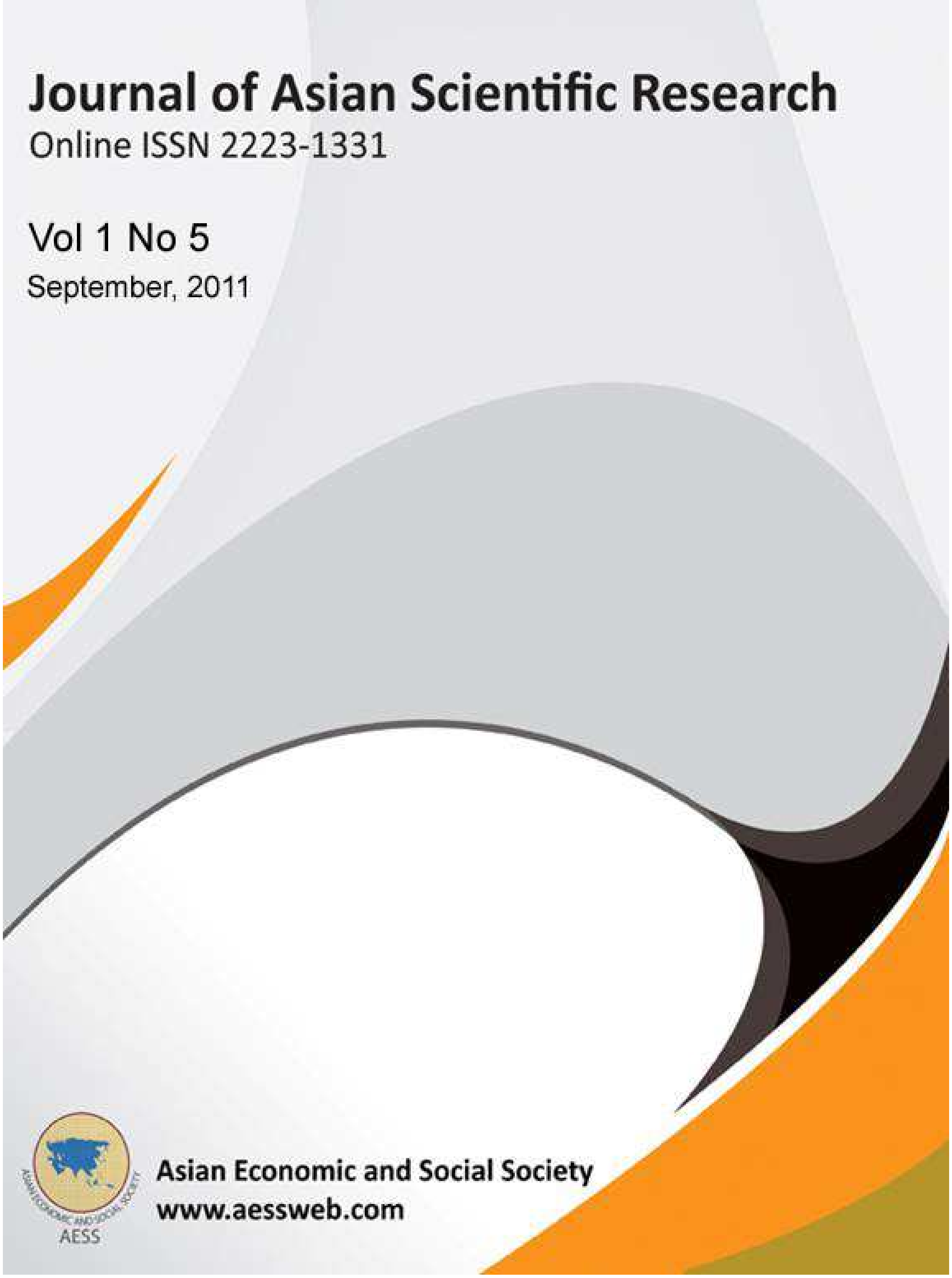

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Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement- A Review

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Abstract

This paper presents the work carried out on the chemical reaction, mechanism, role of materials, applications and microstructure of fly ash geopolymer cement. Geopolymer is a type of amorphous alumino-silicate cementitious material. Geopolymer can be synthesized by polycondensation reaction of geopolymeric precursor, and alkali polysilicates. Literature demonstrates that the exact geopolymerization mechanism is not well understood because the geopolymerization process involves a substantially fast chemical reaction. However, the most proposed mechanism includes three stages: (1) dissolution of Si and Al atoms from the source material through the action of hydroxide ions, (2) transportation or orientation or condensation of precursor ions into monomers, (3) setting or polycondensation/polymerisation of monomers into polymeric structures. Every materials used in geopolymer cement have their own function and role to create a chemical reaction and mechanism. The atomic ratio Si:Al in the polysialate structure determines the application fields. A low ratio Si:Al (1,2,3) initiates a 3D-Network that is very rigid. A high ratio Si:Al, higher than 15, provides polymeric character to the geopolymeric material.

Introduction

During the last decade, considerable research efforts have been directed towards the development of inorganic geopolymers, due to the wide range of potential applications for these materials. Several reports can be found in the literature on the synthesis, properties and applications of geopolymers (Silva *et al*., 2007). The development of geopolymer cement is an important step towards the production of environmentally friendly cements. Geopolymer is a type of amorphous alumino-silicate cementitious material. Geopolymer can be synthesized by polycondensation reaction of geopolymeric precursor and alkali polysilicates known as geopolymerization process. Geopolymerization is an innovative technology that can transform several aluminosilicate materials into useful products called geopolymers or inorganic polymers. Geopolymerization involves a heterogeneous chemical reaction between solid aluminosilicate oxides and alkali metal silicate solutions at highly alkaline conditions and mild temperatures yielding amorphous to semi-crystalline polymeric structures, which consist of Si–O–Al and Si–O–Si bonds (Dimas *et al*., 2009). Geopolymerization is a geosynthesis (reaction that chemically integrates minerals) that depend on the ability of the aluminium ion (6-fold or 4-fold coordination) to induce crystallographical and chemical changes in a silica backbone (Davidovits, 2005). The geopolymer cement is produced by totally replacing the Ordinary Portland Cement (OPC). Therefore, the use of geopolymer technology not only substantially reduces the CO_2 emissions by the cement industries, but also utilises the waste materials such as fly ash. It is to be noted that fly ash, one of the possible sources for making geopolymer binders, is available abundantly worldwide, and yet its usage to date is very limited (Hardjito *et al.*, 2004). Consumption of fly ash in the manufacture of geopolymers is an important strategy in making concrete more environmentally friendly. For this reason, fly ash has been chosen as a base material for this project in order to better utilise this industrial waste.

The Role of Materials in Geopolymer

Starting material plays an important role in the formation of geopolymer. Materials rich in Si (like fly ash, slag and rice husk) and materials rich in Al (clays like kaolin) are the primary requirement to undergo geopolymerization. The majority of studies conducted to date have used alkali silicate solutions for dissolution of raw materials to form the reactive precursors required for geopolymerisation. It has been shown that silicate activation increases the dissolution of the starting materials and gives rise to favourable mechanical properties (Rees *et al.*, 2004).

Fly Ash

Fly ash consists of finely divided ashes produced by pulverized coal in power stations. The chemical composition depends on the mineral composition of the coal gangue (the inorganic part of the coal). Silica usually varies from 40 to 60% and alumina from 20 to 30%. The iron content varies quite widely. Alkalis are present in an appreciable amount and potassium prevails over sodium (Khale and Chaudhary, 2007). The biggest reason to use fly ash in concrete is the increased life cycle expectancy and increase in durability associated with its use. During the hydration process, fly ash chemically reacts with the calcium hydroxide forming calcium silicate hydrate and calcium aluminate, which reduces the risk of leaching calcium hydroxide and concrete's permeability. Fly ash also improves the permeability of concrete by lowering the water-to-cement ratio, which reduces the volume of capillary pores remaining in the mass. The spherical shape of fly ash improves the consolidation of concrete, which also reduces permeability (Pacheco-Torgal *et al.*, 2008).

Alkali Activation

Figure 1 shows the dissolution process of the Si and Al occurs when the fly ashes are submitted to the alkaline solution. Then the higher molecules condense in a gel form and the alkali attack on the surface of particle, and then expand to larger hole, exposing smaller particles whether hollow or partially filled with other yet smaller ashes to bi-directional alkaline attack from the outside in and from the inside out. Consequently, reaction product is generated both inside and outside the shell of the sphere, until the ash particle is completely or almost completely consumed (Pacheco-Torgal *et al.*, 2008).

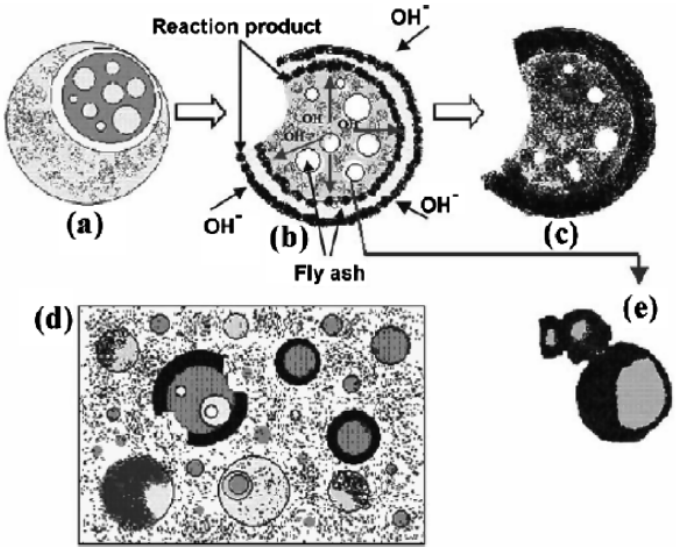


Figure 1 Descriptive model of the alkali activation of fly ash (Pacheco-Torgal *et al.*, 2008).

Alkali activation of alumino-silicate materials represents a complex process that has not been described to the full yet. The reaction of alumino-silicate materials in a strong alkaline environment results, first of all, in a breakdown of Si-O-Si bonds; later, new phases arise and the mechanism of their formation seems to be a process that includes a solution ("synthesis via solution"). The penetration of Al atoms into the original Si-O-Si structure represents a substantial feature of this reaction. Alumino-silicate gels (geopolymer precursors) are mostly formed. Their composition can be characterized by the formula Mn[-(Si-O)z - Al–O]n. wH_2O. The C-S-H and C-A-H phases may also be originated in dependence on the composition of the starting materials and the conditions of the reaction. Even secondary H_2O may be formed during these (poly-condensation) reactions. Amorphous (gel-like) or partially amorphous or crystalline substances may be originated in dependence on the character of starting raw materials and on the conditions of the reaction. The concentration of the solid matter plays a substantial role in the process of alkali activation (Skvara, 2007).

Sodium Hydroxide (NaOH) solution

The most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate (Hardjito, 2005). The type and concentration of alkali solution affect the dissolution of fly ash. Leaching of Al^{3+} and Si^{4+} ions are generally high with sodium hydroxide solution compared to potassium hydroxide solution. Therefore, alkali concentration is a significant factorin controlling the leaching of alumina and silica from fly ash particles, subsequent geopolymerization and mechanical properties of hardened geopolymer (Rattanasak and Chindaprasirt, 2009). Duchesne *et al*. (2010) confirmed that in presence of NaOH in the activating solution, the reaction proceeds more rapidly and the gel is less smooth. The gel composition analysed in the sample activated with the mixture of sodium silicate and NaOH is enriched in Na and Al.

Sodium Silicate solution

Palomo *et al*. (1999) concluded that the type of activator plays an important role in the polymerization process. Reactions occur at a high rate when the alkaline activator contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. A study conducted by Xu and Van Deventer (2000), showed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline activator enhanced the reaction between the source material and the solution. Tempest *et al.* (2009), state that the sodium silicate activator dissolves rapidly and begins to bond fly ash particles. Open porosity can be observed and is rapidly filled with gel as soon as the liquid phase is able to reach the ash particles. The liquid phase is important as a fluid transport medium permitting the activator to reach and react with the fly ash particles.

The Geopolymerization and Application

The chemical structure and geopolymerization of Geopolymer cement

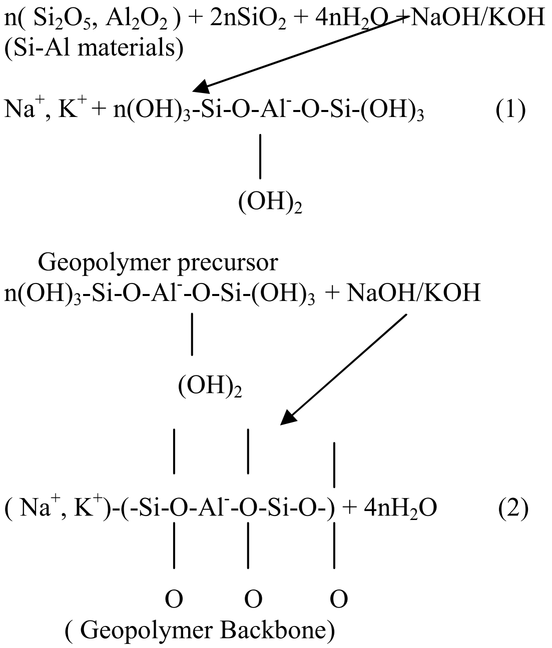
The geopolymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals that result in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows:

$Mn\,[-(SiO_2)z\text{-}AlO_2]n.\ wH_2O$

Where: M = the alkaline element or cation such as potassium, sodium or calcium

n = the degree of polycondensation or polymerisation

z = 1,2,3 or higher [15]



$$n(\,Si_2O_5,\ Al_2O_2\,) + 2nSiO_2 + 4nH_2O + NaOH/KOH$$

(Si-Al materials)

$$Na^+,\ K^+ + n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\underset{|}{Al^-}}\text{-O-Si-}(OH)_3 \qquad (1)$$

Geopolymer precursor

$$n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\underset{|}{Al^-}}\text{-O-Si-}(OH)_3 + NaOH/KOH$$

$$(\,Na^+,\ K^+)\text{-}(\text{-}\underset{O}{\underset{|}{\overset{|}{Si}}}\text{-O-}\underset{O}{\underset{|}{\overset{|}{Al^-}}}\text{-O-}\underset{O}{\underset{|}{\overset{|}{Si}}}\text{-O-}) + 4nH_2O \qquad (2)$$

(Geopolymer Backbone)

Figure 2 The schematic formation of geopolymer material can be shown as described by equations (1) and (2) (Chanh *et al*., 2008).

The exact mechanism of setting and hardening of the geopolymer material is not clear. However, most proposed mechanism consists the chemical reaction may comprise the following steps:

(1) Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
(2) Transportation or orientation or condensation of precursor ions into monomers.
(3) Setting or polycondensation/polymerisation of monomers into polymeric structures (Chanh *et al*., 2008).

Such frameworks are called polysialates, where sialate stands for the silicon-oxo-aluminate building unit. The sialate network consists of SiO_4 and AlO_4 tetrahedra linked by sharing all oxygen atoms. Positive ions (Na^+, K^+, Ca^{2+}, etc) must be present to balance the negative charge of Al in 4-fold coordination. Chains and rings may be formed and cross-linked together, always through a sialate Si-O-Al bridge. Polysialates are chain and ring polymers with Si^{4+} and Al^{3+} in 4-fold coordination with oxygen and range from amorphous to semi-crystalline. The amorphous to semi-crystalline three dimensional silico-aluminate structures were classified 'geopolymer' of the types (Van Deventer *et al*., 2007).

Applications on geopolymer cement

Geopolymeric materials have a wide range of applications in the field of industries such as in the automobile and aerospace, non-ferrous foundries and metallurgy, civil engineering and plastic industries. The type of application of geopolymeric materials is determined by the chemical structure in terms of the atomic ratio Si: Al in the polysialate. The type of application can be classified according to the Si: Al ratio as presented in the table below. A low ratio of Si: Al of 1,2 or 3 initiates a 3D-Network that is very rigid, while Si: Al ratio higher than 15 provides a polymeric character to the geopolymeric material. For many applications in the civil engineering fields, a low Si: Al ratio is suitable (Davidovits, 1999).

Table 1: Applications of Geopolymeric Materials Based on The Silica-toAlumina Atomic Ratio (Davidovits, 1999)**.**

Si: Al ratio	Applications
1	Bricks Ceramics Fire protection
2	Low CO2 cements and concretes Radioactive and toxic waste encapsulation
3	Fire protection fibre glass composite Foundry equipments Heat resistant composites, 200°C to 1000°C Tooling for aeronautics titanium process
>3	Sealants for industry, 200°C to 600°C Tooling for aeronautics SPF aluminium
20-35	Fire resistant and heat resistant fibre composites

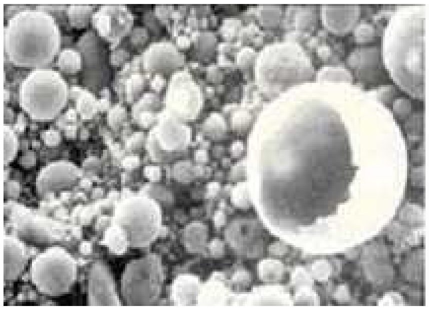
4.0 Microstructure of The Geopolymer Cement

Unlike ordinary portland cement, geopolymer do not form calciumsilicate-hydrates (CSHs) for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors and a high alkali content to attain structural strength. Composition of the geopolymer is similar to natural zeolitic materials, but the microstructure is amorphous instead of crystalline. Fly ash particles: SEM was used to investigate the surface of fly ash, before and after reacting with NaOH. NaOH reacted with fly ash particles resulted in the roughness of surface as shown in figure 3,4 and 5 (Chanh *et al*., 2008).

Geopolymer frameworks

Geopolymerization process forms aluminosilicate frameworks as shown in figure 6. Sialate is an abbreviate form for alkali silicon-oxo-aluminate, the alkali being (Na,K,Li,Ca) and the term poly(sialate) covers all geopolymers containing at least one (Na,K,Li,Ca)(Si-O-Al), (Na,K,Li,Ca)-sialate unit. Sodalite frameworks and kalsilite frameworks have structural molecules Na-(-Si-O-Al-O-) and K-(-Si-O-Al-O-) are chain and ring polymers that are the result of the polycondensation of the monomer, ortho-sialate $(OH)_3$-Si-O-Al-$(OH)_3$. Sanidine frameworks, K-(-Si-O-Al-O-Si-O-Si-O-) may be considered as the condensation result of orthosialate with two ortho-silicic $Si(OH)_4$.

The sialate unit may be at the beginning, in the middle or at the end of the sequence. There are six isomorphs: 2 linear, 2 branched and 2 cycles. Leucite frameworks with structural molecule K-(-Si-O-Al-O-Si-O-) may be considered as the condensation result of orthosialate with ortho-silicic acid $Si(OH)_4$. There are three isomorphs, a linear (-Si-O-Si-O-Al-O-), mono-siloxo-sialate and 3 cycles. Anorthite frameworks containing 2 sialate unit, Ca-(-Si-O-Al-O-Si-O-Al-O-) are ring polymers that are result of the polycondensation of the monomer (Davidovits, 2008).



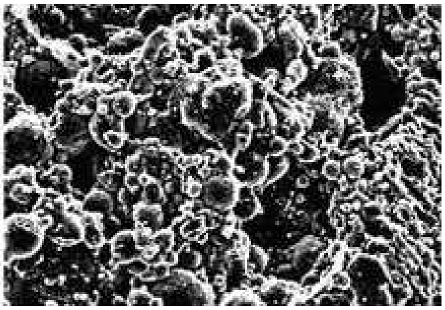


Figure 3 Fly ash before reacting with NaOH. **Figure 4** Fly ash after reacting with NaOH (Chanh *et al*., 2008).

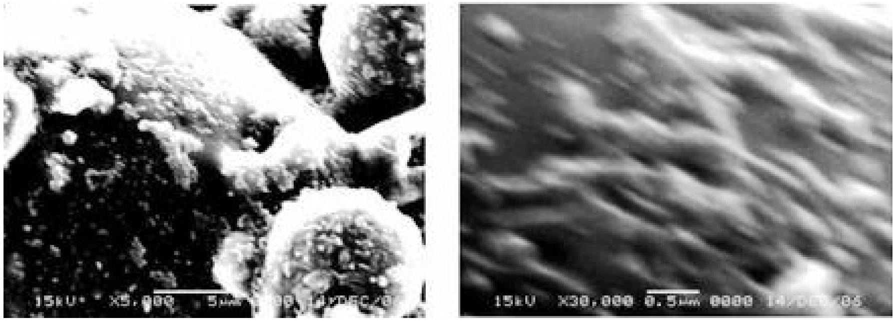


Figure 5 Fly ash after reacting with NaOH (x5000 and x30 000) (Chanh *et al*., 2008).

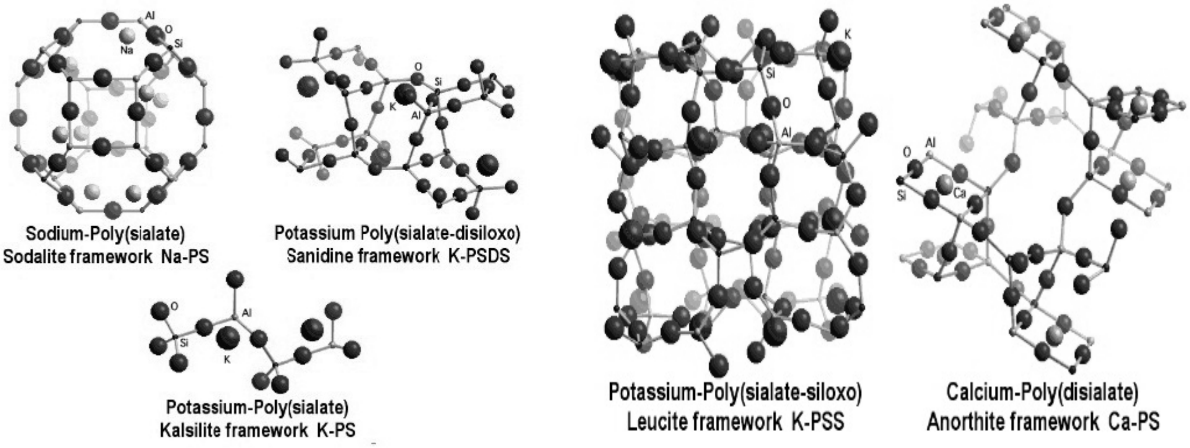


Figure 6 Polymeric structures from polymerisation of monomers (Davidovits, 2008).

Fly Ash Geopolymer Cement

Fly ash geopolymer cement can be used to produce structural strength concrete without the considerable carbon dioxide emissions that characterize Portland cement manufacture. Geopolymers are formed when alumino-silicates, such as fly ashes, dissolve in a strong alkaline solution, reorganize and precipitate in a hardened state (Tempest *et al*., 2009) Class C Fly ashes from Manjung, Malaysia were tested on their suitability for geopolymeric cements. Fly ash suitable for use in geopolymer consists mostly of glassy, hollow, spherical particles, which are cenospheres (thin walled hollow spheres) (Davidovits, 2008). Sodium silicate (Na_2SiO_3) mixed with sodium hydroxide (NaOH) as an alkaline activator was used in this study. NaOH powder was dissolved in distilled water to form sodium hydroxide (NaOH) solution. The ratio of fly ash to alkaline activator and Na_2SiO_3/NaOH ratio were fixed as 2.5 and applied for all samples. The use of this ratio is due to the work done by Hardjito et al. which states that a ratio of fly ash to alkaline activator of 2.5 produced the highest compressive strength on the 28th day of testing. Their study results also indicated that the optimum Na_2SiO_3/NaOH ratio was 2.5 which give high compressive strength (Mustafa Al Bakri, 2010). In this research, the curing is taking place at temperature 80°C in first cycle preparation of fly ash geopolymer cement paste with modified water to cement ratio in second cycle. In the second cycle, the geopolymer cement paste was crushed and milled for 2 hours for the formation of cement powder. The cement powder then mixed with certain amount of water to make a second cycle geopolymeric cement paste. The best ratio of water to cement ratio result (higher compressive strength) was further study.

Conclusion

It is clear that the chemistry of geopolymeric aluminosilicate materials is only just beginning to be understood. With the further development of this understanding will come the ability to design geopolymers with specific applications in mind, which will be a critical step in the acceptance of these materials as alternatives to existing cement and ceramic technology and as binders for hazardous waste immobilization. This paper reviews on mechanism and chemical reaction of Fly Ash geopolymer cement. From the review, it can be concluded that an extensive research has already been carried out. The right name for these binders is alkali-activated binders for the general case although the term ''geopolymer'' is accepted in some cases. The exact reaction mechanism of alkali-activated binders is not yet quite understood, although it depends on the prime materials and on the alkaline activator. Despite that, most authors agree it consists in a three step model of dissolution, orientation and hardening.

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