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# FLY ASH BASED GEOPOLYMER CONCRETE: A REVIEW

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Geopolymer binder is an emerging alternative of ordinary Portland cement (OPC) for concrete because of its comparable physical and mechanical properties shown in the recent studies. The current published literature indicates the prospect of geopolymer concrete for structural use. However, the overall performance and functionality under various environmental conditions has not yet been well documented. This paper reviews the works conducted on the fly ash based geopolymer concrete (FGPC) and summarizes its performance as a concrete material. The properties of FGPC are influenced by many factors such as the types and composition of fly ash (aluminosilicate source), final composition of chemical ingredients (alkaline activators), water to solid ratio and curing condition (temperature and relative humidity). Most of the previous studies were based on heat-cured or steam-cured samples. The implications of the current studies were analyzed to identify the critical factors holding back the wide application of FGPC. Further research areas for the improvement of FGPC were identified.

*Keywords*: Alkali activation, fly ash, geopolymer, inorganic polymer.

## 1 Introduction

In recent years, there is an increasing awareness on the environmental impact and sustainability of concrete production. Portland cement is one of the major contributors of green house gas. Several alternative binders are now gaining more attention to replace cement fully or partially (Juenger *et al.* 2011). Geopolymer binder is an attractive alternative to cement which is produced by alkali activation of various aluminosilicate materials originated naturally or as a by-product from other industry (Davidovits 2008). Geopolymer binders can play a major role in producing environment-friendly concrete by replacing cement and by utilizing waste by-product materials such as fly ash and blast furnace slag. Geopolymer materials also show great potential in encapsulation of toxic solid wastes and heavy metals (van Jaarsveld *et al.* 1997).

The term geopolymer is generally used to describe the amorphous to crystalline reaction products of aluminosilicate materials and alkali hydroxide or alkali silicate solutions. Geopolymer is a subset of inorganic polymer in the wider group of alkali activated materials (van Deventer *et al.* 2010). In the geopolymerization process, aluminosilicate materials, when dissolved into alkaline solution, release free $SiO_4$ and $AlO_4$ tetrahedral units which forms polymeric gel by linking and sharing all oxygen atoms between tetrahedral units (Duxson *et al.* 2007). The final geopolymer products are characterized by many factors regarding chemical composition of the source materials and alkaline activators (Diaz *et al.* 2010).

Geopolymer and alkali-activation technology has been known to the cement and concrete industry for more than seven decades. Purdon (1940) developed the first alkali-activated binder using blast furnace slag and sodium hydroxide. In the mid-1950s, Glukhovsky (1994) began to investigate the binders used in ancient Roman and Egyptian structures to find an alternative to OPC concrete in former Soviet Union. He produced a binder, called 'soil cement', combining various types of slags with alkaline industrial waste solutions. This formula was applied in the various structural applications throughout the 1960s, however the mixture techniques were mostly patented and was inaccessible. In late 1970s, Davidovits developed a mineral polymer with 3D polysialate chains, which resulted from the hydroxylation and poly-condensation reaction of natural minerals such as clay, slag, fly ash and pozzolan on alkaline activation (Davidovits and Sawyer 1985). Davidovits coined the term "geopolymer" for a range of alkali-activated metakaolinite binders. In 1984, Lone Star Industries inc. of USA started to utilise geopolymer binders blended with OPC (named as PYRAMENT) which resembles closely to alkali activated pozzolanic cement. This concrete achieved a high early strength and been used in many structural application in USA until 1996 (Davidovits 2008). Vigorous research on geopolymer materials was accelerated and started to appear as publication in late 1990s. The team of Fernandez-Jimenez and Palomo in Spain and a team of van Jaarsveld and van Deventer in Australia reported numerous studies on geopolymer technology. The types and composition of aluminosilicate source materials and alkaline activator varied widely.

## 2 Fly ash based geopolymer

Fly ash is one of the major potential source materials for geopolymer due to the presence of silica and alumina as major constituents. Jiang and Roy (1992) presented about fly ash cement. Silverstrim *et al.* (1997) patented the first fly ash based cementitous material making method. The research on fly ash based geopolymer intensified in late 1990s. Most of the studies were conducted on various properties of pastes and mortar samples. Studies on heat cured fly ash geopolymer concrete were initiated in 2001 at Curtin University of Technology in Australia led by Rangan (Hardjito and Rangan 2005).

### 2.1 *Mixture parameters*

The properties of geopolymer binder greatly depend on the chemical composition of source materials and activator solutions. Davidovits (2008) suggested certain synthesis limits for the formation of strong geopolymer products: $M_2O/SiO_2$ from 0.2 to 0.48; $SiO_2/Al_2O_3$ from 3.3 to 4.5; $H_2O/M_2O$ from 10 to 25; and $M_2O/Al_2O_3$ from 0.8 to 1.6. Hardjito *et al.* (2004) studied the effect of the test variables on compressive strength of Class F fly ash based geopolymer concrete by using the $H_2O/Na_2O$ molar ratio from 10 to 14 and the $Na_2O/SiO_2$ molar ratio from 0.095 to 0.120. Outside these ranges, geopolymer concrete mixtures were either too dry or too wet causing segregation of aggregates. The water-to-geopolymer solids ratio by mass in the geopolymer paste varied from 0.17 to 0.22.

Fernandez-Jimenez and Palomo (2003) reported some main characteristics of a fly ash with optimal binding properties for alkali activation are: percentage of unburned material < 5%; $Fe_2O_3$ content < 10%; low content of CaO; content of reactive silica between 40–50%; percentage of particles with size lower than 45 µm between 80–90%; and also high content of vitreous phase. An European Union sponsored project named GEOASH, carried out in 2004-2007, tested the suitability of 17 European fly ashes with conventional method of alkali activation (zeolitic Method) and geopolymeric method ((K, Ca)-based system) for curing in ambient temperature (Davidovits 2008). It indicated that for a given fly ash alkali activation provides lower strength than (Ca, K)-based geopolymeric procedure. To achieve high compressive strength the fly ashes should be with Mullite ($Al_6Si_2O_{13}$) content below 5%, relatively higher glass content and moderate particle size in the range of 10-40 µm. The presence of high $Fe_2O_3$ content, unburned carbon particles and unusual mineral components in fly ash may disrupt the geopolymerization reaction. Hence class F fly ash is noted as the most suitable for (Ca, K)-based geopolymer cement.

Various types of alkaline activator solutions were studied which include mainly alkali hydroxides, silicates, carbonates and sulfates with a variety of concentration. The microstructure as well as the Si/Al and Na/Al ratios of the aluminosilicate gel change as a function of the activator type used in the system (Fernandez-Jimenez and Palomo 2005). Recently Ma *et al* (2012) reported that increasing the sodium oxide content in alkali activated fly ash leads to a higher extent of reaction, denser matrix, higher possibility of crystallization, and higher compressive strength. The addition of silica in the alkaline solution retards the reaction rate and zeolite formation, while improves the microstructure of the matrix. They indicated an optimal value for $SiO_2$ with respect to the $Na_2O$ content for the alkali activated fly ash mixtures.

The extra water added to improve the workability of mixture generally reduces compressive strength. However it remains outside of the geopolymeric network, acting as a lubricating agent and has a diluting effect. (Davidovits 2008).

### 2.2 *Curing process*

A comparative study of different curing conditions (Krivenko and Kovalchuk 2002) showed that temperature and humidity play a key role in the development of the microstructure and consequently the properties of alkali activated fly ash materials. Most research has been conducted with curing conditions of about 95% relative humidity and temperatures generally range from 30$^o$C to 85$^o$C. The time of curing ranges from few hours to several days. Criadoa *et al*. (2010) found that when the material is cured in air-tight containers, a dense and compact product can be achieved, because the silicon content of the initial aluminium-rich material gradually increases. However, when samples are exposed to the atmosphere, early age carbonation takes place, resulting in water loss and persistence of a high-aluminium content. This resulting material is granular and develops lower mechanical strength than the paste cured under high RH conditions. Another study (Palomo *et al*. 2004) found that raising the curing temperature from 45$^o$C to 65$^o$C increased the rate of mechanical strength development fivefold; and a 10-fold rise was recorded between 65$^o$C and 85$^o$C. They indicated existence of a threshold value beyond which strength increases at a slower rate. Kovalchuk *et al*. (2007) reported that curing of alkali activated fly ash materials in a covered mold at 95$^o$C yields the highest compressive strength (102 MPa after 8 hours of curing) as compared to dry curing at 150$^o$C, or steam curing at 95$^o$C. They recommended dry curing only for NaOH-based systems (low $SiO_2/Al_2O_3$ ratio), since waterglass-based mixes tend to retard reaction kinetics. Steam curing showed an intermediate effect on strength development, as compared to cover mold curing at 95$^o$C and dry curing at 150$^o$C.

The geopolymer mixture solely made of fly ash as the binder shows very slow rate of setting and low compressive strength when cured in ambient temperature. Fly ash blended with slag and metakaolin were tested by some researcher and found suitable for ambient curing temperature (Puertas *et al*. 2000, Davidovits 2008).

### 2.3 *Structural properties*

According to Hardjito (2005) compressive strength of heat cured samples increase due to increase of concentration of sodium hydroxide, increase of the ratio of sodium silicate to sodium hydroxide by mass, increase of curing temperature from 30$^o$C to 90$^o$C and curing time from four to 96 hours, increase of the $H_2O/Na_2O$ molar ratio and decrease of water to solid ratio. The value of Young's modulus and stress-strain relation in compression of fly ash based geopolymer concrete are similar to those of OPC concrete using the same aggregate type. The poison's ratio falls between 0.12 and 0.16, which is also in the range observed for OPC. Fernandez-Jimenez et al. (2006) tested bond strength, modulus of elasticity and drying shrinkage of heat cured fly ash geopolymer concrete activated with different activators. According to their study, silicate ions present in the activator solutions improves strength and modulus of elasticity substantially, but cause a slightly adverse effect on bond and shrinkage. However geopolymers performed better than OPC concrete. Sofi *et al*. (2007a) also reported similar engineering properties.

Wallah (2006) studied the long term properties of heat cured FGPC. He found very low creep and little drying shrinkage of FGPC. The drying shrinkage strain after 52 weeks under sustained load of 40 % of the compressive strength was approximately 100 $\times 10^{-6}$ and the creep factor (the ratio of creep strain to elastic strain) was found to vary between 0.44 and 0.63 when the compressive strength of concrete was 60 MPa. Sumajouw *et al.* (2005, 2007) studied the behavior of structural columns and beams made of steam cured FGPC. Concrete strength varied from 40-60 MPa. The behavior of these reinforced columns and beams was similar to that of members made of OPC. The results have also shown that the design provisions of the Australian Standard (AS 3600) and American Concrete Institute Building Code (ACI 318–02) are applicable to reinforced FGPC. Sarker (2009) reported the properties of fly ash based geopolymer columns. He used conventional equations and analysis technique generally applied for OPC concrete and found good correlations with respect to stress–strain curve, ultimate load (test–prediction ratio is 1.03 and standard deviation is 5%) and mid-height deflection of columns (test–prediction ratio of 1.14 and standard deviation of 11%).

Bonding characteristics (Sofi *et al.* 2007b, Sarker 2011) and fracture properties (Sarker *et al.* 2013) of alkali activated heat cured FGPC were reported to be similar or superior to the OPC concrete properties.

### 2.4 *Durability properties*

Fly ash based geopolymer generally shows better resistance to aggressive elements such as chloride, sulfate, acid and alkali-silica reaction as compared to OPC concrete (Fernandez-Jimenez *et al.* 2007). Wallah *et al.* (2005) exposed FGPC specimens in sodium sulfate solution (5%) for 52 weeks and found no sign of sulfate attack or degradation in properties. However, the compressive strength significantly decreased when the FGPC was immersed in 2% sulfuric acid solution.

Contrary to standard OPC binders alkali-activated binders show a high stability when tested in high temperatures of 1000$^{o}$C (Pawlasova and Skavara 2007). Alkali-activated fly ash binders show a high resistance to freeze–thaw cycles (Yunsheng and Wei 2006).

## 3 Economic and environmental benefits of fly ash based geopolymer

Fly ash, being a by-product material, is associated with no extra production cost. Unlike cement, fly ash can be directly used in the geopolymer mixture without any further processing. The cost of one ton of fly ash is only a small fraction of the cost of one ton of Portland cement. After allowing for the cost of activator liquids, it has been estimated that the cost of FGPC may be about 10 to 30 percent cheaper than that of OPC concrete. The superior durability offered by the FGPC may yield additional economic benefits in long term when it is utilized in infrastructure. Fly ash based geopolymeric cement emits up to nine times less $CO_2$ than OPC, whereas kaolin based geopolymer cement emits six times less than OPC (Davidovits 2008). By substituting alkali activated binders for OPC in concrete, $CO_2$ emissions can be reduced by more than 80% (Duxson *et al*. 2007). The life cycle assessment of Habert et al (2011) indicated that, FGPC has a lower environmental impact than geopolymer concrete made from pure metakaolin.

## 4 Challenges

Though geopolymer binders show superiority over OPC, taking them from the laboratory to the real-world is technically challenging. The participation of the industry to accept geopolymer cement in place of OPC is still out of sight. It is because of lack of sufficient information regarding mixture design and long term performance of the end product. Conventional geopolymerization is not a user friendly technique, as it is associated with corrosive alkali activators which are a potential source of hazards (Davidovits 2008). The key ambiguity in the development and application of alkali activation technology is the durability which is strongly dependent on the application of adequate curing at high temperature. While heat curing is not always applicable in cast-in-situ construction, materials suitable for ambient curing is not adequately addressed. Another important issue is the lack of appropriate admixtures for modifying mixture properties such as superplasticizer, setting accelerator and retarder, shrinkage reducer etc.

## 5 Further research

Significant amount of study on alkali activated materials was reported over the past two decades. Yet, the whole process of alkali activation is somewhat ambiguous. Hence a definite mechanism for alkali activation of aluminosilicate materials is necessary to develop. The relationship between reaction mechanisms, the chemistry of alkaline activating solutions and the property of end product properties needs to be explored. The effect and reaction process of different types of alkaline activators need to be clarified with respect to the reaction kinetics and the composition of the end product. Further study is necessary to understand the role of calcium in geopolymer gel processes and phase formation. Much works needed in developing geopolymer concrete products for ambient curing condition, as the reaction mechanism and kinetics influences the final property of the concrete. It is also necessary to develop appropriate admixtures for geopolymeric mixtures.

## 6 Conclusion

Fly ash has been recognized as an important source for making geopolymer binder due to its favorable features stated above. Significant progress has been made in developing an understanding of the phenomena underlying geopolymerization of aluminosilicates. Fly ash based geopolymer concrete has shown excellent properties and was recommended for structural applications by the researchers. However, lack of standard specifications and regulations related to processing and application in the industry level hinder its wide use in real structures. It is hoped that concentrating over such issues and needs and researching elaborately in this field will help to emerge fly ash based geopolymer concrete as a commercial and environment-friendly material and ensure the sustainability of construction industry.

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