

Chemical Reactions in the Geopolymerisation Process Using Fly Ash–Based Geopolymer: A Review

¹A.M. Mustafa Al Bakri, ¹H. Kamarudin, ³M. Bnhussain, ²I. Khairul Nizar,
¹A.R. Rafiza & ¹A.M. Izzat

¹Green Concrete@UniMAP, School of Materials Engineering

²School of Environmental EngineeringUniversiti Malaysia Perlis (UniMAP)

P.O. Box 77, d/a Pejabat, Pos Besar, 01007 Kangar, Perlis Malaysia

³King Abdul Aziz City Science & Technology (KACST),

P.O. Box 6086, Riyadh 11442, Kingdom of Saudi Arabia

Abstract: The development of our world, demanding the power supply which is produced by combustion of coal. Unfortunately, the million of tons of fly ash and related-products have been generated. To overcome these problems, fly ash was used in term of geopolymer to produce precast structure, non structural elements, concrete pavements, concrete products and immobilization of toxic waste that are resistant to toxic waste that are resistant to heat and aggressive environment Geopolymer is a material produced by inorganic poly-condensation, i.e., by so-called “geopolymerization.” The process comprises dissolution of aluminosilicate followed by condensation of free silicate and aluminate species to form a three-dimensional structure of silico-aluminate structures. This process involving alumino-silicate materials is a complex process that has yet to be described fully. Several studies focused the dissolution reaction of fly ash, rate of reaction, thermodynamic properties of the reaction and mechanism of hardening process involved in geopolymerisation. The raw materials of geopolymer, such as kaolinitic clays, metakaolin, fly ashes, blast furnace slag, mixtures of fly ashes and slag, mixtures of fly ashes and metakaolin, mixtures of slag and metakaolin, mixtures of slag and red mud, and mixtures of fly ashes and non-calcined materials like kaolin and stilbite have significant effects on the properties of the resulting geopolymer. Recent studies have been conducted to determine the effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios on the properties of the geopolymer, such as compressive strength, setting time, strength development, composition of the gel phase, and the microstructure of the alkali-activated material. It is evident that several factors related to the chemistry of the raw materials and the production of the geopolymer affect the performance of the final geopolymer products.

Key words: Chemical Composition, Crystallinity, Geopolymer, Fly Ash

INTRODUCTION

In general, inorganic geopolymers can be synthesized by the alkali activation of materials that are rich in SiO_2 and Al_2O_3 . Although the entire process has yet to be fully described, there is evidence that the geopolymerisation mechanisms include the dissolution of Al and Si in the alkali medium, transportation (orientation) of the dissolved species, and polycondensation, which forms a 3D network of silico-aluminate structures (De Silva *et al.*, 2007). The geopolymer is a type of alkali aluminosilicate cement that can have superior mechanical, chemical, and thermal properties compared to ordinary Portland cement (OPC) (Duxson *et al.*, 2007). Geopolymer binders generally consist of reactive solid components that contain SiO_2 and Al_2O_3 and an alkaline activator solution. When these two components, i.e., reactive solids and an alkaline activation solution react, an *aluminosilicate network*, ranging from amorphous aluminosilicate to partially crystalline aluminosilicate, forms, creating a hardened product that is resistant to water (Duxson *et al.*, 2007a; Duxson *et al.*, 2007b). Hence, geopolymers can also be characterized as amorphous precursors of zeolite (Buchwald *et al.*, 2006).

The geopolymer structure consists of cross-linked, SiO_4 and AlO_4^- tetrahedral species where the negative charge on Al^{3+} in IV-fold coordination is balanced with the positive charges of the alkali ions (Na^+ , K^+). The geopolymerisation reaction can be expressed as shown in Figure 1 below.

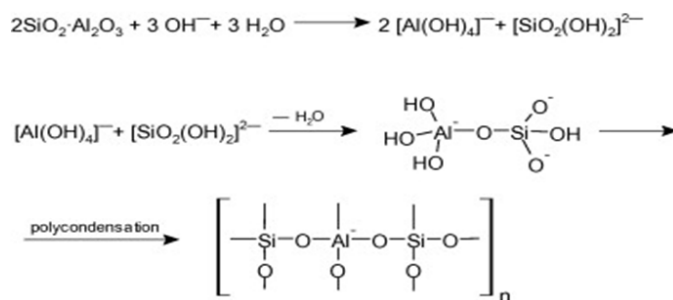


Fig. 1: Geopolymerisation reaction (Duxson *et al.*, 2007)

There are three types of geopolymer structures, i.e., poly(sialate) (-Si-O-Al-O-), poly(sialate-siloxo) (-Si-O-Al-O-Si-O-) and poly(sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-) (Duxson *et al.*, 2007b). Geopolymers that have poly(sialate-siloxo) and poly(sialate-disiloxo) structures are more rigid, more stable, and stronger than poly(sialate) structures (De Silva *et al.*, 2007).

Past research (Brouwers and Van Eijk, 2003) has conducted a theoretical study of the dissolution (reaction) of fly ash and used the reaction product to derive the thermodynamic properties of the fly ash, including the free energy, enthalpy, and entropy of the reaction. The effects of initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios on the compressive strength and microstructure of alkali-activated metakaolin systems have been reported (Provis *et al.*, 2005). Researchers (Alvarez-Ayuso *et al.*, 2008) stated that increasing the crystallinity of the geopolymer products increased their compressive strength. This paper presents a review of the chemistry associated with the inorganic geopolymerisation process.

Preliminary Literature Review:

Chemical Characterization Of Fly Ash:

According to the classification of the American Society for Testing and Materials (ASTM C618-92a, 1994) various fly ash products can be classified into two types:

- Class F. Fly ash products in this group have pozzolanic properties and are characterized by (a) $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$; (b) $\text{SO}_3 < 5\%$; (c) moisture content $< 3\%$; and (d) loss on ignition (LOI) $< 6\%$.
- Class C. Fly ash products in this group have combinations of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 < 70\%$. Class C fly ash shows cementitious properties and is characterized by (a) $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 < 70\%$ due to high Ca and Mg contents (27 and 3.8%, respectively). Class C fly ash, in the range of 20-35% of the mass of the cementitious material, can be used to replace Portland cement.

The mineral composition of the various fly ash samples was determined by X-Ray diffraction (XRD) using a SIEMENS D501 powder diffractometer with a graphite monochromator, a NaI(Tl) detector, and $\text{Cu K}\alpha$ radiation. Researchers (Moreno *et al.*, 2005) have classified the fly ash materials as shown in Table 1 depending on their major oxide content, as follows:

- Sialic-type fly ash. Soto de Ribera, Acid, Espiel, Monfalcone, Puertollano, and CCB fly ash products contain very high alumina and silica contents (80–87 wt%) and very low contents of major impurities (Fe, Ca, S). The Soto de Ribera, Espiel, Compostilla, and Narcea fly ashes are characterised by a relatively high K_2O content (4%).
- Robla and Meirama fly ash products have low $\text{SiO}_2 + \text{Al}_2\text{O}_3$ contents (around 67 wt%).
- Ferro-calco-sialic-type fly ash. The other fly ash products have very similar contents of alumina and silica ($\text{SiO}_2 + \text{Al}_2\text{O}_3 = 70\text{--}79$ wt%) and different concentrations of impurities.
- Escucha, As Pontes Teruel and Robla fly ash samples are characterised by a relatively high Fe content, whereas Meirama, Sardegna, Robla, and Barrios fly ash samples have relatively high Ca content. Levels of Mg or Mn are also relatively high due to the similar atomic radii.

Chemical Reactions Involved in Fly Ash-Based Geopolymers:

Past research (Brouwers and Van Eijk, 2003) proposed that the hydration process for vitreous silica with a $\text{pH} > 12$ are:



and that Al_2O_3 is hydrated according to:



and that CaO and MgO react as follows:



that Na_2O and K_2O react as follows:



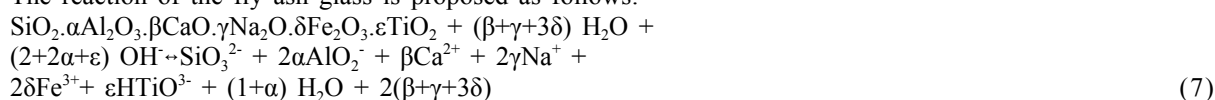
that Fe_2O_3 reacts as follows:



and that TiO_2 hydrates as follows:



The reaction of the fly ash glass is proposed as follows:



From reactions (1-7), the thermodynamic properties of the studied fly ashes, i.e., enthalpy and entropy of reaction, were derived (Brouwers and Van Eijk, 2003). Silica, aluminium oxide and titanium oxide consume hydroxides, whereas the Earth alkalis (CaO, MgO), alkalis (Na_2O , K_2O), and iron oxide produce hydroxides. Fly ash contains a high percentage of amorphous alumina and silica that make it very suitable for making geopolymers. After the fly ash is mixed with an alkaline solution, dissolution of silicate species begins (Fletcher *et al.*, 2005). The type and concentration of alkali solution affect the dissolution of fly ash. Leaching of Al^{3+} and Si^{4+} ions is generally high with sodium hydroxide solution compared to potassium hydroxide solution (Alvarez-Ayuso *et al.*, 2008; ASTM C618-92a, 1994).

Table 1: Major element concentrations, moisture, and LOI values of various fly ash samples in wt% (Moreno *et al.*, 2005)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	MnO	SO ₃	N	C	Moisture	LOI	SiO ₂ /Al ₂ O ₃
Narcea	55.2	23.3	6.9	4	2.5	0.7	3.8	0.3	0.9	0.1	0.4	0.03	1.4	0.03	1.9	2.4
Barrios	42.6	35.6	2.6	8.4	2.1	0.3	0.6	1.7	1.6	0.1	0.6	0.05	3.4	0.01	3.8	1.2
Escucha	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.2	0.9	0.03	0.3	0.08	4.6	0.03	4.7	1.9
Meirama	49.2	17.6	10.4	11.8	2	0.4	0.4	0.2	0.5	0.1	2.2	0.03	0.7	2.4	5.2	2.8
Teruel	48.3	23.9	16	5.4	1	0.2	1.4	0.2	0.8	0.03	0.8	0.02	0.6	0.1	2	2
Espiel	52.3	28.5	5.9	2	1.5	0.5	4	0.4	1	0.1	0.1	0.03	2.4	0.1	3.7	1.8
Compostilla	51.2	25.5	7.5	2.8	2	0.8	3.9	0.4	0.9	0.1	0.6	0.04	3.2	0.1	4.3	2
La Robla	44.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8	0.9	0.1	1.1	0.03	1.1	0.1	1.9	1.9
As Pontes	41.5	30.1	12.6	5.6	1.6	0.6	1.9	0.2	0.6	0.1	1.4	0.04	1.4	0.3	3.8	1.4
S. de Ribera	48.9	30.6	7.2	3	1.6	0.6	3.9	0.1	0.8	0.03	0.3	0.03	1.2	0.2	3	1.6
Puertollano	58.6	27.4	7.3	0.8	1	0.3	2.4	0.1	0.7	0.1	0.2	0.02	0.7	0.1	1.1	2.1
Alkaline	46.8	24.8	9	6.8	3.7	1.2	2	0.7	0.9	0.1	1	0.04	1.9	0.2	3	1.9
Nijmegen	45.3	25	8.8	6.4	1.4	0.8	1.1	1	1.3	0.03	1.3	0.09	6.2	0.2	7.5	1.8
Neutral	53.3	26.1	7.4	3.1	0.6	0.1	0.6	1.5	1.8	0.1	0.5	0.06	4	0.3	4.8	2
CCB	59.6	27	3.3	0.5	0.9	0.3	2.9	0.1	1.4	0.03	0.2	0.05	3.4	0.3	3.7	2.2
Acid	51.3	28.9	8.4	1.8	1	0.5	2.5	0.2	1.5	0.03	0.5	0.05	2.7	0.1	3.3	1.8
Amer-8	45.2	26.5	7.1	6.1	1.6	0.8	1.2	1.1	1.3	0.03	1.1	0.11	7	<0.1	8.1	1.7
Amer-9	52.4	25.8	7	5.6	1.6	0.7	1.4	0.9	1.3	0.1	0.6	0.04	2.3	0.1	2.8	2
Hemweg-8	53.2	26	8.6	2.4	1.6	0.5	2.7	0.3	1.3	0.1	0.6	0.04	2.3	0.2	2.7	2
Lignite	28.5	17.9	8.4	27.3	3.8	0.2	1	0.3	1	0.03	8.6	0.06	1	0.1	3	1.6
Fusina	48.2	25.9	8.8	2.3	1.5	0.5	2.6	0.3	1.3	0.1	0.6	0.14	7.6	0.1	7.9	1.9
Monfalcone	50.8	33.4	6.4	2.4	0.8	0.4	0.7	0.3	2.6	0.03	0.3	0.04	1.6	0.1	1.9	1.5
Sardegna	41.7	29	3.8	10	2.4	0.5	0.8	1.5	1.7	0.1	0.9	0.08	6.5	0.2	7.6	1.4
UKQAA	48-52	24-32	7-15	1.8-5.3	1.2-2.1	0.8-1.8	2.3-4.5	ND	0.9-1.1	ND	0.3-1.7	ND	ND	ND	3.2	1.6-2.2
NBS 1633 ^b	51.2	27	10.5	2	0.8	0.3	2.4	0.5	1.2	0	0.5	ND	ND	ND	ND	1.9
NBS 1633 ^b certified	49.2	28.4	11.1	2.1	0.8	0.3	2.5	0.5	1.3	0.02	0.5	ND	ND	ND	ND	1.7

Composition Range Of Aluminosilicate Geopolymers:

There are three steps involved in geopolymerisation, i.e., dissolution of Al and Si in the alkali medium, orientation, and polycondensation. The dissolution and hydrolysis reactions (8-10) can be written as (De Silva *et al.*, 2007):





The presence of $[\text{SiO}_2(\text{OH})_2]^{2-}$ is preferred to $[\text{SiO}(\text{OH})_3]^-$ in very high alkaline solution. Condensation can take place between aluminate and silicate or between silicates themselves, depending on the concentration of Si in the solution. With mixtures that have low Si/Al ratios (approximately 1), condensation occurs predominantly between aluminate and silicate species resulting in poly(sialate) polymer structures. It is well known that poly(sialate) structures is the backbone structures of bricks and ceramics (Comrie and Kriven, 2003).

However, when the Si/Al ratio increases (> 1), the silicate species tends to condense among themselves to form oligomeric silicates. Then, these oligomeric silicates condense with $\text{Al}(\text{OH})_4^-$, forming a rigid 3D network of polymer structures, poly(sialate-siloxo) and poly(sialate-disiloxo) (Moreno *et al.*, 2005). According to past research (Van Jaarsveld and Van Deventer, 1999), the condensation rate between silicate species is slower than the rate between silicate and aluminate species.

Aluminosilicate geopolymers with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been studied by several authors (Xu and Van Deventer, 1999; Weng *et al.*, 2002). Researchers (Stevenson and Sagoe-Crenstil, 2005) have discussed the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio and concluded that the optimum ratio must be 12, but other researchers (De Silva *et al.*, 2007) kept the mixture formulations at a ratio of 13.6 to provide good workability and to lower the rate of reaction, thereby making it easier to determine early-stage development. Table 2 shows the composition and properties of the present series of geopolymers with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (change the amount SiO_2 or Al_2O_3) while keeping the amounts of H_2O and Na_2O constant.

Table 2: Mixture Formulations (De Silva *et al.*, 2007)

Sample	Initial composition	$\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio)	$\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ (molar ratio)	$\text{SiO}_2/\text{Na}_2\text{O}$ (molar ratio)	$\text{H}_2\text{O}/\text{Na}_2\text{O}$ (molar ratio)	Final setting time (min)
Si38	$\text{Na}_2\text{O}.1.0\text{Al}_2\text{O}_3.3.8\text{SiO}_2.13.6\text{H}_2\text{O}$	3.81	1.0	3.8	13.6	155
Si34	$\text{Na}_2\text{O}.1.0\text{Al}_2\text{O}_3.3.4\text{SiO}_2.13.6\text{H}_2\text{O}$	3.41	1.0	3.4	13.6	70
Si30	$\text{Na}_2\text{O}.1.0\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	3.00	1.0	3.0	13.6	46
Si25	$\text{Na}_2\text{O}.1.0\text{Al}_2\text{O}_3.2.5\text{SiO}_2.13.6\text{H}_2\text{O}$	2.50	1.0	2.5	13.6	30
Al06	$\text{Na}_2\text{O}.0.6\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	5.01	0.6	3.0	13.6	220
Al07	$\text{Na}_2\text{O}.0.7\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	4.28	0.7	3.0	13.6	180
Al08	$\text{Na}_2\text{O}.0.8\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	3.76	0.8	3.0	13.6	58
Al10	$\text{Na}_2\text{O}.1.0\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	3.00	1.0	3.0	13.6	46
Al12	$\text{Na}_2\text{O}.1.2\text{Al}_2\text{O}_3.3.0\text{SiO}_2.13.6\text{H}_2\text{O}$	2.50	1.2	3.0	13.6	30

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was calculated by dividing the moles of SiO_2 by the moles of Al_2O_3 . Researcher (Davidovits, 2008) had prepared the 317 grams of reactant mixture containing 8.1 moles H_2O , 0.47 mole of Na_2O , 1.65 moles of SiO_2 , and 0.41 mole of Al_2O_3 . The author explained the source of each component, i.e., Al_2O_3 was from the alumino-silicate oxide prepared by dehydroxylating a natural polyhydroxy-alumino-silicate Si_2O_5 , $\text{Al}_2(\text{OH})_4$, was from alumino-silicate oxide, SiO_2 was from alkali silicate, and Na_2O was from sodium hydroxide.

Better strength properties are reported for mixtures with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the range of 3.4 – 3.8, with an $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of about 1 (De Silva *et al.*, 2007).

Conclusion:

The desirable properties of geopolymer products made from fly ash in alkaline solutions, such as mechanical strength, workability, and resistance to adverse environmental conditions, can be enhanced by careful control of the relative quantities of reactants used and control of the conditions at which the reactions take place.

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