

Review on Development of Geopolymer Composites from Aluminosilicate Materials

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Abstract: Geopolymerization is the chemical reaction between aluminosilicate oxides with silicates under highly alkaline condition to form polymers called geopolymers. Geopolymer is an alternate to the Ordinary Portland Cement. This paper tries to review the literatures on geopolymers. Geopolymer is synthesized from materials rich in reactive silica and alumina of geological origin or industrial by products such as fly ash, metakaolin, rice husk ash, red mud etc. The chemical composition of geopolymer is same as to that of zeolite, but amorphous in structure. Type and nature of raw materials, alkaline activators and curing conditions are the main factors affecting the geopolymerisation reaction. The leaching of alumina and silica from raw materials depend on the concentration of the alkali. Alkaline concentration is different for different raw materials. Curing conditions are also different for different raw materials and different activators.

Keywords: Geopolymer, Aluminosilicate, Alkaline activators, Alkaline concentration, Activator-binder ratio

1. Introduction

In the middle of 18th century Portland cement was invented. Since then concrete is the main construction material for all the civil engineering structures. During the early day's world's annual consumption of Portland cement was about 2 million tons. But now it is raised to 2 billion tons.

Manufacture of Portland cement is a complicated process. During the production of 1 Kg of Portland cement about 0.9 Kg of CO₂ will be emitted to the atmosphere. The increase in atmospheric CO₂ causes global warming and climate changes. The production of Portland cement will consume a high energy. So the production and use of Portland cement is a severe threat to the environment and ecology.

This made the scientists to think about a substitute to the Portland cement. In 1972 the French materials scientist Prof. Joseph Davidovits found out the geopolymerization process. According to Davidovits geopolymers are inorganic polymers having amorphous to semi-crystalline three dimensional silico-aluminate structures possessing SiO₄ and AlO₄ tetrahedra linkage by sharing all the oxygen atoms. It

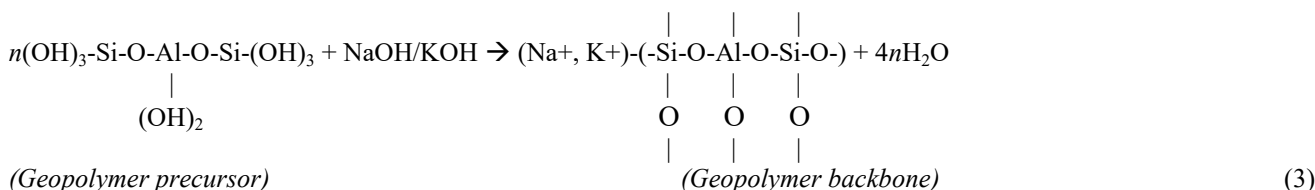
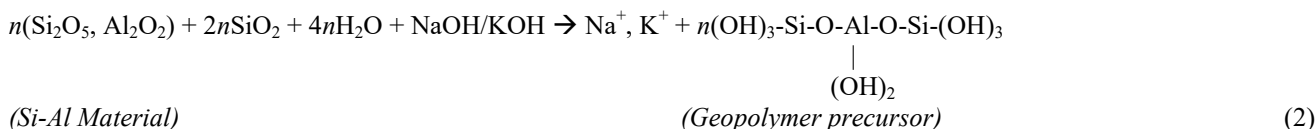
can be designated as (-Si-O-Al-O-). He proposed an empirical formula as follows.

$$M^+_n \{-(SiO_2)_z-AlO_2-\}_n \quad (1)$$

Where M⁺ is an alkali cation (K⁺, Na⁺), n is the degree of polymerisation and z is Si/Al ratio which may vary 1, 2, 3 up to 300. Si/Al up to 3 lead to three-dimensional cross-linked rigid networks and stiff and brittle properties (such as cements and ceramics); high ratios result in two-dimensional networks or linearly linked polymeric structures with adhesive or rubbery properties, respectively [5].

2. Geopolymerization

Usually polymerization reaction takes place in organic compounds, due to the tetra valency of the carbon atom. Geopolymerisation is an inorganic polymerization. In geopolymers during the setting actually poly condensation reaction take place leading to the formation of amorphous to semi-crystalline aluminosilicate polymers. The schematic representations of the actual reaction are as follow.



From the above reactions we can understand that any material that contains silica and alumina in amorphous phase is a possible source for the production of geopolymers [18].

2.1. Raw materials for Geopolymer formation

Materials that contain mostly Silica and Alumina in amorphous form are the best raw materials for the manufacture of geopolymers. The raw materials have a significant role in the polymerization reaction. They affect the properties and structures of the geopolymer. The main raw materials used in geo polymerization are natural minerals such as kaolinite, clays etc. and by-products such as fly ash, silica fume, slag, rice-husk ash, red mud etc. But now many other substances like metakaolin, coal ashes, palm oil fuel ash, steel slag, waste glass etc. are also used as the source for silicates and aluminates. The particle size and chemical composition of the raw materials have an important role in the polymerisation reaction.

2.1.1. Chemical Composition

Chemical composition of the raw materials is an important factor in geopolymerization. According to Azizul Islam [3] the rate of polymerization is influenced by parameters such as alkali concentration, initial solids content, silicate and aluminate ratio, water content, pH and the type of activators used. Lime (CaO) has an important role in polymerization. It controls strength and safe but excess lime causes expansion and disintegration. The free calcium ions present at the slag prolong fly ash dissolution and enhances geopolymer gel formation. According to Jian He the mechanical properties of the Red mud and Rice husk ash (RHA) geopolymers are highly complex and its qualities depend up on the factors like alkalinity, mix proportion of the raw materials, particle size of rice husk ash [8]. He also suggests that incomplete reaction and side reaction will also affect the qualities of the geopolymer.

2.1.2. Particle size and reactivity of raw materials

Particle size of the raw materials is also important factors in geopolymerization. Finer particle sizes of the RHA improve its reactivity and thereby higher degree of geopolymerization can be achieved. Higher degree of geopolymerization makes the resulting geopolymer more ductile and stronger. As the particle size of the RHA decrease the surface area increase. The increased surface area also results in the formation of more ductile and stronger geopolymers. This suggests that the mechanical properties of geopolymers are depending upon the physical property, the particle size of the raw materials [8]. S.Detphan and P.Chindapasirt also suggest that particle size is an important factor in geopolymerization. They have the opinion that – the strength of geopolymer mortars are affected by the fineness of RHA. The increase in the fineness of RHA increases its reactivity and strength of mortars. RHAs with 1% - 5% retained on No.325 sieve are suitable for making geopolymer mortars [15]. Ali Nazari has the opinion that the compressive strength of the geopolymer depends on the particle size of the raw materials. The finer the particle size the stronger the geopolymer [1]. According to Navid Ranjbar the shape, particle size and surface area of the raw materials affect the hardened mechanical properties of geopolymer mortars [12].

2.2. Alkaline activators

Alkaline activators are the alkalis or alkali silicates that are used in the geopolymerization reactions. The commonly used alkaline activators are sodium hydroxide (NaOH), potassium

hydroxide (KOH), sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3). The alkaline activators play an important role in the geopolymerization reaction. When the alkali hydroxide contains a soluble silicate, reactions will occur in higher rate. Xu and Van Deventer found that when a mixture of sodium hydroxide solution and sodium silicate solution is used as an alkaline activator the reaction between the source material and the solution will be at a higher rate. They also found that sodium hydroxide is a better alkaline activator than potassium hydroxide [6]. But Jian He used only sodium hydroxide as alkaline activator in the synthesis of geopolymer using Red mud and Rice husk ash [8].

2.2.1. Concentration

Alkali concentration is a significant factor in the production of geopolymer. Sodium hydroxide concentration is different for different raw materials. Jian He found out that a more caustic alkalinity results in faster and more extensive dissolution of the source material and induces more reactive silica and alumina species. Because of the generation of more geopolymeric binder higher alkali concentration improves the compressive strength and stiffness of the final geopolymeric products [7]. Ali Nazari suggests that the concentration of alkali activator has a main effect on the strength of geopolymeric specimens. In the production of geopolymer using fly ash and rice husk ash the highest strength was achieved by the use of 12M sodium hydroxide solution [1]. According to Jian He a higher Si/Al ratio exhibit poorer mechanical properties. He explained that the reason for this is relatively larger RHA solid particles cause negative influence on the rate and extent of geopolymerization reaction. A higher concentration of soluble Si results in a reduced skeletal density of the geopolymer binder which also makes the geopolymers weaker [8].

2.2.2. Activator liquid to solid binder material mass ratio

In geopolymerization the quantity of activator solution taking part in the dissolution of the raw material will change with activator liquid material mass ratio. Liew et al [19] found that the calcined Kaolin based geopolymer can acquire high compressive strength with solid to liquid ratio as 0.8 and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio as 0.2. According to Joshi and Kadu [9], by keeping water to binder ratio as 0.26, the optimum combination of mix for development geopolymerconcrete from fly ash with alkaline liquid to fly ash mass ratio must be 0.35. Kaolin based geopolymer was optimised with solid to alkaline solution ratio as 1.

2.2.3. Sodium silicate to sodium hydroxide solution mass ratio

The most common alkaline activators used in geopolymerization are sodium hydroxide (NaOH) with sodium silicate (Na_2SiO_3) or potassium hydroxide (KOH) with potassium silicate (K_2SiO_3). Nowadays sodium hydroxide alone is used as an activator. Fly ash when activated with NaOH and soluble silicates, the reaction rates and mechanical properties would be higher compared to that activated with hydroxides only [13]. According to Jian He different alkalinities affect the rate and extend of polymerizations and thereby mechanical properties of the geopolymer must be different [7]. S. Detphan and P. Chindapasirt studied the fly ash and rice husk ash based geopolymers and found that the optimum mass ratio of

sodium silicate to sodium hydroxide is 4. When increasing the mass ratio from 4.0 to 5.5 the result is a viscous mix. In such condition water is needed to produce a workable mortar. But the resulting geopolymer's strength is very low [15].

3. Curing Process

Curing time of geopolymers depend on several factors such as the concentration of alkaline solution, composition of alkaline solution, nature of the raw material, ratio of alkaline liquid to raw material, curing temperature, presence of water. During the setting of geopolymer water has an important role. It serves as a carrier of the alkali activating agent. So care must be taken to minimize the loss of water. It was found that different geopolymers made from different raw materials and different alkali activators have different curing conditions. In the case of many geopolymers setting is slow at normal temperature. But at elevated temperature the setting will become fast.

3.1. Normal temperature curing

In practical applications geopolymers curing at normal temperature is more convenient. Since heat accelerates the reaction, curing of geopolymer is carried out mostly at an elevated temperature. N A Lloyd and B V Rangan have the opinion that temperature specification for curing should be correlated to actual specimen temperature for high and very high strength geopolymer concretes. The introduction of a rest day, that is normal curing for 24 hours prior to steam curing, resulted in elevated compressive strengths of the order of 20% [21] S Jayadeep and B J Chakravarthy found by experiment that oven cured geopolymers have the higher compressive strength than that of by sun light curing. But sun light curing is convenient for practical conditions [16].

3.2. Elevated temperature curing

Most of the geopolymers can get the maximum compressive strength only by curing at an elevated temperature. S. Detphan and P. Chindaprasirt studied the fly ash and rice husk ash based geopolymers and found that the influence of curing temperature is more significant in the mix containing a large amount of fly ash (FA). The curing temperature will vary from 60°C to 90°C as the amounts of FA vary from 100% to 80%. They also found that the optimum temperature was 60°C for all series [15]. Azizul Islam and others made geopolymer using ground granulated blast furnace slag (GGBS) palm oil fuel ash (POFA) and fly ash (FA). They found that the mixes were cured at 65°C instead of 100°C. They have the opinion that the reduction in the curing temperature allowed the mixtures with high calcium content able to achieve the higher strength. They have also the opinion that long pre-curing at room temperature is helpful for developing strength to the geopolymers containing FA as a source material [3]. According to M.Catauro the thermal treatment improves the geopolymerization. He has the opinion that this is because of the removal of the water formed during the condensation process. The water removal will cause empty areas formation. So the activation procedure must require the addition of required amount alkali activator and the heat treatment at 60°C [10].

4. Conclusion

- Geopolymer is an eco-friendly substitute to ordinary Portland cement which can be prepared from raw materials which contain silicates and aluminates in amorphous phase.
- The particle size and chemical composition of the raw materials have an important role in the geopolymerization reaction.
- Incomplete reaction and side reaction affect the qualities of the geopolymer.
- Finely powdered raw materials can produce geopolymers with reasonable strength and ductility.
- An alkali activator must be need for the production of geopolymer. The commonly used alkaline activators are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na₂SiO₃) and potassium silicate (K₂SiO₃).
- Higher alkali concentration improves the compressive strength and stiffness of the final geopolymeric products.
- Quantity of activator solution taking part in the dissolution of the raw material will change with activator liquid-material mass ratio.
- For different raw materials the optimum alkaline concentration would be different.
- Curing conditions for geopolymers produced from different raw materials are different.
- Normal temperature curing is convenient for practical conditions.
- Majority of geopolymers achieve reasonable strength only by curing at an elevated temperature for 24-48 hours and a long curing period. Also pre-curing at room temperature is helpful for developing strength.

Combining locally available materials having silicates and aluminates in amorphous phase in addition with different alkaline activators can produce eco-friendly geopolymer composites. This idea leads to the scope for the future works in production of geopolymer composites.

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