

THE PROCESSING, CHARACTERIZATION, AND PROPERTIES OF FLY ASH BASED GEOPOLYMER CONCRETE

A.M. Mustafa Al Bakri^{1,3}, H. Kamarudin^{1,3}, M. Bnhussain², I. Khairul Nizar³,
A. R.Rafiza^{1,3} and Y. Zarina^{1,3}

¹Center of Excellence Geopolymer System Research, School of Material Engineering, Perlis (UniMAP), 01000, P.O. Box 77, D/A PejabatPosBesar, Kangar, Perlis, Malaysia

²King Abdul Aziz City Science & Technology (KACST), P.O. Box 6086, Riyadh 11442, Kingdom of Saudi Arabia

³School of Environmental Engineering, Universiti Malaysia Perlis (UniMAP), 01000, P.O. Box 77, D/A PejabatPosBesar, Kangar, Perlis, Malaysia

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Abstract. In recent years, attempts to increase the utilization of fly ash as a replacement for ordinary Portland cement (OPC) in concrete have increased in significance. Geopolymer concrete does not need the presence of Portland cement as a binder. Instead, an activating geopolymer can be utilized with an alkaline activator. Moreover, the use of fly ash is more environmentally friendly due to the reduced CO₂ emissions and costs compared to OPC, which requires the burning of large quantities of fuel and the decomposition of limestone and can result in significant CO₂ emissions. The compressive strength increases with the optimum NaOH molarity, fly ash/alkaline activator ratio, Na₂SiO₃/NaOH ratio used, and curing process handled. Fly ash-based geopolymer also provides superior performance given its better resistance to aggressive environments compared to normal concrete. This paper summarizes the current knowledge about the properties and characteristics of fly ash-based geopolymer by reviewing previous research work.

1. INTRODUCTION

The demand for concrete as a construction material has increased as the demand for infrastructure development has increased. However, the utilization of cement pollutes the environment and reduces raw materials (limestone). The manufacturing of ordinary Portland cement (OPC) requires the burning of large quantities of fuel as well as the decomposition of limestone, resulting in significant emissions of CO₂ [1]. For every ton of OPC manufactured, nearly one ton of CO₂ is produced, depending on the production process adopted [2]. Cement plants have been reported to emit up to 1.5 billion tons of CO₂ into the atmosphere annually [3]. As such, geopolymer concrete has been introduced to reduce this problem. Fly ash is abundantly available to replace totally

manufactured cement and make a concrete-like material. This paper summarizes the current knowledge of the properties of fly ash-based geopolymer in utilizing this material to produce valuable products in concrete technology.

2. RAW MATERIALS

The two main constituents of geopolymers are source materials and alkaline liquids. Source materials for geopolymers based on alumina-silicate should be rich in silicon (Si) and aluminum (Al). These could be natural minerals such as kaolin and clays. Alternatively, fly ash, silica fume, slag, rice-husk ash, red mud, and metakaolin, among others, could be used as source materials as by-product materials [4]. However, fly ash has

Corresponding author: A.M. Mustafa Al Bakri, e-mail: mustafa_albakri@unimap.edu.my

advantages over metakaolin in that it is waste resource produced in huge quantities by coal-fired power stations, making it an ideal environmentally friendly feedstock [5].

An alkaline liquid could be used to react with silicon (Si) and aluminum (Al) in a source material of natural minerals or in by-product materials to produce binders [6]. The alkaline activation of materials can be defined as a chemical process that provides a rapid change of some specific structures, partially or totally amorphous, into compact cemented frameworks [7]. Alkali activation of fly ash is a process that differs widely from Portland cement hydration and is very similar to the chemistry involved in the synthesis of large groups of zeolites. The most used alkaline activators are a mixture of sodium or potassium hydroxide (NaOH, KOH) and sodium silicate or potassium silicate [4,8].

3. MIXING PROCESS

Rattanasak *et al.* [9] proposed two types of mixing procedures—namely, separate mixing and normal mixing—and mixed fly ash with an NaOH solution to prepare a geopolymer paste. For separate mixing, the NaOH solution was mixed with fly ash for the first 10 minutes; a sodium silicate solution was subsequently added to the mixture. However, for normal mixing, fly ash, sodium hydroxide, and sodium silicate solution were mixed at the same time. From the results produced, separate mixing produced a slightly stronger mortar than normal mixing.

Some authors believe that the optimum mixing order for alkali-activated binders is as follows. First, solids are mixed (fly ash and/or aggregates). The prepared activator is mixed with the solids, and the mixture is placed in molds [10,11]. The samples in molds are then compacted in three layers of equal weight with standard compaction using a rod and vibrating table [12]. Therefore, it is important to confirm whether the mixing order remains the same for other prime materials as well as how it is influenced by the type of alkaline activator [8].

3.1. Various molarity of NaOH

According to Rangan [4], mixing both solutions together at least 24 hours prior to use for the alkaline liquid is recommended. The use of the sodium silicate solution A53 with an SiO_2 -to- Na_2O ratio by mass of approximately 2 and sodium hydroxide with 97-98% purity is also recommended. The concentrations of the sodium hydroxide solution that can be used range from 8 to 16 M.

In our study, we found that the 12 M NaOH solution gives the highest compressive strength. This result is supported by past studies [13] that also found that a 12 M NaOH solution produced better results than the corresponding 18 M NaOH solution. However, other researchers [14] found that increasing NaOH molarity increases the compressive strength of the geopolymer. According to findings [15] reported in such studies, when the activator concentration is above a 10 M NaOH solution, a lower rate of polymer formation is produced due to the high concentration of NaOH, resulting in a decreased strength. However, the study carried out by Tushar *et al.* [16] stated that the highest compressive strength of geopolymer was affected when a 16 M NaOH solution is used.

3.2. Various fly ash/alkaline activator ratios and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios

Previous researchers [14,17] have stated that the compressive strength increases as the fly ash content and activator solution increase. Some researchers [10,13] have stated that geopolymer fly ash with a fly ash/alkaline activator ratio of 3.3-4.0 can be used. However, other researchers [13] have stated that the fly ash/alkaline activator ratio is not a relevant parameter influencing the compressive strength. This conclusion has been contradicted by other researchers. Previous research [9] has concluded that the use of an $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 1.0 gives a strength of up to 70 MPa. One study [14] indicated that the use of an $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 2.5 gives the highest compressive strength compared to the use of an $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 0.4. Sathonawaphak *et al.* [18] further stated that geopolymer with a fly ash/alkaline activator ratio of 1.4-2.3 showed a high compressive strength of 42-52 MPa. In addition, the optimum $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was 1.5 while the maximum strength of 48 MPa was obtained in their study. However, in our study, the highest compressive strength - up to 71 MPa - was observed at the 2.0 fly ash/alkaline activator ratio and 2.5 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio.

4. CURING PROCESS

The curing temperature is the most important factor for the geopolymer. When the curing temperature increases, the setting time of the concrete decreases [19]. During the curing process, the geopolymer concrete experiences the polymerization process. Due to the increased temperature, polymerization becomes more rapid,

Table 1. Chemical composition of fly ash.

Chemical	Fly ash component (wt. %)				
	Kong <i>et al.</i> [32]	Temuujin and Riessen [33]	Thokchom <i>et al.</i> [34]	Hardjito <i>et al.</i> [35]	Mustafa <i>et al.</i> [36]
Al ₂ O ₃	27.0	23.63	29.8	26.49	23.59
SiO ₂	48.8	-	56.01	53.36	52.11
CaO	6.2	1.74	2.36	1.34	2.61
Fe ₂ O ₃	10.2	15.3	3.58	10.86	7.39
K ₂ O	0.85	0.84	0.73	0.80	0.80
MgO	1.4	1.2	0.30	0.77	0.78
Na ₂ O	0.37	0.38	0.61	0.37	0.42
P ₂ O ₅	1.2	1.31	0.44	1.43	1.31
TiO ₂	1.3	1.32	1.75	1.47	0.88
BaO	0.19	-	-	-	-
MnO	0.15	0.13	-	-	0.03
SrO	0.16	-	-	-	-
SO ₃	0.22	0.28	Nil	0.20	0.49
ZrO ₂	-	-	-	-	-
LOI	1.7	1.78	0.40	1.39	-

and the concrete can gain 70% of its strength within 3 to 4 hours of curing [1].

Generally, heat-curing is recommended for fly-ash-based polymers. Rangan [4] stated that heat-curing (steam curing or dry curing) can assist in the chemical reaction that occurs in the geopolymer paste. The results demonstrate that the compressive strength of dry-cured geopolymer concrete is 15% higher than that of steam-cured geopolymer concrete. Nuruddin *et al.* [20] found that externally exposed curing is better than hot gunny and ambient curing. Both curing time and curing temperature influence the results for compressive strength of geopolymer concrete. A higher curing temperature results in a higher compressive strength. However, a curing temperature beyond 60 °C does not increase the compressive strength [4]. Our research found that the optimum curing temperature of 60 °C gives the highest compressive strength. Meanwhile, the 60 °C curing temperature was also recommended in manufacturing fly ash and kaolinite geopolymer [4,10].

5. CHARACTERIZATION OF GEOPOLYMER

5.1. X-ray fluorescence (XRF)

The chemical composition of the aluminosilicate precursors was determined using XRF. Table 1 shows the chemical composition of fly ash (determined by researchers using different sources).

5.2. X-ray diffraction (XRD)

The basic material of the geopolymer-based fly ash is of a prevailingly amorphous character only seldom containing needle-shaped minority crystals. The X-ray diffraction (XRD) pattern of fly ash in its as-received condition is shown in Fig. 1, which also illustrates the phases present in the fly ash—namely, silica (SiO₂), alumina (Al₂O₃), and quartz [21,22].

5.3. Scanning electron micrograph (SEM)

Fig. 2a is a SEM image showing the characteristic morphology of the original fly ash. The majority of the fly ash particles are spherical in nature and are precipitator type fly ash [21]. This ash consists of a series of spherical vitreous particles of different sizes (diameters ranging from 200 to 10 Am). Although usually hollow, some of these spheres may contain other particles of a smaller size in their interiors. Fig. 2b highlights the first changes detected in the microstructure of the fly ash system as a consequence of the caustic dissolution attack and posterior thermal curing (5 hours at 85 °C). Here, the spheres seem to be almost intact or appear within other spheres, depending on the degree of local reactivity. Indeed, in the early stages of the process, the alkaline dissolution dissolves part of the shells of the spheres, exposing the smaller particles (trapped inside the larger ones) to the

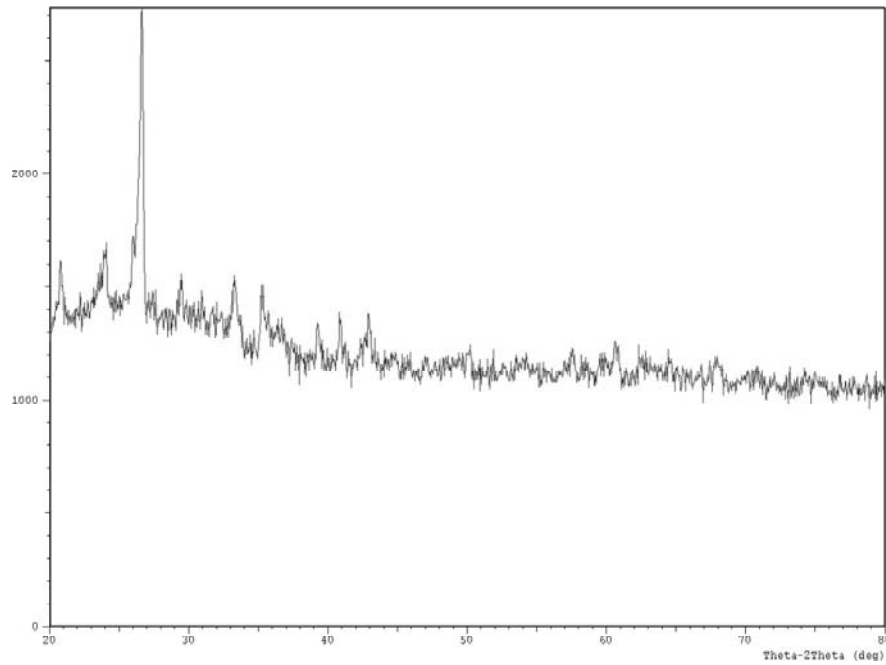


Fig. 1. X-ray diffractogram of fly ash.

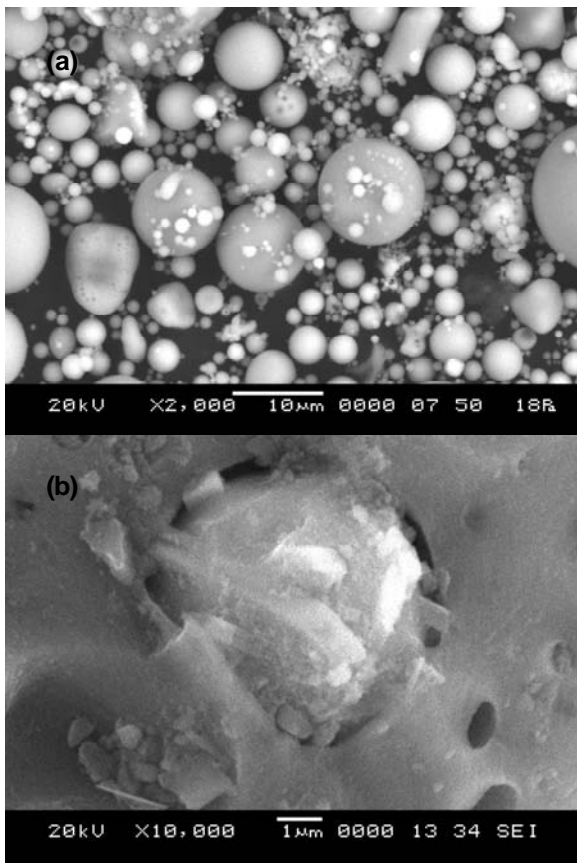


Fig. 2. SEM pictures: (a) original fly ash, (b) fly ash activated with alkaline activator [37].

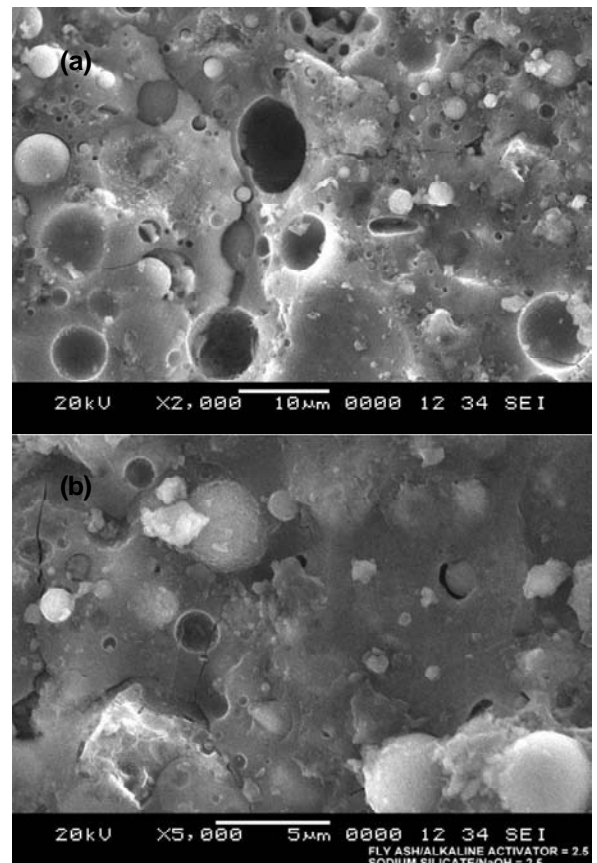


Fig. 3. Appearance of fly ash-based geopolymer [37].

alkaline attack as well. At this particular reaction time, the reaction product is a sodium silicoaluminate [23].

The process of geopolymeration causing the hardening of the material is different from the processes of hydration of the inorganic binders, such

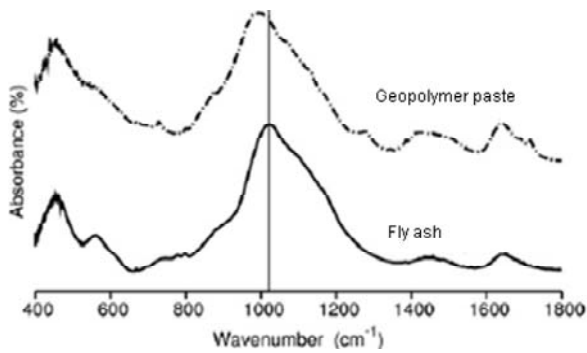


Fig. 4. FTIR of fly ash and fly ash-based geopolymer.

as in Portland cement. This process is primarily run by a “through the solution” mechanism, when parts of the fly ash are initially dissolved in strong alkali-surrounding solution and then a new geopolymer structure is developed in this solution (see Fig. 3). The gel produced was in a colloid form varying in size from less than 1 μm to about 20 μm . As more gel was formed, it overwhelmed the fly ash particles and formed a continuous mass of aluminosilicate [9].

5.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra for both raw fly ash and geopolymer paste demonstrated remarkable differences (see Fig. 4). The vibration at 1020 cm^{-1} corresponding to Si–O and Al–O in the raw fly ash was shifted to less than 1000 cm^{-1} . Such a shift is understood to be a penetration of Al^{4+} atoms into the original arrangement of the Si–O–Si skeletal structure. A similar phenomenon appears in a zeolite structure. The greater the shift of the vibration spectrum, the greater the intrusion of Al^{4+} from raw fly ash into the $[\text{SiO}_4]^{4-}$ [24]. The line obviously corresponds to the C–S–H phase formed. A clear difference exists among original fly ash and geopolymer paste on the FTIR spectra [24,25].

5.5. Differential scanning calorimetry (DSC)

DSC was used to measure a number of characteristic properties of the geopolymer pastes. Using this technique, it is possible to observe exothermic and endothermic events as well as glass transition temperatures (T_g). The range of investigation is between -30 and $100\text{ }^\circ\text{C}$ [26]. DSC thermograms (exothermal up) of the geopolymer studied by Chindaprasirt and Rattanasak [26] are shown in Fig. 5. As this figure indicates, the DSC thermogram of fly ash is smooth, with no sign of

reaction. The fly ash geopolymer demonstrated some peaks in the matrix. When the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio is 0.5, the exothermal peaks occurred at a temperature between 20 and $50\text{ }^\circ\text{C}$. A significant peak of the water’s melting point was observed in all geopolymer samples at $0\text{ }^\circ\text{C}$ [5].

5.6. Thermal gravimetric analysis (TGA)

In this TGA test, the mass loss was measured while the specimens were gradually exposed to increasing temperatures. Powdered specimens were used in TGA to ensure the achievement of thermal equilibrium during transient heating [1]. Fig. 6 shows the results of the TGA/DTG analysis of the geopolymer paste from Kong and Sanjayan’s study [12]. The sharp decrease in weight before $250\text{ }^\circ\text{C}$ as recorded in the TGA thermogram is attributed to the loss of evaporable water in the geopolymer. The decrease in weight peaked at $127\text{ }^\circ\text{C}$, as indicated by the DTG curve. After the initial rapid decline, the geopolymer’s rate of weight loss stabilized between $250\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$. Little change occurred in the percentage of weight remaining beyond $700\text{ }^\circ\text{C}$. The average total percentage of weight remaining after $800\text{ }^\circ\text{C}$ exposure was 89%.

6. PROPERTIES OF GEOPOLYMER

6.1. Workability of fresh geopolymer

Water plays as an important role in geopolymer concrete as it does in normal concrete. Water is used in geopolymer to improve the workability, but it increases the porosity in concrete due to the evaporation of water during the curing process at the elevated temperature [17]. Chindaprasirt *et al.* [27] discovered that an increase in sodium hydroxide and sodium silicate concentration reduces the flow of mortar. The workable flow of geopolymer mortar occurred in the 110 ± 5 to $135 \pm 5\%$ range. To improve the workability of mortar, superplasticiser or extra water can be added. However, the use of superplasticiser has an adverse effect on the strength of geopolymer. As such, extra water gives greater strength than the addition of superplasticiser. Reddy *et al.* [28] stated that, as the molarity of the NaOH solution increases, the workability of concrete decreases.

6.2. Compressive strength

Compressive strength is an essential property for all concrete as it also depends on curing time and curing temperature. When the curing time and

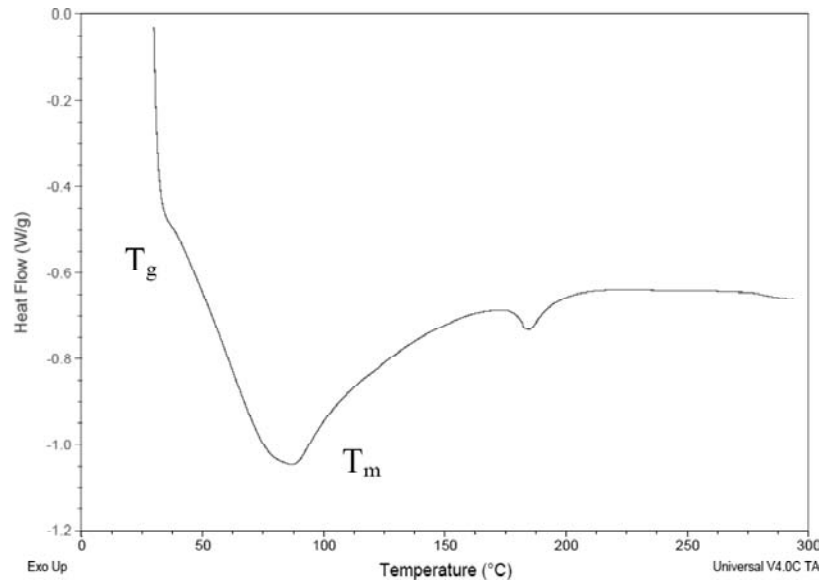


Fig. 5. DSC Thermogram geopolymer paste with fly ash.

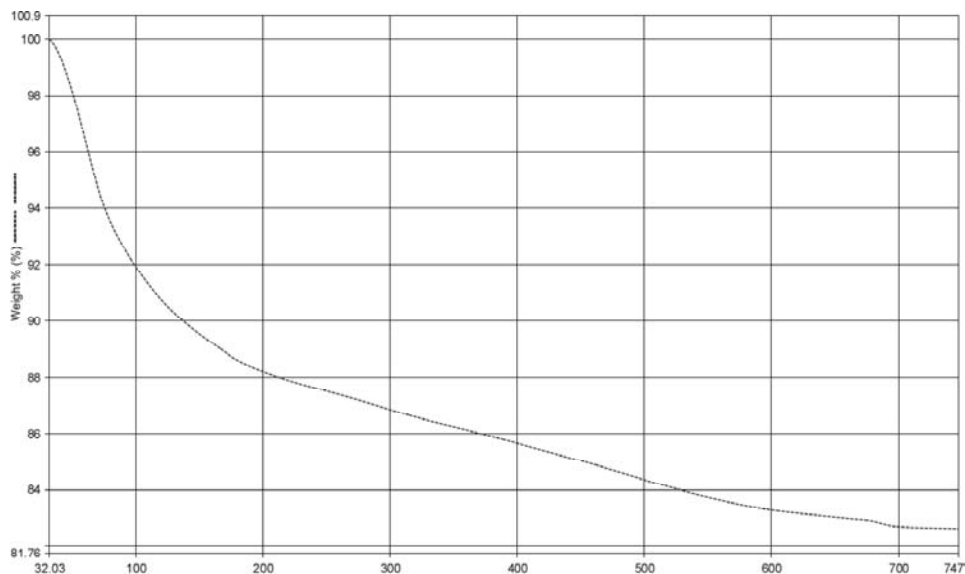


Fig. 6. TGA of fly ash geopolymer paste.

temperature increase, the compressive strength also increases. With curing temperatures ranging from 60 to 90 °C within a time ranging from 24 to 72 hours, the compressive strength of concrete can be obtained at approximately 400 to 500 kg/cm² [19]. In addition, the compressive strength of geopolymers also depend primarily on the content of fine particles of fly ash (smaller than 43 μm). The compressive strength increases as the finest of fly ash increases. Hence, the nature and concentration of activators are dominant factors in the reaction of alkali activation. The highest compressive strength was obtained using a solution of sodium silicate as an activator ($n = 1.5$; 10% Na₂O). Sodium silicate is most suitable as an alkaline activator because it contains dissolved and partially polymerized silicon,

which reacts easily, incorporates into the reaction products, and significantly contributes to improving the mortar characteristics [29].

6.3. Resistance to aggressive environment

The durability of concrete is an important requirement for the performance of the structure in aggressive environments throughout its design life period. The durability of concrete primarily depends upon its permeability characteristics. Impermeable concretes can resist the ingress of aggressive ions into the concrete, thereby reducing the damage occurring due to the deterioration of concrete and the corrosion of steel in concrete.

Fly ash-based geopolymer has been shown by many studies to provide better resistance to an aggressive environment. As such, this advantage can be used to construct a structure exposed to a marine environment [19]. The exposure of the geopolymer in the acid solution shows that the weight loss due to the exposure is only 0.5% compared to normal concrete when immersed in 3% sulfuric acid. [17] According to Bakharev [30], in acidic exposure, high-performance geopolymer materials deteriorate with the formation of fissures in an amorphous polymer matrix whereas low-performance geopolymers deteriorate through the crystallization of zeolites and the formation of fragile grainy structures. The formation of aluminosilicate gel is important for determining the stability of the geopolymer. Crystalline geopolymer material prepared with sodium hydroxide is more stable in the aggressive environment of sulfuric and acetic acid solutions than amorphous geopolymers prepared with a sodium silicate activator.

Thokchom *et al.* [31] exposed the geopolymer mortar to 10% sulfuric acid and found specimens that were still intact and did not show any recognizable change in color after 18 weeks. When observed under an optical microscope, the exposed surface revealed a corroded structure that progressed with exposure over time. In addition, the weight loss results obtained in this study showed better performance than OPC; specimens with a higher alkali content were observed to lose more weight than specimens with a lower alkali content. At 18 weeks, the specimens were fully dealkalinized by the sulfuric acid, but they still had substantial residual compressive strength to prove the higher resistance against acid exposure [31].

7. CONCLUSION

Investigations about fly ash-based geopolymer have found a potential material for replacing the used of OPC in infrastructure development. However, it must be noted that different samples of fly ash may give different reactivity due to their varying chemical compositions. The current knowledge shows that the influence of NaOH molarity, fly ash/alkaline activator ratio, $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, and curing temperature are essential for achieving the optimum strength of geopolymer. Moreover, the durability of the fly ash-based geopolymer is better than OPC when exposed to an aggressive environment.

REFERENCES

- [1] D.L.Y. Kong and J.G. Sanjayan // *Cem. Concr. Compos.* **30** (2008) 986.
- [2] J. Davidovits // *Global Warming Impact on the Cement and Aggregates Industries. World Resource Review.* **6** (1994) 263.
- [3] V.M. Malhotra, *Introduction: Sustainable Development and Concrete Technology*, (Concrete International, 2002).
- [4] B.V. Rangan, *Low-Calcium Fly-Ash-Based Geopolymer Concrete. Faculty of Engineering* (Curtin University of Technology, Perth, Australia, 2008).
- [5] M. Steveson and K. Sagoe-Crentsil // *J. Mater. Sci.* **40** (2005) 4247.
- [6] J. Davidovits, *High-alkali cements for 21st century concretes*. In: *Concrete Technology, Past, Present and Future*, ed by P.K. Metha (American Concrete Institute, Farmington Hills, 1994).
- [7] A. Fernandez-Jimenez and A. Palomo // *Fuel* **82** (2003) 2259.
- [8] F. Pacheco-Torgal, J. Castro-Gomes and S. Jalali // *J. Constr. Build. Mater.* **22** (2008) 1315.
- [9] U. Rattanasak and P. Chindaprasirt // *Minerals Eng.* **22** (2009) 1073.
- [10] J.C. Swanepoel and C.A. Strydom // *Appl. Geochem.* **17(8)** (2002) 1143.
- [11] T.W. Cheng and J.P. Chiu // *Minerals Eng.* **16** (2003) 205.
- [12] D.L.Y. Kong and J.G. Sanjayan // *Cem. Concr. Res.* **40** (2010) 334.
- [13] A. Palomo, M.W. Grutzeck and M.T. Blanco // *Cem. Concr. Res.* **29** (1999) 1323.
- [14] D. Hardjito // *ACI Mater. J.* **101** (2004) 467.
- [15] S. Alonso and A. Palomo // *Mater. Lett.* **47 (1-2)** (2001) 55.
- [16] T.K. Mandal *et al.*, In: *Study on the Strength of Fly Ash-Based Geopolymer Concrete* (700032, Jadavpur University: Kolkata), p. 1.
- [17] R. Sathia, K.G. Babu and M. Santhanam, In: *Durability Study of Low Calcium Fly Ash Geopolymer Concrete*, (The 3rd ACF International Conference-ACF/VCA, 2008).
- [18] A. Sathonsaowaphak, P. Chindaprasirt and K. Pimaraksa // *J. Hazard. Mater.* **168(1)** (2009) 44.
- [19] N.V. Chanh, B.D. Trung and D.V. Tuan, In: *Recent Research Geopolymer Concrete*, (The 3rd ACF International Conference-ACF/VCA. Faculty of Civil Engineering - University of Technology Ho Chi Minh City, Vietnam, 2008).
- [20] M.F. Nuruddin *et al.*, *Polymeric Concrete: Complete Elimination of Cement for Sustainable Futures*, (CSBI, Kuala Lumpur, 2010).

- [21] J.B. Rao, P. Narayanaswami and K.S. Prasad // *Inter. J. Eng. Sci. Tech.* **2(5)** (2010) 284.
- [22] K.T. Paul *et al.* // *Nanoscale Res. Lett.* **2** (2007) 397.
- [23] A. Fernandez-Jimenez, A. Palomo and M. Criado // *Cem. Concr. Res.* **35** (2005) 1204.
- [24] F. Skvara *et al.* // *J. Hazard. Mater.* **168** (2009) 711.
- [25] F. Skvara *et al.* // *Ceramics Silikaty* **50(4)** (2006) 208.
- [26] P. Chindapasirt and U. Rattanasak, In: *Utilization of coal ash in geopolymeric material*, (Technology and Innovation for Sustainable Development Conference, TISD Thailand, 2008), p. 77.
- [27] P. Chindapasirt, T. Chareerat and V. Sirivivatnanon // *Cem. Concr. Compos.* **29(3)** (2007) 224.
- [28] B.S.K. Reddy, J. Varaprasad and K.N.K. Reddy // *Indian J. Sci. Tech.* **3(12)** (2010) 1188.
- [29] M. Komljenovic, Z. Bascarevic and V. Bradic // *J. Hazard. Mater.* **181** (2010) 35.
- [30] T. Bakharev // *Cem. Concr. Res.* **36** (2006) 1134.
- [31] S. Thokchom, P. Ghosh and S. Ghosh // *ARPJ. Eng. Appl. Sci.* 2009.
- [32] D.L.Y. Kong, J.G. Sanjayan and K. Sagoe-Crentsil // *Cem. Concr. Res.* **37** (2007) 1583.
- [33] J. Temuujin and A.V. Riessen // *J. Hazard. Mater.* **164** (2009) 634.
- [34] S. Thokchom, P. Ghosh and S. Ghosh // *ARPJ. Eng. Appl. Sci.* **4(7)** (2009) 28.
- [35] D. Hardjito *et al.* // *Australian J. Struc. Eng.* **6** (2005) 1.
- [36] A.M. Mustafa *et al.*, In: *2nd International Conference on Mechanical, Industrial, and Manufacturing Technologies* (MIMT, Singapore, 2011).
- [37] A.M. Mustafa Al Bakri *et al.* // *J. Eng. Tech. Res.* **3(2)** (2011) 44.