



# Review

# Geopolymers as sustainable alternates for portland cement in constructive concrete: systematic review

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**KEYWORDS:** Aluminosilicate, raw materials, wastes, management, sustainable.

|               | ABSTRACT: This systematic review presenting fundamentals of geopolymer (GP) for concrete technology.   |
|---------------|--|
|               | Geopolymer formulated by activation of sustainable aluminosilicate (minerals) binders (eco-friendly, available,  |
| Received:     | cheap, sustainable natural raw materials fly ash and slag wastes). Geopolymer concrete decrease scarcity of global ordinary Portland cement and decrease energy 0.110 kWh per gram and $CO_{2(g)}$ emission (800 kg ton <sup>-1</sup> ). Durability, |
| May 19, 2024  | mechanical strength, resistance to water and leaching improved via by TiO <sub>2</sub> nanoparticles as nanofiller.  |
| Accepted:     | Polycondensation yield and physicochemical characteristics of GP are monotonic functions of (binder's chemistry, alkali concentration& types, reinforcing fibers, Si to Al ratio, precursors firing, types of solid wastes, heating                  |
| June 30, 2024 | activation, types and curing conditions. Concrete quality is controlled by geopolymer (composition, additives,   |
| Published:    | mechanical strength and compressive strength). Nano fillers materials $SiO_2$ , $Fe_2O_4$ and $Al_2O_3$ improved (mechanical characteristics, microstructure, functionality, durability, mortar strength, slurry mobility, permeability, impact, and |
| July 22, 2024 | rheology (hydration and chemical interactions in GP paste system) as well as decreasing shrinkage and micro  |
|               | cracks on aging. Fumed nano silica showed be added at small 0.5% wt. with 4% wt. % superplasticizer with low   |
|               | water: cement ratio. Appropriate curing and optimum 7% super plasticizer improved workability, flow and fluidity.  |
|               | Limestone (CaCO <sub>3</sub> ) is an ideal filler increases tensile strength and flexural strength, however decreasing the   |
|               | thermal expansion coefficient. The obstacle is the scale up using CaCO <sub>3</sub> in GP cement.  |

# **1. INTRODCTION**

Construction industry controls economy. Production portland cement release hazardous pollutants specifically  $CO_2$  (g) into environment. Ordinary Portland Cement (OPC) production is

 $2^{nd}$  source of CO<sub>2</sub> global emission causing global warming [1], 12% CO<sub>2</sub>in 2020 [2]. Using 2.0 tons raw materials to produce 1.0 ton cement release 1.0 ton CO<sub>2</sub> and NO gases [3].

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For every 1000 kg cement produced, 110 kWh electricity consumed and 800 kg CO<sub>2</sub> released [4]. Recent urbanization in developing countries has further increased demand and cement utilization, consequently environmental sustainability has been compromised [5]. Because global cement demand is expected to increase by 2.5 times by 2050, production of sustainable building materials is a must [6] to minimize environmental pollution caused by traditional concrete. Due to environmental impact of OPC, recent studies have concentrated on production an eco-friendly geopolymer cement (GPC) [7]. GPC is sustainable [8], during its production, CO<sub>2</sub> emissions decreased by up to 90% than OPC depending upon precursor. FA-based GP produces as little as 90 kg CO<sub>2</sub> per ton cement and maximum limit 250 kg  $CO_2$  ton<sup>-1</sup>. Thus, 70% to 80% less emissions GPC than OPC [9]. Raw materials (silica-alumina) required for GP are available and cheaper than OPC which uses untarnished raw materials Ca(di-, tri-silicates and aluminates). However, costs of alkali-activator are high. Optimizing alkali concentration could render GPC production is economically supported for management of industrial wastes [10].

#### 1.1. What is geopolymer?

Davidovits discovered low cost GP in 1970 during as fireproof

materials and green alternative for OPC. Inorganic polymer alkali-activated aluminosilicate [11]. GPs produced by exploitation industrial wastes such as FA, and slag instead of improper disposal harming environment [12]. Durable resist (water absorption, leaching by sulfates and acids), better mechanical strength, GPC Portland Concrete Cement (PCC) substitutes [13]. Compressive strength and durability enhanced by nanoparticles (NPs) such as TiO<sub>2</sub>. GPC is 3<sup>rd</sup> generation cement [14], 3D polymer, empirical formula  $\{M_n[-(SiO_2)_2-$ AlO<sub>2</sub>]<sub>n</sub>.wH<sub>2</sub>O}: where n is polymerization degree, w is water content and M is alkali metal cation. Initial dissolution of aluminosilicate in strong alkaline aqueous solution giving Si, oxide. Then, a mixture silicate, aluminate, and Al aluminosilicate species is formed, Si-O-Si bonds broken and aluminosilicate oxide gel formed (precursor of polycondensation involved elimination water molecule, Al(III) ions incorporated into silicate backbone (6 or 4 folds coordination) [15] [16]. Geo-polymerization is sensitive [8] and yield controlled by chemical composition of binder (high molecular weight polymer resin) and alkali [17]. Geopolymerization process can diagrammatically as shown in (Figure. 1).

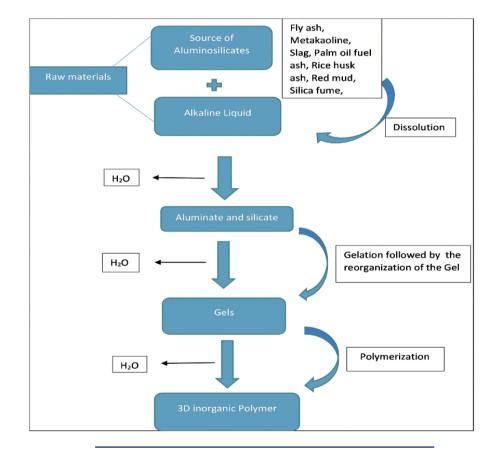


Figure 1. The diagrammatic of geo-polymerization.

Si-O-Si bonds cleavage occurs in the sol-gel polymerization that involved conversion of aluminosilicate into a colloidal *sol* acts as the precursor for an integrated gel polymeric network.

Efficiency of GPC depends on alkaline liquid solution and aluminosilicates resources. Mechanical and physical properties like thermal stability and compressive strength influenced by alkali concentration. Example, low viscous GP produced by reacting kaolinite clay material with a suitable amount of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>). Similarly, a convenient calcination temperature of Kaolinite was determined. Optimum alkali concentration maximized mechanical properties [18]. KOH or NaOH and silicates (K<sub>2</sub>SiO<sub>3</sub> or Na<sub>2</sub>SiO<sub>3</sub>) are common alkali [19]. Structural reliability enhanced by recycled fibers additives [20].

#### 1.2. Classification of geopolymers

Based on monomer type into: poly (siliates, sialate-siloxo (-Si-O-Al-O-)<sub>n</sub> or silico-aluminates and polysialate-disiloxo (-Si-O-Al-O-Si-O-). Alkali-activated GPs were classified by Davidovits [16] [8]. Aluminosilicates chains consist of specific Si: Al ratio depicted in (Figure. 2). Classification into conventional two parts liquid-activated and modern one-part powder-activated GPs using liquid-, and powder alkali respectively.

Concentrated aqueous alkali solutions and water added into solid aluminosilicates. In one-part GP, solid alkali is blended with aluminosilicates and calcined if necessary. Reaction is initiated by little water to minimize corrosion [21]. One-part GP comprise Na aluminate, Na silicate, Ca(OH)<sub>2</sub>, Na<sub>2</sub>O, LiOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na silicate.5H<sub>2</sub>O and their different combinations have been created [22]. FA, slag or a mixture of two are the common precursors due to accentuated pozzolanic activity (slow reaction involves dissolution of all GP constituents yielding 3D network matrix). If some non-fired starting aluminosilicates, pretreatment activates since theses inert reactants such as natural minerals (Example: shales, clays, feldspars, plagioclase, quartz, amphibole) and industrial wastes (red mud and mine tailings, etc.) [23].

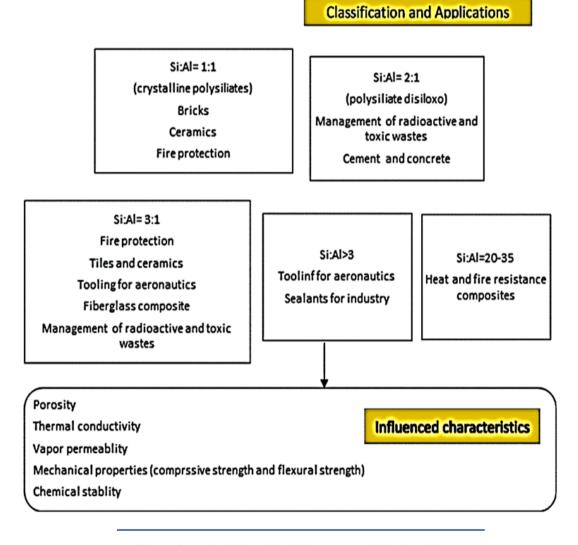


Figure 2. Ratio of Si to Al in different types of aluminosilicates.

Despite liquid-activated GP is eco-friendly having excellent physical and mechanical properties. Challenges in mixing and handling alkali solution affects both safety and economic costs, small change in alkali concentration change geopolymerization degree. One-part GP is safe [25]. This solid phase formulation of GP to avoid risks of contact with very high concentrations alkali such as NaOH that cause severe burns to eyes, skin, gastrointestinal tract or lungs causing permanent damage and death; dermatitis on prolonged or repeated skin contact and permanent lung damage on repeated inhalation NaOH.

#### 1.3. Classification based on raw materials

Different GPs of variable properties depicted in Table 1. Based on precursors, GP categorized into metakaolin-based GP cements (MGCs), FA-based GP cements (FAGCs), natural minerals-based GP cements (NGCs), and hybrid GP cements (HGCs). Metakoaline (MK) is not an industrial byproduct but produced from kaolinite minerals sources under specific calcination conditions. Pozzolanic properties and less energy consumption is required for production MK-based GPC making it more eco-friendly [26]. Rock-based GP discussed by Davidovits are precursors for one-part GP[27] and comprised of high kaolinite content [9]. Industrial by-products blast furnace slag and FA are primary aluminosilicates source. Slag Based Geopolymer (SGPC) has a stronger cross-linked aluminosilicate structure than FAGPC. Cross linking improved higher durability and strength.

Cross linker (such as radiation, silane, peroxide (favored)) possessed react reactive functional groups (FGs) binding FGs of the polymer chains yielding intercalated 3D network polymer chains. For an example, include grafting by adding initiator benzoyl peroxide, cross linking proceeds *via* free radical mechanism. Crosslinking improved chemical, thermal, shrinkage, stress cracking resistance.

FA shortcomings are: Annealing developed primary strength [28]. Mechanical and physical properties of FAGPC affected by impurities in FA. Pure raw materials, such as pumice-type natural pozzolana, natural zeolite, volcanic ash, feldspar, quartz, biotite, and mining wastes are used in synthesis of NGCs containing higher Si content in comparison to FA and metakaolin [26]. Hybrid GP cement is synthesized by compounding GP with OPC or other binders to enhance physical and mechanical properties [26] [29]. Compressive strength increased from 11.4 MPa to 33.4 MPa in 28 d *by* incorporated 10%OPC in GP composites [30]. Rice husk ash functional filler improved strength and permeability [26].

| Raw materials  | Municipal waste           | Industrial waste      | Agricultural ash |
|----------------|---------------------------|-----------------------|------------------|
| Kaolin         | Wastewater                | Fly ash               | Rice husk        |
| Metakaolin     | Rubber                    | Silica fume           | Corn cob         |
| Volcanic ash   | Glass wool fiber          | Blast furnace slag    | Palm oil fuel    |
| Zeolite        | Paper                     | Red mud               | Coconut husk     |
| Dolomite       | Effluent waste and sludge | Recycled glass        | Sawdust          |
| Calcined clays | Plastic, cow dung ash     | Tailings foundry sand | -                |

# 2. General synthesis methods

#### 2.1. Heat Curing Method

In 1970, Joseph Davidovits synthesized GP from finely divided silicaceous materials or salicaceous and aluminous materials e.g. FA, etc. are reactants for endothermic reaction. Annealing enhanced strength and properties. Heat curing form gentle thermal gradients inside material enhanced geo-polymerization that is slow and incomplete through conventional heating. Curing at 50-80°C, 24 h by hot air oven allow heat transfer from outer surface GP to inside surfaces by thermal convection. Curing include [31]: (self, room temperature, hot weather, microwave radiation [32, 33], steam [34] solar [35], hot and advanced cold press) curing. Curing conditions impart different strengths and characteristics to GP [36]. Curing is important for OPC to gain strength and enhance geopolymerization process. OPC undergoes water curing whereas (steam, heat, and ambient) curing are applied for GP concrete. Heat Curing speed up geo-polymerization which is comparatively slow at room temperature. Mechanical and compressive strength are improved via heat curing than ambient curing [37]. Curing temperatures and time affect microstructure and strength [38]. Optimum conditions 60-90°C, 24 h complete geo-polymerization. Above optimum range decrease compressive strengths and weaken microstructure. Superior Microwave causes uniform rapid heating of sample [39]. Increased compressive strengths, i.e. 70 Mpa, 77 Mpa, 90 Mpa larger than ( 4 Mpa, 58 Mpa, 66 Mpa) for oven heat curing [37]. The best curing method is microwave curing. Microwave (frequency range 300MHz-300 GHz ) is an electromagnetic radiation consists of oscillates perpendicular magnetic and electric fields. Penetration of microwave into certain GP with the polar components generate heat affect molecules (of dielectric materials) by ionic conduction and dipole rotation. Ionic conduction is exothermic process generates heat due to the ions flow resistance in the medium. Also during dipole rotation, ions continue changing directions along with field charge creating molecular collisions and heat generation. Microwave curing (via increased temperature and pressure) is a faster curing technique gave better quality GP at short curing time (few min.) relative to 20 h time consuming for room temperature [39].

There are three steps involved in the microwave-assisted extraction process. First, the solute is separated from the active site of sample matrix under increased pressure and temperature; second, the solvent is diffused across sample matrix; and third, solutes get released from sample matrix to solvent <sup>[196]</sup>. MAE is a faster operational technique through which the efficiency of extraction of high-value bioactive compounds is enhanced. The various advantages include faster heating of the material, better extraction yield, better quality of extracts, reduced time required for extraction and reduced solvent quantity as compared to conventional extraction methods and also restricts the degradation of thermolabile compounds. Green tea leaves were used for the extraction of polyphenols and caffeine. It was reported that MAE has a higher extraction yield at 4 min than by other methods of extraction for 20 h at room temperature <sup>[197]</sup>.

#### 2.2. Mix Design Methods

For developing conventional concrete [40], rational practice code is also available [41]. For GPC replacement to OPC variables affect synthesis and properties of GP. For example type of curing and curing conditions, type and source of raw materials, Na2SiO3/NaOH and SiO2/Al2O3 ratio, alkali to binder ratio [41] and type and alkali dose. Therefore no proper design and guidelines have been reported for GPs synthesis until now. Design universal mix design method for GPC is developed [37] [42] [43].Mix designs for FA-based GPC [42] [44] as well as conventional GPC are based on trial and error methods [43]. These methods are based mainly on mix design method available for conventional concrete that is mainly dependent on water to cement (w/c) ratio and physical and mechanical properties control performance [37] like mechanical and compressive strength, quantity of source material, time duration, and alkali concentration. Taguchi approach method [41], particle packing fraction method and response surface methodology optimized mix design of GPs [37]. Three mix design methods have been reported for GPC mixed with FA and slag namely target strength method, performance-based method, and statistical factorial model method [43]. Target strength method includes fixed water content method, fixed binder strength method, and fixed paste content method. Whereas mixture design method based on factorial models is further divided into Taguchi methods and multivariate regression models [43].

Desirable mechanical strength [42] [43] and costs [41] can be obtained *via* develop suitable mix designs for GPC commercialization [42] [43]. Proper mix designs can even produce good mechanical strengths in GPC even at ambient curing conditions. In mix design method, alkaline to binder ratio, FA to GGBS ratio, type, and curing time are focused [41]. Limitations as sometimes alkali to binder ratio is not included and precursor composition ignored as the biggest hindrance factor in developing suitable universal mix design [37]. The required proportion of mixes for producing GPC of desired compressive strength predicted accurately by employing machine learning however neglecting some variables limits applications [37].

#### 2.3. Electromagnetic field curing

Electromagnetic (EM) induction accelerates curing [45]. Sensitivity of nonconductive GP increased by susceptor additives inherent to EM induction. Sensitive conductive materials are Al and Si [46]. Heat production and transfer [47] as changing magnetic field altering current in induction media, conductive part heated and heat transfer by conduction. Bonded components exposed to electromagnetic field (EMF) kHz or MHz frequency range [46]. Heat is produced in heat-sensitive components like Al or susceptors and other conductive mixed materials GP like fibers or additives particles. Careful monitoring of temperature program avoid rapid overheating [45]. Curing accelerates geopolymerization by accelerates dissolution Si, Al atoms from FA surface and heats all sample sections evenly due to heat induction. Less water evaporation as compared to classical heat curing. Moisture accelerated polymerization. Since about 24 to 48 h are required for heat transfer to GP core from surface in heat curing. Temperatures 55°C to 65°C reached in 15 min. EMF curing method is more (economical and sustainable in terms of energy consumption and duration time) than other curing methods. Compressive and flexural strengths 76.8 MPa and 11.3 MPa achieved after 28 d curing. Ferromagnetic Fe powder used for heat generation. Compressive and flexural strengths improved (76.8 MPa and 11.3 MPa respectively) than heat curing. EMF conserves about 99.70% energy compared to conventional heat curing[36].

# **3. Properties**

Room temperature setting, nontoxicity, bleed-freeness, and a protracted working life before stiffening, impermeability, high resistance to heat and inorganic solvents increased compressive strength. GPC has higher Early strength and compressive strength than Portland cement concrete (PCC). For same mix, compressive strength of GPC is approximately 1.5 folds greater than PCC. GPC demonstrated good workability similar to PCC [48]. GPs have unlimited applications, from straightforward, low-cost materials to sophisticated compounds for specialized uses. Si/Al atomic ratio 1-3 for cheap products (metakaolin, blast furnace slag, FA, and among others). Atomic ratio up to 35 for synthesis more complex materials [49, 50]. (Figure. 3) describes different types of materials according to Si/Al ratio, application area, and technical intervention [49, 51].

Fire retardants additives to GP included  $Mg(OH)_2$ ,  $Al_2O_3$  (alumina), red phosphorus, ammonium polyphosphate.

# **3.1. Mechanical properties**

### 3.1.1 Compressive strength of geopolymer cement

Influenced by nano fillers and grinding raw materials [52, 53]. Comparing compressive strengths of GP and PC cement paste after 3 d at various temperatures, (Figure. 4a). GP cement paste's compressive strength are much higher. At 1000°C, 2.0 h, shears of GP specimens used to estimate their thermal stability. GP shrank even throughout thermal exposures, (Figure. 4b) [54].

3.1.2. Split tensile strength and flexural strength of concrete Split tensile strength (TS) and flexural strength (FS) are crucial mechanical characteristics. Fractures initiation and growth in concrete structures, shearing and anchoring of bars, and other phenomena are all related to split TS. Flexural strength measures resistance to bending and breaking [55]. Fang et al. [56] reported slag content affected split TS and FS FA-based GPC. (Figure. 5) showed GPC's split TS and FS increased with a higher proportion of ground-granulated blast-furnace slag (GGBFS). Increased activity of GGBFS, promoted production C-A-S-H gel N-A-S-H gel accelerated and and geopolymerization [57].

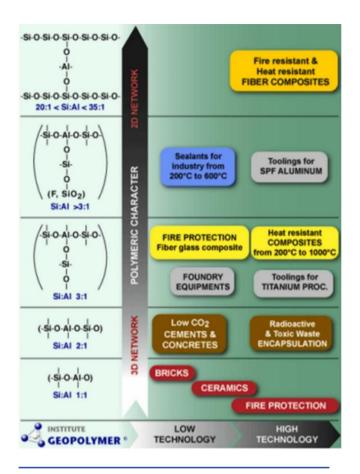


Figure 3. Properties and applications of GPs (Adapted with permission from Ref. [50], Copyright 2022, and Elsevier).

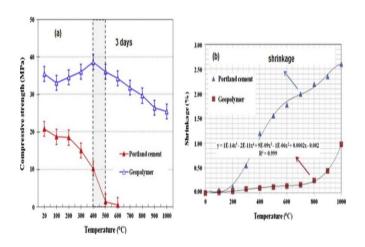


Figure 4. (a) Compressive strength at various curing temperatures and (b) shrinkage.(Adapted with permission from Ref. [54], Copyright 2015, Elsevier).

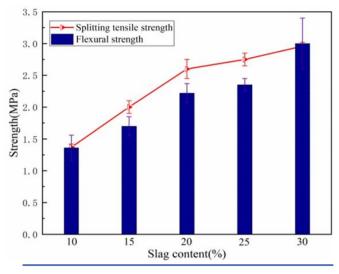


Figure 5. Split tensile strength and flexural strength of GPC concerning the slag content at 28 d. (Adapted with permission from Ref. [56], Copyright 2018, and Elsevier).

#### **3.1.3. Bond properties**

Strength of bonding interaction via chemical adhesion, friction, and mechanical occlusion of concrete to bars determines bearing capacity and performance of reinforced concrete [58-60]. Pulling out of bar or cracking concrete cover causing failure. When a pull-out attempt fails, bar pushed out while concrete between ribs is crushed. Cracks growth along specimen's longitudinal axis occurs, causes splitting failure. Diameter of steel bar, concrete cover's confinement, and transverse reinforcements affect failure. Pull-out failure happens when confinement is satisfactory. In instance that it is not, splitting failure occurs. Prior knowledge bond stress versus slip relation enabled simulation bonding behavior [60]. Numerous variables affect bond strength and characteristics of GPC, (Figure. 6). Bond stress to free-end slide broken as linear bond stress-slip, nonlinear then maximum bonding and longitudinal fissures [55].

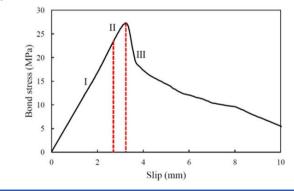
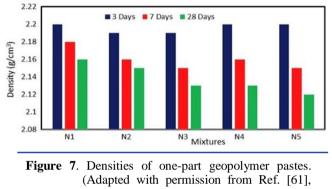


Figure 6. Vaciation of bond stress versus slip (Adapted with permission from Ref. [56],Copyright 2018, Elsevier).

#### 3.1.4. Hardened density

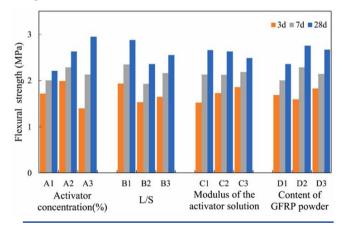
Weighing mass and measurements of cube specimens per mix enabled determination hardened density of one-part GP paste. Initially, 2 cubes per mix were measured, but if there was a more than 5 percentage variation in densities, 3<sup>rd</sup> cube was utilized. When one-part GP pastes mature, hardened densities gradually decrease on aging due to a rather slow geopolymerization reaction. Drop linked to dehydration during reaction by water evaporation. Faster response observed at beginning phase [61] in contrary to the finding in reference [62]. Densities of various mixtures shown in (**Figure. 7**) are nearly the same demonstrating that alkali content has little or no effect [61].



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#### 3.1.5. Fracture behavior of geopolymer concrete

Influenced by material characteristics including aggregate type and mixing composition. To ensure GPs as constructions materials, fracture behaviors are important, properties thoroughly investigated before application as cement substitutes [63]. Early flexural strength of GPC influenced by OPC content, water to solid ratio, Na silicate modulus, and alkali dose [64]. Components, (Figure. 8) demonstrates variation flexural strength and compressive strength are comparable.



**Figure 8**. Relationship between flexural strength and mix factors for GFRP powder/FA-based GP pastes. (Adapted with permission from Ref. [66],Copyright 2022, Elsevier).

At 3, 7, and 28 d, GPs' highest ratios of compressive strength to flexural strength (RCF) were 3.89, 3.63, and 5.52, respectively. At long curing time, RCF grow indicating brittleness. Greater RCF values suggest more fragile. In comparison to glass fiber reinforced polymer (GFRP) powder/FA-based GPs, the greatest RCF values of FA/steel slag (FA/SS)-based GPs were 6.77, 6.92, and 7.46, respectively [65]. Resin in GFRP powder increase GP brittleness. GP early flexural strength evolved faster than their early compressive strength [66].

#### 3.2. Durability

Service life of structural building and bridges is influenced by concrete's durability that lowers concrete spalling by chemicals and inhibited corrosion of embedded reinforcing steel [67]. Durability increased corrosion resistance by (acids, carbonates, sulfides, chlorides, and high temperatures [50]) and resistance to acid assault, freeze-thaw cycles and thermal degradation. Freeze-thaw (ice-liquid water equilibrium) cycles impacts on concrete corrosion, decreased mechanical strength. Exothermic heat flow create differential corrosion temperature for steel [67].

#### 3.2.1. Resistance to acid attack

Reaction of Ca compounds with acid solution damages cement binder system by creating tensile stress cracking. FA/GGBFSbased GPC exceptionally resist acids [55]. (Figure. 9) demonstrated 2% H<sub>2</sub>SO<sub>4</sub> solution affected stability of FAGPC and OPCC over 90 d. Sample's appearance demonstrated that GPC, contains 20% SiO<sub>2</sub> fume showed degradation or corrosion. PCC, however, showed edge breaking and corrosion. PCC sample underwent the most weight loss and compressive strength reduction [68]. OPCC suffered edge breaking, corrosion, and weak compressive strength.



Figure 9. Visual appearance of four blocks of concrete samples exposed to 2% H<sub>2</sub>SO<sub>4</sub> for 90 d:a) FAGPC and b) OPCC (Adapted with permission from Ref. [68],Copyright 2017, Elsevier).

#### 3.2.2. Resistance to freeze-thaw cycles

Performance of GPC is impacted by damage from freezing, endangering strength and security of GPC structures [55]. Systematic evaluations of fundamental qualities of GP mortars have been conducted. However, there hasn't been much system study done on freeze-thaw resistance. In northern China, particularly in chilly northeast and northwest, freeze-thaw cycle is the common cause of concrete degradation. For preparation GP mortar samples, water to class C FA ratios of 0.35 and 0.40, and 45% and 100% Cano with various compositions were used. Until mass loss exceeded 5% or relative dynamic elastic modulus fell below 60%, specimens were frozen and thawed repeatedly [69]. Both concrete specimens continuously lose mass on increasing number of freeze-thaw cycles. However, conventional concrete specimens exhibit greater stability under freezing-thawing conditions. GPC had a larger mass loss than typical concrete specimens [70].

#### 3.2.3. Resistance to thermal degradation

The best attainable shrinkage for GPC 17% at 1000°C decreased to 12%% by alumina and quartz [71]. GP has 3D zeolite-like network structure destroyed at higher temperature than that of cemented cement. GPC resist high-temperature and tolerate 800-1000°C. According to (Figure. 10), FA-based GPCs had a brownish-gray color after curing. On exposure to heat, color began to "redden" (after firing). Iron (Fe) species confined inside FA particles oxidized during prolonged heating. When compared to identical FA-based GPC derived from a separate source with 4.1wt% Fe<sub>2</sub>O<sub>3</sub>, degree of "reddening" of GPC with 16.4 wt. % Fe<sub>2</sub>O<sub>3</sub> is proportional to Fe content. Structural changes post firing, macro cracks above over 600°C, Figure 10 [72].



Figure 10. Photographs of GPCs fired to different temperatures. (Adapted with permission from Ref. [72],Copyright 2015, Elsevier).

# 4. Factors affecting geopolymers properties

In (Figure. 11), these factors including chemical composition, alkali molarity, curing conditions, residual-, tensile strength, and surrounding environment. Concentrations Nano-SiO<sub>2</sub> affects compressive strength, microstructure, setting time, shear bond strength, and durability.

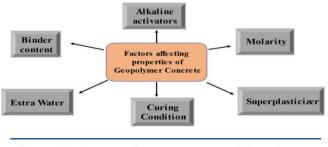


Figure 11. Factors affecting properties of Geopolymer Concrete

## 4.1. Factors affecting mix properties

Geopolymers have poor strength because geopolymerization conducting at ambient temperature [73]. High-temperature curing followed by GP molding formulated concrete that limited to prefabricated components [74]. Specific volcanic ash behavior and nano fillers such as SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> enhanced mechanical characteristics and microstructure of GP composites [75]. Nanofillers boost functionality of GP cement. Zhou et al [76] reported optimum content SiO<sub>2</sub> NPs to sand increases compressive strength, dynamic elastic modulus, and durability, while also decreasing its shrinkage and micro cracks on aging. SiO<sub>2</sub> influence cement mortar strength, cement slurry mobility, dynamic elastic modulus, concrete strength, and effectiveness of permeability was analyzed by Zhuang and Chen [77]. Impact of cement hydration products grew steadily in proportion to amount nano-SiO<sub>2</sub> additive. Incorporating SiO<sub>2</sub> into concrete drastically alter rheology (ASTM D3835). Nanosilica has quantum dot particle size improved: concrete's setting time, collapse, shrinkage (melt apparent viscosity made GP materials exhibiting non-Newtonian melt behavior) [78], mechanical characteristics, and durability[76].

#### 4.1.1. Influence of mixed design

Despite significant differences in binder type and reaction kinetics, impacts of paste volume compared to total aggregate volume and fine-to-coarse combined volume ratio on compressive strength of GP concrete are similar to Ordinary Portland Concrete Cement (OPCC) [79]. Increases in paste volume to a modest level improve aggregate packing, which boosts compressive strength at low to moderate strength grade typical of AAC. For a paste-to-binder ratio below 0.4, range of which is equivalent to described for OPCCs [80], and ignoring long-term effects of AAC binder on aggregates in (e.g. alkaline-silica reaction). More fine aggregate yield uniform matrix with better mechanical characteristics [81].

#### 4.1.2. Influence of curing of geopolymer pastes

Curing atmosphere and annealing enhance geo-polymerization. The common curing methods use conventional heat and microwaves. In Heat curing, specimen not be overheated during curing. Internal temperature may increase significantly boiling point of water on heating to 90°C) Developed because of internal residual tensions, even though original silicate solution has a far higher boiling point than water. Mechanical strength is greatly diminished [82, 83]. Micro-cracks result from curing at low temperature (75°C) for longer periods (72 h). Microwave curing improved compressive strength [84]. Electromagnetic wave (frequency up to 300 GHz) penetrated cement paste interact with polar components generate heat affect molecules by ionic conduction and dipole rotation (ions continue changing direction along with field charge, molecular collisions generating heat. Microwave curing used for curing under precautions. Maximum penetration depth is few centimeters (depending on constant wavelength) as shown in (Figure. 12).

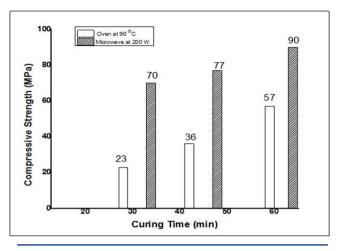


Figure 12. Curing time and compressive strength of geopolymer paste in an oven and a microwave. (Adapted with permission from Ref. [84], Copyright 2018, Elsevier).

The best compressive strength (90 M Pa) was attained at the longest time of curing (90 min.) in microwave curing. The optimum curing time (compressive strength (77 M Pa) is 50 min.

Solar curing is an innovative, eco-friendly alternative to traditional normal curing (oven or ambient conditions. Structures with lots of exposed surface area simply treated. Sun energy affect strength of GP mortars, samples coated with solar curing black (SCB) and 40% black (grey SCG) [85]. Hotpressing technique is good alternative, annealing at a constant 350°C under applied pressure improved compressive strength. Density increases by compressing out trapped air holes [86]. Because water is essential to alkaline activation and curing regime humidity influence structural and mechanical characteristics FA GP pastes, mortars, and concretes. Water throughout GP curing phase is critical and temperature accelerates curing. Rapid geo-polymerization produced by heat curing rapidly attain satisfactory strength [87]. Curing at 400 to 500° C for 4 to 48 h was described by J. Temuujin et al. [88], Figure 4 was a key prerequisite for GPs synthesis. Hardjito et al. [89] noted that enhancing curing temperature does not automatically result in a greater final product compressive strength. Curing temperatures affect mechanical and chemical characteristics [90].

#### 4.2. Influence of admixture and other additives

Electrostatic repulsion between particles in super plasticizer (SP) dispersion agent much as it does in OPC-based concrete, making mixture easier to work with by particles dispersion [91]. With "combined admixtures" (i.e. PC with whichever sucrose or borax), the compatibility of PC was higher with sucrose than borax. Compared to PC and borax paste, PC and sucrose paste displayed greater compressive strength, more workability, and longer setting time. Compressive strength decrease up to 26% when paste was made with "mixed admixtures. Possible explanations include the retarder and SP's combined slowing effects. Paste made with "combined admixtures" was up to 32% less workable than paste made with

only PC due to competitive absorption with sucrose or borax. Inclusion sucrose or borax inhibited PC absorption, hence decreasing paste's fluidity. There was 18% increase in 1<sup>st</sup> setting time of paste containing "mixed admixtures" compared to paste having only sucrose or borax retarder. PC had a fluidizing impact and/or because PC contained more water than usual, both of which inhibited setting [92].

# 4.2.1. Influence of super-plasticizer (SP)

Since high viscosity of GP concrete mix reduces workability, SP (examples are trimellitate, adipate, and phthalate esters (the most common SP.).An adequate amount improve flowability and fluidity. SP enhance GP flexibility and workability, decrease elastic modulus of binder melt and enhance processing and flow (modify properties of natural polymers) and develop a new property to native binder.

External SP physically interacts with polymer chains have a low volatility and lost by migration, evaporation or extraction. Internal SP are main part GP matrix (one component of GP, or reacted or copolymerized with binder. Bulky structures provide polymers to move around due to space provided from crowded structure to keep GPs from getting enclose and softening (decreasing glass transition temperature (Tg), so elastic modulus reduced. SP during ambient curing improved workability with slight decrease in strength, Jithendra and Elavenil [93]. Table 2 demonstrates according to Memon et al., SP makes concrete it easier to work and increases compressive strength. Up to 5% SP is insufficient for achieving desired fluidity level [94]. Workability achieved with both 6% and 7% SP (highest compressive strength with 7% SP across all ages tested). Demie et al. provided a similar idea concerning SP dosage. Increasing SP dose increased compressive strength of GC and gave superior microstructure by decreasing thickness of Interfacial Transition Zone (ITZ) [95]. To compare fresh and hardened characteristics, Sashidhar et al. used 3% SP and 25% water addition [96]. While researching malleability and durability of SCGC, Ushaa et al. used 6% SP and a water-topowder ratio of 0.33 in their experiments [97]. Strength and microstructural and workability properties improved by SP. In addition to SP age, more water is needed to keep GC workable. When it comes to SP dose of less than 5% is inadequate for appropriate workability. Adding 7% SP to GC mix increases final products and enhanced compounding. To achieve the best ambient curing GPC, 6% SP and 12 M NaOH are recommended [98].

| Super<br>plasticizer | Remarks   | Reference |
|----------------------|---|-----------|
| 2% - 6%              | Maximum strength and workability at 6% SP       | [93]      |
| 3% - 7%              | 7% SP enhanced outcome                          | [99]      |
| 3% - 7%              | At 7% SP, microstructure and strength maximized | [100]     |
| 3%                   | Ideal workability at 12 M NaOH.                 | [96]      |
| 6%                   | 6% SP mandatory for fluidity                    | [97]      |

Table 2: Reported studies on superplasticizers

#### 4.2.2. Influence of nano and micro silica fume

Accumulation silica fume improves rheology of liquid activated GP [101]. Ultra high compressive strength values (>150 MPa) achieved after 28 d or even after 2 d for a mortar with maximum aggregate size of 2 mm cured at 60°C, 24 h [102]. Water to binder ratio reduced to 0.25 or even lower to accomplish this [86]. GPC is limited in application since it requires heat curing. These problems solved by adding optimum quantity of silica NPs to the activated mixture [103]. Adding 6 % silica improving concrete's structural behavior at several ages without heating activation [86,104]. Silica (SiO<sub>2</sub>) nanoparticles (NPs) catalyzed sol gel reaction increasing adhesion cement slurry to steel in concrete. SiO<sub>2</sub>NPs efficiently increased mechanical strength than properties SiO<sub>2</sub> powder of concrete. Small weight percent SiO<sub>2</sub>NPs keep porosity cement slurry unaffected. SiO<sub>2</sub>NPs elevated resistance of steel in concrete against stress corrosion cracking and water. Silica is nanofiller decease blustering of GP, increasing softening temperature. Although temperatures of glass transition and decomposition may decreased by increasing silica wt. % but heat of decomposition and weight loss data reflect thermal stability.

#### 4.2.3. Influence of limestone filler

Limestone (CaCO<sub>3</sub>) is setting retarder in pastes enhanced setting performance and reductions in efflorescence of hardened pastes achieved by high NaOH concentration and limestone blends. Percentage CaCO<sub>3</sub> in mixture affect shrinkage degree that is more pronounced at 5.0M NaOH rather than 8.0M or 10.0M NaOH solution. Samples shrink by less than 1%; as proportion CaCO<sub>3</sub> powder in pastes rise, water absorption fell, and vice versa, up to 45% mix. While density rise [105]. Mixtures of 45% CaCO<sub>3</sub> powder with maximum activation temperature replace thermally activated halloysite based GP, improving mechanical strength through densification of matrix and improved particles packing [106]. Calcium carbonate, notably increases modulus, and flexural strength, but decreases the thermal expansion coefficient (TEC). The challenge is to convert these benefits into marketable commercial products. GPC containing CaCO<sub>3</sub> aggregate has lower TEC than GPC concrete containing silica aggregate [106]. Using CaCO<sub>3</sub> in small micron particle size improve TEC of GPC [49].

In summary, geopolymerization can be represented by equation 1[107]:

Aluminosilicate + conc. NaOH
$$\rightarrow$$
 SiO<sub>2</sub> + A<sub>12</sub>O<sub>3</sub> (1)

This reaction followed by the formation of a mixture silicate, aluminate, and aluminosilicate species is formed, Si-O-Si bonds cleavage +aluminosilicate oxide gel formed (precursor of polycondensation with elimination H<sub>2</sub>O molecule).

Chemical structure of aluminosilicate contains Al-O, Al-OH octahedral (Oh) sheets sandwiched by 2 Si-O tetrahedral (Td) sheets. Layers in 2:1 triple sheets bounded by weak Van der Waals forces. Layer (thickness 1.0 nm and lateral layers dimensions 100-1000 nm. Swelling by hydration of interlayer cation enable intercalation with positively charged biomolecules. Si<sup>+4</sup> and Al<sup>+3</sup>cations in tetrahedral sheet. On substitution of Si<sup>+4</sup> ion in Td and/or Oh sheets by Al<sup>+3</sup>, layer framework become negatively containing exchangeable

Na<sup>+</sup> or K<sup>+</sup> cation [107].

#### Conclusion

This review enabled developing test application ecofriendly low cost GP in concrete with considering challenge alkali costs. Production not cause climate changes due to low CO<sub>2(g)</sub> emissions. Alkaline activation of raw minerals materials enabled commercial GP. GP cements with good mechanical and durability produced from various aluminosilicates and alkali solutions with optimizing curing temperature, alkali concentrations, additives, Na<sub>2</sub>O/SiO<sub>2</sub> ratio, etc. GPC are safe construction material. Curing enhanced mechanical strength. Several mix design of FA and slag GPs optimized statistically. Fixed (H<sub>2</sub>O content, binder strength, paste) methods. Mechanical strength, suitable proper universal mix designs of GP enabled commercialization. Application specified by Si/Al ratio. Mechanical strength of GPC exceeded that OPC. GP shrinking is much less at 1000°C. Concrete's split tensile such as fractures, shearing and bars anchoring. Flexural strength (bending and breaking resistance) increased by slag content that catalyzed gelation. Amount solid alkali slightly affect density change of aged GPC. Concrete's fracture influenced by aggregation and mixing composition. Properties investigation prior cementations eliminates fracture. Brittleness is due high glass fiber content. GP is durable, chemical& thermal stable and resists corrosion. Optimum Ca content mitigated acid cracking. SiO<sub>2</sub> fume inhibited erosion corrosion. Stability against icing required further studies. Resistance to shrinkage of GPC is more than OPC. High-temperature curing, molding, concrete kind limited prefabricated GPs components. Curing enhance geopolymerization, favored curing methods are hotpressing and microwave. Super plasticizer improved at 6%SP, 12M NaOH improved workability. maximized strength, workability and fluidity. Nano Silica improved rheology, improving structural behavior on aging without heat activation. This nanofiller randomly distribute without causing any voids in GP increasing the mechanical strength. The best curing methods of GP are: magnetic field (application of magnetic water fluids. Ions rapidly peetrated cement pores achieving complete hydration that improving hydraulic strength of GPC depending on the strength of the magnetic field. Radiation microwave curing (time-saving eddicient technology) improved compressive strengths.

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