

Microstructure Studies on the Effect of the Alkaline Activators Ratio in Preparation of Fly Ash-Based Geopolymer

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Abstract. Fly ash-based geopolymers are new binding materials produced to replace the ordinary Portland cement (OPC) used in concrete. In this research, the effect of alkaline activators on the compressive strength and the microstructure of low-calcium (Class F) fly ash-based geopolymers were studied. Fly ash and the alkaline activator were mixed with alkaline activator to fly ash ratios of 0.30, 0.35, and 0.40 at a constant ratio of water glass (sodium silicate) to sodium hydroxide (NaOH). The alkaline activator solution was prepared by mixing water glass with a 15 M NaOH solution. The samples were cured at a temperature 70 °C for 24 hr and maintained at room temperature until the testing was conducted. After the geopolymers were aged for seven days, the test results indicated that the compressive strength (i.e., the geopolymerization rate) increased when the ratio of alkaline activator to fly ash was increased. The ratio of 0.4 produced the maximum compressive strength, which was 8.61 MPa. This was due to high reaction rate between the fly ash and the alkaline activator solution. Morphology studies, conducted by SEM analysis of the geopolymer samples, indicated that geopolymers synthesized at a ratio of 0.4 also had the most homogeneous and less porous microstructures, which was attributed to the high dissolution of the fly ash particles in the alkaline activator solution.

Keywords: alkaline activator, geopolymerization, compressive strength, SEM analysis, geopolymer

1. Introduction

Over the last 20 years, geopolymers, which are also known as mineral polymers or inorganic polymer glasses, have received much attention as a promising new form of inorganic polymer material that could be used as a substitute for conventional or ordinary Portland cement, plastics, and many other mineral-based products. However, to date, the exact mechanisms that govern geopolymerization still are not fully understood [1].

Geopolymers are members of the family of inorganic polymers in which the chemical compositions of the geopolymer materials are similar to natural zeolitic materials, but the microstructure is amorphous. The composition of zeolites is based on an aluminosilicate framework and a three-dimensional network of inorganic polymers made of SiO₄ and AlO₄ tetrahedra that are linked by shared oxygen atoms into rings and cages. The polymerization process (geopolymerization) involves a substantially fast chemical reaction under alkaline conditions with Si and Al minerals that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [2].

In addition, since the geopolymer synthesis technology is based on the alkaline activation of source materials that contain mostly silicon (Si) and aluminum (Al) in amorphous form [3], the similarity of some

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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 for making cement with special properties [4-5]. The successful stabilization and immobilization of some toxic heavy metals in geopolymeric material by Jaarsveld *et al.* [6] and Jaarsveld and Deventer [7], have also encouraged the use of this fairly new technology.

Hos *et al.* [8] systematically analyzed the microstructure of an aluminosilicate inorganic polymer. By using scanning electron microscopy (SEM), they observed that the polymer had a nonporous microstructure. According to the authors, the structure is a result of the extensive dissolution of aluminosilicate species that occurs before polycondensation begins, resulting in the consolidation of the shapes of the specimen through a chaotic, three-dimensional network of polysodium aluminosilicate. In addition, fly ash-based geopolymers also exhibit the extensive formation of pores (or air bubbles). Palomo *et al.* [9] reported that fly ash-based geopolymer material is very porous and that the microspheres (originating from fly ash grains) are surrounded by a crust of reaction products. The adherence of the crust to the sphere does not appear to be very strong, and the bonding between grains is produced through the necks of the reaction products, as indicated in Fig. 1a. The development of cracks, which is likely to have been initiated from the pore, is evident in the middle of the matrix (Fig. 1b).

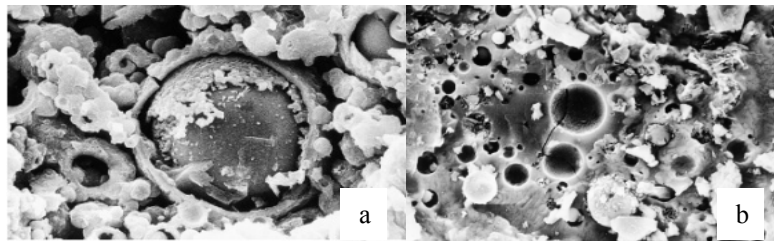


Fig. 1: Microstructure of the fly ash-based geopolymer (Palomo *et al.*, 1999).

2. Materials and Experimental Details

2.1. Raw Materials

The raw materials used to prepare the samples were fly ash (class F) and alkaline activator, which consisted of sodium silicate (water glass) mixed with a 15 M sodium hydroxide (NaOH) solution. Solid NaOH pellets with 97% purity were obtained from Sigma-Aldrich Pty. Ltd., Germany, were used to prepare the 15 M NaOH solution. Technical grade sodium silicate liquid (water glass) was supplied by South Pacific Chemical Industries Sdn Bhd (SPCI), Malaysia. The chemical composition of the water glass solution was 9.4% Na_2O , 30.1% SiO_2 , and 60.5% H_2O , with a weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 3.20-3.30), a specific gravity of 1.4 at 20 °C, and a viscosity of 400 cP at 20 °C. The fly ash was obtained from Sultan Abdul Aziz Power Station in Kapar, Selangor, Malaysia, and it was equivalent to ASTM Class F. It was used as the base material for the production of the geopolymers. The composition of the fly ash is given in Table 1.

Table 1: XRF analysis data of Fly ash composition

Compound	Percentage in Fly ash
SiO_2	52.11 %
Al_2O_3	23.59 %
Fe_2O_3	7.39 %
TiO_2	0.88 %
CaO	2.61 %
MgO	0.78 %
Na_2O	0.42 %
K_2O	0.80 %
P_2O_5	1.31 %
SO_3	0.49 %
MnO	0.03

2.2. Mix Proportion and Mixing Process

The geopolymers were synthesized by the activation of fly ash with alkaline activator solution at alkaline activator to fly ash ratios of 0.30, 0.35, and 0.40 at a constant ratio of water glass/NaOH solution. The alkaline activator, which consisted of a mixture water glass and NaOH solution, was prepared and mixed at constant waterglass to NaOH solution ratio of 1.0. The NaOH solution was prepared by dissolving sodium hydroxide pellets in deionized water, and the concentration of the NaOH solution was kept constant at 15 M. It is preferable to mix the water glass and the NaOH solution at least one day before adding the liquid to the solid constituent. Geopolymer samples were synthesized by adding the alkaline activator gradually at the different alkaline activator/fly ash ratios. Additional water, which amounted to a constant 17% of the weight of the samples, was added to achieve suitable workability. The ratio of alkaline activator to fly ash that was 0.25 was not used because it required the addition of water that would have amounted to more than 17% of the weight of the sample. Table 2 shows the details of the mixing proportions.

Table 2: Detailed of mix proportion

AA/FA	Water glass/NaOH	FA (g)	Activators (g)			H ₂ O (g)
			NaOH solid	H ₂ O in NaOH solution	Water glass	
0.30	1.00	450.00	25.312	42.188	67.50	102.45
0.35	1.00	450.00	29.531	49.219	78.75	103.27
0.40	1.00	450.00	33.750	56.250	90.00	107.10

*AA – Alkaline Activator, FA – Fly Ash

2.3. Molding, Curing and Compressive Strength Test

After 15 minutes of mechanical mixing, the fresh, homogeneous, geopolymer paste was poured into standard steel molds that measured 50 x 50 x 50 mm. The samples were compacted with two layer placing, as described in ASTM C109. The samples were maintained at room temperature for 24 hr prior to being cured in an electrical, low-temperature furnace (L T Furnace, L6-1200) for 24 hr at 70 °C. The evaporation of water was prevented by sealing the top of the molds with a thin plastic layer during storage as well as during the curing stage. When curing was completed, the samples were removed from the furnace and left at room temperature for seven days. The samples were sealed and not exposed to ambient air during the aging period. In accordance with ASTM C109, after seven days of aging, the samples were tested using an Instron mechanical testing machine (Instron 5569, USA). Three compression strength tests were conducted for samples prepared with each ratio, and the values reported were the averages of the three compressions strength values.

2.4. Microstructure Analysis

Scanning electron microscopy (SEM) was performed using the SEM JSM-6460 LA, Jeol, Japan, located in School of Material Engineering, Universiti Malaysia Perlis (UniMAP), to analyze the microstructure of the fly ash and the geopolymer samples. The tests were conducted using secondary as well as backscattered electron detectors. The samples were cut into 0.5-mm-thick slices and then ground into the powder form needed for the SEM analysis.

3. Result and Discussion References

Fig. 2 shows the effect of increasing the alkaline activator/fly ash ratio on the compressive strength of the fly ash-based geopolymer. A rapid increase in the compressive strength from 3.695 to 8.325 MPa was observed as the alkaline activator/fly ash ratio was increased from 0.30 to 0.35. When the ratio was increased from 0.35 to 0.40, the compressive strength increased from 8.325 to 8.610 Mpa. This result was obtained due to the change in the alkaline activator content, which affected the contents of Si species, base water, and Na⁺ ions. All of these factors have a major effect on the geopolymerization process and on the strength of the resulting geopolymer. An increase in the alkaline activator content (alkaline activator/fly ash ratio) increased the content of Si species because the alkaline activator contained sodium water glass (more Si species),

increased the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and also increased the geopolymer strength since the increased the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio resulted in more Si-O-Si bonds, which are stronger than Si-O-Al bonds.

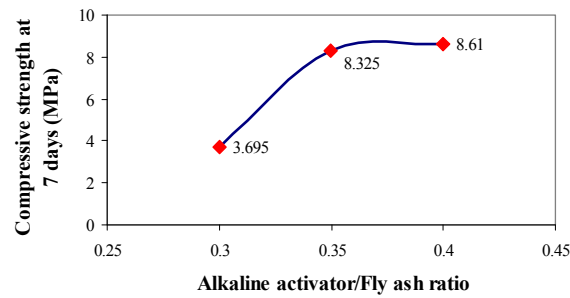


Fig. 2: Effect of alkaline activator/fly ash ratio on the compressive strength of fly ash-based geopolymer.

Fig. 3 shows the SEM-determined microstructure of the original fly ash used in preparation of the fly ash-based geopolymer. The fly ash consisted mostly of glassy, hollow, spherical particles, which were cenospheres (thin-walled, hollow spheres); the appearance of the microstructure of the original fly ash agreed well with that reported by Davidovits [10]. Although the fly ash particles were essentially the same, variations in shape did occur (rounded to angular) with some crystals of mullite and iron [11]. Furthermore, the surface texture appeared to be smooth and dense to highly porous, and the surfaces sometimes had coatings, such as magnetite.

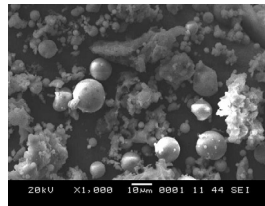


Fig. 3: SEM analysis of fly ash

Fig. 4 illustrates the SEM-determined microstructure characteristics of the original fly ash and the prepared fly ash-based geopolymers synthesized at alkaline activator/fly ash ratios of 0.30, 0.35, and 0.40 with a water glass/NaOH mass ratio of 1.0. The micrograph of the geopolymer synthesized with an alkaline activator/fly ash ratio of 0.30 showed the typical microstructure associated with a low geopolymerization rate, i.e., a porous, heterogeneous matrix with a high content of unreacted fly ash microspheres, which gives low compressive strength (3.695 MPa). However, the geopolymers synthesized with alkaline activator/fly ash ratio of 0.35 and 0.40 had microstructure appearances that showed the formation of continuous, less porous, homogenous matrices that had microcracks that resulted when water evaporated during the curing and aging processes. The samples prepared using an alkaline activator/fly ash ratio of 0.40 also contained unreacted fly ash. The higher dissolution rates associated with samples synthesized with alkaline activator/fly ash ratios of 0.35 and 0.40 resulted in high geopolymerization rates, more homogeneous matrices, and the highest compressive strength.

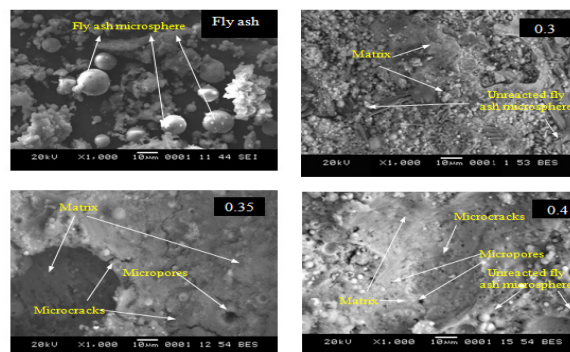


Fig. 4: SEM micrographs of the original fly ash and the synthesized geopolymers at activator/fly ash ratios of 0.30, 0.35, and 0.40 and a water glass/NaOH solution ratio of 1.0

4. Conclusion

An increasing ratio of alkaline activator/fly ash resulted in increasing compressive strength of the samples. The highest compressive strength (8.61 MPa) was obtained at an alkaline activator/fly ash ratio of 0.40:1.0. The SEM study indicated that significant changes occurred in the microstructure of original fly ash when it was mixed with the alkaline activator due to the formation of a matrix during the geopolymerization reaction. The microstructure of the optimum strength geopolymer appeared to be homogenous and contained the minimum proportion of unreacted fly ash microspheres. It also had continuous matrices of aluminosilicate and microcracks.

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6. References

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