore structure, only open porosity is beneficial to absorption

behavior, as the poro-acoustic interaction into the cement medium is encouraged, and sound reflection is minimized. Leiva et al. [76] reported acoustic absorption coefficients (α) over 0.40 at middle-high frequencies (1000–2000 Hz) and high frequency (3500–4000 Hz) in a porous FA-geopolymer concrete (22% open porosity) based on Pavai (a solid waste steam from the Al industry) as the foaming agent. Gao et al. [77] founded high α -values (0.81 at 500 Hz and 0.54 at 5000 Hz) in aerated geopolymer compounds (~90% of maximum porosity) made of kaolinite aggregates and hydrogen peroxide (H_2O_2) pore generation reagent. Stolz et al. [78] investigated the sound absorption properties of cellular FA-based geopolymer concrete reinforced with glass microfibers (GM) and foamed with a protein-based agent. They noted high efficiency in the low-frequency range (125–250 Hz) where the α -coefficient reached a maximum value of 0.9, indicating a good attenuation against the low-frequency noise, which is harmful to human health.

Sound insulation is another key indicator of the damping and noise reduction peculiarities of building materials. It refers to the ability of a medium to hinder the sound diffusion between two ambient and to attenuate the vibratory phenomena that arise in unwanted noise emissions. In the civil sector, scientific research works on the development of cementitious materials capable of optimizing comfort and life quality in urban and domestic environments, reducing the transmission of noise from a room to another and the sound propagation from vehicles and industrial activities [79]. Contrary to ordinary PC, studies on the acoustic insulation properties of geopolymeric concrete/mortars are very limited. The major finding can be found in Gandoman and Kokabi's work [80]. The authors investigated the insulating behavior of eco-friendly sound barriers made of MK-based geopolymer concrete functionalized with ground rubber (GR) deriving from end-of-life tires, comparing its performance with that of conventional PC concrete panels. The addition of polymer aggregates enhanced the sound transmission class (STC) of geopolymeric panels: 6 wt % of GR provided about 45 dB attenuation against 37 dB STC-value in PC panel. As confirmed in similar research on tire rubber-modified PC-based mortar [81], viscoelastic nature of rubber inclusions improves the material's vibroacoustic damping and sound retention.

4. Recent Applications and Upgrading of Geopolymer Technology in Construction Sector

In this section, some emerging evolutions and applicability examples of geopolymer concrete materials in the civil-architectural sectors are discussed.

4.1. GC-Based Mixes for 3D Printing Fabrication Technologies

In the last 30 years, PC technology has strongly evolved by the study, development, and optimization of cementitious mixes suitable for additive manufacturing (AM) methodologies. Attractive perspectives can arise from the application of AM in civil-architectural fields: (a) reduction in labor requirements, which would result in a lowered production cost and increased safety; (b) reduction in construction time, especially for large-scale application; (c) optimized use of raw material, implying less waste and low production costs; and (d) high architectural freedom, resulting in more complex and sophisticated designs for structural, insulating, and aesthetic purposes [82]. The combination of digital fabrication and cement-based printable materials has led to the development of two forms of methods for manufacturing concrete-like components or structures: extrusion 3D printing (EP) and particle-bed 3D printing (PP) techniques. In the EP method, a digitally controlled deposition nozzle, mounted on a gantry or robotic arm, lays fresh concrete or mortar layer by layer. The PP technique consists of two iterative work stages: (a) deposition of a layer of dry very fine aggregates (typically sand < 1 mm); (b) selective application of a fluid cementitious binder onto the particle packing by a print nozzle to bind the mineral particles. Finally, the non-bonded particles are removed, and the strength of the final product is improved by proper thermal treatments [83]. Each method has very specific features regarding the print resolution, feasibility, material properties, and process parameters. In the PP technique, the shape and size of powder particles determine the deposition quality,

the resolution of printed layers, and the buildability of the final object. This technique is suitable for small-scale and high-resolution (order of mm) applications. In the EP method, the cementitious mix rheology (slump, flow, and setting time), the deposition parameters (pressure and speed of printer head), and the architecture of the printing system (nozzle section and shape) affect the print quality in terms of filaments dimensions, inter-layer adhesion, extrusion regularity, and structural solidity of the printed object. The method does not allow high-print resolutions (4–6 mm maximum resolution) but is suitable for both small-scale and large-scale manufacturing processes allowing, in the latter case, easy implementation of structural reinforcements [84,85].

To enhance the eco-efficiency of concrete 3D printing, in the last 5 years, a lot of efforts have been made to integrate alternative “green” cementitious binders, such as geopolymer compounds, into digital fabrication. Below are some recent research works on the application and optimization of geopolymer-based mixes in AM technologies. However, more information and technical details on 3D printing automation and robotic processes in the geopolymer construction sector can be found in the review work conducted by Luhar S. and Luhar I. [86].

4.1.1. Muthukrishnan et al. Research

The technical details, methods, and aims of this experimental study are reported in Table 4.

Table 4. Details of [87] research work.

Method	Process Parameter	Mix Composition	Primary Findings
EP	3-axis extruder, 25 mm × 15 mm rectangular nozzle, 12 mm/s printing speed, 15 mm nozzle height	FA-GBFS geopolymer mix, coarse, and fine silica sand, PVA fibers, Na ₂ SiO ₃ activating solution, no chemical admixtures	Use of microwave heating as a rapid and efficient mode to increase the filaments bond strength and improve the buildability of 3D printed elements

The authors investigated the effect of microwave curing on the bond strength, stiffness properties, and lateral deformation of printed geopolymer filaments, considering four different microwave exposures (0, 5, 10, and 20 s at constant power of 1200 W and operating frequency of 2.45 GHz). Regarding the inter-filament bond strength, 10 s represents the optimal microwaving time where maximum adhesion force occurs compared to the untreated sample (87.5% of strength gain at 28 days). This condition implied a proper malleability (related to surface moisture content), higher stiffness (related to the accelerated geopolymerization reaction), and greater contact area between the printed filaments. As a result, the lateral deformations of the printed structure were reduced by 87%, thereby improving the structural stability of the 3D printed element. Above 10 s, the bond strength was lowest, exhibiting an average 30% reduction from the control sample (no microwaving exposure). Prolonged thermal treatment promoted the excessive moisture evaporation and malleability loss, resulting in effective overlapping between the extruded filaments.

4.1.2. Chougan et al. Research

The technical details, method, and aims of this experimental study are reported in Table 5.

In this work, the authors analyzed the synergistic influence of nano-clay additive and PVA reinforced fibers on the rheology and structural properties of printable geopolymer mortars. The functionalization with nano-additives and fibers similarly contributed to a significant enhancement in strength performance. The extrusion process promotes the uniform distribution and alignment of polymer reinforcement in the geopolymeric matrix, where a good interfacial bond occurs. This maximizes the crack-bridging and crack-blocking effect induced by the incorporation of fibers (0.25 wt %), increasing the flexural

and compressive strength by 49% (~13 MPa) and 16% (~70 MPa), respectively, to that of the printed neat sample. The addition of nano-clay (1 wt %) accelerates the alkali-activation process, leading to a more compact matrix structure and lower unreacted precursors. This effect increased the flexural and compressive strength by 44% and 7%, respectively. The hybrid formulation (0.25 wt % of PVA and 1 wt % of nano-clay) was found to be optimum in terms of buildability properties (Figure 16).

Table 5. Details of [88] research work.

Method	Process Parameter	Mix Composition	Primary Findings
EP	Gantry-type extruder, 20 mm circular nozzle, 20 mm/s printing speed, 10 mm nozzle height	FA-GBFS geopolymer mix, fine river sand, silica fume, KOH- Na_2SiO_3 activating solution, no chemical admixtures	Addition of nano additive reinforcements (attapulgite nano-clay) and PVA fibers to increase the printability and mechanical strength properties



Figure 16. Buildability of geopolymeric printable composites reinforced with nano-clay additives and PVA fibers (reproduced with permission from Chougan, M. et al., *Materials and Design*; Elsevier, 2021).

4.1.3. Li et al. Research

The technical details, method, and aims of this experimental study are reported in Table 6.

By the automated incorporation of steel micro-cables within the extruded filaments (Figure 17), a remarkable increase in compressive strength, strain at peak strength, and toughness were observed, reducing the structural effect of weak planes between the printed layers. Cable reinforcements perform higher tensile strength (82.5% increase) and greater bond strength (19% increase) than the non-reinforced configuration. However, this research is being optimized regarding the study of pre-treatment methods to improve the steel fiber-matrix compatibilization and the possibility of integrating polymer cables to enhance the corrosion resistance behavior.

Table 6. Details of [89] research work.

Method	Process Parameter	Mix Composition	Primary Findings
EP	3-axis extruder, 12 mm circular nozzle, 10 mm/s printing speed, 50 mm nozzle height	FA-GBFS geopolymer mix, fine river sand, silica fume, penta- Na_2SiO_3 , no chemical admixtures	Implementation of printing device with an automated micro-cable reinforcing method to incorporate steel fibers into the printed filaments for mechanical bearing capacity optimization

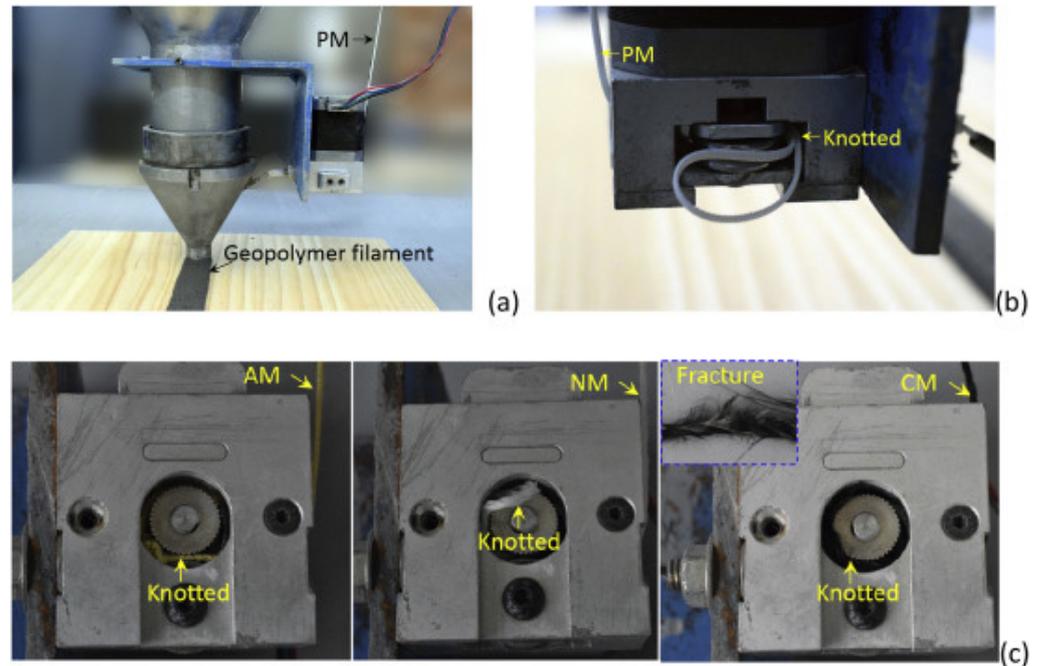


Figure 17. Extrusion 3D printing system implemented with micro-cable reinforcing device (reproduced with permission from Li et al., *Composites Part B: Engineering*; Elsevier, 2020).

4.1.4. Voney et al. Research

The technical details, method, and aims of this experimental study are reported in Table 7.

Table 7. Details of [90] research work.

Method	Process Parameter	Mix Composition	Primary Findings
PP	Powder-based system, 0.2 mm circular nozzle, 0.8 mm line spacing, 2.5 mm layer height, 0.5–1 $\mu\text{L}/\text{mm}$ injection volume	MK reactive powder, silica sand, ground quarry waste, K_2SiO_3 activating solution	The replacement of natural aggregates with ground quarry waste preserves the print quality and the structural properties of the printed elements, resulting in a more eco-sustainable approach

The use of waste stone (quarry waste) as a replacement of natural silica sand in the binder jet 3D printing process does not alter the mechanical behavior of the printed material, resulting in a compressive strength ranging from 10 to 12 MPa. In terms of printing accuracy, evaluated on 40 mm-side printed cubes, the use of quarry waste as mineral aggregates implied better results than traditional sand (about 30% increase). However, printed materials were lower in strength than their corresponding cast (37 and 42 MPa

for quarry waste and silica sand, respectively). This evidence was attributed to the high porosity and the presence of unimpregnated powder in the printed sample

4.1.5. Xia et al. Research

The technical details, method, and aims of this experimental study are reported in Table 8.

Table 8. Details of [91] research work.

Method	Process Parameter	Mix Composition	Primary Findings
PP	Powder-based system, 2.5 pL drop volume, 0.1 mm layer height, 2–4 layers/min printing speed	FA-GBFS powder blend, silica sand, anhydrous Na ₂ SiO ₃ activating solution	The use of GBFS in the mix design (min. 50 wt %) is always necessary to ensure an adequate material setting at room temperature and higher mechanical properties. The exclusive use of FA does not allow to reach adequate green strength due to the low reactivity of the particles. The increase in FA amount increases the binder droplet penetration time.

In this work, the author mainly focused on the effect of FA-GBFS mix proportion on the print quality and strength properties of powder-based 3D printable geopolymer compounds. Concerning the mechanical properties, 100 wt % GBFS mix exhibited the highest green and post-processed compressive strength (0.91 MPa and 29.6 MPa along the X-printing direction referred to the binder jetting direction, and 0.76 MPa and 26.5 MPa along the Z-printing direction referred to the layer stacking direction, respectively). The addition of FA gradually reduces the mechanical strength of the printed materials, which is mainly due to the low alkaline reactivity of the particles at room temperature. For 75 wt % of FA, the powder did not have enough green strength (<0.3 MPa) to resist the de-powdering process, making the post-processed samples untestable. The FA-GBFS ratio was crucial in terms of droplet penetration behavior. A certain FA fraction is necessary to ensure a proper penetration time of the binder during the printing process, which affects the bond strength between layers. Insufficient droplet penetration implies a partial powder–binder reaction between deposited layers, resulting in low green strength. On the other hand, excessive droplet penetration negatively affects the printing resolution [92]. FAs reduce the powder bed hydrophilicity, regulating the droplet penetration. In this research, better dimensional accuracy was obtained in the mix based on 50 wt % of FA and 50 wt % of GBFS.

4.2. Adopting Geopolymer Technology: Companies and Applications

In Australia, geopolymer technology is a highly consolidated reality in the civil and construction sectors, as is clearly shown by the contributions reported below. The Australian company Wagners [93] has patented and commercialized Earth Friendly Concrete® (EFC), which is a pre-mixed FA-GGBFS-based geopolymer binder used in numerous large-scale applications. Brisbane West Wellcamp Airport (Figure 18) is the largest civil project in the world based on geopolymer concrete technology. The EFC compound was employed for the construction of 435 mm-thick heavy pavements, by the slip-forming method, in the aircraft turning areas. The work was completed in 2014 and involved the use of approximately 25,000 m³ of EFC for pavement fabrication and an additional 15,000 m³ for other structural elements in the airport, including bridges, road barriers, tunnel slabs, and sewer tanks. In this project, a saving of around 8640 tonnes of CO₂ emissions has been estimated [94]. More recently, EFC precast floor panels were used to implement the

Australian Global Change Institute. Geopolymer concrete was included in the design for 33 precast floor beams (320 m^3) that formed three suspended floors in the building. Zeobond Pty Ltd. [95] is a manufacturer company of geopolymer pre-cast and pre-mixed concrete products (E-Crete[®]) developed by using FA, coal, and steel by-product. E-Crete[®] technology was implemented in numerous infrastructural renovation projects. Pre-mixed product was used for the manufacture of river retaining walls (Yarra river in Melbourne), road footpath (footpath along Westgate freeway in Melbourne), and pavements works (Thomastown recreative center and Ceres environment park in Brunswick). Precast E-Crete[®] units were fabricated and installed at the Salmon Street bridge (Melbourne), for a total of 180 footway and footpath panels.



Figure 18. Brisbane West Wellcamp Airport: The largest civil project based on geopolymer concrete.

Unlike the Australian scenario, in other countries, the applicability of geopolymer materials is still limited for civil interventions, but several start-ups are emerging, focusing on the development of innovative products and technologies based on geopolymeric binders. Geopolymer Solutions (Conroe, TX, USA) deals with the design of FA-based geopolymeric compounds (aggregate materials and protection sprayed coatings), named Cold Fusion Concretes, with optimized durability performances in terms of acid resistance, corrosion inertia, and fireproofing [96]. Renca (Moscow, Russia) develops pre-mixed compounds suitable for fire-resistant panels, low-temperature burning bricks, high-performance concrete (compressive strength more than 120 MPa), and 3D-printable mortars (named 3D ink) for extrusion-based AM processes [97]. Agma (Italy) devised various geopolymer-based products by incorporating natural fillers (such as hemp fibers) or aerating agents to obtain blocks, panels, and tiles with optimized fireproof, anti-seismic, and thermo-acoustic insulation properties [98].

4.3. InnoWEE Project

InnoWEE [99] is a four-year research project (2016–2020) funded by the European Union (EU) in the context of “Horizon 2020 research and innovation program”. The activity was coordinated by the Institution of Construction Technologies Institute National Research Council (Milan, Italy) with the scientific cooperation of various research partners, including the Institute of Condensed Matter Chemistry and Technologies for Energy National Research Council (Padua, Italy), Slovenian National Building and Civil Engineering Institute (Ljubljana, Slovenia), Advanced Management Solutions Ltd. (Acharnes, Greece), and Pietre

Edil Srl (București, Romania). The main purpose of InnoWEE project is the design of geopolymer binders obtained by the incorporation of demolition and construction wastes (bricks, mortars, crushed wood pallets, grounded glass) to produce novel insulating and radiant pre-cast panels with high performance in terms of energy efficiency and environmental impact. A brief description of some prefabricated InnoWEE components is reported below.

- *ETICs-like panels.* ETICs-like panels (Figure 19a) consist of sandwich panels (400 mm × 900 mm) composed of an outer high-density geopolymer layer (8 mm thin) and 70 mm-thick expanded polystyrene (EPS) insulating core. The geopolymeric binder is an FA-MK blend implemented with 50 wt % of inorganic aggregates consisting in a mixture of fired clay and concrete waste. A preliminary thermal insulation performance analysis was performed by installing these panels in some residential and urban buildings located in various European countries, such as “Don Orione” residential assistance center (Bucharest, Romania), Volua municipal building (Athens, Greece), and pilot eco-buildings (Padova, Italy). In terms of energy efficiency, the results demonstrated an annual energy saving of over 400 kW/h per year, meeting the new building efficiency requirements imposed by the EU.
- *Ventilated façade cladding panels.* Innovative lightweight façade panels (Figure 19b), with dimensions of 595 mm × 595 mm, were developed by bonding an outer high-density geopolymer (such as the ETICs-like one) layer to an inner wood–geopolymer panel (incorporating 40 wt % of crushed wood). The element combines the specific behavior of its components. The geopolymer layer acts as a barrier to protect the structure from adverse weather phenomena (wind load, rain, and ice). The wood–geopolymer panel provides additional strength and lightweight. As for ETICs, insulating and durability studies were performed both in the laboratory and on site by the installation of prefabricated cladding panels in European pilot buildings.

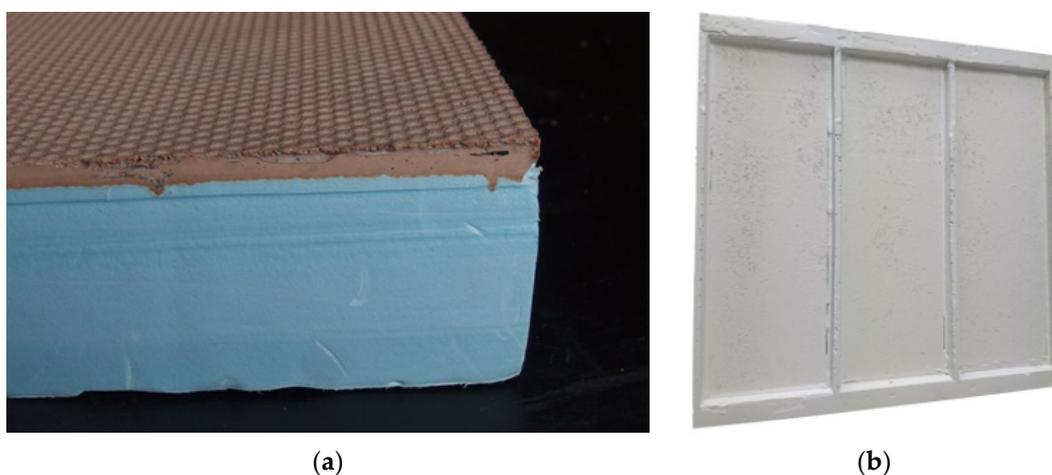


Figure 19. InnoWEE geopolymer-based prototypes: ETICs panel (a) and ventilated façade cladding panel (b) (reproduced with permission from InnoWEE Consortium).

5. Discussion and Conclusions

The current review assessed the major advances, recent findings, and direction for future investigations of geopolymer technology in the construction industry. This topic has remarkably attracted many researchers in the past decade due to being a potentially efficient alternative solution to common PC-based binders both in terms of technological properties and eco-sustainability (CO₂ emission reduction and industrial waste recycling valorization). In addition to investigating recent research trends on the influence of synthesis parameters (type of alumino-silicate precursors, activating alkaline solution molarity, curing regime, water-to-binder ratio) on the performance of geopolymer concrete materials, this paper also

discussed the effect of variables, such as the type of chemical admixtures, characteristics of the natural aggregates, incorporation of reinforcement fillers, and the use of aerating agents or functionalizing additives that enhance the thermo-acoustic properties, which have not received sufficient attention over the years. The following conclusions may be emphasized from the comprehensive analysis reported in the manuscript:

- Reactivity, SiO_2 and Al_2O_3 monomers concentration, and the morphological finesse of the precursors are crucial for the compaction and microstructural features of a geopolymer matrix. A finer size gradation and a high (but balanced) Si/Al ratio are favorable conditions to ensure the formation of a less porous and dense geopolymer gel, promoting the mechanical strength properties.
- Activating solution molarity should be properly balanced to obtain an efficient dissolution of the alumino-silicate precursors and proper rheology of the fresh paste in terms of setting time and slump. The addition of superplasticizers reduces the water requirement, preserving optimal mechanical properties.
- Curing at room temperature or thermal-induced provides similar performance in terms of long-term mechanical strength. High curing temperatures promote the geopolymerization process but, on the other hand, they can negatively affect the microstructure and strength of the material due to the micro-crack generation deriving from accelerated water evaporation.
- The Si-content and the specific surface of the natural inert incorporated in the geopolymer compounds affect the microstructure and mechanical properties. The very Si-rich and finer mineral aggregates promote a more compact and cohesive ITZ.
- The incorporation of reinforcement fibers and micro and nano-fillers is a novel and viable approach to improve the mechanical strength and stiffness of geopolymer concrete and mortars.
- Some current investigations on the durability performance of geopolymeric compounds revealed better characteristics than PC-based materials in terms of water sorptivity, permeability, long-term resistance to corrosion, and fireproofing.
- GFCs are an emerging class of geopolymer formulations with improved thermal insulation and sound absorption properties, resulting in attractive technologies to optimize the energy-efficiency for building application. However, the sound insulation performances of geopolymers concrete are poorly covered in the literature, and therefore, more investigations need to be conducted in this field.

Significant advances were also made in terms of technological innovation and applicability. One of the main interesting goals achieved concerns the possibility of modifying geopolymer mixes for advanced AM processes, opening up to a new design approach, and engineer optimization in the construction industry. In this regard, future work must be done to better understand the possibility of using 3D printing technology to develop functional geopolymer-based applications in the building–architectural fields.

Although more progress has been made regarding the diffusion of these building materials in the civil sector (multi-cooperation scientific projects and extensive development of start-up companies), their use would still seem weak. The main limiting factors, on which more investigation will be needed, are summarized in the following points:

- The high sensitivity of the geopolymerization process to environmental factors and synthesis parameters requires skilled and highly trained labor to obtain materials of suitable quality. The instability in the chemical composition of precursors can be another severely limiting factor.
- High costs and toxicity of activating alkaline solutions. In this regard, the study of more eco-friendly and cheap activators could be a possible way of research to optimize the geopolymer technology.
- Long-term availability of raw materials. The stringent environmental regulations adopted in many industrialized countries on the use of renewable resources as primary energy supplies have led to a slight decline in many power plants, from which geopolymeric raw materials are extracted (for example, coal-fired power stations

for FA supply). If this trend continues, it may further affect the diffusion of GC as a replacement of ordinary PC. However, in accordance with current production rates, availability, and costs, possible replacements of PC concrete with geopolymer aggregates of at least 75% are feasible [100].

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