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Full Length Research Paper

Microstructure of different NaOH molarity of fly ash-based green polymeric cement

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Every 1 ton of concrete leads to CO_2 emissions which vary between 0.05 to 0.13 tons. About 95% of all CO_2 emissions from a cubic yard of concrete are from cement manufacturing. It is important to reduce CO_2 emissions through the greater use of substitute to ordinary Portland cement (OPC) such as fly ash, clay and others geo-based material. This paper, report on the study of the processing of geopolymer using fly ash and alkaline activator with geopolymerization process. The factors that influence the early age compressive strength such as molarity of sodium hydroxide (NaOH) have been studied. Sodium hydroxide and sodium silicate solution were used as an alkaline activator. The geopolymer paste samples were cured at 70°C for 1 day and keep in room temperature until the testing days. The compressive strength was done at 1, 2, 3 and 7 days. The result showed that the geopolymer paste with NaOH concentration of 12 M produced maximum compressive strength.

Key words: Green polymeric concrete, fly ash, molarity, compressive strength.

INTRODUCTION

The term geopolymer was first applied by Davidovits (1994) to alkali aluminosilicate binders formed by the alkali silicate activation of aluminosilicate materials. Geopolymer (green polymeric concrete) are amorphous to semi-crystalline equivalent of certain zeolitic materials with excellent properties, such as high fire and erosion resistances, and high strength materials. Recent works have shown that the addition of moderate amount of minerals to a geopolymer can give significant improvements on the geopolymer structure and properties (Hu Mingyu et al., 2009).

The alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in a source material of natural minerals or in by-product materials such as fly ash and rice-husk ash to produce binders (Davidovits, 1994). The alkaline activation of materials can be defined as a chemical process that provides a rapid change of some specific structures, partial or totally amorphous, into compact cemented frameworks (Fernandez and Palomo, 2003). Alkali activation of fly ash is a process that differs widely from Portland cement hydration, and very similar to the chemistry involved in the synthesis of a large groups of zeolites (Criado et al., 2005). Some researchers described the alkali activation of fly ash (AAFA) as a physical–chemical process in which this powdery solid is mixed with a concentrated alkali solution (in a suitable proportion to produce a workable and mouldable paste) and stored at mild temperatures (< 100°C) for a short period of time to produce a material with good binding properties (Fernandez et al., 2006; Fernandez and Palomo, 2005). At the end of this process, an amorphous alkaline aluminosilicate gel is formed as the main reaction product. In addition, Na-Herschelite-type zeolites and hydroxysodalite are formed as secondary reaction products (Criado et al., 2005;

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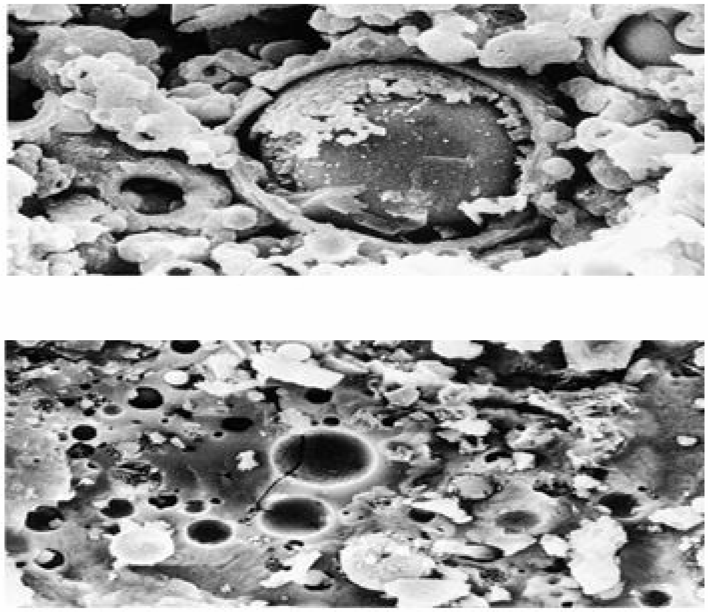

Figure 1. Microstructure of the fly ash-based geopolymer (Palomo et al., 1999a).

Fernandez et al., 2006; Fernandez and Palomo, 2005). The most used alkaline activators are a mixture of sodium or potassium hydroxide (NaOH, KOH) with sodium waterglass ($nSiO_2Na_2O$) or potassium waterglass ($nSiO_2K_2O$) (Davidovits, 1994; Palomo et al., 1999a; Vijaya Rangan, 2008; Fernando et al., 2008). The concentrations of sodium hydroxide solution that can be used are in the range of 8-16 M (Vijaya Rangan, 2008). The studies on the effect of different molarity of NaOH to the geopolymer have been done by some researchers. Puertas et al. (2000) stated that at 28 days of reaction, the mixture of 50% fly ash/ 50% slag activated with 10 M NaOH and cured at 25℃, developed compressive mechanical strengths at about 50 MPa. Rattanasak and Chindaprasirt (2009) concluded that when the mixture was formulated with NaOH molarity of 10 M and ratio of sodium silicate to NaOH of 1.0, the strength of geopolymer mortar up to 70 Mpa was obtained. Palomo et al. (1999a) reported that an activator with a 12 M of NaOH concentration leads to better results than a 18 M of NaOH concentration.

In this study, the effect of various molarity of NaOH to fly ash geopolymer paste was studied. There were six different molarity of NaOH (6, 8, 10, 12, 14, and 16 M) have been utilised in this study. The properties of the geopolymer such as compressive strength, water absorption, porosity, and density will plays a role as an indicator to prove that the geopolymer have similar properties to OPC (ordinary Portland cement).

Microstructure of geopolymers

Hos et al. (2002) systematically analyzed the microstructure of aluminosilicate inorganic polymer. By using scanning electron microscopy (SEM), they observed the nonporous microstructure of their materials. According to Hos et al. (2002), the nonporous microstructure is a result of extensive dissolution of aluminosilicate species that occurs before polycondensation commences and consolidates the shapes of the specimen through a chaotic three-dimensional network of polysodium aluminosilicate.

Moreover, fly ash-based geopolymer has also exhibits a high density of pores or air bubbles. Palomo et al. (1999a) reported that the fly ash-based geopolymer material is very porous and the microspheres (originating from fly ash grains) are surrounded by a curst of reaction product. The curst adhere to the sphere is not very strong and the bond between grains is produced through the necks of reaction product as indicated in (Figure 1A). Crack development is evident in the middle of the matrix and is likely been initiated from the pore (Figure 1B).

EXPERIMENTAL PROCEDURES

Materials

In the research work, low calcium, Class F (American Society for Testing and Materials, 2001) dry fly ash (Hos et al., 2002) obtained from Sultan Abdul Aziz power station in Kapar, Selangor, Malaysia was used as base material to make the geopolymers.

Sodium silicate (Na_2SiO_3) mixed with sodium hydroxide (NaOH) as an alkaline activator has been used in this study. NaOH in pellet form with 97% purity (Vijaya Rangan, 2008; Buchwald and Schulz, 2005; Steenie, 2009) and Na_2SiO_3 consists of Na_2O = 9.4%, SiO_2 = 30.1% and H_2O = 60.5%, with weight ratio SiO_2/Na_2O = 3.20-3.30),

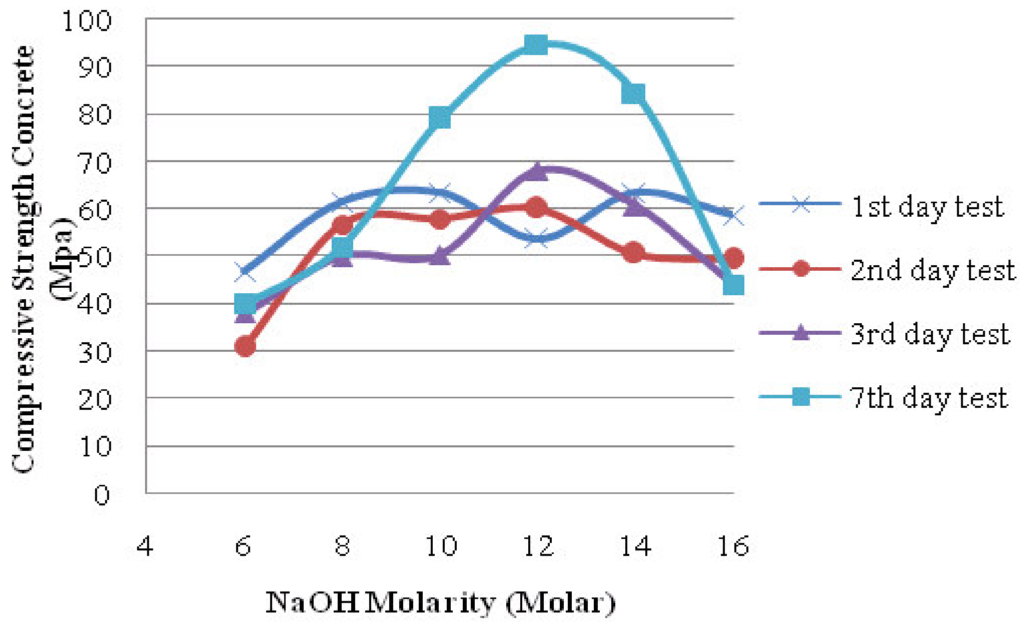

Figure 2. Compressive strength of various molarity of NaOH.

Table 1. Mixture proportions of geopolymer paste.

Mixture of geopolymer	Mass ratios (g)
Ratio fly ash/alkaline activator	2.50
Ratio Na_2SiO_3/NaOH	2.50
Mass of fly ash (g)	334.82
Mass of NaOH (g)	38.27
Mass of Na_2SiO_3 (g)	95.66

and specific gravity at 20ºC = 1.4 gm/cc were used in this study.

Method of mixing

In preparation of NaOH solution, NaOH pellets was dissolved in one liter of distilled water in a volumetric flask for six different concentration of NaOH (6, 8, 10, 12, 14 and 16 M). Alkaline activator with the combination of NaOH and Na_2SiO_3 was prepared just before mixing with fly ash. The addition of sodium silicate is to enhance the process of geopolymerization process (Xu and Deventer, 2000).

The ratio of fly ash/alkaline activator and Na_2SiO_3/NaOH is 2.5 and fixed for all mixture. The used of this ratio is due to Hardjito et al. (2008) which stated that ratio of fly ash/alkaline activator of 2.5 produced the highest compressive strength at 28th day of testing. Hardjito et al. (2004) used ratio of Na_2SiO_3/NaOH 2.5 and 0.4 in the preparation for geopolymer concrete.

The fly ash and alkaline activator were mixed together in the mixer until homogeneous paste was obtained. This mixing process can be handled within 5 min for each mixture with different molarity of NaOH. The total mass of each material used is kept constant for geopolymer paste for all the six different types of samples (6, 8, 10, 12, 14, and 16 M) with different molarity as shown in Table 1.

Casting and curing

The geopolymer paste was placed in 50 x 50 x 50mm cube mould and cured in the oven for 1, 2, 3 and 7 days at constant temperature of 70°C.

Compressive strength test and microstructure

The compressive strength test was performed on geopolymer paste samples accordance to BS 1881-116:1983 by using mechanical testing with Automatic Max (Instron, 5569 USA) in order to obtain the ultimate strength of geopolymer. The samples were loaded with 50 KN and the utilized with speed rate of 5 mm/min. The compressive strength values are determined by the average of 3 samples testing for each different types of mixture.

Scanning electron microscopy (SEM) was performed by using SEM JSM-6460 LA Jeol Japan in School of Materials Engineering, University of Malaysia Perlis (UniMAP) to study the microstructure of the base material (fly ash) and the resulting geopolymer samples. The test was carried out using secondary and backscattered electron detectors. The SEM samples must be prepared in powder form. The prepared samples were cut into 0.5 mm thick slices and then grinded into powder form for the test

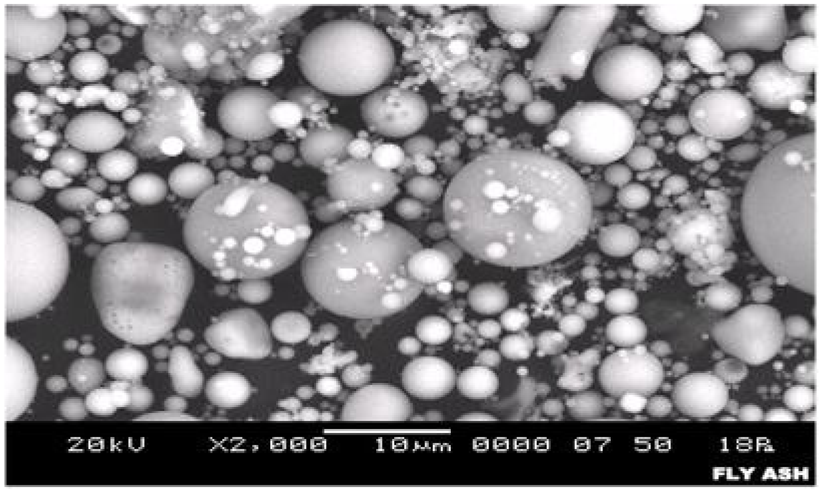

Figure 3. SEM micrograph of fly ash.

requirement.

RESULT AND DISCUSSION

Compressive strength due to different molarity of NaOH solution

The compressive strength result for 1st, 2nd, 3rd and 7th days of testing are shown in Figure 2. For 1st day of testing, 10 M NaOH solutions showed the highest compressive strength of 63.41 Mpa. However, for the 2nd, 3rd and 7th days of testing, samples with 12 M NaOH solution produced highest compressive strength of 60.15, 68.1 and 94.59 MPa respectively.

Study carried by Alonso and Palomo (2001) stated that when activator concentration increased above 10 M, a lower rate of polymer formation was produced resulting in the decrease of strength. This might be due to differences in the type of source materials which their study use metakaolin but in this work, the source material use is fly ash.

The perfect curve has been shown for 7th day testing. After 12 M of NaOH solution, the compressive strength has decreased. Palomo et al. (1999b) also found that alkaline activator with 12 M NaOH solution produced better result compared to 18 M NaOH. However, Hardjito et al. (2008) stated that the increase of NaOH molarity will increase the compressive strength of samples. The strength increased with the increased of NaOH concentration mainly through the leaching out of silica and alumina (Chindaprasirt et al., 2009).

Microstructure of fly ash

The microstructure of fly ash was analyzed using scanning electron microscope (SEM). From Figure 3, the microstructure of fly ash appeared to be a glassy, hollow, spherical particle which is cenospheres (thin walled hollow spheres). The microstructure appearance of the original fly ash is well agreed as reported by Davidovits (1994).

Although fly ash particles are essentially the same, variations do occur in shape (rounded to angular) with some crystals of mullite and iron (Fernandez and Palomo, 2003). Furthermore, surface texture appears to be smooth and dense to highly porous.

SEM analysis for geopolymer paste

The microstructure of geopolymer with different molarity of NaOH are shown in Figures 4(a and b). The formation of pores heterogonous matrix which does not exist in the original fly ash was observed in Figures 4 a-f. The formation of matrix was due to geopolymerization reaction occurred after mixing the original fly ash with the alkaline activator liquid and for further preparation processes. The gel formation was in colloidal form with the sizes <1 µm up to 20 µm. As the molarity of NaOH increased from 6 to 16 M, the microstructure of the resulted geopolymer appeared to contain relatively less unreacted fly ash microspheres proportions. Based on Figure 4 (a) and (b), a large proportion of fly ash still did not completely dissolve. Figure 4 (d) shows most less unreacted fly ash with alkaline activator which give higher compressive strength of 94 MPa for 7th days test. Pores as indicated on the figures by arrow sign, and cracks which could limit the strength of geopolymer also found in the matrix [Figure 4 (a), (b), (c), (e)] that leads to lower compressive strength. The results obtained suggested that the composition of aluminosilicate gel formed by the reaction between fly ash and alkaline activator is variable

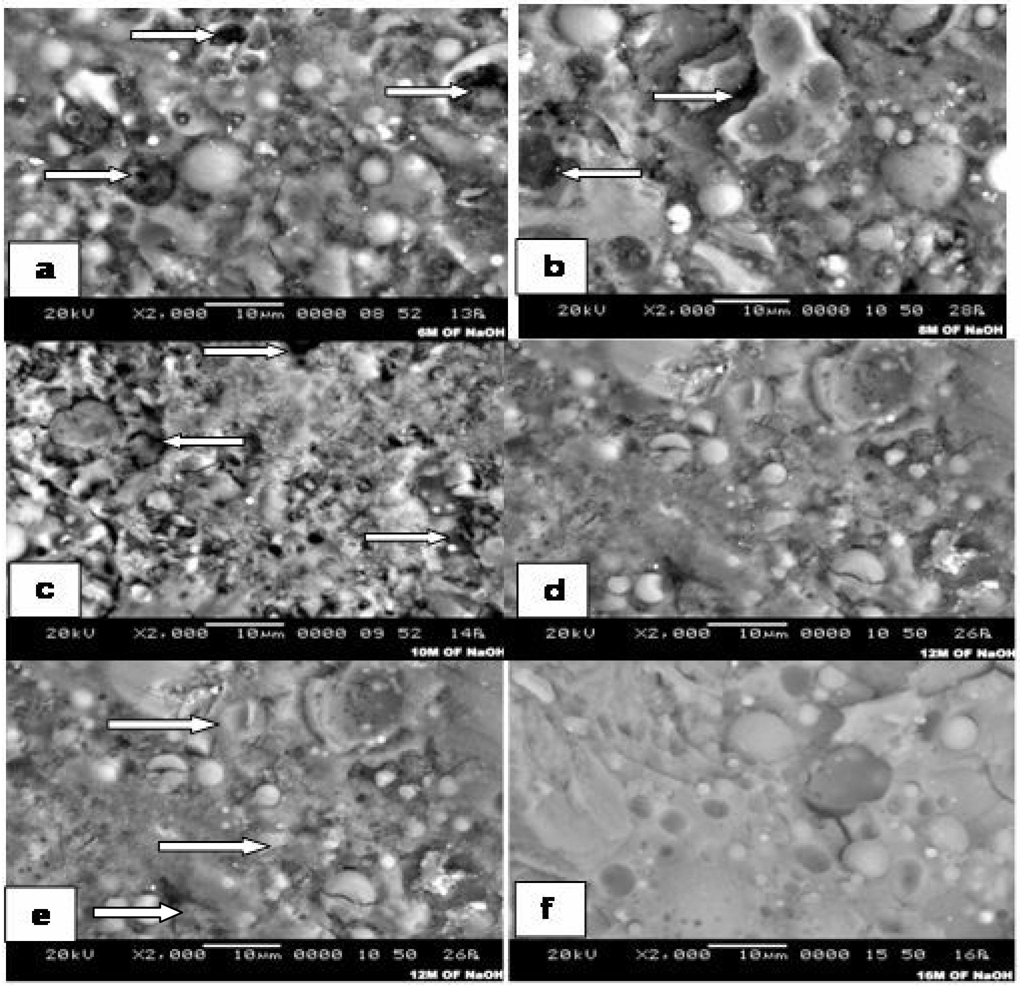

Figure 4. (a) SEM of geopolymer with 6 M of NaOH solution (b) SEM of geopolymer with 8 M of NaOH solution (c) SEM of geopolymer with 10 M of NaOH solution (d) SEM of geopolymer with 12 M of NaOH solution. (e) SEM of geopolymer with 14 M of NaOH solution (f) SEM of geopolymer with 16 M of NaOH solution.

and depends on the reactivity, type and concentration of activators (Duchesne et al., 2010)

Conclusion

Fly ash from Sultan Abdul Aziz power station combined with sodium hydroxide and sodium silicate as geopolymer can be enhanced to the use of OPC which often used in construction due to high compressive strength produced. Fly ash-based geopolymer with 12 M NaOH concentration shows excellent result with high compressive strength (94.59 MPa) for 7th days of testing. The microstructure of the optimum strength geopolymer appears to be homogenous and contains minimum proportion of unreacted fly ash microspheres, with continuous matrices of aluminosilicate and microcracks.

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