Synthesis and Characterization of Fly ash based Geopolymer Ceramics: Effect of NaOH Concentration

Romisuhani Ahmad\textsuperscript{1*}, Wan Mastura Wan Ibrahim\textsuperscript{1}, Mohd Mustafa AlBakri Abdullah\textsuperscript{2}, Andrei Victor Sandu\textsuperscript{3}, Nurul Aida Mohd Mortar\textsuperscript{2}, Noratikah Hashim\textsuperscript{1} and Warid Wazien Ahmad Zaitani\textsuperscript{4}

\textsuperscript{1}Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
\textsuperscript{2}Center of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
\textsuperscript{3}Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, Iasi, Romania
\textsuperscript{4}Faculty of Civil Engineering, Universiti Teknologi MARA, Shah Alam, Selangor

Email: romisuhani@unimap.edu.my

Abstract. Ceramic materials have demonstrated impressive performance under severe conditions in a wide number of areas including health, energy and environment, transportation and electronic applications. In order to meet the growing demand of specific properties of ceramics, the use of geopolymer method were introduced as an alternate way by providing new material to fabricate geopolymer as ceramic precursor and moving towards green technology. Geopolymer ceramic was produced using fly ash as source materials. Different molarities of sodium hydroxide solution in the range of 8 M to 14 M were used in the preparation of fly ash geopolymer ceramic. The ratio of fly ash/alkaline solution and alkaline activator were kept constant at 2.0 and 2.5 respectively. Physical and mechanical properties such as density, flexural strength and shrinkage were determined. The optimum flexural strength of 61.6 MPa is obtained at the sodium hydroxide concentration of 12 M with the density of 2.21 g/cm\textsuperscript{3}. The formation of almost fully crystalline phase with appearance of albite contribute to the flexural strength of fly ash geopolymer ceramic. Microstructure image result shows that a presence of pores due to sintering effect and smoother matrix which gives denser structure as supported by the excellent density.

1. Introduction

Ceramic are non-metallic inorganic material with high melting point and high hardness. Typical ceramics are thermal and electrical insulators with good strength in compression and good chemical stability. Ceramics play are critical role in a wide array of electronic, optical, magnetic and energy-related technologies [1]. Advanced ceramics play important role in providing thermal insulation and higher temperature properties. Several method are available for fabricating ceramic materials and fabrication method is important since it can affect the properties of product. More recently, geopolymers have been suggested as a low cost ceramic binder with application in some ceramic and high-technology applications [2]. Besides, the alternative way to produce ceramic materials using geopolymer since the amorphous to semi-crystalline behaviour of geopolymer will transform into
crystalline ceramic phase upon heating. Furthermore, geopolymer can design the chemical composition of final product and directly converted into final structural ceramic part of interest.

The properties and characteristics of geopolymer depending on the raw materials and the processing conditions used. Davidovits (2002) was the first that introduced geopolymer technology. Geopolymer is an inorganic polymeric material that contain silicon (Si) and aluminum (Al) that formed with alkaline solution or alkaline silicate solution at higher temperature level [3]. Geopolymer shows numerous outstanding properties, for example high compressive strength, low shrinkage in addition to corrosive and fire resistance [4]. The strength of geopolymers is dependent on the nature of the source materials, with geopolymers synthesized from calcined source materials such as slag, fly ash and metakaolinite exhibiting a higher compressive strength than those from non-calcined materials, for example kaolinite and naturally occurring minerals. On the other hand, the abundant availability of fly ash worldwide creates opportunity to utilize this by-product of burning coal to manufacture ceramic [5-8].

The geopolymerization process need alkaline solution which consist of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and glassy silicate that consist of sodium silicate or potassium silicate [9]. The most frequent alkaline solution used in geopolymerization are sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) commonly used to be incorporated with source materials that in rich in silica and alumina due to it cost and availability [10]. In production of geopolymer material, the concentration of sodium hydroxide (NaOH) solution play important roles. The solubility of aluminosilicates in alkaline solution depends on the charge of aluminum and silicon as well as on hydroxide concentration. In this study, the fabrication of geopolymer ceramic is carried out by using fly ash and powder metallurgy method. Thus, this paper study the effect of sodium hydroxide (NaOH) solution on fly ash based geopolymer ceramic.

2. Experimental

2.1 Material

Fly ash is a fine grey powder that consist of spherical, glassy particles that are produced as a byproduct in coal fired power stations. The fly ash used in this study was obtained from Manjung power station, Lumut, Perak, Malaysia. The physical forms of fly ash used were in powder state with the mean particle size (X50) of 46.22 µm. The components of fly ash typically include SiO2, Al2O3, CaO and Fe2O3, which exists in the form of amorphous and crystalline oxides or various minerals as shown in Table 1.0.

| Composition | SiO2 | Al2O3 | Fe2O3 | CaO | TiO2 | K2O | SrO | SO3 | RuO2 | ZrO2 | LOI |
|-------------|------|-------|-------|-----|------|-----|-----|-----|------|------|-----|
| Percentage  | 55.9 | 27.8  | 7.093 | 3.95| 2.25 | 1.55| 0.371| 0.33| 0.24 | 0.134| 0.382|

The alkali activator used were a combination of sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) solutions. The NaOH used is Formosoda-P brand name made in Taiwan supplied by Formosa Plastic Corporation, Taiwan while Na2SiO3 was supplied by South Pacific Chemicals Industries Sdn. Bhd. Malaysia with a chemical composition of 30.1 % SiO2, 9.4 % Na2O and 60.5 % H2O as stated by the supplier upon purchased.

2.2 Experimental method

The alkaline activator solution was formed by mixing Na2SiO3 to NaOH solution at a ratio of 2.5 until clear solution was obtained for 24 hours. An alkaline activator with a combination of NaOH and Na2SiO3 was prepared just before mixing with fly ash to ensure the reactivity of the solution. In order to produce geopolymer paste, fly ash powder was mixed with the alkaline solution with 2.0 solid to
liquid ratio and stirred well until no clumps were visible. The mixture then mixed well for a few minutes and poured into high-density polyethylene (HDPE) mould. Then, the samples were put into oven at 60 °C for 24 hours for the curing process.

To obtained fine powder, the samples were sieved manually to a 150 micron. In order to produce geopolymer ceramic, the sieved powders were compacted using uniaxial isostatic pressing with a 12-mm-diameter cylindrical stainless steel die at 5 tonnes for 2 minutes. After being shaped into a pellet, the samples were sintered at a fixed temperature of 1000 °C with soaking time of 180 minutes and heating and cooling rate of 5 °C/minutes.

2.3 Testing
2.3.1 Flexural Strength
Flexural strength measurements of fly ash geopolymer ceramics were conducted on specimens (7 mm x 5 mm x 52 mm) using a three-point-bending fixture on an Instron-500 tester machine with a span length of 30 mm at a crosshead speed of 0.5 mm/min. The three-point test configuration exposes only a very small portion of the specimen to the maximum stress. Minimum of five samples were subjected to flexural strength testing in accordance with ASTM C1161-02c.

2.3.2 Density
The theoretical density was measured using densitometer (DH-300X DahoMeter. A cylinder shaped sample with a diameter of 12 mm and a length of 5 mm were used in this testing.

2.3.3 Morphology Analysis
The morphology characterization in this study was done by scanning electron microscopy (SEM) using Hitachi TM3000. Geopolymers are non-conductive materials, therefore samples were coated with platinum using Auto Fine Coater JEOL JFC 1600 model as a conductive layer to obtain better quality of microstructural images. Imaged in a scanning mode using conventional SEM techniques (magnification used were 500x and 1000x).

2.3.4 Phase Analysis
The phase analysis and crystallinity test was performed on fly ash, fly ash geopolymer and fly ash geopolymer ceramic using XRD 6000, Shimadzu diffractometer. The test was performed at operating conditions of 40 kV and 30 Ma using Cu-Kα radiation. In collecting data sets, the range diffraction were performed from 10 ° - 80 ° 2θ with a step size of 0.02 °at a rate of 2 °/minutes. To analyses the results of diffraction patterns, The X’Pert High Score Plus software.

3. Results and Discussion
3.1 Flexural Strength
Figure 1 shows the flexural strength of fly ash geopolymer ceramic with different NaOH concentration. The flexural strength increased with the increasing of NaOH concentration and unsintered sample was expected to have a lowest flexural strength at 3.13 MPa compared to the sintered samples. As for sintered samples, the flexural strength at 8 M having the lowest strength among the other NaOH concentration which at 48 MPa due to lower alkalinity and insufficient of Na⁺ and OH⁻ at for the dissolution of fly ash. Therefore, would cause poor geopolymerization due to low leaching rate of Al 3⁺ and Si 4⁺ from fly ash thus lowering the flexural strength of the samples [11]. The maximum of flexural strength of 61.60 MPa was achieved at 12 M due to sufficient alkalinity (Na concentration) for activating the fly ash geopolymer. However, the flexural strength started to decrease at 14 M with 49.73 MPa contributes the excess of Na⁺ cation could weaken the structure [12].
Figure 1. Flexural strength of fly ash geopolymer ceramic at different NaOH concentration.

3.2 Density
Figure 2 represents density of fly ash geopolymer ceramic as function of NaOH concentration. The densities vary in the range of 1.85 to 2.25 kg/m$^3$. Increasing of NaOH concentration from 8 M to 14 M increased the density of the fly ash geopolymer. As for sintered samples, the density at 8 M having the lowest density among the other NaOH concentration which at 2.05 g/cm$^3$ attributed to the less concentration of NaOH in the activating solution to produce a dense structure of fly ash geopolymer ceramic at low molarity. Concentration of NaOH at 14 M shows the highest density which is at 2.25 kg/m$^3$ while the lowest density was depicted for unsintered sample at 1.85 g/cm$^3$. High concentration of NaOH caused the greater dissolution process due to the leaching of alumina and silica which contribute to the increases in geopolymerization reaction and also produced denser structure [10].

Figure 2. Density of fly ash geopolymer ceramic at different concentration of NaOH.
3.3 Morphology Analysis

Figure 3 shows the microstructure of the fly ash geopolymer and fly ash geopolymer ceramic at 1000x and 2000x magnifications. According to the illustrated micrograph, the microstructure of fly ash geopolymer are porous and heterogeneous mixture of non or partly-reacted fly ash grains, consist of a dense continuous gel-like with microcracks and micropores which can be clearly observed on the surface. The micro-crack was caused by the drying shrinkage, a physical property, inherent of the gel. The gel shrinkage occurs because the removal of water during polycondensation creates capillary tension within the gel matrices [13]. While the microstructure image of fly ash geopolymer ceramic at 12 M NaOH concentrations shows an appearance of pores. The samples appeared to have a smoother geopolymer matrix and denser as the concentration increases indicate that geopolymerization has occurred well contributes to high strength as proved by density and flexural strength results as well as the effect of the densification process during sintering.

![Figure 3](image_url)

**Figure 3.** Microstructure images of fly ash geopolymer a) 1000x, b) 2000x and fly ash geopolymer ceramic at 12 M of NaOH concentration with different magnification c) 1000x, d) 2000x.

3.4 Phase Analysis

For the phase analysis, the sample with optimum flexural strength at 12 M of NaOH is shown in Figure 4. The broad reflection pattern of fly ash geopolymer begins to show a sharp peak in fly ash geopolymer ceramic indicates the transformation of amorphous to crystalline phase upon sintering. Fly ash consist of minerals such as quartz, mullite and hematite. The dilution effect caused the disappearance of quartz, mullite and hematite peaks. During geopolymerization, new crystalline phase of formed. The crystalline phases (quartz, mullite) detected in the initial material remained apparently unaltered with activation. The use of NaOH as activators in geopolymers lead to the formation of quartz structure [14]. Geopolymers with low NaOH concentration shows low intensity of quartz formation. These indicates that the formation of geopolymer products were slow giving a low flexural strength. At higher NaOH concentrations, the quartz peak was detected to be high, gave a high level and better of geopolymerization has occurred [10]. A higher NaOH concentration have better result due to ability of dissolving the fly ash particles during geopolymerization process.
Figure 4. Phase analysis of fly ash geopolymer and fly ash geopolymer ceramic at 12 M NaOH concentration (Q= Quartz, M= Mullite, Al= Albite).

4. Conclusion
The aims of this paper is to synthesize and characterize fly ash geopolymer ceramic with the optimum sodium hydroxide based on flexural strength. The results concluded that the 12 M is the optimum NaOH concentration to produce highest flexural strength at 61.60 MPa for fly ash geopolymer ceramic. The broad, amorphous peak showed by phase analysis indicates that geopolymerization has occurred. Microstructure image shows smoother and having geopolymer matrix which gives denser structure as supported by excellent density. Thus, it can be conclude that the concentration of NaOH solution affects the dissolution ability of the fly ash as the higher of concentration provides a better dissolving ability of raw materials and accelerate the monomer condensation, hence increase the geopolymer bonding strength.

5. References
[1] Askeland, D. and Wright, W. (2016). The science and engineering of materials, 7th ed. Boston: Cengage Learning, pp. 532–564.
[2] Van Jaarsveld, J. G. S., Van Deventer, J. S. J., & Lukey, G. C. (2003). The characterisation of source materials in fly ash-based geopolymers. Materials Letters, 57(7), 1272–1280.
[3] Tabassum, R. K., Khadwal, A., & Ash, F. (2015). Effect of sodium hydroxide concentration on various properties of geopolymer concrete, 0869(10), 28–32.
[4] Bakri, A. M. M. Al, Kamarudin, H., Bnhussain, M., Nizar, I. K., Rafiza, A. R., & Zarina, Y. (2012). The processing, characterization, and properties of fly ash based geopolymer concrete, 90–97.
[5] Yahya, Z., Abdullah, M. M. A. B., Hussin, K., Ismail, K. N., Sandu, A. V., Vizureanu, P., & Razak, R. A. (2013). Chemical and physical characterization of boiler ash from palm oil industry waste for geopolymer composite. Revista de Chimie, 64(12), 1408–1412.
[6] Wazien, A.Z.W., Abdullah, M.M.A.B., Abd Razak, R., Rozainy, M.A.Z.M.R., Tahir, M.F.M. Strength and Density of Geopolymer Mortar Cured at Ambient Temperature for Use as Repair Material. (2016) IOP Conference Series: Materials Science and Engineering, 133 (1)
[7] Heah, C. Y., Kamarudin, H., Bakri, A. M. M. Al, Luqman, M., & Nizar, I. K. (2011). Potential Application of Kaolin Without Calcine as Greener Concrete: A Review, Australian Journal of Basic and Applied Sciences, 5(7), 1026–1035.
[8] Liew, Y. M., Heah, C. Y., Li, L. yuan, Jaya, N. A., Abdullah, M. M. A. B., Tan, S. J., & Hussin, K. (2017). Formation of one-part-mixing geopolymers and geopolymer ceramics from geopolymer powder. Construction and Building Materials, 156, 9–18.
[9] Muhammad Faheem, M.T., Mustafa Al Bakri, A.M., Kamarudin, H., Ruzaidi, C.M., Binhussain, M., Izzat, A.M. The relationship of Na2SiO3/NaOH ratio, Kaolin/Alkaline activator ratio and sand/kaolin ratio to the strength of kaolin-based non load bearing Geopolymer Brick(2013) International Review of Mechanical Engineering, 7 (1), pp. 161-166.

[10] Sani, N. A. M., Man, Z., Shamsuddin, R. M., Azizli, K. A., & Shaari, K. Z. K. (2016). Determination of excess sodium hydroxide in geopolymer by volumetric analysis. Procedia Engineering, 148, 298–301.

[11] Heikal, M., Nassar, M. Y., El-Sayed, G., & Ibrahim, S. M. (2014). Physico-chemical, mechanical, microstructure and durability characteristics of alkali activated Egyptian slag. Construction and Building Materials, 69, 60–72.

[12] Alehyen, S., & Achouri, M. T. (2017). Characterization, microstructure and properties of fly ash based geopolymer. Journal of Materials and Environmental Sciences, 8(5), 1783–1796.

[13] Provis, J. L., Yong, C. Z., Duxson, P., & van Deventer, J. S. J. (2009). Correlating mechanical and thermal properties of sodium silicate-fly ash geopolymers. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 336(1–3), 57–63.

[14] Jaya, N. A., Al Bakri Abdullah, M. M., Ghazali, C. M. R., Binhussain, M., Hussin, K., & Ahmad, R. (2016). Effect of NaOH concentration on flexural strength, phase formation and microstructural development of kaolin geopolymer ceramic. Materials Science Forum, 857, 405-411.