

Review on Processing of Low Calcium Fly Ash Geopolymer Concrete

A.M. Mustafa Al Bakri, Omar A. Abdulkareem, A.R. Rafiza, Y. Zarina, M.N. Norazian
and H. Kamarudin

Center of Excellence Geopolymer and Green Technology (CEGeoGtech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), P.O. Box 77, D/A Pejabat Pos Besar, 01000, Kangar, Perlis, Malaysia

Abstract: Concrete usage around the world is second only to water. Ordinary Portland cement (OPC) is conventionally used as the primary binder to produce concrete. Any material that contains mostly Silicon (Si) and aluminum (Al) in amorphous form is possible source material for the manufacture of geopolymer. The calcined source materials, such as fly ash, slag, calcined kaolinite, demonstrated a higher final compressive strength. Alkaline activator liquid plays an important role in the polymerization process. Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of geopolymer concrete. As the H_2O/Na_2O molar ratio increases, the compressive strength of the geopolymer concrete decrease. Activator/Fly ash mass mixing ratio of the range 0.3-0.45 are recommended in the synthesized of low-calcium (Class F) based geopolymers. Waterglass/NaOH molar ratio of 2.5 leads to expressive strength increase of the geopolymers. The best curing condition is reported as being 60°C for 24 hours.

Key words: geopolymer, H_2O/Na_2O ratio, activator/fly ash ratio, waterglass/NaOH, curing.

Background:

The environmental issues associated with the production of OPC are well known (Hardjito *et al.*, 2005). The amount of carbon dioxide released during the manufacture of OPC due to the calcination of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC production. In additional, the extent of energy required to produce OPC is only next to steel and aluminum.

As early as the 1980s Davidovits proposed a controversial theory that some of the Pyramids in Egypt were not built by mining limestone blocks and moving them into place but were cast in place and allowed to set, creating an artificial zeolitic rock. This theory, which gained acceptance, culminated in a book “*The Pyramids An Enigma Solved*”, written together with Magie Morris and published in 1988. Intensive research, initiated by Davidovits and co-workers, to prove this theory has resulted in the rediscovery of a new family of mineral polymers, which they called *alkali -activated aluminosilicate geopolymer* or simply *geopolymers*. This name was chosen because of the similarities with organic condensation polymers in regards to their hydrothermal synthesis conditions (Davidovits, 1982; Davidovits & Sawyer, 1985; Davidovits, 1988; Davidovits, 1994a).

Over the last twenty years, geopolymer also known as *mineral polymer* or *inorganic polymer glasses*, have received much attention as a promising new form of inorganic polymer material that could substantially substitute for conventional or ordinary Portland cement, plastics and many mineral-based products. However, to date the exact mechanisms that cavern geopolymerization are still not fully understood (Hardjito *et al.*, 2005).

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. Zeolites composition is based on aluminosilicate framework and three dimensional network inorganic polymers built up of (Si, Al) O_4 tetrahedra linked by sharing oxygen atoms into rings and cages. The polymerization process (geopolymerization) involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals that result in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds (Davidovits, 1994a).

Moreover, as the geopolymers synthesizing technology is basing on the alkaline activation of source materials contains mostly Silicon (Si) and Aluminum (Al) in amorphous form (Hardjito *et al.*, 2004), the similarity of some fly ashes to natural aluminosilicates (due to the presence of SiO_2 and Al_2O_3 in the ash) has encouraged the use of geopolymerization as a possible technology solution in the making of special cement (Silvestrim *et al.*, 1997, 1999). The successful stabilization and immobilization of some toxic heavy metals in geopolymeric material by Jaarsveld *et al.* (1998), Jaarsveld & Deventer (1999), has also encouraged the use of this fairly new technology.

Fly Ash:

Fly ash according to the American Concrete Institute (ACI) Committee 116R, is defined as ‘*the finely divided that results from the combustion of ground or powdered coal and that is transported by flue gasses from*

Corresponding Author: A.M. Mustafa Al Bakri, Center of Excellence Geopolymer and Green Technology (CEGeoGtech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), P.O. Box 77, D/A Pejabat Pos Besar, 01000, Kangar, Perlis, Malaysia

the combustion zone to the particle removal system' (ACI Committee 232, 2004). 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. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 μm to no more than 150 μm (Hardjito & Rangan, 2005).

The types and relative amounts of incombustible matter in the coal determined the chemical composition of fly ash. The chemical composition is mainly composed of the oxides of silicon (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3), and calcium (CaO), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount. The major influence on the fly ash chemical composition comes from the type of coal. The combustion of sub-bituminous coal contains more calcium and less iron than fly ash from bituminous coal. The physical and chemical characteristics depend on the combustion methods, coal source and particle shape. The chemical compositions of various fly ashes show a wide range, indicating that there is a wide variation in coal used in power plants all over the world (Malhotra & Ramezaniapour, 1994).

Fly ash that results from burning sub-bituminous coals is referred as ASTM Class C fly ash or high-calcium fly ash, as it typically contains more than 10 percent CaO . On the other hand, fly ash from the bituminous and anthracite coals is referred as ASTM Class F fly ash or low-calcium fly ash (Davidovits, 2008). The color of fly ash can be tan to dark grey, depending upon the chemical and mineral constituents (Malhotra and Ramezaniapour, 1994; ACAA, 2003). The typical fly ash produced from Malaysia power stations is light to mid-grey in color, similar to the color of cement powder.

Aside from the chemical composition, the other characteristics of fly ash that generally considered are loss on ignition (LOI), fineness of fly ash mostly depend on the operating conditions of coal crushers and grinding process of the coal itself. Finer gradation generally results in a more reactive ash and contains less carbon.

Worldwide, the estimated annual production of coal ash in 1998 was more than 390 million tons. The main contributors for this amount were China and India. Only about 14% of this fly ash was utilized, while the rest was disposed in landfills (Malhotra, 1999). By the year 2010, the amount of the fly ash produced worldwide is estimated to be about 780 million tons annually (Malhotra, 2002). The utilization of fly ash, especially in concrete production, has significant environmental benefits, via, improved concrete durability, reduced use of energy, diminished greenhouse gas production, reduced amount of fly ash that must be disposed in landfills, and saving of the other natural resources and materials (ACAA, 2003).

Introduction of Geopolymers:

In 1978, Davidovits proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in a source material of geological origin or in by-product materials such as fly ash and rice husk ash to produce binders. Davidovits coined the term "Geopolymer" in 1979 (Davidovits, 1979) to describe a new family of material binder whose matrix is based on a poly(sialate) Si-O-Al-O framework structure with alternating SiO_4 and AlO_4 tetrahedra joined together in three directions by sharing all the oxygen atoms. The replacements of Al^{3+} (four-fold coordination) for Si^{4+} causes a negative charge, which needs alkalis or alkali-earth to balance, like (Na^+ , K^+ , Ca^{2+} or Mg^{2+}). The empirical formula (Davidovits, 1988) is:



Where M = 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 polymerization; z is 1, 2, 3, or higher, up to 32.

Geopolymer is also known in other names, such as low temperature aluminosilicate glass (Rahier *et al.*, 1996a), alkali-activated material (Malek & Roy, 1997; Palomo *et al.*, 1999b; Roy, 1999; Jahanian and Rostami, 2001; Xie and Xi, 2001) and Geocement (Krivenko, 1997).

Constituents Of Geopolymer:

Source Materials:

Any material that contains mostly Silicon (Si) and aluminum (Al) in amorphous form is possible source material for the manufacture of geopolymer (Hardjito & Rangan, 2005). Several minerals and industrial by-product materials have been investigated in the past. Metakaolinite or calcined kaolin (Davidovits, 1999; Barbosa *et al.*, 2000; Teixeira-Pinto *et al.*, 2002), low-calcium ASTM Class F fly ash (Palomo *et al.*, 1999a; Swanepoel & Strydom, 2002), natural Al-Si minerals (Xu & Deventer, 2000), combination of calcined mineral and non-calcined material (Xu & Deventer, 2002), combination of fly ash and metakaolinite (Swanepoel & Strydom, 2002; Jaarsveld *et al.*, 2002; Zuhua *et al.*, 2009), and combination of granulated blast furnace slag and metakaolinite (Cheng & Chiu, 2003) have been studied as source materials.

Metakaolinite is preferred by the niche geopolymer product developers due to its high rate of dissolution in the reactant solution, easier control on the Si/Al ratio and the white color (Gourley, 2003). Low-calcium (ASTM Class F) fly ash is preferred as a source material than high-calcium (ASTM Class C) fly ash. The presence of

calcium in high amount may interfere with the polymerization process and alter the microstructure (Gourley, 2003).

Davidovits (1999) calcined kaolinite clay for 6 hours at 750°C. He termed this metakaolinite as KANDOXI (**KA**olinite, **Na**crite, **D**ickite **O**Xide), and used it to make geopolymers. For the purpose of making geopolymer cement and concrete, he suggested that the molar ratio of Si-Al of the material should be about 2.0.

On the nature of the source material, it was stated that the calcined source materials, such as fly ash, slag, calcined kaolinite, demonstrated a higher final compressive strength when compared to those made using non-calcined materials, for instance kaolinite clay, mine tailings, and naturally occurring materials (Barbosa *et al.*, 2000). However, Xu & Deventer (2002) found that using a combination of calcined (e.g. fly ash) and non-calcined material (e.g. kaolinite or kaolin clay and albite) resulted in significant improvement in compressive strength and reduction in reaction time.

Natural Al-Si minerals have shown the potential to be the source materials for geopolymerization, although quantitative prediction on the suitability of the specific mineral as the source material is still not available, due to the complexity of the reaction mechanisms involved (Xu & Deventer, 2000). Among the by-product materials, only fly ash and slag have been proved to be potential source materials for making geopolymers. Fly ash is considered to be advantageous due to high reactivity that comes from its finer particle size than slag. Moreover, low-calcium fly ash is more desirable than slag for geopolymer feedstock material.

The suitability of various types of fly ash to be geopolymer source material has been studied by Fernandez-Jimenez & Palomo (2003). These researchers claimed that to produce optimal binding properties, the low-calcium fly ash should have the percentage of unburned material (LOI) less than 5%, Fe₂O₃ content should not exceed 10%, and 80-90% of particles should be smaller than 45µm. On the contrary, Jaarsveld *et al.*, (2003) found that the fly ash with higher amount of CaO produced higher compressive strength, due to the formation of calcium-aluminate-hydrate and other calcium compounds, especially in the early ages. The other characteristics that influenced the suitability of the fly ash to be source material for geopolymers are the particle size, amorphous content, as well as morphology and the origin of fly ash.

Alkaline Activator Liquid:

The most common alkaline activator 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.* 1999b; Xu & Deventer, 2002; Bakharev, 2005; Duxson *et al.*, 2006; Chareerat *et al.*, 2007; Chindaprasirt *et al.*, 2009). The use of single alkaline activator has been reported (Palomo *et al.*, 1999b; Teixeira-Pinto *et al.*, 2002).

Palomo *et al.* (1999b) concluded the type of alkaline activator liquid plays an important role in the polymerization process. Reactions occur at a high rate when the alkaline activator liquid contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxide. That statement is also shared by Criado *et al.* (2005). Furthermore, Xu & Deventer (2000) confirmed that the addition of sodium silicate solution to the sodium hydroxide enhanced the reaction between the source material and the solution. Although, after a study of the geopolymerization of sixteen natural Al-Si minerals, they found that the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution.

Mixture Proportions:

Most of the reported works on geopolymer material to date were related to the properties of geopolymer paste or mortar, measured by using small size specimens (Katz, 1998; Palomo *et al.*, 1999a; Pinto, 2004; Hongling *et al.*, 2005 Chindaprasirt *et al.*, 2009). In addition, the complete details of the mixtures composition of the geopolymer paste were not reported.

Katz (1998) studied the alkali-activated slags reporting an increasing in the geopolymerization degree (high mechanical compressive strength) when the concentration of the activators increases. Other authors have reported the same behavior using alkali-activated metakaolinite (Pinto, 2004; Hongling *et al.*, 2005). However, for the fly ash-based geopolymers, Palomo *et al.* (1999a) reported that the activator (NaOH or KOH) with concentration of 12M leads to better results than 18M concentration. Chindaprasirt *et al.* (2009), studied the alkali- activation of fly ash and bottom ash by alkaline activator consisted of waterglass+ NaOH solution, these authors reported that using NaOH of 10M leads to better result than using solution with 5M. This statement is also shared by Zuhua *et al.* (2009). While, Hardjito & Rangan (2005) reported that the concentration of the NaOH can vary in the range between 8M to16M.

Jaarsveld *et al.* (1997), and Jaarsveld & Deventer (1999) claims that the H₂O/SiO₂ molar ratio is very important in the study of geopolymers based on the fly ash. However, this statement is not confirmed by others, Hardjito *et al.* (2002). Hardjito & Rangan (2005), studied the fly ash-based geopolymer concrete, they reported that the compressive strength and the workability of the geopolymer concrete influenced by the proportions and the properties of the constituent materials that make the geopolymer paste. Their results had shown that:

- Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of geopolymer concrete.
- As the H_2O/Na_2O molar ratio increases, the compressive strength of the geopolymer concrete decrease as indicated in Figure (2.2).

Barbosa *et al.* (2000) reported that using mixture with high water content $H_2O/Na_2O=25$, developed very low compressive strength, and thus underlying the important of the water content in the mixture.

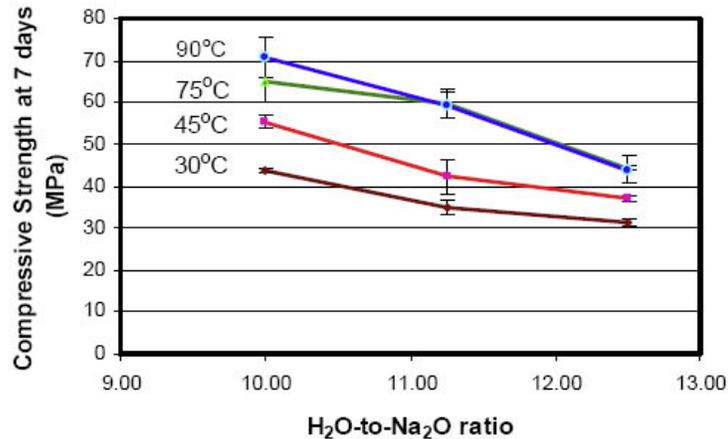


Fig. 2.2: Effect of H_2O/Na_2O molar ratio on compressive strength (Hardjito & Rangan, 2005).

The mass mixing ratio of Activator/Fly ash:

Palomo *et al.* (1999a) studied the geopolymerization of low-calcium ASTM (Class F) fly ash (molar $Si/Al=1.81$) using four different solutions with the Activator/ Fly ash ratio by mass of 0.25 to 0.3. The molar SiO_2/K_2O or SiO_2/Na_2O of the solutions was in the range of 0.36 to 1.23. The specimens were $10 \times 10 \times 60$ mm in size. The best compressive strength obtained was more than 60 MPa for mixtures that used alkaline activator consisted of waterglass+ NaOH solution. Xu & Deventer (2000) reported that the proportion of alkaline activator to the alumino-silicate powder by mass should be approximately 0.33 to allow the geopolymerization reactions to occur. Alkaline activator solution formed a thick gel instantaneously upon mixing with the source material. The specimen size in their study was $20 \times 20 \times 20$ mm, and the maximum compressive strength achieved was 19 MPa. Bakharev (2005) used Activator/ Fly ash of 0.3 to prepare low-calcium (Class F) fly ash-based geopolymers, in his study the fly ash was activated using either sodium silicate (waterglass) or with solution of NaOH to providing up to 10% Na_2O in mixture. He used cylindrical molds of $\varnothing 25 \times 50$ mm. Moreover, Hardjito & Rangan (2005), utilized ratio of Activator/Fly ash of 0.35 in the preparation of low-calcium (Class F) fly ash-based geopolymer concrete with two different NaOH concentrations of 8M and 14M.

In general, Rangan (2008) reported that Activator/Fly ash mass mixing ratio of the range 0.3-0.45 are recommended in the synthesized of low-calcium (Class F) based geopolymers, based on the results obtained from numerous mixtures made in laboratory over period of four years. While, Chindaprasirt *et al.* (2009), studied geopolymer mixtures based on High-calcium (Class C) fly ash and bottom ash by using Activators/Fly ash ratio of 0.66. A mixture of waterglass and NaOH solution used as alkaline activators, with different NaOH solution concentrations of (5 M, 10M, and 15M). The specimens size of 25mm diameter \times 25 mm height cylinder. The Class C fly ash-based geopolymers were having the molar ratios indicated in Table 2.1:

Table 2.1: Composition of geopolymers prepared from fly ash and bottom ash (Chindaprasirt *et al.*, 2009).

| Sample | NaOH | Molar ratio | | | |
|------------------|------|---------------|-----------------|-------------|-----------------|
| | | Na_2O/SiO_2 | SiO_2/Al_2O_3 | $H_2O/NaOH$ | Na_2O/Al_2O_3 |
| Fly ash based | 5 | 0.15 | 4.14 | 19.95 | 0.64 |
| Fly ash based | 10 | 0.21 | 4.14 | 13.33 | 0.89 |
| Fly ash based | 15 | 0.26 | 4.14 | 10.40 | 1.08 |
| Bottom ash based | 5 | 0.15 | 4.05 | 19.95 | 0.62 |
| Bottom ash based | 10 | 0.12 | 4.05 | 13.33 | 0.87 |
| Bottom ash based | 15 | 0.26 | 4.05 | 10.40 | 1.05 |

The mass mixing ratio of waterglass/NaOH:

For the geopolymers synthesized by activation the source material using alkaline activator of (waterglass and NaOH), only limited researches notice the range of waterglass/NaOH mass mixing ratios. For the fly ash-based geopolymers, Pinto (2004) reported that the waterglass/NaOH molar ratio influences the compressive

strength, as the use of molar ratio of 2.5 leads to expressive strength increase of the geopolymers. Hardjito & Rangan (2005), used waterglass/NaOH mass mixing ratio of 0.4 and 2.5 in the preparation of low-calcium (Class F) fly ash-based geopolymer concrete. They reported an increasing in the compressive strength with the increasing waterglass/NaOH ratio for different concentration of NaOH solution as indicated in Table 2.2.

Table 2.2: Effect of waterglass/NaOH solution and NaOH concentration of (Class F) fly ash-based geopolymers. (Hardjito & Rangan, 2005).

| Mixture | Concentration of NaOH liquid (in Molars) | Waterglass/NaOH solution (by mass) | Compressive strength at 7 th day (MPa) |
|---------|--|------------------------------------|---|
| | | | Cured for 24 hours at 60°C |
| 1 | 8M | 0.4 | 17 |
| 2 | 8M | 2.5 | 57 |
| 3 | 14M | 0.4 | 48 |
| 4 | 14M | 2.5 | 67 |

Furthermore, the synthesized of high-calcium (Class C) fly ash-based geopolymers, Chindaprasirt *et al.*, (2007) reported the effect of waterglass/NaOH solution in details using waterglass/NaOH solution mass mixing ratios range of 0.67, 1.00, 1.5, and 3.0. The optimum compressive strength reported was in the range of (0.67-1.00), with variation in the NaOH solution concentration of 10M to 20M. While Chindaprasirt *et al.*, (2009) used waterglass/NaOH mass mixing ratio of 1.5 in preparation of geopolymers based on high-calcium fly ash and bottom ash.

Curing Conditions:

Curing condition includes the curing temperature and heating period. Hardjito *et al.*, (2002) studied the effect of curing temperature in range of (30 °C, 60 °C and 91°C) on the compressive strength as indicated in Figure 2.3. It can be concluded that the benefit of evaluated temperature curing is significant. The best curing condition is reported as being 60°C for 24 hours.

In fact, a number of researchers have studied the influence of curing conditions on fly ash-based geopolymer, but there is no clear statement as to which temperature and heating period are the best. Table 2.4, presents the adoption values suggested of different authors. It is clear that the curing conditions varied from one case to another but the evaluated temperature curing is a general trend. Such curing regimes limit the application of geopolymer in the precast industry.

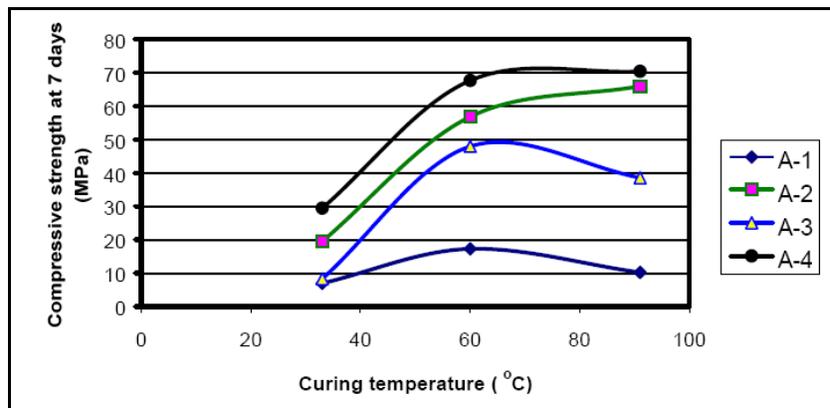


Fig. 2.3: Influence of curing temperature (30°C, 60°C & 90°C) on strength development (Hardjito *et al.*, 2002).

Table 2.4: Curing regimes on fly ash-based geopolymer development.

| No | Range | Adoption | Reference |
|----|------------------------|-----------|-------------------------------------|
| 1 | 30, 60, 91°C for 24 hr | 60°C 24hr | (Hardjito <i>et al.</i> 2002) |
| 2 | 30, 75°C for 24 hr | 75°C 24hr | (Sindhunata <i>et al.</i> 2004) |
| 3 | 75, 95°C for 6 or 24hr | 95°C 24hr | (Bakharev 2005) |
| 4 | 45, 65, 85°C for 24hr | 85°C 24hr | (Fernandez-Jimenez and Palomo 2002) |

Additionally, Sindhunata *et al.* (2004) claimed that the variation in relative humidity (75% or 30%) during curing has little effect on the physical properties of geopolymer, the wet sample is normally covered or sealed

before being cured in an oven at evaluated temperature. the main reason is to reduce the rate of water evaporation.

Though the evaluated temperature curing was widely used previously, for example the curing regimes of 60°C for 24 hours by Wastiels *et al.* (1993) and Hardjito *et al.* (2002), and 95°C for 24 hours by Bakharev(2005). The negative effect of continuous high temperature curing on strength development cannot be overlooked. Jaarsveld *et al.* (2002) reported that the prolonged curing at a high temperature (70°C for 24 hours) could break down the gel structure in the geopolymer matrix, resulting in the lower strength at longer curing hours. Heating of geopolymer for curing is actually an advantage in the precast industry for quicker hardening results in more rapid turnover of molds decreasing costs. However, a requirement for heating would be a disadvantage in the ready-mix industry. Yet there is a challenge in synthesizing fly ash-based geopolymers at ambient temperatures because others have found that geopolymers did not set at 23°C (Bakharev, 2005).

Conclusion:

From the past research, it can be concluded that the concentration of NaOH, H₂O/Na₂O ratio, activator/fly ash ratio, waterglass/NaOH ratio, and curing temperature affect the strength of the fly ash geopolymer concrete. Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of geopolymer concrete. As the H₂O/Na₂O molar ratio increases, the compressive strength of the geopolymer concrete decrease. Activator/Fly ash mass mixing ratio of the range 0.3-0.45 are recommended in the synthesized of low-calcium (Class F) based geopolymers. Waterglass/NaOH molar ratio of 2.5 leads to expressive strength increase of the geopolymers. The best curing condition is reported as being 60°C for 24 hours.

REFERENCES

- ACAA, 2003. Fly Ash Facts for Highway Engineers. Aurora, USA, American Coal Ash Association: 74.
- ACI Committee 232, 2004. Use of Fly Ash in Concrete. Farmington Hills, Michigan, USA, American Concrete Institute: 41.
- American Society for Testing Materials. ASTM C618, 2001. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzoaln for Use as a Mineral Admixture in Concrete. Philadelphia, USA: 4.
- Bakharev, T., 2005. Geopolymeric materials prepared using Class F fly ash and elevated temperature curing. *Cement and Concrete Research*, 25(6): 1224-1232.
- Barbosa, V., K. MacKenzie, & C. Thaumaturgo, 2000. Synthesis and Characterization of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers. *International Journal of Inorganic Materials*, 2(4): 309-317.
- Cheng, T. & J. Chiu, 2003. Fire-resistant Geopolymer Produced by Granulated Blast Furnace Slag. *Minerals Engineering*, 16(3): 205-210.
- Chindapasirt, P., T. Chareerat, & V. Sirivivatnanon, 2007. Workability and strength of coarse high calcium fly ash geopolymer. *Cement and Concrete Composites*, 29(3): 224-229.
- Chindapasirt, P., C. Jaturapitakkul, W. Chalee, & U. Rattanasak, 2009. Comparative study on the characteristics of fly ash and bottom ash geopolymers. *Waste Management*, 29(2): 538-543.
- Criado, M., A. Palomo, & A. Fernandez-Jimenez, 2005. Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products. *Fuel*, 87: 1141-5.
- Daniel, L., Y. Kong, J. Sanjayan, & K. Sagoe-Crentsil, 2008. Factors affecting the performance of metakaolin geopolymers exposed to elevated temperatures. *Journal of Materials Science*, 43: 824-831.
- Davidovits, J., 1979. Synthesis of new high-temperature Geopolymers for reinforced plastics and composites, SPE PACTEC'79, Costa Mesa, California, Society of Plastics Engineers, USA, pp: 151-154.
- Davidovits, J., 1982. Mineral polymers and methods of making them, 4,349,386 United States Patent.
- Davidovits, J., 1988. Geopolymers of the first generation: SILIFACE-Process, Geopolymer '88; First European Conference on Soft Mineralogy, Compiègne, France, pp: 49-67.
- Davidovits, J., 1991. Geopolymers: Inorganic Polymeric New Materials. *Journal of Thermal Analysis*, 37: 1633-1656.
- Davidovits, J., 1994a. Global warming impact on the cement and aggregates industries. *World Resource Review*, 6(2): 263-278.
- Davidovits, J., 1994b. Properties of geopolymer cements, Alkaline Cement and Concretes, Kiev State Technical University, Ukraine, pp: 131-149.
- Davidovits, J., 1999. Chemistry of geopolymeric system, terminology, Geopolymere '99, Saint-Quentine, France, pp: 9-93.
- Davidovits, J., 2005. Geopolymer chemistry and sustainable development. The poly (sialate) terminology: a very useful and simple model for the promotion and understanding of green-chemistry, In proceeding of 2005 geopolymere conference, (1): 9-15.

- Davidovits, J., 2008. Geopolymer Chemistry and Applications. Institut Geopolymere, Saint- Quentin, France.
- Davidovits, J. & J.L. Sawyer, 1985. Early-high strength mineral polymer, 4, 509.958 United States Patent.
- De Jong, B. & G. Brown, 1980. *Geochim Cosmochim Acta*, 44(3): 491.
- Duxson, P., G. Lukey, & J.S.J. Deventer, 2007. Physical evolution of Na-geopolymer derived from metakaolin up to 1000°C. *Journal of Materials Science*, 42: 3044-3054.
- Fernandez-Jimenez, A. & A. Palomo, 2002. Alkali activated fly ash concrete: alternative material for the precast industry, *Geopolymer 2002 -- Turn Potential into Profit*, ISBN: 0975024205, Melbourne, Australia.
- Fernandez-Jimenez, A. & A. Palomo, 2003. Characterization of fly ashes, potential reactivity as alkaline cements, *Fuel*, 82: 2259-2265.
- Fernandez-Jimenez, A. & A. Palomo, 2005. Composition and microstructure of alkali activated fly ash binder: Effect of the activator, *Cement and Concrete Research*, 35(10): 1984-1992.
- Fernandez-Jimenez, A., A. Palomo, I. Sobrados, & J. Sanz, 2006. The role played by reactive alumina in the alkaline activation of fly ashes. *Microporous and Mesoporous Materials*, 91:111-9.
- Glukhovskiy, V.D., G.S. Rostovskaja, G.V. Rumyna, 1980. High strength slag alkaline cements. In: *Proceeding of the seventh international congress on the chemistry of cement*, (3): 164-8.
- Gourley, J., 2003. Geopolymers; Opportunities for Environmentally Friendly Construction Materials. *Materials 2003 Conference: Adaptive Materials for a Modern Society*, Sydney, Institute of Materials Engineering Australia.
- Hardjito, D. & B.V. Rangan, 2005. Development and Properties of Low-calcium Fly ash-based geopolymer concrete, Research report GC1. Faculty of Engineering Curtin University of Technology, Perth, Australia.
- Hardjito, D., S. Wallah, & B. Rangan, 2002. Study on engineering properties of fly- ash based concrete, *Journal of Australian Ceramic Society*, 38: 44-7.
- Hardjito, D., S. Wallah, D. Sumajouw, & B. Rangan, 2004. Properties of Geopolymer concrete with fly ash as source material: effect of mixture composition, the 7th CANMET/ACI International Conference on Recent Advance in Concrete Technology, Las Vegas, USA.
- Hongling, W. & J.S.J. Deventer, 2003. Synthesis and mechanical properties of metakaolinite-based geopolymer, *Colloids Surf. A: Physicochem. Eng. Asp.* 268: 1-6.
- Hongling, W., L. Haihong, & Y. Fengyuan, 2005. Synthesis and mechanical properties of metakaolinite-based geopolymer, *Colloids Surf.*, 268: 1-6.
- Hos, J., P. McCormick, and L. Byrne, 2002. Investigation of the synthetic aluminosilicate inorganic polymer, *Journal of Materials Science*, 37: 2311-6.
- Jaarsveld, J., 2000. The physical and chemical characterisation of fly ash based Geopolymers, The University of Melbourne, Australia, PhD thesis, pp: 381.
- Jaarsveld, J., J. Deventer, & L. Lorenzen, 1997. "The potential use of Geopolymeric materials to immobilise toxic metals: Part I. Theory and applications." *Minerals Engineering*, 10(7): 659-669.
- Jaarsveld, J., & J. Deventer, 1999. The effect of alkali metal activator on the properties of the fly ash-based geopolymers, *Ind Eng Res.*, 38: 3932-41.
- Jaarsveld, J., J. Deventer, & L. Lorenzen, 1998. Factors affecting the immobilization of metals in geopolymerised fly ash, *Metall Mater Trans B*. 29B: 283-91.
- Jaarsveld, J., J. Deventer, & G. Lukey, 2002. The Effect of Composition and Temperature on the Properties of Fly Ash and kaolinite based Geopolymers." *Chemical Engineering Journal.*, 89(1-3): 63-73.
- Jaarsveld, J., J. Deventer, & G. Lukey, 2003. The Characterisation of Source Materials in Fly Ash-based Geopolymers, *Materials Letters.*, 57(7): 1272-1280.
- Jahanian, S. & H. Rostami, 2001. Alkali ash material, a novel material for infrastructure enhancement, *Engineering Structures*, 23(6), pp.736-742.
- Jiang, W. & D. Roy, 1992. Hydrothermal processing of new fly ash cement, *Ceramic Bulletin*, 71(4): 642-647.
- Katz, A., 1998. Microstructure study of alkali-activation fly ash, *Cement and Concrete Research*, 28:197-208.
- Krivenko, P., 1997. Alkaline cements: terminology, classification, aspects of durability (4iv04, 6pp), *Proceedings of the 10th International Congress on the Chemistry of Cement*, Gothenburg, Sweden.
- Malek, R. & D. Roy, 1997. Synthesis and Characterization of New Alkali-activated Cements (1i024, 8 pp), *Proceedings of the 10th International Congress on the Chemistry of Cement*, Gothenburg, Sweden.
- Malhotra, V., 1999. Making Concrete "Greener" With Fly Ash, *ACI Concrete International*, 21(5): 61-66.
- Malhotra, V., 2002. High-Performance High-Volume Fly Ash Concrete, *ACI Concrete International*, 24(7): 1-5.
- Malhotra, V. & A. Ramezani pour, 1994. Fly Ash in Concrete, Ottawa, Ontario, Canada, CANMET.
- Palomo, A., M. Grutzeck, & M.T. Blanco, 1999a. Alkali-activated fly ashes: A cement for the future, *Cement and Concrete Research*, 29(8):1323-1329.

- Palomo, A., M. Blanco, M. Granizo, F. Puertas, T. Vazquez, & M. Grutzeck, 1999b. "Chemical stability of cementitious materials based on metakaolin, *Cement and Concrete Research*, 29(7): 997-1004.
- Pinto, A., 2004. Alkali-activated metakaolin based binders, PhD Thesis. University of Minho: 2004 [only in Portuguese].
- Puertas, F., S. Martinez-Ramirez, S. Alonso, & T. Vazquez, 2000. Alkali-activated fly ash/slag cements: Strength behaviour and hydration products, *Cement and Concrete Research*, 30(10): 1625-1632.
- Rahier, H., B. van Mele, M. Biesemans, J. Wastiels, & X. Wu, 1996. Low-temperature synthesised aluminosilicate glass: Part I low temperature reaction stoichiometry and structure of a model compound, *Journal of Materials Science*, 31: 71-79.
- Roy, D., 1999. Alkali activated cements: opportunities and challenges, *Cement and Concrete Research*, 29(2): 294-254.
- Silverstrim, T., H. Rostami, B. Clark and J. Martin, 1997. Microstructure and properties of chemically activated fly ash concrete, The 19th International Cement Microscopy Association, Cincinnati, OH, USA, pp: 355-373.
- Silverstrim, T., J. Martin, & H. Rostami, 1999. Geopolymeric Fly Ash Cement, *Proceeding of Geopolymere'99*, Saint-Quentine, France, pp: 107-108.
- Sindhunata, Lukey, G., H. Xu, & J. Deventer, 2004. The effect of curing conditions on the properties of Geopolymeric materials derived from fly ash, *Proceedings of Advances in Concrete through Science and Engineering*, North-western University, Evanston, IL, USA.
- Swanepoel, J. & C. Strydom, 2002. Utilisation of fly ash in a geopolymeric material, *Applied Geochemistry*, 17(8): 1143-1148.
- Teixeira-Pinto, A., P. Fernandes & S. Jalali, 2002. Geopolymer Manufacture and Application - Main problems When Using Concrete Technology, *Geopolymers 2002 International Conference*, Melbourne, Australia, Siloxo Pty. Ltd.
- Xie, Z. & Y. Xi, 2001. Hardening mechanisms of an alkali activated class F fly ash. *Cement and Concrete Research*, 31(9): 1245-1249.
- Xu, H. & J. Deventer, 2000. The Geopolymerisation of aluminosilicate minerals, *International Journal of Mineral Processing*, 59(3): 247-266.
- Xu, H. & J. Deventer, 2002. Geopolymerisation of Multiple Minerals, *Minerals Engineering*, 15(12): 1131-1139.
- Wang, S-D., K. Scrivener & P. Pratt, 1994. Factors affecting the strength of alkali-activated Slag, *Cement and Concrete Research*, 24:1033-43.
- Wastiels, J., X. Wu, S. Faignet and G. Patfoort, 1993. Mineral polymer based on fly ash, *Proceedings of the 9th International Conference on Solid Waste Management*, 14-17November, Philadelphia, PA, USA.