Microstructural Analysis of Fly Ash-based Geopolymers with various Alkali Concentration

Ng Hui-Teng, Heah Cheng-Yong, Liew Yun-Ming, Mohd Mustafa Al Bakri Abdullah, Ng Yong-Sing
Center of Excellence Geopolymer & Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
E-mail: cyheah@unimap.edu.my

Abstract. In the present work, a comparative study on the effect of different concentration of sodium hydroxide (NaOH) on fly ash-based geopolymer was investigated. The geopolymer synthesis by mixing fly ash with alkali activator (a mixture of NaOH and sodium silicate) at solid/liquid ratio of 2.5. The NaOH were used 6M, 8M, 10M, 12M and 14M with constant sodium silicate/NaOH ratio of 2.5. The geopolymers were cured at room temperature (29°C) for 24 hours and 60°C in oven for another 24 hours. The testing and analysis of the fly ash-based geopolymers were performed after 28 days. The adequate Na⁺ ions and densified microstructure were observed at optimum 8M-NaOH-activated fly ash-based geopolymers.

1. Introduction
There has been growing attention on new construction materials with low greenhouse gas emissions and sustainability for the past few decades. Therefore, Davidovits [1] invented geopolymers as a new type of discovered materials with inorganic polymeric structure which can replace ordinary Portland cement. Geopolymer synthesis is considered as a sustainable binding material due to waste utilization and low greenhouse footprint [2].

Geopolymers are formed once the aluminosilicate material (fly ash and slag) is mixed with the alkaline solution through geopolymerization process. The alkaline solution acts as a character to dissolve the active aluminosilicate species at the early stage of geopolymerization process [3]. There contain a few stages in geopolymerization [4]. First stage consist of starting materials (silicate (SiO₄) and aluminate (AlO₄)) which activated by alkali and geopolymer gel produced. Hydrolysis occurred in the next stage when water molecules help to further break the bond and let SiO₄ and AlO₄ tetrahedral units to connect each other to yield polymeric precursors. Finally, polycondensation process occurred as geopolymer gel solidified and the three-dimensional aluminosilicate network is formed.

Different parameters such as raw materials, alkali concentration, solid/liquid ratio, alkali activator ratio, curing time and any other factors could influence the mechanisms formation and properties of geopolymer synthesis. Among of the parameters, the sodium oxide concentration of the activator solution play an important role as it determines the degree of reaction and the densification of microstructure on geopolymer synthesis [5]. Several researchers were also studied on the consequence of using different NaOH content on geopolymer synthesis [6, 7]. Thus, the aim of this paper was to investigate the effect of NaOH concentration on fly ash-based geopolymers. The compressive strength, elemental composition and microstructural analysis of fly ash-based geopolymers with various NaOH concentration were examined.
2. Methodology

2.1. Material
Fly ash (FA) collected from Cement Industries of Malaysia Berhad (CIMA) Perlis Plant, Malaysia was used as the source of aluminosilicate materials. The chemical composition of FA is tabulated in Table 1, which was obtained from XRF analysis. Referring to Table 1, the lime (CaO) content was 3.89% which can be classified as Class F FA according to ASTM C618 due to less than 20%. Figure 1 displayed the SEM micrograph of FA particles which were sieved (75μm) with spherical in shape and smooth surfaces.

The alkaline solution used was a mixture of sodium hydroxide (NaOH) and liquid sodium silicate (Na₂SiO₃). The NaOH used was caustic soda flakes with the brand name Formosoda-P supplied by Formosa Plastic Corporation Taiwan. The liquid Na₂SiO₃ was supplied by South Pacific Chemicals Industries Sdn. Bhd. (SPCI), Malaysia with SiO₂/Na₂O modulus of 3.2.

Table 1. Chemical composition of fly ash as determined by XRF analysis.

| Chemical | Wt% |
|----------|-----|
| SiO₂     | 56.3|
| Al₂O₃    | 28.0|
| Fe₂O₃    | 6.86|
| TiO₂     | 2.17|
| CaO      | 3.89|
| K₂O      | 1.49|
| Others   | 1.24|

2.2. Samples Preparation
The Na₂SiO₃/NaOH ratio of 2.5 and solid to liquid ratio of 2.5 was fixed in FA-based geopolymers synthesis. Three sets of geopolymer samples were formed for each molarities of NaOH (6M, 8M, 10M, 12M and 14M). The geopolymer paste was moulded into 50mm × 50mm × 50mm plastic moulds. The moulded samples were cured at room temperature for 24 hours followed by curing at 60°C in oven for another 24 hours. The cured samples were sealed with plastic covering in order to avoid substantial loss of moisture and kept curing for 28 days in room temperature before testing.

2.3. Testing and Analysis
The compressive strength was carried out according to ASTM C109 by using the Instron machine series 5569 Mechanical Tester. Microstructural and elemental composition analysis were performed by using SEM machine with model JEOL JFC 1600. Before undergoing SEM characterization, specimens were cut in small pieces from coated with platinum using an Auto Fine Coater.

3. Results and Discussions

3.1. Compressive Strength
According to the previous studied on Ng et al. [8], the compressive strength (Figure 5) showed increasing trend as the NaOH concentration utilized in geopolymer synthesis increases from 6M to 8M (optimum strength) but beyond of that the compressive strength reduced. The highest strength obtained at 8M was due to the sufficient OH− and Na+ concentration as mention before. When NaOH concentration exceed 8M, a lower strength obtained in the FA geopolymer synthesis. It is reasonable suggest that the presence of excess OH− and Na+ ions content caused aluminosilicate gel precipitation at the very early stages [9]. It was consistence with the results on EDX (Table 2) where higher mass percentage of Na observed from 14M over 8M and 6M.

3.2. Microstructural Analysis
Figure 2 revealed the SEM micrographs of fly ash geopolymer synthesis with 6M, 8M and 14M-NaOH. After mixing the original FA and alkaline activator solution, there were undergoing geopolymerization reaction (arrow sign) as shown in Figure 2a and thus geopolymeric gel was formed, indicating that the structure experiences growth. In other words, the alkaline activator solution has dissolved the FA to release Al3+ and Si4+ for geopolymerization reaction to take place. However, the porous heterogeneous matrix formed at Figure 2a which does not exist in the original FA (Figure 1).

![Figure 2. SEM micrographs of fly ash geopolymer with](image-url)
a) geopolymerization reaction, b) 6M, c) 8M, and d) 14M-NaOH-activated.)
Referring to Figure 2b, there showed a large proportion of un-reacted and/or partially reacted FA which did not completely dissolve with alkaline activator. A lot of FA particles were loosely bonded to the matrix and interfacial boundaries can be detected in the structure easily. The imperfect microstructures (cracks, pores) appear on FA geopolymers caused of poor compressive strength [10].

According to Figure 2c, it can be seen that the geopolymeric gel was enough to bind the constituents and some of the FA particles are firmly connected to the geopolymer structure, which indicates a greater extent of geopolymerization. The microstructures showed the more densified and homogeneous as compared to Figure 2b and 2d. The densified micro-structures (8M-NaOH) correlated well with the results on compressive strength [8], possessing a greater amount of geopolymeric gels. The results obtained suggested that the increase of alkali concentration contribute to higher geopolymerization rate and enhance the growth of geopolymeric gels, hence the compressive strength increased as observed for 8M-NaOH.

However, the excess content of alkali (14M) on Table 2 further increased the rate of geopolymerization caused the reaction products not enough time to disperse in the geopolymer matrix and it deposed on the surface of the FA particles (Figure 2d), as a result hindered further dissolution reactions. Therefore, Figure 2d produced lesser geopolymeric gel lead to strength reduction as compared to Figure 2c. These observations indicate that the geopolymeric gels formed by the reaction between FA and activator are rely on the reactivity and concentration of alkali activators solution [11].

3.3. Elemental Composition Analysis

Table 2 tabulated the elemental composition of 6M, 8M and 14M-NaOH-activated on FA geopolymers, as determined using EDX analysis. The Na\(^+\) constituent of the activator solution was detected apart from the Si\(^4+\) and Al\(^3+\) constituent of FA. The presence of Na\(^+\) cation was due to the formation of reactants via the condensation process caused by geopolymerization. These reactants combined with the Na\(^+\) cation depart from the external NaOH, leading the reaction products to agglomerate and developing the strength at 8M-NaOH-activated geopolymers through the combinations of FA particles [12].

| Molarity of NaOH | Element with mass percentage |
|-----------------|----------------------------|
|                 | Si (wt%)   | Al (wt%) | Na (wt%) | O (wt%) |
| 6M              | 39.82      | 42.39    | 0.99     | 16.8    |
| 8M              | 47.21      | 35.3     | 3.57     | 13.92   |
| 14M             | 51.23      | 18.12    | 10.00    | 20.65   |

Geopolymeric system was under constant sodium silicate content but with the continuous addition of NaOH causes a reduction on Si/Na ratio. This reduced Si/Na ratio leading to the gradual change of the chemical system from the larger rings species, complex structures and polymers to monosilicates, chains and smaller rings species [13]. The predominance of monosilicates and species with smaller rings at high concentration of NaOH slows down the polycondensation process [13, 14] and causing the compressive strength reduced beyond 8M [8].

4. Conclusions

This paper presented the effect of different concentration of NaOH solution (6-14M) on fly ash-based geopolymers synthesis. The optimum NaOH concentration was revealed at 8M for the formation of FA geopolymers. It was supposed that there are sufficient of Na\(^+\) ions for complete geopolymerization reaction which in agreement with the results on EDX analysis. There were also observed denser microstructure at 8M-NaOH with smoother surface than 6M and 14M-NaOH.
Acknowledgement
The authors wish to gratefully acknowledge the funding by Fundamental Research Grant Scheme (FRGS/1/2015/TK05/UNIMAP/02/1) sponsored by Ministry of Education Malaysia.

References
[1] Davidovits J 1989 J Therm Anal 35 441.
[2] Bakri, A M M et al 2013 Revista de Chimie, 64 382.
[3] Bakri A M M et al 2012 Applied Mechanics and Materials 110 734.
[4] Izzat, A M et al 2013 Materiale Plastice 50 171.
[5] Lloyd R R et al 2009 Micropor Mesopor Mat 126, 32-39.
[6] Al Bakri Abdullah et al 2015 Revista de Chimie 66 1001.
[7] Yahya Z et al 2015 Materials 8 2227.
[8] Ng H T et al 2018 AIP Conf Proc 2045 020098
[9] Lee W K W et al 2002 Colloid Surface A 211, 115.
[10] Granizo M L et al 2007 J Mater Sci. 42 2934.
[11] Duchesne J et al 2010 Waste Biomass Valori 1 367-377.
[12] Xu H et al 2000 Int. J. Miner Process 59 266.
[13] Panias D et al 2007 Colloid Surface A 301 254.
[14] Zuhua Z et al 2009 Appl. Clay. Sci. 43 223.