

USE OF GEOPOLYMER CONCRETE AS GREEN CONSTRUCTION MATERIAL- A REVIEW

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Abstract- Geopolymer is the alternate binder of Ordinary Portland cement (OPC) which was first introduced to reduce the carbon dioxide emission by using these industrial by products as base material. These are advance mineral binders possessing physico-chemical properties which are entirely different from those of conventional OPC. The main objective of this paper is to present the state of art report on the use of geopolymer concrete as reflected on various research articles. This report covers the study on polymerization process, mix design, strength characteristics and behavior under aggressive environments, economy and sustainability of geopolymer materials. It has seen that the geopolymer binders are environmental friendly and can also be used as cost saving construction materials.

Keywords: Geopolymer, Green concrete, Sustainability, Alkali activators

1. INTRODUCTION

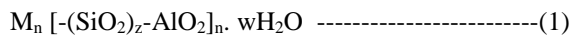
Concrete is the world's most versatile, durable, reliable and most widely used construction material. The main component of concrete is the Ordinary Portland cement (OPC) which is conveniently used as binder in concrete still now. But the environmental impact induced during production stage of OPC is a concerning issue now a days. Statistics show that the amount of carbon dioxide production is almost one ton for every ton of OPC produced. This carbon dioxide contributes in greenhouse gas emission approx. 7% of the total greenhouse gas (GHG) emission to the earth's atmosphere. Among the GHGs, CO₂ contributes 65% of total global warming [1]. In addition, the extent of energy required to produce OPC is only next to steel and aluminium. Each year the concrete industry produced almost 12 billion tons of concrete globally and utilized 1.65 billion tons of cement for that purpose [1]. Cement production has been increased almost 3% per year. The Portland cement production is a hazardous procedure itself for environment. Cement is also among the most energy-intensive construction materials, after aluminium and steel. Furthermore, it has been reported that the durability of Ordinary Portland cement (OPC) concrete is under examination, as many concrete structures, especially those built in corrosive environments, start to deteriorate after 20 to 30 years, even though they have been designed for more than 50 years of service life [2]. The concrete industry has recognized these issues. For example, the U.S. Concrete Industry has developed plans to address these issues in 'Vision 2030: A Vision for the U.S. Concrete Industry'. The document states that 'Concrete technologists are faced with the challenge of leading future development in a way that protects

environmental quality while projecting concrete as a construction material of choice. Public concern will be responsibly addressed regarding climate change resulting from the increased concentration of global warming gases. In this document, strategies to retain concrete as a construction material of choice for infrastructure development, and at the same time to make it an environmentally friendly material for the future have been outlined [2].

On the other hand, there is abundant availability of fly ash and ground granulated blast furnace slag (GGBS) which are the byproduct of burning coal and steel manufacturing process respectively. The development and application of high volume fly ash concrete is reported to enable the replacement of OPC up to 60% by mass in concrete production. But the geopolymer concrete is a good alternative to overcome the abundant of fly ash [3]. The role of binder in geopolymer concrete is replaced by fly ash or slag which also possesses pozzolanic properties as OPC and rich with alumina and silicate. Geopolymer concrete also showed good properties such as high compressive strength, low creep, good acid resistance and low shrinkage [4].

2. GEOPOLYMER

Geopolymers are members of the family of inorganic polymers. The chemical composition of the geopolymer material is similar to natural zeolitic materials, but the microstructure is amorphous instead of crystalline [5]. The polymerisation process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals, that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows [3]:



Where:

M_n = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or polymerisation; z is 1, 2, 3, or higher, up to 32.

The schematic formation of geopolymer material was described by H. Xu [6] with the chemical reaction that may comprise the following steps:

- Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
- Transportation or orientation or condensation of precursor ions into monomers.
- Setting or polycondensation/polymerisation of monomers into polymeric structures.

However, these three steps can overlap with each other and occur almost simultaneously, thus making it difficult to isolate and examine each of them separately [4]. A geopolymer can take one of the three basic forms [3]:

- Poly (sialate), which has [-Si-O-Al-O-] as the repeating unit.
- Poly (sialate-siloxo), which has [-Si-O-Al-O-Si-O-] as the repeating unit.
- Poly (sialate-disiloxo), which has [-Si-O-Al-O-Si-O-Si-O-] as the repeating unit.

From the fundamental process of polymerization it has been seen that the water is released during chemical reaction process of polymerization. This water, expelled from the geopolymer matrix during the curing and further drying periods, leaves behind discontinuous nano-pores in the matrix, which provide benefits to the performance of geopolymers. Thus the water play no important role in chemical reaction takes place, it just provides workability of the mixture. This is the basic difference in role of water on polymerization and hydration of Portland cement. The following constituents are generally used to produce geopolymer concrete.

2.1 Binder Materials

Fly-ash (FA)/ slag (GGBS) rich in Silica and alumina are commonly used as binder material of geopolymer concrete. Higher proportion of silicon dioxide (SiO_2) or sum of silicon dioxide and alumina ($SiO_2+Al_2SiO_3$) is required to ensure sufficient potential reactive glassy constituent that is present in fly ash. When such kind of fly ash is activated by an alkaline environment, the effect of high calcium concentration leads to accelerate the rate of reaction. Therefore, class F fly ash is most suitable in geopolymer due to its high content of amorphous aluminosilicate phases and greater workability. Loss of ignition (LOI) is a measure of unburnt carbon present in flyash which affects the quality by increasing water demand and reducing the fineness. According to ASTM C618, maximum 6% of LOI is allowable. The majority of Bangladesh fly ash falls in the category of ASTM Class F low calcium fly ash. However; the Oxide components of different class of fly ash shown in **table 1**.

Table 1: Specifications of flyash requirement for geopolymer [5]

Composition	Class C Fly Ash	Class F Fly Ash
SiO ₂	23.1-50.5	45-64.4
Al ₂ O ₃	13.3-21.3	19.6-30.1
Fe ₂ O ₃	3.7-22.6	3.8-23.9
MnO	---	---
CaO Total	11.6-29	0.7-7.5
CaO Free	---	---
MgO	1.5-7.5	0.7-1.7
Na ₂ O	0.4-1.9	0.7-2.10
K ₂ O	0.5-7.3	0.3-2.9
LOI	0.3-1.9	0.4-7.2

The chemical composition of slag vary depending upon the source, which are generally iron blast furnace slag and hydraulic while nickel and copper slag only have the pozzolanic properties [7]. The most common cementitious materials for Alkali activating slag (AAS) binder is grounded granulated blast furnace slag (GGBS). This is the only material to be used worldwide for AAS production.

2.2 Alkaline Solution

The most common alkaline liquid used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate [3,4, 5]. The use of a single alkaline activator has been reported by A. Palomo [5]; he concluded that the type of alkaline liquid plays an important role in the polymerisation process. Reactions occur at a high rate when the alkaline liquid contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. H. Xu [6] confirmed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline liquid enhanced the reaction between the source material and the solution. Furthermore, after a study of the geopolymerisation of sixteen natural Al-Si minerals, they found that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution.

2.3 Properties of Geopolymer Binder

The superior properties of Geopolymer concrete, based on D. Hardijito, B. V. Rangan [8], are

- sets at room temperature
- nontoxic, bleed free
- long working life before stiffening
- impermeable
- higher resistance to heat and resist all inorganic solvents
- higher compressive strength

Compressive strength of Geopolymer concrete is very high compared to the Ordinary Portland cement concrete. Geopolymer concrete also showed very high early strength. The compressive strength of Geopolymer concrete is about 1.5 times more than that of the compressive strength with the Ordinary Portland cement concrete, for the similar mix. Similarly the Geopolymer

Concrete shows good workability as that of the Ordinary Portland Cement Concrete.

3. FACTORS AFFECTING THE PROPERTIES OF GEOPOLYMER

Several factors have been identified as the controlling parameters that can affect the properties of geopolymer. The type of base material, type of activator solution, dosage of Na_2O and modulus of activator, mixing procedure, curing temperature, curing period etc. are considered as the governing factors [9].

3.1 Type of Base Materials

The most common base materials for geopolymer are FA and GGBS used as binder. The alkali activated slag (AAS) is a product of activation of GGBS, whereas the FA-based geopolymer binder is a product of the activation of low-calcium fly ash. According to A. Adam [10] GGBS can be activated easily rather than geopolymer mortar made of low calcium fly ash with an same mixing proportions. Consequently less amount of activator solution is required for GGBS to find same compressive strength.

3.2 Type of Activator

V. D Glukhovskiy [11] classified alkaline activator into six groups according to their chemical composition: (1) Caustic alkalis: MOH ; (2) Non-silicate weak acid salts: M_2CO_3 , M_2SO_4 , M_3PO_4 , MF , etc; (3) Silicates: $\text{M}_2\text{O} \cdot n\text{SiO}_2$ (4) Aluminates: $\text{M}_2\text{O} \cdot n\text{Al}_2\text{O}_3$; (5) Aluminosilicates $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (2-6)\text{SiO}_2$; and (6) Non-silicate strong acid salts: M_2SO_4 .

In spite of the fact that NaOH , Na_2SO_4 and Na_2CO_3 are often used as activators of slag and can be effective [12], the majority of research support that activation with sodium silicate or sodium silicate blended with NaOH gives the best strength.

3.3 Dosages and Modulus of Activator

The term dosages denote the ratio of the Na_2O content of the alkaline activator solution to the mass of binder (GGBS or FA) and expressed in terms of % Na_2O . Whereas the activator modulus (M_s) is the mass ratio of the SiO_2 to the Na_2O in the activator solution. Both dosages and modulus of activator have significant contribution on strength of AAS mortar [13]. Increasing the modulus means increasing the concentration of anions of sodium silicate. The anion in the sodium silicate reacts with Ca^{2+} dissolving from the surface of the slag grains and forms the primary C-S-H [14]. However; many of the researchers consider the Molarity (M) of sodium hydroxide solution and arbitrary ratio of sodium hydroxide solution to sodium silicate solution [9,15]. These literature show that the strength is gradually increased with the increase of molarity & solution ratio. Although the basic concept is almost same with previous system But the dosage and activator modulus system is often taken as more accurate mixing procedure as it consider the % of Na_2O present, as well as the ratio of the SiO_2 to the Na_2O . The SiO_2 and Na_2O content of sodium silicate is variable and depends on source and production process. According to J. Davidovits [3], the polymerization process requires highly alkaline solutions

to dissolve the silica and alumina ions in the FA as the quantity of cations in the alkaline solutions, the extent of dissolution of Si and the molar Si to Al ratio in FA are significant factors in geopolymerisation.

3.4 Curing Regimes for Geopolymer

The geopolymer needs heat curing rather than moist curing often used for Portland cement. The polymerization process depends on the curing temperature, time and curing condition. Steam curing is the best condition for geopolymer specimen but heat curing is adopted by majority researcher due to simplicity. D. Hardjito et.al.[8] conducted a wide study over curing temperature and conclude that the strength gaining is gradually increased with the increase of curing temperature. Geopolymer concrete specimens should be wrapped during curing at elevated temperatures in a dry environment (in the oven) to prevent excessive evaporation. The optimum range of curing temperature is upto 100°C and the curing period is range is 4 hours to 96 hours, after 4 days of curing the polymerization process goes slow down. Higher curing temperature resulted in larger compressive strength, although an increase in the curing temperature beyond 60°C did not increase the compressive strength substantially. The rate of increase in strength was rapid up to 24 hours of curing time. The results indicate that longer curing time did not decrease the compressive strength of geopolymer concrete as claimed by V. Jaarsveld [16].

After completion of curing, the geopolymer is kept in ambient temperature. AAS mortar provides satisfactory strength in ambient temperature without heat curing but the FA based geopolymer mortar can't gain the binding property without high temperature (greater than 60°C) even after 24 hour [9].

3.5 Rest Period Prior to Curing

The term 'Rest Period' was coined to indicate the time taken from the completion of casting of test specimens to the start of curing at an elevated temperature. This may be important in certain practical applications. For instance, when fly ash-based geopolymer concrete is used in precast concrete industry, there must be sufficient time available between casting of products and sending them to the curing chamber. According to D. Hardjito[8] the extent of strength gain was significant, in the range of 20 to 50 percent of the compressive strength of specimens with no rest period but the exact reason for this strength gain is not clear.

4. RESEARCH ON GEOPOLYMER

Slag was the first cementitious materials which is activated by alkali due to its latent hydraulic property. From observation of many researcher, a hydrated calcium silicate gel C-S-H is the most abundant product of hardened AAS paste. The microstructure of AAS gel and FA based geopolymer was observed by several researcher. P. Duxson et.al.[17] proposed a model shown in figure-1 for activation mechanism of geopolymer which consists of: (a) dissolution, (b) speciation equilibrium, (c) gelation, (d) reorganization, and (e) polymerization and hardening.

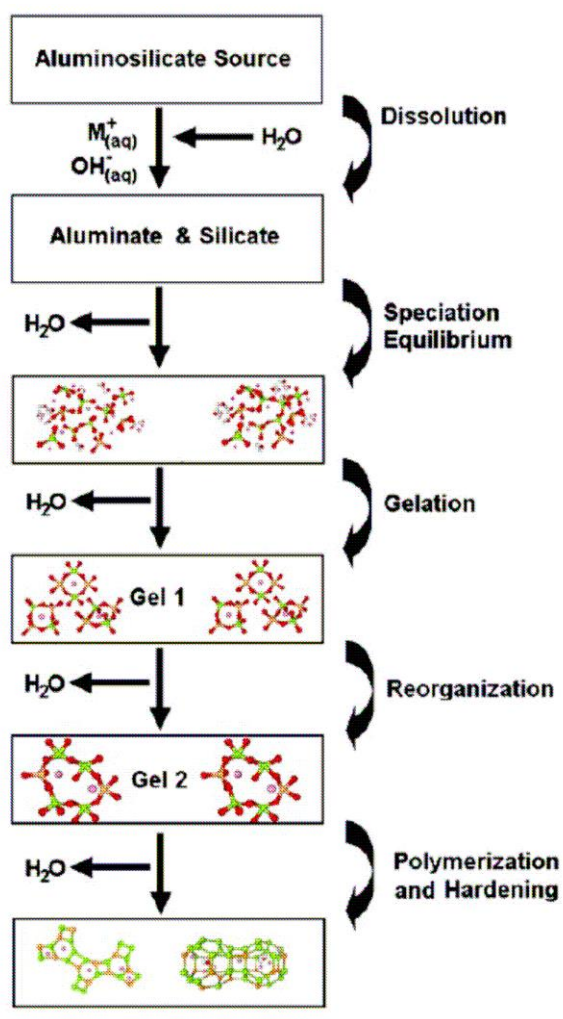


Fig.1: Conceptual model of geopolymerisation [17]

4.1 Geopolymer on Aggressive Environment

K. M. Gopalet.al.[18]exposed geopolymer concrete as well as conventional concrete in 5% acidic solutions (HCl, H₂SO₄, MgSO₄) for 7,14,28 days exposure period and found that geopolymer concrete mixes resisted acid attack in a better way as compared to conventional concrete at all age of exposure to HCl and H₂SO₄. It was observed that the percentage loss of Compressive strength of all Geopolymer Concrete mixes are considerably lower than that of Conventional concrete mixes at all ages of acid exposure. It is also observed that the maximum loss of compressive strength and weight occurs in case of H₂SO₄ acid immersion as compared to HCl and MgSO₄. The detail result found by [18] is shown in figure -2, where the loss of compressive strength of conventional concrete is almost double the loss of compressive strength of geopolymer concrete in H₂SO₄ acid immersion at all ages. According to this report percentage weight loss of Conventional concrete is more when compared to Geopolymer concrete. This is true for all the acids tried in this investigation. It is observed that the loss of compressive strength of Geopolymer concrete is more when compared to conventional concrete in MgSO₄immersion. So Geopolymer concrete is sensitive to MgSO₄ environment. The weight loss of Geopolymer

concrete is very low when Geopolymer concrete mixes are exposed to 5% acid attack.

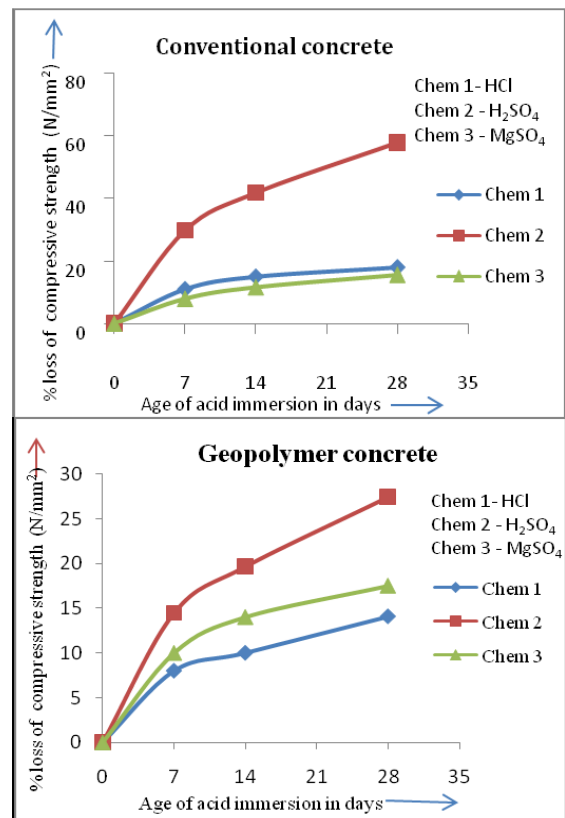


Fig.2: % loss of compressive strength in (a) conventional concrete and (b) geopolymer concrete (K. M. Gopal et al. [18])

N. Singh [19] investigated the durability of geopolymer concrete in sulfuric acid, sodium chloride and sodium sulphate environment. Result shows that the effect of sulphate chloride salt on compressive strength for both types decrease on exposure of 30, 60 and 90 days duration where the decrease in case of OPC is more in comparison to GPC which shows that the Geopolymer concrete exhibits significant resistance to sulphate and chloride attack. [19] Observed that the mass changes of the samples exposed to acidic solutions and results obtained from XRD analyses shows the depolymerisation of aluminosilicate polymer gel. The better performance of geopolymeric materials than that of Portland cement concrete in acidic environment might be attributed to the lower calcium content of the source material as a main possible factor since geopolymer concrete does not rely on lime like Portland cement concrete. Heat cured Geopolymer concrete has an excellent resistance to chloride attack. This proves Geopolymer concrete can be used in sea water area.

K. Chandan [20] measured the performance of geopolymer concrete at elevated temperature and also its behavior under aggressive environment. In this study the specimens were subjected to the elevated temperature in an electric air heated muffled and after cooling they were tested for compressive strength. The thermal stability of geopolymer concrete material prepared with sodium containing activators rather low and significant changes

in the microstructure occurred. At 1000°C, the strength of the concrete was reduced due to increase in the average pore size where amorphous structure were replaced by the crystalline Na-feldspars. Fly ash based geopolymer prepared using class F fly ash with sodium silicate shows high shrinkage as well as large cracks in compressive strength with increasing fire temperature in the range 800-1000°C. The compressive strength and loss of weight at different elevated temperature as found are listed in **table- 2.4**

Table 2: Compressive strength and % weight loss at elevated temperature [20]

Elevated temperature (°C)	Residual compressive strength (MPa)	% loss of weight of concrete
Room temperature	51.0	0
200	47.8	0.972
400	40.83	2.855
600	33.27	3.94
800	29.42	5.81
1000	20.33	8.5

5. APPLICATION OF GEOPOLYMER

There is a large potential for geopolymer concrete applications for bridges, precast pavers & slabs for paving, bricks and precast pipes. It is advantageous for precast structural elements and decks as well as structural retrofits to use geopolymer-fibercomposites. Geopolymer technology is most advanced in precast applications due to the relative ease in handling sensitive materials (e.g., high-alkali activating solutions) and the need for a controlled high-temperature curing environment required for many current geopolymer which can easily be provided in factory. Based on the molar ratio of Si to Al, J. Davidovits [3] proposed the possible applications of the geopolymers as given in Table 3.

Table 3: Applications of Geopolymers

Si/Al	Application areas
1	Bricks, ceramics, fire protection
2	Low CO ₂ cements, concrete, radioactive & toxic waste encapsulation
3	Heat resistance composites, foundry equipments, fibre glass Composites
>3	Sealants for industry
20<Si/Al<35	Fire resistance and heat resistance fibre composites

6. LIMITATIONS OF GEOPOLYMER

The followings are the limitations of geopolymer:

- Bringing the base material fly ash to the required location
- High cost for the alkaline solution
- Safety risk associated with the high alkalinity of the activating solution.
- Practical difficulties in applying Steam curing / high temperature curing process

Considerable research is ongoing to develop geopolymer systems that address these technical hurdles.

7. CONCLUSION

Following conclusions can be drawn from this theoretical study.

- i. The geopolymer concrete is more sustainable, environmental friendly construction material
- ii. It can provide greater resistance against aggressive environment rather than Ordinary portland cement concrete.
- iii. It can be used under conditions similar to those suitable for Ordinary portland cement concrete.
- iv. The geopolymer concrete shall be very effective for using in precast industries due to its high early strength. Thus huge production is possible within a short duration and reduces the damage of elements during transportation and handling.
- v. Geopolymer concrete possesses excellent mechanical properties and durability in chloride environment as compared to OPC concrete, so the Geopolymer Concrete can also be used in the Infrastructure development works in marine environment and in industrial areas where the concrete is subjected to chloride/sulphate attack.
- vi. Fly-ash can be effectively used as a binder material and hence no landfills are required to dump the Fly-ash and thus it helps to create a healthy environment for future generation.

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