A Review on Fly Ash-Based Geopolymer Concrete

Ramin Hosseini Kupaei, U. Johnson Alengaram, Mohd Zamin Bin Jumaat

Department of Civil Engineering, University of Malaya, Kuala Lumpur, Malaysia

ABSTRACT:
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. Binders could be produced by a polymeric reaction of alkaline liquids with the silicon and the aluminium in source materials of geological origin or by-product materials such as fly ash. Low-calcium fly ash-based geopolymer is used as the binder, instead of Portland or other hydraulic cement paste, to produce concrete. The manufacture of geopolymer concrete is carried out using the usual concrete technology methods. As in the case of OPC concrete, the aggregates occupy about 75-80% by mass, in geopolymer concrete. The silicon and the aluminium in the fly ash react with an alkaline liquid that is a combination of sodium silicate and sodium hydroxide solutions to form the geopolymer paste. Geopolymerisation in fly ash based concrete could be occur by using different solutions with the solution-to-fly ash ratio by mass of 0.25 to 0.30. The best compressive strength will be more than 60 MPa for mixtures that used a combination of sodium hydroxide and sodium silicate solution, after curing the specimens for 24 hours at 65°C. The proportion of alkaline solution to alumino-silicate powder by mass should be approximately 0.33 to allow the geopolymeric reactions to occur. Alkaline solutions forms a thick gel instantaneously upon mixing with the alumino-silicate powder. By the use of the mass ratio of the solution to the powder of about 0.39 and mixing 57% fly ash with 15% kaolin or calcined kaolin and the alkaline liquid comprise 3.5% sodium silicate, 20% water and 4% sodium or potassium hydroxide the maximum compressive strength will be 75 MPa when fly ash and builders’ waste are used as the source material.

1 INTRODUCTION
Climate change due to global warming, one of the greatest environmental issues has become a major concern during the last decade. The global warming is caused by the emission of greenhouse gases, such as CO$_2$, to the atmosphere by human activities. The cement industry is responsible for about 6% of all CO$_2$ emissions. Geopolymeric cements are becoming the focus of increasing research efforts as the need to reduce global CO2 emissions intensifies. Displaying excellent mechanical strength and resistance to attack by aggressive environments, these materials represent an opportunity to simultaneously improve both environmental and engineering performance compared to traditional technologies [1]. Although the use of OPC is still unavoidable until the foreseeable future, many efforts are being made in order to reduce the use of OPC in concrete. Geopolymers, a new form of binder used in cement and concrete composites, are produced by the reaction of aluminosilicate material with alkaline solutions. Instead of using metakaolin as the main binding material in concrete, slag and fly ash have become popular source materials for geopolymers because they have high silica and alumina content sand are abundantly available in landfill sites. Fly ash is a heterogeneous material of variable chemical composition that can affect the final geopolymer product. Low calcium fly ash is preferred because high calcium poses the risk of fast setting. The main parameters affecting the fly ash geopolymer mixtures are the composition of the raw materials, the concentrations of alkaline solutions used, and the curing method [2]. low-calcium (ASTM Class F) fly ash-based geopolymer is proposed as the binder, instead of ordinary OPC paste, to produce concrete. The fly ash-based geopolymer paste binds the loose coarse aggregates, fine aggregates and other un-reacted materials together to form the geopolymer concrete, with or without the presence of admixtures [3-6].

2 GEOPOLYMERS
The term ‘geopolymer’ was first introduced by Davidovits in 1978 to describe a family of mineral binders with chemical composition similar to zeolites but with an amorphous microstructure. He also suggested the use of the term ‘poly(sialate)’ for the chemical designation of geopolymers based on silico-aluminate; Sialate is an abbreviation for silicon-
oxo-aluminate. Poly(sialates) are chain and ring polymers with Si$^{4+}$ and Al$^{3+}$ in IV-fold coordination with oxygen and range from amorphous to semicrystalline with the empirical formula which is shown in formula $[M_n\left(-\left(\text{SiO}_2\right)_z\text{-AlO}_2\right)_n\cdot \text{H}_2\text{O}]$ where “z” is 1, 2 or 3 or higher up to 32; M is a monovalent cation such as potassium or sodium, and “n” is a degree of polycondensation. Davidovits has also distinguished 3 types of polysialates, namely the Poly(sialate), the Poly(sialate-siloxo) and the Poly(sialate-disiloxo) [7]. The structures of these polysialates can be schematised as in Figure 1. Geopolymerization involves the chemical reaction of aluminosilicate oxides (Si$_2$O$_5$, Al$_2$O$_3$) with alkali polysilicates yielding polymeric Si–O–Al bonds. Polysilicates are generally sodium or potassium silicate supplied by chemical industry or manufactured fine silica powder as a by-product of ferro-silicon metallurgy. Figure 2 shows equation of an example of polycondensation by alkali into poly (sialate-siloxo).

Unlike OPC, geopolymers do not form calciumsilicate-hydrate (CSH) for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors and a high alkali content to attain structural strength. Therefore, geopolymers are sometimes referred to as alkaliactivated aluminosilicate binders [8].

In figure 2 the last term of equation indicates that water is released during the chemical reaction that occurs in the formation of geopolymers. This water is expelled from the mixture during the curing process. Seeding enhances the dissolution of silica by inducing nucleation of geopolymer gel in the initially Al-rich reaction mixture. This prevents dissolved alumina from sorbing onto the surface of silica particles and impeding their dissolution. Also, by controlling the silica release rate, seeding provides a means of directly manipulating the physical properties of geopolymers. The enhancement of the nucleation process leads to the formation of an additional silica-rich phase in the early stages of the reaction, which leaves more Al available to contribute to bulk gel formation and improves the early strength development of geopolymer binders. The later release of more silica from the Si-rich phase then also enhances final strength [9].

3 SOURCE MATERIALS AND ALKALINE LIQUIDS

There are two main constituents of geopolymers, namely the source materials and the alkaline liquids. The source materials for geopolymers based on aluminosilicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, micas, andalusolite, spinel, etc whose empirical formula contains Si, Al, and oxygen (O) [10]. Alternatively, by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc could be used as source materials. The alkaline liquids are from soluble alkali metals that are usually Sodium or Potassium based. Since 1972, researchers worked with kaolinite source material with alkalis (NaOH, KOH) to produce geopolymers [11]. It was found that a wide range of natural aluminosilicate minerals provided potential sources for synthesis of geopolymers. For alkaline solutions, they used sodium or potassium hydroxide. The test results have shown that potassium hydroxide (KOH) gave better results in terms of the compressive strength and the extent of dissolution. Among the waste or by-product materials, fly ash and slag are the most potential source of geopolymers [12-13]. A high compressive strength is obtained when the class C fly ash (CFA) is activated by the mixed alkali activator (sodium hydroxide and sodium silicate solution) with the optimum modulus viz., molar ratio of SiO2/Na2O of 1.5. The proper content of this mixed activator is 10% as evaluated by the mass proportion of Na2O to CFA. The compressive strength of these
samples is 63.4 MPa when they are cured at 75°C for 8 h followed by curing at 23°C for 28 d [14].

3.1 Fly Ash

Fly ash, generated during the combustion of coal for energy production, is an industrial by-product which is recognized as an environmental pollutant. Because of the environmental problems presented by the fly ash, considerable research has been undertaken on the subject worldwide [15]. According to the American Concrete Institute (ACI) Committee 116R, fly ash is defined as ‘the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system’ [16]. Fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere. The degree of vitrification during cooling of the fly ash plays an important role in geopolymerization. Fly ash with high content of glass phase will lead to higher degree of geopolymerization, therefore higher compressive strength. The cooling rate of the fly ash can be controlled at the power plant, thus increasing the suitability of the fly ash to geopolymerization [17]. Fly ash particles are typically spherical, finer than OPC and lime, ranging in diameter from less than 1 μm to no more than 150 μm. The types and relative amounts of incombustible matter in the coal determine the chemical composition of fly ash. The chemical composition is mainly composed of the oxides of silicon (SiO₂), aluminium (Al₂O₃), iron (Fe₂O₃), and calcium (CaO), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount [18]. The particle size, calcium content, alkalai metal content, amorphous content, and morphology and origin of the fly ash affected the properties of geopolymers. It was also revealed that the calcium content in fly ash [19] played a significant role in strength development and final compressive strength as the higher the calcium content resulted in faster strength development and higher compressive strength. However, in order to obtain the optimal binding properties of the material, fly ash as a source material should have low calcium content and other characteristics such as unburned material lower than 5%, Fe₂O₃ content not higher than 10%, reactive silica content between 40-50%, 80-90% particles with size lower than 45 mm and high content of vitreous phase [20]. Circulating fluidized bed combustion fly ashes (CFAs) have long posed more severe challenges than conventional pulverized coal combustion fly ashes (PFAs) to waste management. Eventually, the low combustion temperature may lead to a low pozzolanic activity, which is partially responsible for the poor feasibility of utilizing CFAs in cement industry. In spite of the cementitious properties, the use of CFAs in concretes may result instructural damage and strength decrease [21].

3.2 Alkaline Liquids (Alkali Activator)

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 [22]. 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 [23]. 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, it was found that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution [24]. The sodium hydroxide (NaOH) solution prepare by dissolving either the flakes or the pellets in water. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M. For instance, NaOH solution with a concentration of 8M consisted of 8x40 = 320 grams of NaOH solids (in flake or pellet form) per litre of the solution, where 40 is the molecular weight of NaOH. The mass of NaOH solids was measured as 262 grams per kg of NaOH solution of 8M concentration [25].

4 PROPERTIES OF GEOPOLYMER CONCRETE

Previous studies have reported that geopolymers possess high early strength, low shrinkage, freeze-thaw resistance, sulfate resistance, corrosion resistance, acid resistance, fire resistance, and no dangerous alkali-aggregate reaction [26-29]. Nonetheless, it is clear that materials exhibiting the following performance properties can be made with both technological and commercial confidence: high compressive strength gain, good abrasion resistance, particularly when mixed with PTFE filler, rapid controllable setting and hardening, fire resistance (up to 1000 °C) and no emission of toxic fumes when
heated—either in the form of a carbon fibre/geopolymer composite or as a pure geopolymer (e.g. a geopolymeric coating on an exposed surface), high level of resistance to a range of different acids and salt solutions, not subject to deleterious alkali–aggregate reactions, low shrinkage and low thermal conductivity, adhesion to fresh and old concrete substrates, steel, glass, ceramics, high surface definition that replicates mould patterns, inherent protection of steel reinforcing due to high residual, pH and low chloride diffusion rates [30]. Geopolymers are generally believed to provide good fire resistance due to their ceramic-like properties [31]. Based on laboratory tests, reported that geopolymer cement can harden rapidly at room temperature and gain the compressive strength in the range of 20 MPa after only 4 hours at 20°C and about 70-100 MPa after 28 days [32]. Most of the 28-day strength gain during the first 2 days of curing. Geopolymeric cement was superior to OPC in terms of heat and fire resistance, as the OPC experienced a rapid deterioration in compressive strength at 300°C, whereas the geopolymeric cements were stable up to 600°C [8]. It has also been shown that compared to OPC, geopolymeric cement has extremely low shrinkage. The presence of alkalis in the normal OPC or concrete could generate dangerous Alkali–Aggregate–Reaction. However, the geopolymeric system is safe from that phenomenon even with higher alkali content. As demonstrated by Davidovits (1994a; 1994b), based on ASTM C227 bar expansion test, geopolymer cements with much higher alkali content compared to OPC did not generate any dangerous alkali-aggregate reaction where the OPC did. Geopolymer cement is also acid-resistant, because unlike the OPC, geopolymer cements do not rely on lime and are not dissolved by acidic solutions. As shown by the tests of exposing the specimens in 5% of sulfuric acid and chloric acid, geopolymer cements were relatively stable with the weight lose in the range of 5-8% while the OPC were destroyed and the calcium alumina cement lost weight about 30-60% [22]. By observing the weight loss after acid exposure, these researchers concluded that geopolymers or geopolymer concrete is superior to OPC concrete in terms of acid resistance as the weight loss is much lower. There is degradation in the compressive strength of test specimens after acid exposure and the rate of degradation depended on the period of exposure.

5 FRESH GEOPOLYMER CONCRETE AND MANUFACTURING PROCESS

Study on geopolymerisation of low-calcium ASTM Class F fly ash (molar Si/Al=1.81) using four different solutions with the solution-to-fly ash ratio by mass of 0.25 to 0.30 and molar SiO$_2$/K$_2$O or SiO$_2$/Na$_2$O of the solutions in the range of 0.63 to 1.23 results the best compressive strength more than 60 MPa for mixtures that use a combination of sodium hydroxide and sodium silicate solution, after curing the specimens for 24 hours at 65°C [18]. The proportion of alkaline solution to alumino-silicate powder by mass should be approximately 0.33 to allow the geopolymeric reactions to occur. Alkaline solutions formed a thick gel instantaneously upon mixing with the alumino-silicate powder [25]. On the other hand, van Jaarsveld et al (1998) reported the use of the mass ratio of the solution to the powder of about 0.39. In their work, 57% fly ash was mixed with 15% kaolin or calcined kaolin. The alkaline liquid comprised 3.5% sodium silicate, 20% water and 4% sodium or potassium hydroxide. In this case, they used specimen size of 50x50x50 mm. The maximum compressive strength obtained was 75 MPa when fly ash and builders’ waste were used as the source material [33]. Only limited information on the behaviour of the fresh geopolymer concrete has been reported. Using Fly ash as the source material, the fresh geopolymer mortar became very stiff and dry while mixing, and exhibited high viscosity and cohesive nature. It is suggested that the forced mixer type should be used in mixing the geopolymer materials, instead of the gravity type mixer. An increase in the mixing time increased the temperature of the fresh geopolymer concrete, and hence reduced the workability. To improve the workability, it is suggested the use of admixtures to reduce the viscosity and cohesion [34]. It is measured the viscosity of fresh geopolymer concrete paste, and reported that the viscosity of the geopolymer concrete paste increased with time. Most of the manufacturing process of making geopolymer concrete paste involved dry mixing of the source materials, followed by adding the alkaline solution and then further mixing for another specified period of time [28].

6 FACTORS AFFECTING ON GEOPOLYMER CONCRETE

Several factors have been identified as important parameters affecting the properties of geopolymer concrete. Using the amorphous composition improves the development of fly ash geopolymer mixture for-
mulation and its adoption will ensure manufacture of improved geopolymer products [35]. The curing temperature was a reaction accelerator in fly ash-based geopolymers, and significantly affected the mechanical strength, together with the curing time and the type of alkaline liquid. Higher curing temperature and longer curing time were proved to result in higher compressive strength. In environmental stress conditions, freeze thaw was found to be more deteriorating than heating thaw. It also withstands conditions with higher threshold limit [36]. Alkaline liquid that contained soluble silicates was proved to increase the rate of reaction compared to alkaline solutions that contained only hydroxide. The water content, and the curing affected the properties of geopolymer concrete. However, Curing at too high temperature caused cracking and a negative effect on the properties of the material. Finally, The use of mild curing to improve the physical properties of the material is suggested [34]. The source materials determine the properties of geopolymer concrete, especially the CaO content, and the water-to-fly ash ratio. Based on a statistical study of the effect of parameters on the polymerisation process of Fly ash-based geopolymer concrete, reported the importance of the molar composition of the oxides present in the mixture and the water content. The cured geopolymer concretes showed an amorphous microstructure and exhibited low bulk densities between 1.3 and 1.9. It is reported that factors such as the percentage of CaO, K2O, and the molar Si-to-Al ratio in the source material, the type of alkali liquid, the extent of dissolution of Si, and the molar Si-to-Al ratio in solution significantly influenced the compressive strength of geopolymer concrete [37].

7 CONCLUSION

The geopolymer concrete structural members could easily be produced using the existing current concrete technology without any significant changes. The engineering performances of the products were excellent, and the drying shrinkage was small. Geopolymer concrete possess high early strength, low shrinkage, freeze-thaw resistance, sulfate resistance, corrosion resistance, acid resistance, fire resistance, and no dangerous alkali-aggregate reaction. Geopolymer composites have been successfully applied to strengthen reinforced concrete beams. Using Geopolymer concrete instead of OPC concrete is recommended because of environment friendly issue and reduction of waste materials.

8 REFERENCES


