

Fly Ash based Geopolymer Concrete a New Technology towards the Greener Environment: A Review

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ABSTRACT: Concrete usage around the world is second only after water. Ordinary Portland Cement (OPC) is conventionally used as the primary binder to produce concrete. The environmental issues associated with the production of OPC are well known. The amount of CO₂ released during the manufacture of OPC due to calcinations of lime stone and combustion of fossil fuel is in order of about one ton for every ton of OPC produced. In addition the extent of energy required to produce OPC is only next to steel and aluminum. Therefore there is urgent need to reduce the CO₂ emission. Geopolymer concrete (GPC) is the material for the future, since it is environmental friendly material as during its production about 80% CO₂ is less emitted as compared to OPC. Geopolymer is a novel binding material produced by polymeric reaction of alkaline liquid with silicon and aluminum rich materials like fly ash, rice husk, blast furnace slag, silica fumes etc. It has been found that higher compressive strength is easily achievable in a short period to time in GPC as compared to OPC and has an excellent resistance to acid and sulphate attack when compared to OPC. It can be said that production of geopolymer concrete has a relative higher strength excellent volume stability and better durability. Thus geopolymer concrete may be the future alternate material to the ordinary portland cement concrete.

KEYWORDS: Geopolymer, Fly Ash, Alkaline Activator, Compressive Strength, Superplasticizer, ordinary portland cement, concrete.

I. INTRODUCTION

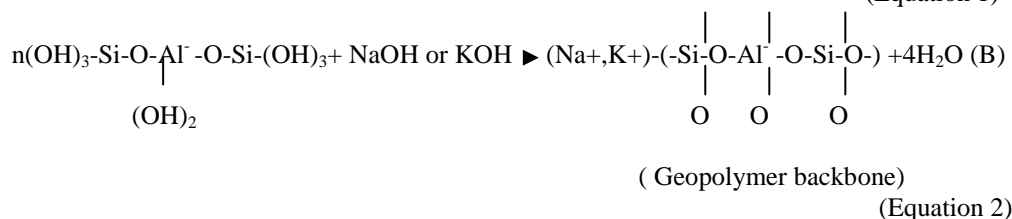
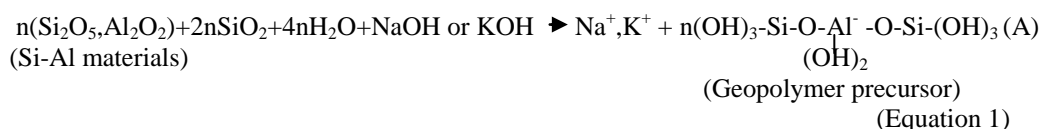
The geopolymer technology was first introduced by Davidovits in 1978. His work considerably shows that the adoption of the geopolymers could reduce the CO₂ emission caused due to cement industries (Shankar H.Sanni and Khadiranaikar R.B 2012) The development of geopolymer concrete is an important step towards the production of environmentally friendly concrete (Hardijito et al.2005) Geopolymerization involves a chemical reaction between various alumino silicate materials with alkali metal silicates under strongly alkaline conditions yielding polymer – Si-O-Al-O- bonds, which lead to geopolymers by polycondensation

The schematic formation of geopolymer material can be shown as described by Equations as (A) and (B)

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.....Eq as (A) and (B) (Panias.D and Giannopoulou.I 2004)

To date the exact mechanism of setting and hardening of geopolymer material is not clear. However, most proposed mechanism consist of the chemical reaction may comprise the following steps.

- Dissolution of Si-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/ polymerization of monomers into polymeric structures.

However, these three steps can overlap with each other and occur simultaneously thus making it difficult to isolate and examine each of them separately (Chanh Van Nguyen et al 2008)

II. CONSTITUENTS OF GEOPOLYMER CONCRETE

There are two main constituents of geopolymers namely the source material and the alkaline liquids. The source material for geopolymers should be rich in silicon (Si) and aluminum (Al). These could be materials such as fly ash, silica fume, rice husk, red mud etc. (Motorwala Ammar et al.2013)

A) Fly Ash

As reported by Nawaz(2013) fly ash is a byproduct material generated by thermal power plants from combustion of Pulverized coal. Presently the annual production of fly ash in India is about 112 million tones and is expected to cross 225 million tons by the year 2017. When pulverized coal is burnt to generate heat the residue contains 80% Fly Ash and 20% bottom ash. If not managed properly Fly Ash disposal in sea/rivers/ponds can cause damage to aquatic life also. Slurry disposal lagoons/settling tanks can become breeding grounds for mosquitoes and bacteria. It can also contaminate the underground water resources with traces of toxic metals present in Fly Ash. In developed countries more than 80% fly ash is used in various fields where in India very less percentages in various segments. It was reported by Alam and Akhtar(2011) that fly ash is one such example that has been treated as waste materials in India till decade back and has now emerged not only as a resource material but also as an environment savior.

B) Alkaline liquids

The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. (Davidovits 1999; Palomo et al 1999; Barbosa et al 2000; Xu and Van Deventer 2000; Swanepoel and Strydom 2002; Xu and Van Deventer 2002). Alkaline liquid plays an important role in polymerization process. Reactions occur at high rate when the alkaline liquid contains soluble silicate either sodium or potassium silicate compared to the use of only alkaline hydroxides. (Palomo et al.1999)

Xu and Van Deventer (2000) confirmed that the addition of sodium silicate to the sodium hydroxide solution as the alkaline liquid enhanced the reaction between the source material and the solution. Furthermore after a study of geopolymerization 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.

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C) Coarse and fine aggregates

Conventionally locally available coarse and fine aggregates may be used for the production of geopolymer concrete.

D) Superplasticizer

In order to improve the workability of fly ash based geopolymer concrete high range water reducing superplasticizer are used. According to the Fiat et al. (2013) superplasticizer are high range water reducers. Their use permits the reduction of water to the extent of 30% without reducing workability. Thus the superplasticizer produces a homogenous cohesive concrete without any tendency of segregation and bleeding. The superplasticizer are synthetic water soluble organic substances that significantly reduce (upto 40%) the amount of water needed to achieve a certain consistency of concrete.

The various superplasticizer that are used for conventional cement concrete are-

- (i) Sulfonated melamin formaldehyde
- (ii) Sulfonated naphthalene formaldehyde
- (iii) Modify lignosulphonates
- (iv) Polyether polycarboxylates

III. LITERATURE SURVEY

- In the year 1978 word geopolymer was coined by Davidovits For the chemical designation of geopolymers based on silico-aluminates, poly(sialate) was suggested. Sialate is an abbreviation for silicon-oxo -aluminate. Polysialates are chain and ring polymers with Si^{4+} and Al^{3+} with oxygen and range from amorphous to semi-crystalline. The new terminology was the key to the successful development of new materials. For the user, geopolymers are polymers and, therefore, by analogy with the organic polymers derived from oil, they are transformed, undergo polycondensation, and set rapidly at low temperature, within few minutes. But they are, in addition, GEO-polymers, i.e. inorganic, hard, stable at temperature up to 1250°C and non-inflammable. This gave a tremendous boost to creativity and innovation. The field of application developed since 1979 includes aeronautical engineering, the nuclear sector, the reproduction of thermal insulation of buildings, furnace insulation mechanical engineering, molding, stamping, foundry work, metal casting, and it even includes archaeological research.

The Invention of Geopolymer High-Strength Cement (1983) (K-Ca) (Si-O-Al-O-Si-O-) Poly(sialate-siloxo) cement

It was discovered that the addition of ground blast furnace slag, which is a latent hydraulic cementitious product, to the poly(sialate) type of geopolymer, accelerates the setting time and significantly improves compressive and flexural strength. Geopolymer cements are acid-resistant cementitious materials with zeolitic properties, developed for the long-term containment of hazardous and toxic wastes Geopolymerization involves the chemical reaction of aluminosilicate oxides, with alkali and calcium polysilicates, yielding polymeric Si-O-Al bonds, for instance:



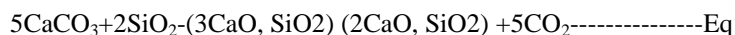
Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions. Portland based cements (plain and slag blended) are destroyed in acidic environment. Calcium aluminate cement is expensive to produce, and does not behave satisfactorily, having 30 to 60% of weight loss (destruction). Geopolymeric cements, Potassium-Poly(sialate-siloxo) type, remain stable with a loss in the 5-8 % range. This acid-resistant cement hardens rapidly at room temperature and provides compressive strength in the range of 20 MPa, after only 4 hours at 20°C, when tested in accordance with the standards applied to hydraulic binder mortars The final 28-day compressive strength is in the range of 70-100 MPa.

- **Davidovits(1994)** studied that CO₂ related energy taxes are focusing essentially on fuel consumption, not on actual CO₂ emission measured at the chimneys. Ordinary Portland cement used in the aggregates industries; result from the calcination of limestone (calcium carbonate) and silica as shown in Eq

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The production of 1 ton of cement directly generates 1T of CO₂. Minor reduction of CO₂ emissions may be achieved through the blending of Portland cement with replacement materials such as coal fly ash and iron blast furnace slag. In the year 2015 assuming that world Global Climate treaties might authorize an amount of this Portland blended cement production in order of 1850 million tones, the complementary need for new low CO₂ cementitious materials in the range of 1650 million tones requires the introduction of different technology. Novel geopolymeric poly (sialate-siloxo) cements, which do not rely on the calcination of limestone (and accompanying release of CO₂), are low CO₂ cementitious materials providing similar properties than current high CO₂ Portland cement. The technology reduces CO₂ emission caused by cement and aggregate industries by 80%.

- **Hardijito et al. (2004)** evaluated the effect of several factors on the properties of fly ash based geopolymer concrete, especially the compressive strength. The test variables included with the age of concrete, curing time, curing temperature, quantity of superplasticizer, the rest period prior to curing and the water content in the mix. The test result shows that the compressive strength of geopolymer concrete does not vary with the age of concrete, Longer curing time improves the polymerization process resulting in higher compressive strength approximately upto 75hours, commercially available Naphthalene based superplasticizer improved the workability of the fresh concrete but had very little effect on the compressive strength upto about two percent of this admixture to the mass of fly ash, beyond this value there is some degraation of the compressive strength and increase in the curing temperature increases the concrete compressive strength upto 75°C.
- Experimental work conducted by **Demie et al. (2011)** focused on the effect of superplasticizer and curing temperature on the workability and compressive strength of self-compacting geopolymer concrete(SCGC). SCGC is an improved way of concreting execution that does not require compaction and is made by complete elimination of ordinary Portland cement content. The parameters investigated were superplasticizer (SP) dosage and curing temperature. SCGC were synthesized from low calcium fly ash, activated by combinations of sodium hydroxide and sodium silicate solutions and by incorporating of superplasticizer for self compactability. The SP dosage were 3%,4%,5%,6% and 7% and the different curing temperature were 60°C,70°C,80°C and 90°C. The effect of SP dosage on workability such as filling ability, passing ability and resistance to segregation was evaluated. Result showed that the workability and compressive strength improved with the increase in SP dosage. An increase in strength was observed with the increase in curing temperature up to 70%. However the strength decreased when the curing temperature increased beyond 70°C. The compressive strength of 51.52MPa was obtained for SCGC with SP dosage of 6% and cured at 70°C oven temperature and the slump was 690mm.
- An experimental investigation conducted by **Dave and Sahu(2012)** with the alkaline liquid(NaOH+Na₂SiO₃). In study three series of geopolymer concrete specimens composing 8M concentration of sodium hydroxide (NaOH) was adopted and 9 cube specimens were prepared.After casting, the specimens were kept in rest period for five days and then they were demoulded. The specimens were wrapped by plastic sheet to prevent loss of moisture and placed in an oven. The test specimens were cured at 60°C in an oven and at ambient condition. The curing time varied from 24hours to 168hours (7days). The result showed that the strength of geopolymer concrete after 24hours was not superior and after 7days the compressive strength of geopolymer concrete was moderate. Another important observation was that the 7days compressive strength of hot cures specimens were about 3 times more than that of ambient cured specimens.
- A study conducted by **Bhosale and Shinde(2012)** using fly ash and alkaline activator with geopolymerization process. The factors that influence the early age compressive strength such as molarities of sodium hydroxide (NaOH) have been studied. Sodium hydroxide and sodium silicate solution were used as an alkaline activator. These studies the comprises the comparison of the ratios of Na₂SiO₃ and NaOH at the values 0.39 and 2.51. The geopolymer paste samples were cured at 60°C for 1 day and kept at room temperature until the testing days. The

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compressive strength tested at 7 and 28 days. The result showed that the geopolymer paste with NaOH concentration, compressive strength increase with molarities increases. It was also found that at ratio of 2.5 of Na_2SiO_3 and NaOH the compressive strength was greater as compared to 0.39 and compressive strength is more for oven drying as compared to specimen left in ambient temperature.

- An experimental investigation conducted by **Sanni and Khadriranaikar(2012)** on the performance of geopolymer concrete subjected to severe environmental conditions. The grades that was chosen for the investigation were M30 M40 M50 and M60 molarity chosen was 8M and 12M and oven curing was done at 60°C. It is well known that mechanisms of attack by sulphuric acid and magnesium sulphates are different. Conventional concrete are generally not resistant to prolonged exposure to very high concentrations of these solutions because decalcification of C-S-H will occur. As a result of this OPC concrete surface becomes soft and could be removed thus exposing the interior concrete layers to deterioration. At the same time the magnesium sulphate attack causes decalcification of C-S-H to form magnesium silicate hydrate (M-S-H). It also destroys the binding capacity of C-S-H and leads to a loss of adhesion and strength in concrete. Durability of specimens were assessed by immersing GPC specimens in 10% sulphuric acid and 10% magnesium sulphate solutions separately, periodically monitoring was done over a period of 15, 30 and 45 days. The result indicates that the heat cured fly ash based geopolymer concrete had an excellent resistance to acid and sulphate attack when compared to conventional concrete. Thus it can be said that the production of geopolymers have a higher strength, excellent volume stability and better durability. 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 concrete. A superplasticizer Conplast SP-430 (Naphthalene based) used for easy working of fresh GPC and found that the workability of GPC decreases with increase in the grade of concrete this is because of the decrease in the ratio of water to geopolymer solids. As the molarity of the NaOH solution increases the workability of GPC decreases. Thus as the grade of the concrete increases the mix become stiffer decreasing the workability.
- Various properties of geopolymer concrete by using fly ash were studied by **Raijiwala et al (2013)**. In this Potassium hydroxide and Sodium Hydroxide were used as an alkali activators in different mix proportion and superplasticizer is added to improve the workability of geopolymer concrete. The actual compressive strength of the concrete depends on various parameters such as the ratio of the activator solution to fly ash, molarity of the alkaline solution, ratio of the activator chemicals, curing temperature etc. The specimens were cured at two different temperature 25°C and 60°C for 24 hours in the oven then left to open air (room temperature 25°C) in the laboratory until testing. Compressive strength, Flexural Strength, Split tensile strength, Pull out strength were evaluated at 1, 7, 14 and 28 days. It was observed that Compressive strength of GPC increases over controlled concrete by 46% higher. (M25 achieves M45). Split tensile strength of GPC increases over controlled concrete by 45% high. Flexural Strength of GPC increased over controlled concrete by 62% higher. In pull out test GPC increases over controlled concrete by 51% higher. It was also observed that strength was greater at curing of 60°C compared to 25°C.
- **Vora and Dave(2013)** conducted the experimental work by casting 20 geopolymer concrete mixes to evaluate the effect of various parameters affecting its the compressive strength in order to enhance its overall performance. Various parameters i.e. ratio of alkaline liquid to fly ash, concentration of sodium hydroxide, ratio of sodium silicate to sodium hydroxide, curing time, curing temperature, dosage of superplasticizer and additional water content in the mix were investigated. The test result showed that the ratio of sodium silicate to sodium hydroxide ratio by mass equal to 2 had resulted into higher compressive strength as compared to 2.5, higher molarity also increases the compressive strength up to 14M, with curing time also compressive strength increases rapid rate of increase in strength had been observed up to the curing time of 24 hours, the compressive strength of geopolymer concrete also increases when the curing temperature is in the range 60°C to 90°C and minor reduction of compressive strength of geopolymer concrete is observed when the superplasticizer dosage is greater than 2%.

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- Maria et al. (2014)** critically analyzed the economic and environmental benefits of geopolymer concrete and address the financial and environmental issues associated with the production and use of Portland cement. Geopolymer concrete products also known to possess far better durability and strength properties than Portland cement concrete. These properties were investigated extensively in laboratory to verify and confirm the superior durability and strength properties. Laboratory tests were conducted on compressive strength, split tensile strength and flexural test for specimens with combination of different molarity(8M,10M,12M,14M,16M). It was found that compressive strength of GPC specimens with 12M is 1.25 times more than that of GPC with other molarities after 28days of hot curing; split tensile strength with 12M was 1.18 times more than other molarities while flexural strength with 12M is 1.058 times more. It was also reported that geopolymer technology does not only contribute to the reduction of green house gas emissions but also reduces disposal costs of industrial waste and geopolymer technology encourages recycling of waste and finally it will be an important step towards sustainable concrete industry.
- Extensive research and development work carried out in the field of geopolymer concrete by **Dr.S.S.Amritphale** chief scientist a renowned person in the field of material science, **Dr. (Er.).Manish Mudgal** and **Er.R.K.Chouhan** renowned person in the field of concrete technology they have designed and developed geopolymer concrete for high compressive and flexural strength upto 80MPa and 6MPa respectively at CSIR-AMPRI,Bhopal.

III. SOME OF THE WORK DONE ON GEOPOLYMERS IN AUSTRALIA

A lot of research work in geopolymer concrete has been done in Australia. Some of the work done on geopolymer concrete in Australia is shown in Figure 1 as Figure 1.1, 1.2 and 1.3. In Figure 1.1 Geopolymer concrete sewer pipes being installed in Toowoomba, Queensland, Australia.(2005) in Figure 1.2 Prestressed geopolymer concrete railway Sleepers installed as spot-replacement sleepers in the Melbourne to Sydney mainline, near Goulburn, NSW Australia.(2005) and in Figure 1.3 Earth Friendly Concrete (EFC) is a proprietary geopolymer concrete developed in Australia and used in a range of precast and in-situ applications.(2014)



Fig 1.1 Geopolymer concrete sewer pipes being installed in Toowoomba, Queensland, Australia.(2005)



Fig 1.2 Prestressed geopolymer concrete railway sleepers installed as spot-replacement sleepers in the Melbourne to Sydney mainline, near Goulburn,NSW, Australia.(2005)



Fig 1.3 Earth Friendly Concrete (EFC) is a proprietary geopolymer concrete developed in Australia and used in a range of precast and in-situ applications .(2014)

Fig. 1 Work Done on Geopolymer Concrete in Australia

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IV. WORK DONE ON GEOPOLYMER CONCRETE IN CSIR-AMPRI, BHOPAL(INDIA)

CSIR-AMPRI Bhopal, India working a lot in the field of geopolymer concrete some of the work has been demonstrated in Figure 2. Figure 2.1 shows the cement free cast in situ structure that was developed in the year 2011 while Figure 2.2 shows the cement free concrete road that was demonstrated in the year 2014 the detailed specification of structure and road has been illustrated along with the figure.



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|  <p style="text-align: center;">Fig 2.1 Cement free Cast-in-Situ Structure</p> <ul style="list-style-type: none"> • Dimension: 1.4 m X 1.4m X 2.4m • Compressive Strength: 25 MPa • Flexural Strength: 3 MPa • Year of Demonstration : 2011 |  <p style="text-align: center;">Fig 2.2 Cement Free Concrete Road</p> <ul style="list-style-type: none"> • Dimension: 34 m X 3.75 m and thickness of pavement quality geopolymer concrete is 150 mm on prepared subgrade • Compressive Strength:35MPa • Flexural Strength: 4 MPa • Year of Demonstration : 2014 |
|---|--|

Fig 2 Work Done on Geopolymer Concrete at CSIR-AMPRI,Bhopal (India)

VI. DISCUSSIONS AND CONCLUSION

On performing the extensive survey on the basis of the literature which is available, it is easy to understand that cement which is key ingredient of concrete has negative impact on the environment releasing carbon dioxide to the atmosphere. In cement manufacturing about one ton of CO₂ is released in one ton clinker production, contributes 7% global CO₂ emission. Hence it is necessary to evaluate the techno physical materials in concrete preparation, which could be eco friendly and reduces the CO₂ gas emissions. Environmental friendly building becoming a crucial issue in construction industry. The course towards sustainable concrete involves mainly minimizing the environmental impact of concrete production by substituting virgin materials by recycled ones as well as reducing the global CO₂ emissions. The approach adopted the use of fly ash as a partial substitute/full substitute of Portland cement for fly ash concrete production.

In 1978 Prof Joseph Davidovits of France developed inorganic polymeric materials and coined the term **Geopolymer**

Due to their unique physical and chemical properties it is widely used in many fields like construction materials, transportation, road building, aerospace materials, metallurgy mining etc. On performing the extensive survey on the basis of literature which is available it was found that Geopolymer Concrete is much better than the cement concrete in terms of strength durability and mostly it protects the environment as it emits less CO₂ about 80% less than Ordinary Portland Cement Concrete.

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The advantage of Geopolymer Concrete is that higher compressive strength is easily achievable in a short period of time. The main factors that influence the compressive strength of Geopolymer Concrete is ratio of alkaline liquid to fly ash, concentration of sodium hydroxide, curing time, curing temperature, dosage of superplasticizer, rest period and additional water content mix. In Geopolymer Concrete curing is provided either in oven or in ambient under natural sunlight. Through the literature a conclusion has been drawn that high strength in Geopolymer Concrete can be achieved when the molarity of NaOH solution is between 10M-16M, ratio of sodium silicate to sodium hydroxide between 0.5-2.5, curing time should be 6to96 hours but it is also reported that beyond 48hours is not significant while the curing temperature should be between 30°C-90°C but beyond 70°C strength decreases.

The literature also reported that Geopolymer Concrete has an excellent resistance to acid and sulphate attack when compared to conventional cement concrete. Thus we can say that the production of geopolymers have a relative higher strength excellent volume stability and better durability. But the main problem that is encountered with geopolymer Concrete is **workability**; it is not as much as workable as compared to conventional cement concrete. The workability in Cement Concrete is generally increased by addition of superplasticizer. The conventional superplasticizer's available are generally Sulfonated melamin formaldehyde condensates, Sulphonated naphthalene formaldehyde condensates, Modify lignosulphonates, Polyether polycarboxylates. Very less literature is available on the workability of geopolymer Concrete.

This is reported that when the dosage of superplasticizer is greater than 2% by mass of fly ash in Geopolymer Concrete there is some segregation and decrease in the compressive strength As it is also reported that higher molarity results in higher strength and lesser in workability. As per most reported literature, the Naphthalene based superplasticizer was used for improving the compressive strength of Geopolymer Concrete whereas ignoring the workability.

In the most research work it is revealed that higher the strength lesser the workability and vice versa. Hence there is need of the day to investigate the remedies of the problem of workability in Geopolymer Concrete.

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