

Review

Fly Ash-Based Geopolymer Binder: A Future Construction Material

Nakshatra B. Singh

Department of Chemistry, Sharda University, Greater Noida-201306, India; nbsingh43@gmail.com

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Abstract: A large amount of waste coming out from industries has posed a great challenge in its disposal and effect on the environment. Particularly fly ash, coming out from thermal power plants, which contains aluminosilicate minerals and creates a lot of environmental problems. In recent years, it has been found that geopolymer may give solutions to waste problems and environmental issues. Geopolymer is an inorganic polymer first introduced by Davidovits. Geopolymer concrete can be considered as an innovative and alternative material to traditional Portland cement concrete. Use of fly ash as a raw material minimizes the waste production of thermal power plants and protects the environment. Geopolymer concretes have high early strength and resistant to an aggressive atmosphere. Methods of preparation and characterization of fly ash-based geopolymers have been presented in this paper. The properties of geopolymer cement/mortar/concrete under different conditions have been highlighted. Fire resistance properties and 3D printing technology have also been discussed.

Keywords: geopolymer; fly ash; compressive strength; microstructure; heat evolution; foam concrete

1. Introduction

Development of a country may be directly linked with the development of a cement industry. Portland cement is the most widely produced man-made material on earth used for the manufacture of concrete, the most prevalent building material on the planet. Demand for cement is increasing continuously and in the next decades, cement and concrete production is expected to increase further. The production of concrete is used by some economists as a measure of a country's economic strength [1,2]. Cement manufacture consumes huge amounts of raw materials and energy. Apart from this, a large amount of solid waste and gaseous emissions particularly CO₂ are produced [3]. Cement industry is considered to be one of the greenhouse gas (GHG) emitters [4]; 0.83 kg CO₂ is produced per kg cement production [5–7] leading to 8% of total global anthropogenic CO₂ emissions.

There are a number of drawbacks to Portland cement manufacture. Some of the major drawbacks are: consumption of huge amounts of natural resources and energy, release of greenhouse gases, etc. Apart from these, Portland cement is poor in immobilization of contaminants and the concretes made from it are not durable in corrosive atmospheres. Atmospheric CO₂ also reacts with the hydration products and deteriorates the structure.

Above demerits of OPC compelled researchers to find new binders as an alternative to traditional OPC so that a better, less energy and raw materials consuming with less emissions of greenhouse gases can be obtained. Now, one of the most important new binding materials is geopolymer cement [8–16]. Geopolymers are binding materials different from OPC and made by activating source materials containing silica and alumina such as (fly ash) FA with alkali solutions and Na₂SiO₃. A three-dimensional amorphous aluminosilicate network is formed due to geopolymerization. Geopolymer binders are becoming important because of utilization of waste materials. One such important source material is FA, which has extensively been used for synthesis of geopolymer concrete

with better mechanical, chemical, thermal and durability properties as compared to OPC concrete [15]. However, there are many other source materials which have potentials to be used as replacement or addition to fly ash in making geopolymers. Geopolymers made from different source materials show different properties. Functionally graded geopolymer specimens have also been fabricated by consecutive pouring of two different pastes with fly ash of different particle size and Si/Al weight ratios. These showed some interesting results [17]. New classes of geopolymers known as boroaluminosilicate geopolymers have also been synthesized from mixtures of fly ash and anhydrous borax [18,19]. These have entirely different microstructures.

The increasing knowledge in understanding the science of geopolymerization is responsible for improving the properties of geopolymers particularly fly ash-based geopolymers. Because of its unique structure, geopolymer is a better substitute for OPC in different applications. A literature survey revealed that geopolymers possess properties superior to OPC and because of various advantages, geopolymer concretes are used in a number of areas. In this article various aspects of fly ash-based geopolymer cement, mortars and concrete have been discussed.

2. Geopolymer Cement

Geopolymer may be treated as one of the most promising and important alternative materials and it was first coined by the French scientist Joseph Davidovits [20]. When inorganic aluminosilicate-based materials react with alkaline solutions, polycondensation reaction forming geopolymers occur. Geopolymer structure may be divided into three basic forms which depend on Si/Al ratios. The three basic units, poly (sialate), poly (sialate-siloxo) and poly (sialate-disiloxo) as reported by Liew et al. [13] are shown in Figure 1.

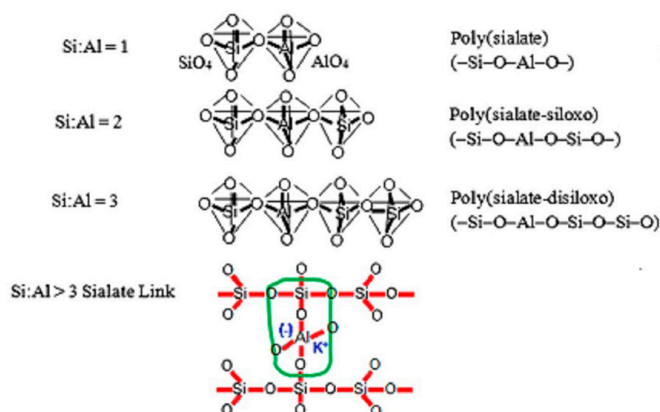
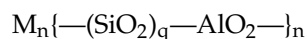


Figure 1. Structure of polysialates [13] (Reproduced with permission from Progress in Materials Science; published by Elsevier, 2016).

On activating aluminosilicate present in FA by alkalis, an inorganic polymer known as geopolymer is formed. The chemical structure is written as:



where M is an alkali cation, n the degree of polycondensation, and q is the Si/Al ratio. In general, geopolymer is a synthetic inorganic polymer and during the chemical reaction under alkaline conditions, a three-dimensional polymeric chain structure is developed. Composition of raw materials and the nature and concentrations of alkaline solutions control the microstructures and mechanical properties of the geopolymers.

The significance of geopolymer binders in replacing OPC binders is based on the fact that there are huge amounts of waste materials containing aluminosilicates obtained from industries and agriculture and result in problems of their disposal [21].

3. Synthesis of Geopolymer Cement

Geopolymers are normally synthesized by mixing source materials having aluminosilicate and the alkaline solutions. Source materials used are kaolinite, clays, zeolite, fly ash, silica fume, slag, POFA, rice-husk ash, red mud, etc. The most common alkaline liquid used in geopolymerization is a combination of NaOH/KOH and sodium silicate. When any of the above source materials (for example fly ash (FA) in solid form) are mixed with alkali solutions of appropriate concentration and sodium silicate, geopolymers are formed. It has been reported by Zhuang et al. [7] that during the polymerization reaction of fly ash, the following processes may take place (Figure 2).



Figure 2. Processes of geopolymerization from FA [7] (Reproduced with permission from Journal of Cleaner Production; published by Elsevier, 2016).

Sometimes the alkali activator in solid form is milled together with source materials (e.g., FA) with a certain composition, resulting in a fine grain similar to cement. This is then mixed with an appropriate amount of water at the time of its use [13,22]. Diagrammatical representation of the method as reported [13] can be seen in Figure 3.

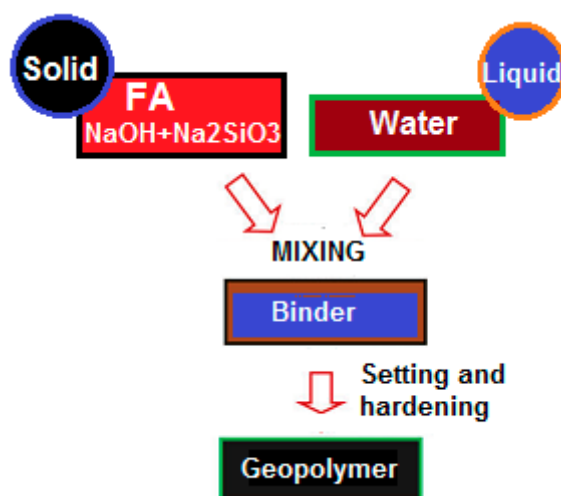


Figure 3. Geopolymerization by dry mixing [13] (Reproduced with permission from Progress in Materials Science; published by Elsevier, 2016).

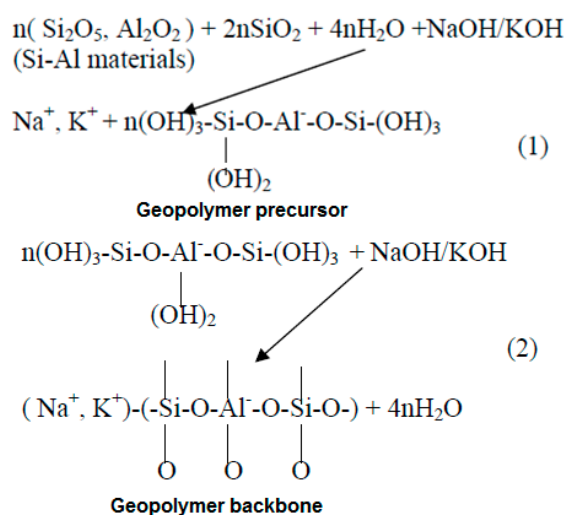
4. Geopolymer Concrete Printing

Use of group of techniques in making 3D structures straightway from a digital model is known as additive manufacturing (AM). This may (1) reduce the number of workers resulting into cost reduction and safety; (2) reduce construction time; (3) reduce the chances of mistakes and (4) increase architectural freedom [23,24]. Now, 3D printing of concrete is developed more in comparison to conventional methods of casting concrete into formwork. Layering processes in geopolymers result in an increase in flexural strength [25].

Three-D printing processes increased compressive strengths of geopolymer mortars made from variety of aluminosilicate materials including FA. It was found that there was anisotropy in the compressive strengths due to layered deposition of the geopolymer mortars [26].

5. Reactions during Geopolymerization

The process of geopolymerization is a chemical reaction between an alkali solution and source material containing aluminosilicate (FA) and gives a three-dimensional polymeric chain and ring structure consisting of Si–O–Al–O bonds, as reported by Scheme 1 [27]. The reactions can occur at room temperature. Therefore, it can be considered as energy and source efficient and much cleaner.



Scheme 1. Reactions during geopolymerization [27].

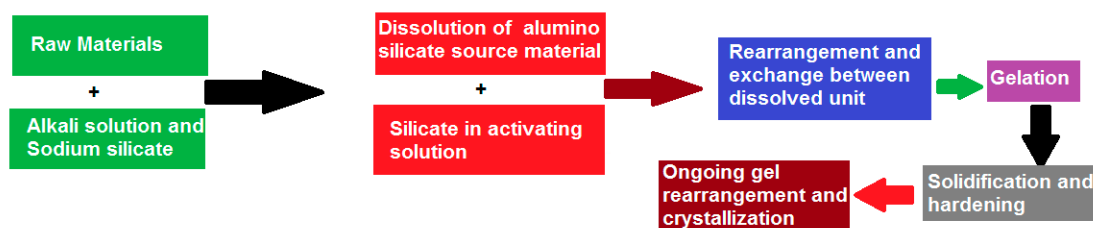
The following steps may be involved during the geopolymerization reaction [28,29]:

- Si and Al atoms present in the fly ash may dissolve by the action of hydroxide ions.
- Precursor ions may be converted into monomers.
- Polycondensation of monomers into polymeric structures.

These three steps can occur almost simultaneously and may also overlap.

Reaction (2) indicates that during polymerization, water is eliminated. On the other hand, during hydration of OPC, water is consumed.

Furthermore, due to different sizes and charge densities, different alkali cations affect the nucleation and growth of aluminosilicate chains in different ways and, as a result, the rate and the extent of polymerization change differently [12,30]. For example, K^+ cation (1.33 Å) having a larger size and lower charge density than that of Na^+ cation (0.97 Å) leads to a higher degree of polymerization of geopolymer matrix [12,31]. The exact mechanism of setting and hardening of the geopolymer material is not well understood. However, based on the findings of Soutsos et al. [32], tentative mechanism of geopolymerization can be proposed by Scheme 2 [32].



Scheme 2. Proposed mechanism of geopolymerization.

When fly ash reacts with alkalis forming geopolymers, its surface gets corroded and amorphous reaction products are formed. Ryu et al. proposed a model (Figure 4) [33]. The reaction products make the structure dense.

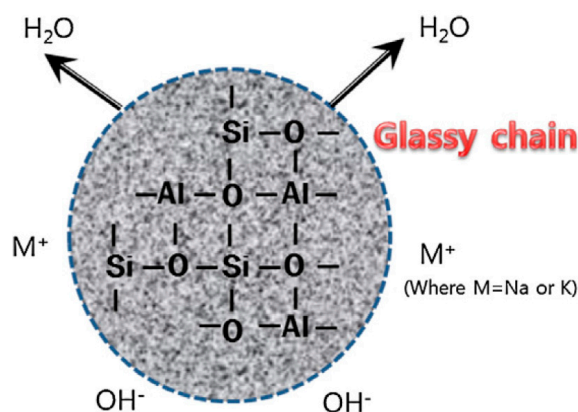


Figure 4. Interaction of fly ash with alkali activator [33] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2013).

6. The Structure of Geopolymers

In spite of large number of studies, a definite structural model could not be proposed for geopolymers. It may be due to its amorphous nature. Small molecules (oligomers) combine together forming 3D network during geopolymerization. Spectroscopic methods have been used to propose structure to polymers. Theoretical models have been proposed and ab initio DFT calculations were made by Koleżyński et al. [14]; the proposed structural model for geopolymer is given in Figure 5. Using solid state MAS NMR, a new model was also proposed for N-A-S-H gel [15].

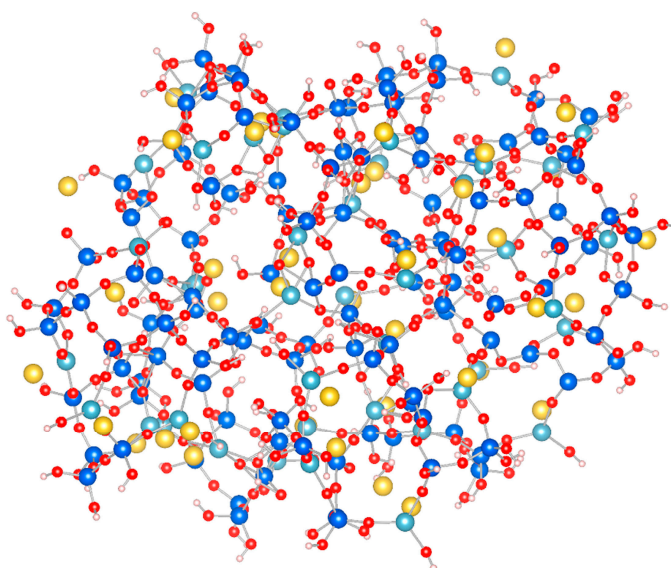


Figure 5. Structural model of geopolymer with 800 (Si:Al = 2.81) [14] (Reproduced with permission from Journal of Molecular Structure; published by Elsevier, 2018).

7. Casting and Curing of Test Specimens

Although there is no standard method prescribed, geopolymer concrete is made in a similar way as conventional Portland cement concrete. First of all, activator solutions as given here are prepared. The required quantity of NaOH pellets is dissolved in water to have to the required concentration. For example, to prepare an 8 M NaOH solution, 320 g of NaOH pellets are dissolved in one liter of solution since the molecular weight of NaOH is 40. This solution is then mixed with the required quantity of Na_2SiO_3 solution to fix the ratio of alkaline activator solution as 1.5, 2.0 and 2.5. Fly ash, sand and the aggregates are first mixed together in dry state and then mixed with alkaline liquid and a small dose of the super plasticizer. Extra water may be added if needed. The fresh concrete was cast and compacted in the molds of standard size. Generally, heat-curing (60–90 °C) of geopolymer concrete is done. It assists the chemical reaction that occurs in the geopolymer paste. Microwave heating can also be used for curing [34].

8. Factors Affecting Geopolymerization

Some of the important factors which affect the process of geopolymerization are given below.

- I. Type of raw materials containing aluminosilicate
- II. Surface area of solid raw materials
- III. Glassy phase content in the raw material
- IV. Amount of aluminum and reactive silicon
- V. Presence of iron, calcium, and inert particles in FA
- VI. Curing temperature and pressure
- VII. Duration of curing
- VIII. Type of curing (conventional heating or microwave heating)
- IX. Type and concentration of alkalies
- X. Alkaline liquid-to-raw material ratio
- XI. H_2O to Na_2O molar ratio
- XII. Water to Geopolymer solids ratio
- XIII. Na_2O to SiO_2 ratio
- XIV. SiO_2 to Al_2O_3 ratio

In general, geopolymerization increase with curing time and curing temperature (up to 90 °C). Higher concentrations of alkalis enhance the geopolymerization, whereas the type of alkalis also affect the process. With the increase of H₂O-to-Na₂O, Water/Geopolymer Solids, Na₂O/SiO₂ ratios, compressive strength decreases indicated lesser geopolymerization.

The variation of compressive strength with SiO₂/Na₂O / Al₂O₃/Na₂O ratio as reported by Ryu et al. [33] is shown in Figure 6. As the ratio increased, the compressive strength decreased.

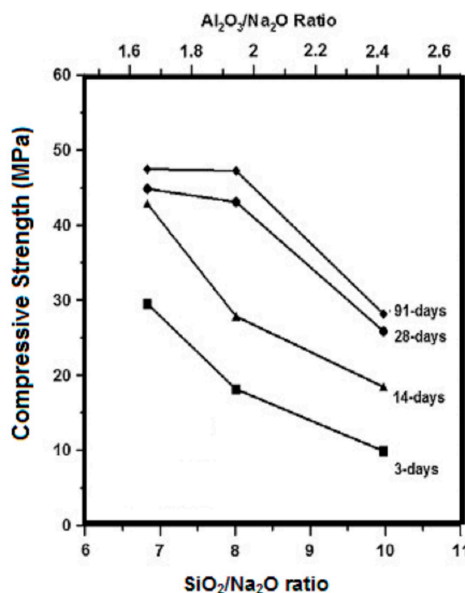


Figure 6. Compressive Strength vs SiO₂/Na₂O and Al₂O₃/Na₂O ratio [33] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2013).

Barbosa et al. [35] found that the optimum Na₂O/SiO₂, H₂O/Na₂O and SiO₂/Al₂O₃ ratios were found to be 0.25, 10.0, and 3.3 for better performance [36]. In order to have an idea about the effect of different parameters on geopolymerization, setting times were determined. Experiments were designed using the Taguchi model [37]. Furthermore, when geopolymers are subjected to high temperature (350 °C) and high pressure known as hot pressing the mechanical properties are enhanced [38].

9. Characterization of Geopolymers

There are a large number of techniques which have been used for the characterization of geopolymer cements. Some of the techniques have been discussed below.

9.1. X-ray Diffraction Technique

XRD patterns of fly ash and geopolymer as recorded by Hanjitsuwan et al. [39] are shown in Figure 7. The fly ash consists of an amorphous phase with broad hump around $2\theta = 20\text{--}38^\circ$. The other peaks are due to some crystalline phases present. In geopolymer the hump is not changed.

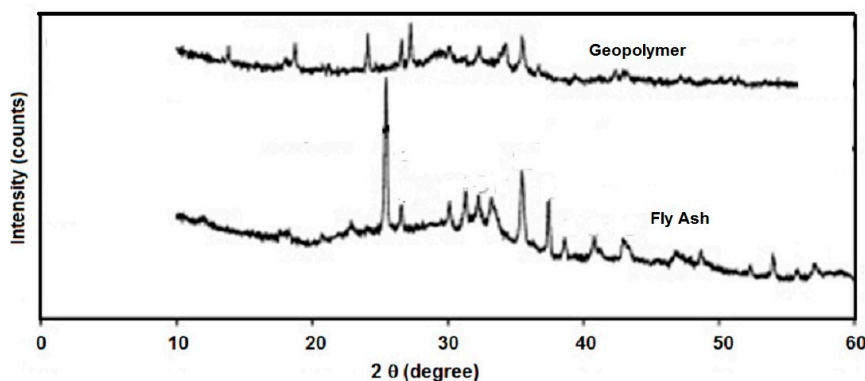


Figure 7. XRD pattern of fly ash and geopolymer [39] (Reproduced with permission from Cement and Concrete Composites; published by Elsevier, 2014).

9.2. FTIR Spectra of Geopolymers

FTIR spectra of geopolymer prepared in the presence of different concentrations of NaOH and cured at 60 °C as reported by Nath et al. [40] are shown in Figure 8. Bands at 460 cm^{-1} and 550 cm^{-1} respectively are assigned to in plane and bending vibrations of Al–O/Si–O [39]. Geopolymer with 8M NaOH showed a much broader peak, may be due to the presence of large amount of structural water. Appearance of a band at $\sim 1456 \text{ cm}^{-1}$ may be due to C=O vibrations, confirming the presence of carbonate groups [40].

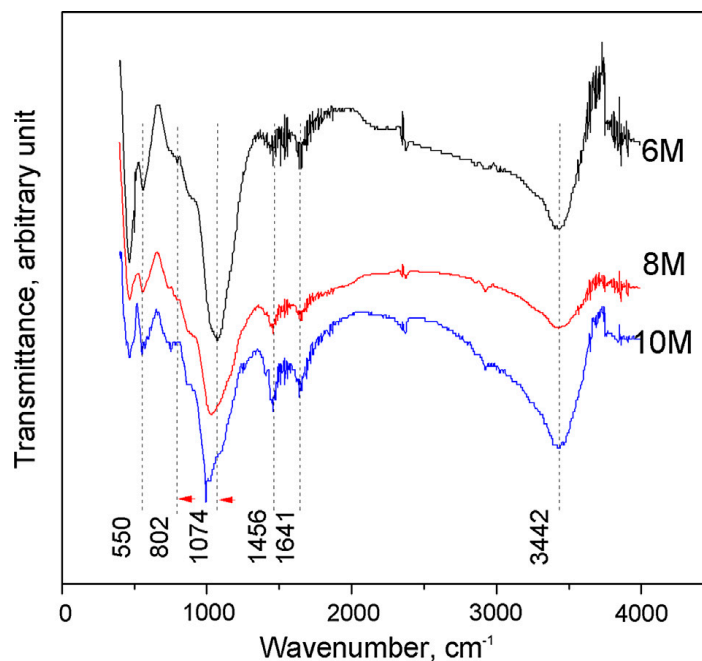


Figure 8. FTIR spectra of geopolymer [40] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2016).

9.3. NMR Spectroscopic Technique

NMR is a technique to derive structural and compositional features (or changes) of most of the compact or porous (zeolitic) natural and synthetic aluminosilicates [41]. ^{29}Si -NMR allows straightforward determination of the framework Si/Al ratios and the resolution of crystallographically non-equivalent sites. The distribution of Al atoms on the various sites can either be random or

specific. ^{27}Al -NMR characterizes Al species in different coordination. MAS NMR spectroscopy is an important tool for the study of inorganic solids such as minerals, zeolites, clays, ceramics and cementitious systems with ^{29}Si and ^{27}Al representing some of the most important nuclei. In ^{29}Si MAS NMR, the chemical shift ($\delta(^{29}\text{Si})$) depends on the local environments of the ^{29}Si nucleus.

The exploratory investigations on silicates with known molecular structure showed that ^{29}Si chemical shift mainly depends on the degree of condensation of SiO_4 tetrahedra with increasing condensation corresponding to a high-field shift, i.e., more negative $\delta(^{29}\text{Si})$. Furthermore, it was shown that each AlO_4 tetrahedron connected to a SiO_4 group increases $\delta(^{29}\text{Si})$ by approximately 5 ppm. In addition, the NMR intensity is directly proportional to the number of ^{29}Si nuclei present which allows quantitative determination of Si components. Thus, ^{29}Si MAS NMR represents a valuable technique for studying amorphous systems, and in the area of cementitious systems to obtain structural and kinetic information. NMR was used for the first time in the 1980s to investigate the structure of metakaolin-based geopolymer by Davidovits.

^{29}Si MAS NMR results showed that fraction of aluminum-rich structural units were found more compared to silicon-rich units with increasing reaction times. The increase in strength was due to (i) more aluminum rich structural units; (ii) higher cross linking and (iii) higher compactness [42].

9.4. Thermal Methods of Characterization of Geopolymer

With heat treatments, shrinkage and weight loss of Na-geopolymers at $1.15 \leq \text{Si}/\text{Al} \leq 2.15$ occurred [40,41]. The shrinkage can be influenced by the Si/Al ratio. TGA of the geopolymers as reported by Nath et al. [40] are shown in Figure 9. Loss in weight between 100 °C and 700 °C could be due to structurally bonded water in the N-A-S-H gel. This indirectly gave an idea about the reaction product.

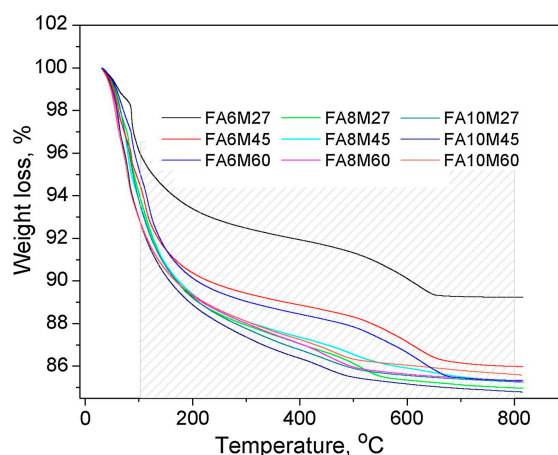


Figure 9. TGA of geopolymer [40] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2016).

9.5. Heat Evolution during Geopolymerization

Sun and Vollpracht [43] studied in detail the heat evolution of FA geopolymerization in the presence of NaOH (Figures 10–12). Sample designation with different parameters is given in Table 1. Effect of NaOH concentration on heat evolution and cumulative heat at 20 °C is given in Figure 10. As soon as the activator solution is mixed with fly ash, an exothermic peak due to wetting appeared [44].

Table 1. Oxide molar ratio of NaOH activated Fly Ash with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.6$ [43].

Sample ID	$\text{SiO}_2/\text{Na}_2\text{O}$	$\text{SiO}_2/(\text{Na}_2\text{O} + \text{CaO})$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	$\text{H}_2\text{O}/(\text{Na}_2\text{O} + \text{CaO})$
FA-6-0.45	4.3	2.8	13.1	8.8
FA-9-0.45	3.5	2.5	10.0	7.1
FA-12-0.45	3.2	2.3	8.8	6.4
FA-9-0.4	3.8	2.6	9.7	6.7
FA-9-0.5	3.2	2.4	10.2	7.4
FA-9-0.6	2.8	2.1	10.6	8.0
FA-9-0.7	2.5	1.9	10.9	8.5

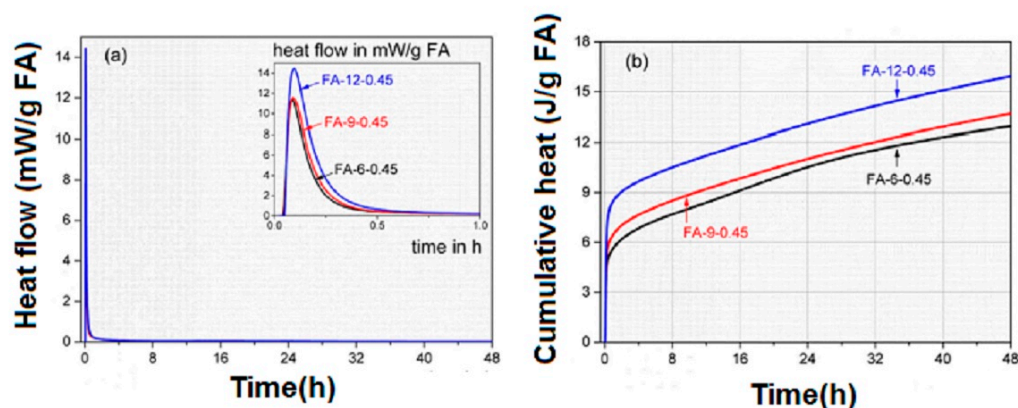
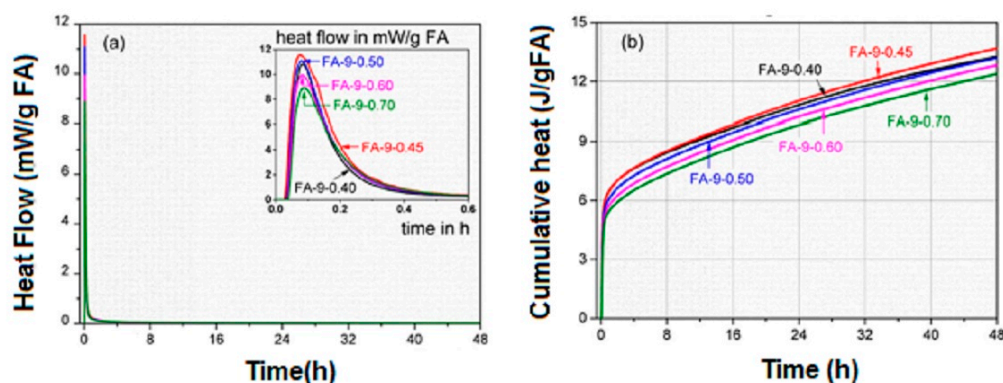
**Figure 10.** Effect of NaOH concentration on heat evolution. (a) Heat flow in mW/g FA, (b) Cumulative heat in J/g FA [43] (Reproduced with permission from Cement and Concrete Research; published by Elsevier, 2018).

Figure 11 gives the effect of liquid/solid ratio on heat of reaction during activation of FA by NaOH. A low liquid/solid ratio retards the process of geopolymerization [45].

**Figure 11.** Heat evolution in the presence of varying liquid/solid ratio. (a) Heat flow in mW/g FA; (b) Cumulative heat in J/g FA [43] (Reproduced with permission from Cement and Concrete Research; published by Elsevier, 2018).

Temperature affects the heat evolution strongly. The increase of curing temperature converts a single peak into a number of peaks (Figure 12). This indicates that multiple chemical steps are involved during geopolymerization.

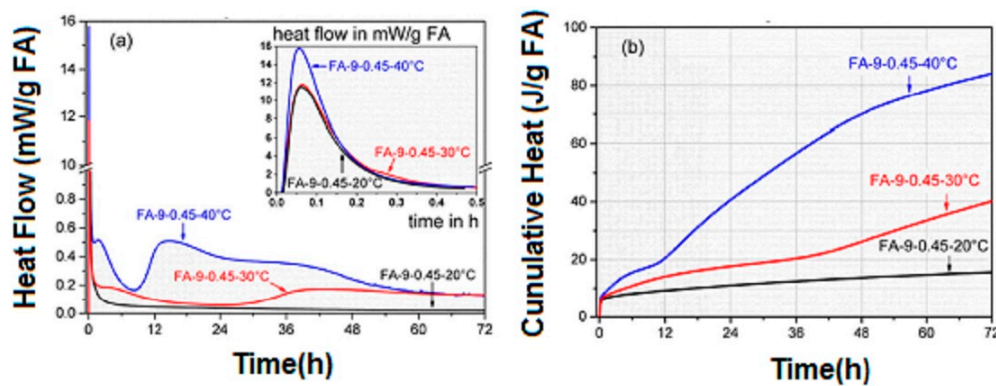


Figure 12. Heat evolution at different temperatures. (a) Heat flow in mW/g FA, (b) Cumulative heat in J/g FA [43] (Reproduced with permission from Cement and Concrete Research; published by Elsevier, 2018).

9.6. SEM of Fly Ash-Based Geopolymer

Nath et al. [40] performed detailed microscopic studies. Figure 13a–i shows SEM pictures of geopolymers. With change in alkali concentrations and curing temperature, the microstructures changed [40].

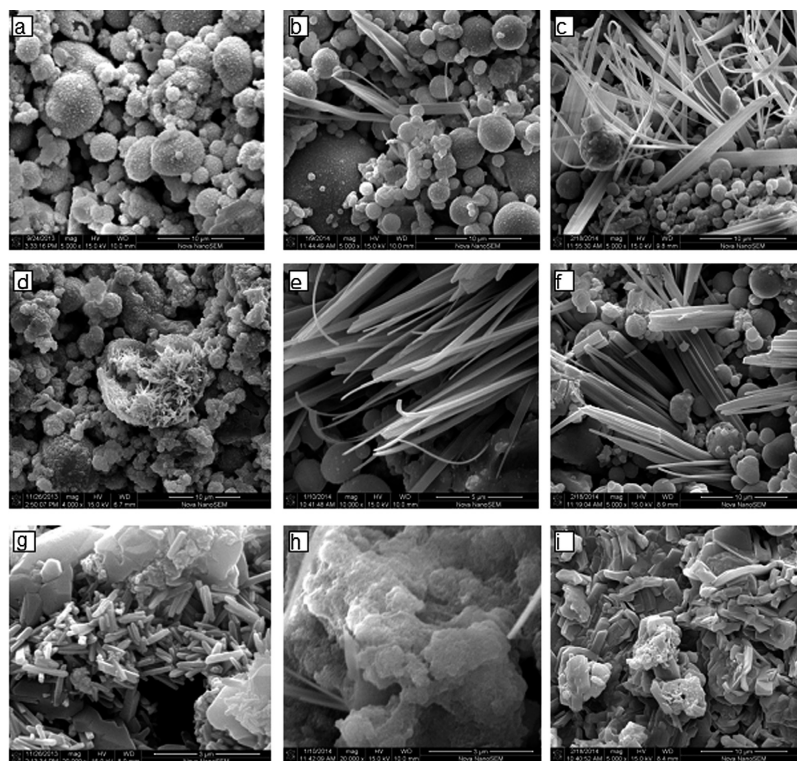


Figure 13. SEM pictures of FA-based geopolymers (a) 6M27; (b) 6M45; (c) 6M60; (d) 8M27; (e) 8M45; (f) 8M60; (g) 10M27; (h) 10M45; (i) 10M60 [40] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2016).

10. Properties of Geopolymer

10.1. Compressive Strength

Compressive strength of geopolymer mortars and concretes is an important property. The strength change in FA geopolymer concrete is due to shape, size distribution, calcium content and high amorphous microstructure of raw material [46]. The silicon and aluminum components of FA are activated by alkali solution which polymerizes into molecular chains and becomes a binder which binds the coarse and fine aggregates into a homogeneous mass and attains optimum strength at elevated temperatures. Calcium content of FA contributes very significantly in the strength development of geopolymer concrete. However, low-calcium FA is preferable for high binding properties since a geopolymer binder depends more on high content of aluminosilicate minerals for performance. Alkali concentrations also affect the strength of geopolymer concrete. As the concentration of alkali was increased, the strength also increased. Blending FA, kaolin and SF in geopolymer concrete increase the compressive strength up to a certain limit. With the increase of kaolin, compressive strength decreased. Furthermore, the addition of slag increased the compressive strength. This is as a result of closer packing of fine particles of slag which fills the pore spaces in the composite mixture. This resulted in fine surface texture and increase in compressive strength [46].

Okoye et al. [47] reported that strength increases up to certain temperatures but after that, it decreases (Figure 14).

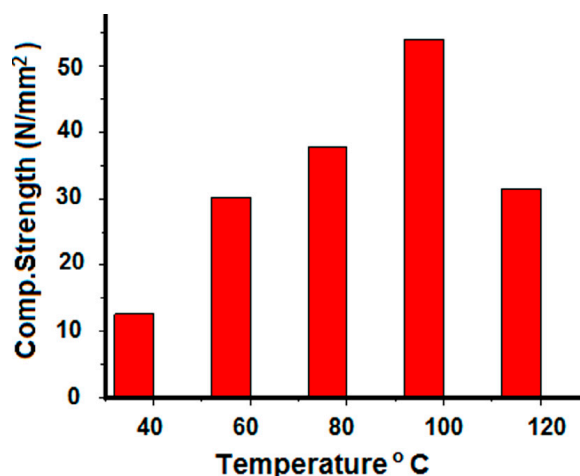


Figure 14. Change in compressive strength of FA-based geopolymer concrete in presence of kaoline at different temperatures [47] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2015).

Silica fume addition decreases the compressive strength of the paste whereas in case of mortar, strength is increased. In the case of paste, porosity is increased, whereas in the case of mortars, porosity is decreased in the presence of silica fume. In the case of mortars/concretes, in addition to reaction of silica fume with alkalies, fine particles also enter into the pores and increase the compactness. According to Okoye et al. [48] in mortars and concretes, increase in strength was found even up to 40% silica fume addition (Figure 15).

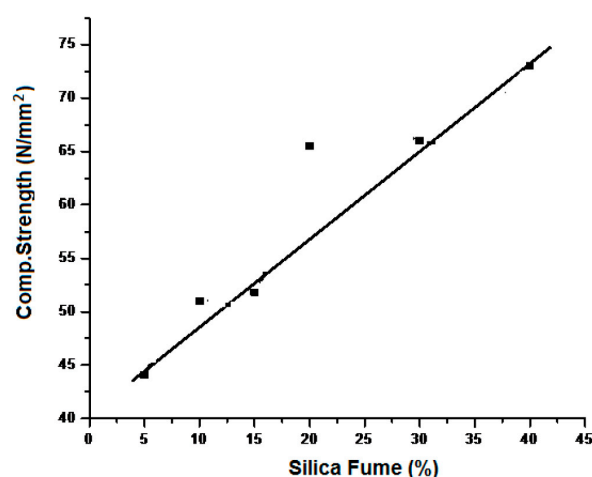


Figure 15. Effect of silica fume on compressive strength [48] (Reproduced with permission from Ceramics International; published by Elsevier, 2016).

Saxena et al. [49] reported that similar to silica fume, Alccofine powder also increased the compressive strength. Curing can alternatively be done by microwave heating, where electromagnetic energy is converted to thermal energy and heat uniformly. This rapidly accelerates the strength gain [50]. Compressive strength of geopolymer mortars cured by conventional and microwave heating are given in Table 2 [34]. The data show that 30 min heating in a microwave oven gives higher strength than 12 h of conventional heating at 80 °C.

Table 2. Mix design with sodium hydroxide (14 M), sodium silicate and lithium silicate and compressive strength by conventional and microwave heating [34].

MIX	Pond Fly Ash (g)	Natural Sand (g)	NaOH Solution (g)	Sodium Silicate (g)	Lithium Silicate (g)	Compr.Str. (MPa) Conventional Curing 80 °C (12 h)	Compr.Str. (MPa) MW Curing (30 min)
Mix-4	200	600	40	80	0	39.0	40.0
Mix-8	200	600	40	0	80	32.6	39.0
Mix-12	200	600	40	80	0	40.6	42.0
Mix-16	200	600	40	0	80	32.0	39.9

10.2. Flexural and Splitting Tensile Strength

Normally, a fly ash-based geopolymer has low tensile strength. It also has low fracture toughness. Because of these properties, fly ash-based geopolymers suffer from brittle failure. These properties can be enhanced if the geopolymer is embedded with chitosan or fibers of steel (ST), polyvinyl alcohol (PVA), sweet sorghum and cotton.

10.3. Electrical Properties of Geopolymer Pastes

Electrical properties of FA-based geopolymer pastes at different NaOH concentrations and frequencies were measured by Hanjitsuwan et al. [39] and are shown in Figure 16. The dielectric constant (16a) decreased and electrical conductivity increased with frequency (16b).

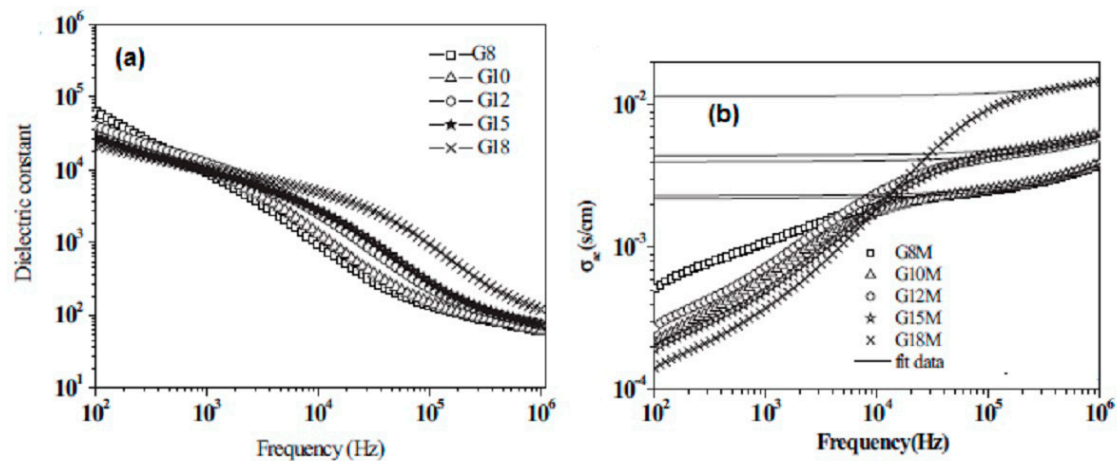


Figure 16. (a) Dielectric constant and (b) AC conductivity (σ_{ac}) of FAGP [39] (Reproduced with permission from Cement and Concrete Composites; published by Elsevier, 2014).

10.4. Fire Retardant Properties

Geopolymers have low thermal conductivity and they do not emit toxic fumes when heated. Geopolymer concretes are one of the most important building materials which can withstand high temperature. Geopolymer concrete is more porous and favors the escape of internal steam pressure during heating and as a result becomes a good fire-resistant material.

Saxena et al. [51] measured compressive strength of FA-based geopolymer mortars in the absence and presence of silica fume at different curing temperatures. Results (Figure 17) [51] showed that in the presence and absence of SF in geopolymer mortars, the compressive strength increased up to 600 °C but after that, there was a continuous decrease.

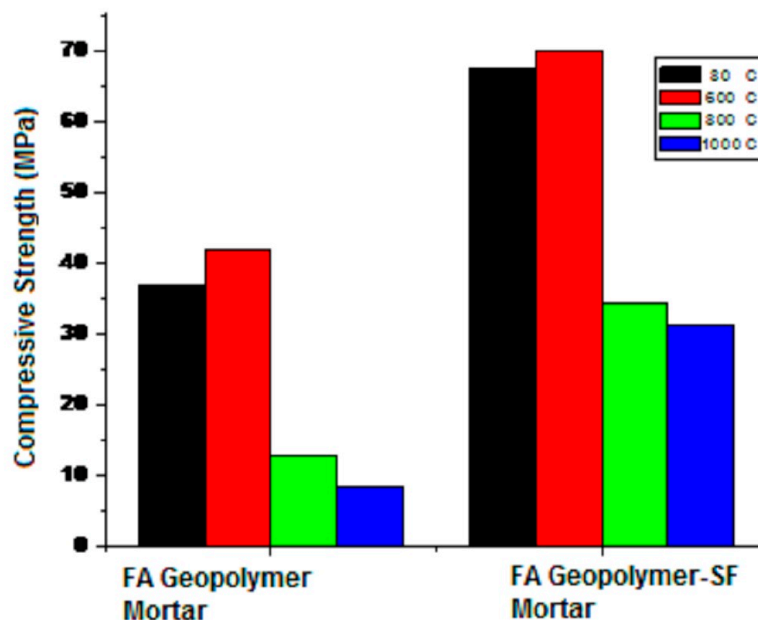


Figure 17. Compressive strength at different temperatures [51] (Reproduced with permission from Materials Today: Proceedings; published by Elsevier, 2017).

10.5. Properties in Presence of Nanomaterials

In the presence of nano-silica, the compressive strength of high volume fly ash mortars at room temperature curing is reported to be improved significantly. The nano-silica enhances the polymerization process because of its high specific area and amorphous nature [52].

When graphene (GR) was incorporated into the matrix of fly ash-based geopolymer (FAG), electroconductive GR/FAG composite was obtained. Photocatalytic degradation of indigo carmine over 1.0GR/FAG composite studied by Zhang et al. [53] is shown in Figure 18. Fe_2O_3 present in FA and in turn in geopolymer is wrapped inside and 1.0GR/FAG composite in presence of sunlight acts as a photocatalyst and degrades the dye.

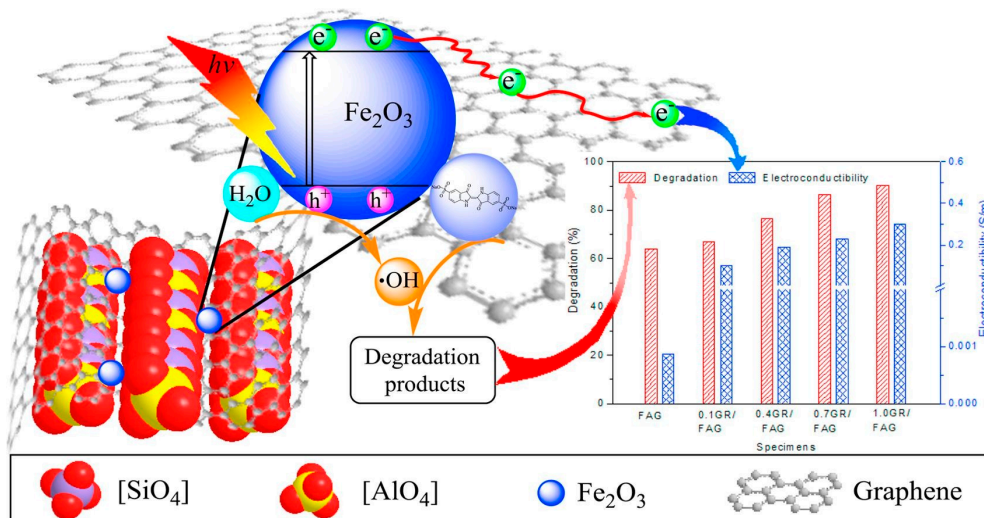


Figure 18. Photocatalytic degradation of indigo carmine over GR/FAG composite [53] (Reproduced with permission from Chemical Engineering Journal; published by Elsevier, 2018).

11. Durability

Durability of geopolymers (resistance to chloride, sulfate, acid, freeze-thaw, thermal and efflorescence) depends on the microstructure and the movement of ions within the structure [54]. Geopolymer made by NaOH is found to be more crystalline and hence more stable, whereas geopolymers made with the sodium silicate activator is amorphous and less stable in acidic medium. Active sites present on the surface of aluminosilicate gel are also responsible for chemical stability. K^+ ions also affect it. If geopolymer deteriorates in acidic medium, it may be due to depolymerization and liberation of silicic acid. Na^+ cations may be replaced by hydrogen ion as given below (Figure 19).

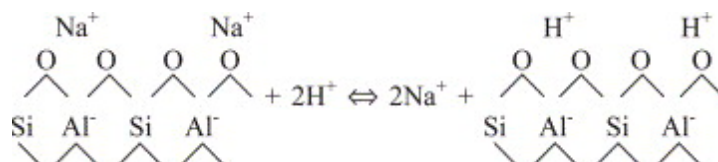


Figure 19. Replacement of Na^+ ions by H^+ ions during depolymerization in acidic medium.

When geopolymer is attacked by acids, Si–O–Al bonds are broken and as a result Si–OH and Al–OH groups get increased in the structure. As a result, the amount of silicic acid and dimmers get increased in the solution leading to mass loss. Because of this, mechanical properties are decreased.

Acid resistance of geopolymer increases with curing temperature. FA-based geopolymer cured at 80 °C for 10 h when immersed in HCl solution did not deteriorate much [55]. Microwave cured

FA-based geopolymer gave enhanced densification comparable to the conventional curing and as a result more durable in acidic environment [56].

Chloride diffusion into the concretes promotes the corrosion of steel bars in the structure. Chloride diffusion can be minimized by using higher concentrations of NaOH. This refines the pore structure due to polycondensation reactions.

Geopolymer when exposed to fire has the tendency for shrinkage and cracking. However, fly ash-based geopolymer has much less effect of fire as compared to OPC-based concretes [57]. There occurs expansion, cracking and scaling mass loss due to freeze-thaw attack [58].

In geopolymers excess of hydroxide solution remain in the pores and excess sodium oxide in pore network. This in contact to atmospheric CO₂ degrade the geopolymer [59,60]. Efflorescence depends on alkali activator, curing temperature and calcium content. KOH instead of NaOH as activator reduces the efflorescence of geopolymer [61].

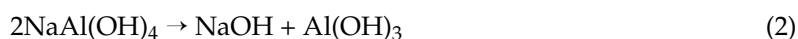
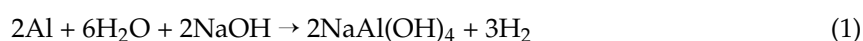
It is reported that heat curing with surface sealing can prevent the early carbonation of FA-based geopolymer paste by increasing polycondensation reaction [62].

12. Foamed Geopolymer Concrete

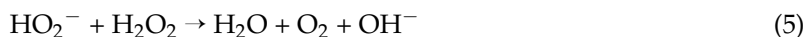
Geopolymer foams (GFs) show a large number of properties and are eco-building materials [63]. Foamed geopolymer concretes are formed by adding foaming agents to a geopolymer and have a porous structure. Because of the foaming agents, gases are evolved and entrapped in the structure before the gel hardens. The gel contains different sizes and types of pores [64]. Chemical and mechanical foaming methods are generally used. In chemical methods, density can be reduced but large voids are generated [65].

When foaming agents are added to FA slurry in alkali activator solutions, geopolymer foam is formed. The number of compounds is known which produce gases on addition to geopolymers and are then entrapped to produce a foamed microstructure in the hardened material [66]. When foaming agents are mixed, chemical reactions liberate different gases which are entrapped in the structure.

Because it is highly reactive, when aluminum metal is kept in alkaline solution, H₂ gas is evolved and aluminum hydroxide is formed. Following reactions (Equations (1)–(3)) occur [67].



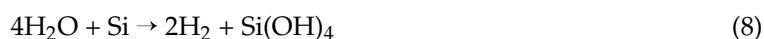
Hydrogen peroxide reacts, evolving oxygen gas, which is entrapped in the paste, giving foamed structure. Equations (4) and (5) represent the reactions [66].



NaOCl also liberates gases as per Equations (6) and (7) and makes foamed geopolymer concrete [68].



Silica fume when added, during geopolymerization, silicon of silica fume is oxidized by water (Equation (8)) liberating H₂ gas [64].



Sodium dodecyl benzene sulfonate and gluten have also been used as foaming agent using fly ash and sheet glass powder as solid materials. The appearance and pore structure of the sintered geopolymer foam studied by Zhang et al. [64] are shown in Figure 20.

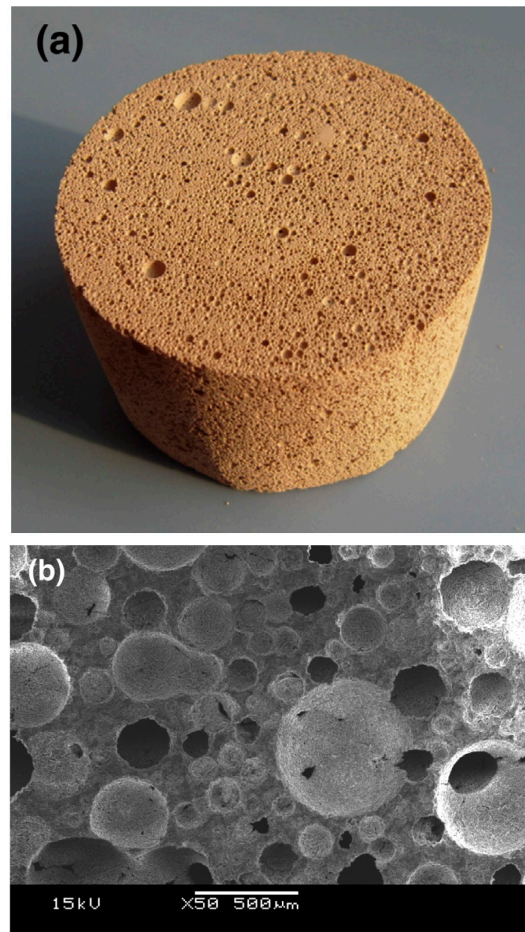


Figure 20. (a) Sintered geopolymer foam and (b) SEM image [64] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2014).

13. Carbon Foot Print in Production and Construction of Portland Cement and Geopolymer Concretes

CO₂ emissions from all the processes involved in the manufacture of 1 m³ of geopolymer and Portland cement concrete were evaluated by Turner and Collins [69] and are shown in Figure 21. The total emissions from the OPC and geopolymer concrete mixes were estimated as 354 kg CO₂ e/m³ and 320 kg CO₂ e/m³ respectively, showing 9% difference.

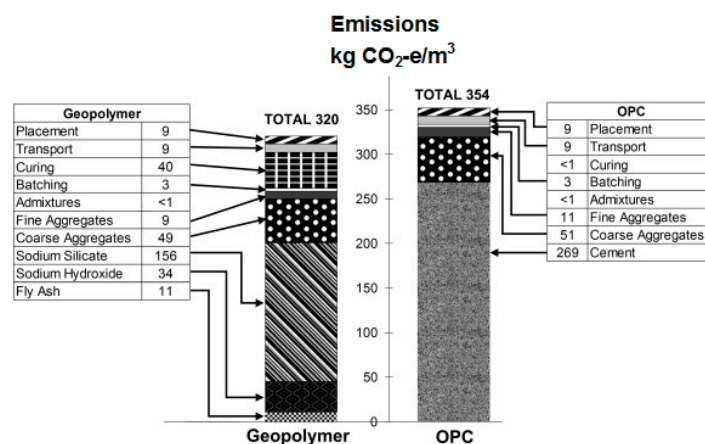


Figure 21. CO₂-e for concrete mixtures with OPC and geopolymer [69] (Reproduced with permission from Construction and Building Materials; published by Elsevier, 2013).

14. Economic Benefits of Geopolymer Concrete

There are a number of economic benefits of Fly ash-based geopolymer concrete over Portland cement concrete. An approximate cost of geopolymer concrete of one cubic meter is reported to be 45 USD whereas that for Portland cements concrete, it is 60 USD. Additional economic benefits may also be due to low drying shrinkage and creep, excellent resistance to sulfate attack and fire resistance offered by geopolymer concrete when it is used in infrastructure applications [46].

15. Conclusions and Future Prospects

Production of geopolymer cement and concretes using fly ash is a better alternative to conventional OPC concrete because it gives high early strength, is durable, economical and emits less carbon. At the same time it minimizes waste generation. The properties of geopolymer cement concrete depend on various factors. However, the most important one is curing conditions, temperature and duration. It can be used as a fire resistant material in the construction industry. Because of variations of composition of fly ash, it is difficult to have standards for this concrete. Attempts should be made to have solid geopolymers which can be easily mixed on the site of construction. Further systems/additives should be found out which can give high strength even at room temperature curing in a shorter period of time. Detailed investigations are required so that geopolymer can become an alternative to Portland cement concrete.

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