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The Low Concentration of Sodium Hydroxide Influence on The Compressive Strength of Fly Ash/Natural Kaolin-Based Geopolymer

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Abstract. Fly ash/natural kaolin-based geopolymer with a low concentration of NaOH has been studied. The fly ash was taken from coal combustion waste of Asam-asam power plant, meanwhile the kaolin clay was taken from Tatakan, South Kalimantan, Indonesia. The kaolin powder was calcined at 750 °C for 3 hours to form pozzolanic metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The silicon content from the X-ray fluorescence (XRF) test of the fly ash and the natural kaolin was respectively 44.58% and 72.98%. The aluminium weight percentage contained in the natural kaolin was roughly three times higher than that in the fly ash. Both starting materials together with the alkali solution ($\text{NaOH}/\text{Na}_2\text{SiO}_3$) were wisely mixed to produce geopolymers with Si/Al ratio of 4. The molarities of NaOH were controlled from 2M to 5M. The mixture was then heated at a curing temperature of 60 °C for 12 hours and dried at setting time of 14 to 28 days. The finest compressive strength, i.e. 91.6 MPa, was shown by the sample with 5M NaOH and 28 days setting time. This sample had a density of 2.04 g/ml and porosity of 5.88%. To the best of our knowledge, there is a prospective feature of using fly ash/natural kaolin-based geopolymer prepared by the low NaOH molarity in infrastructural industries.

Keywords: Geopolymer, natural kaolin, fly ash, compressive strength

1. Introduction

The widespread use of portland cement as one of the most demanding materials for binders in concrete structures requires a huge amount of energy consumption and brings adverse effects on the environment. Portland cements production starts with raw materials extraction, clinker manufacturing, cement grinding, and packing. The normal temperature for the cement calcination Portland is around 1400 °C and the energy consumption to produce cement reaches 8 GJ/ton [1]. In addition, CO₂ emission into the air can be 0.9 tons for every ton of cement production, i.e. 0.53 tons CO₂ emission from the decomposition of raw materials and the other 0.37 tons from the fuel. It implies that the cement production and concrete industrial sectors conduce to serious environmental pollution [2]. Therefore, an environmentally friendly material is important to fabricate to overcome those problems, and the geopolymers have shown their ability to minimum defilement.



The concept of geopolymer was firstly introduced by Joseph Davidovits in the 1980s. It is a new form of inorganic polymer for alumino-silicate established in the alkali environment. The geopolymerization process occurs due to the chemical reaction between alumino-silicate oxides and alkali metal solutions under highly alkaline conditions. This process produces a three-dimensional polymer structure from amorphous to semi-crystalline [3]. The alumino-silicate sources are found in kaolin and industrial waste materials such as slag and fly ash [1]. The use of geopolymers in concrete structures is believed to reduce energy consumption and is safe for the environment. On the other hand, fly ash is a waste from the coal combustion of power plants. It can be directly used as a solid material of geopolymers without further recalcination process, unlike kaolin that must be calcined at 750 °C to transform into metakaolin [4,5]. By means of geopolymers, the CO₂ emission can be reduced by 80% than that of the use of portland cement; besides, they are excellent in terms of mechanical properties, heat resistance, and good acid resistance [6–8].

Enhancing the mechanical performances, like compressive strength, the fly ash-based geopolymers have been carried out by many experts. Addition of slag, red mud, rice husk, and kaolin to the fly-ash will increase its mechanical properties [4–6]. Furthermore, different alkaline solutions, e.g. sodium hydroxide (NaOH) and potassium hydroxide (KOH), bring different effects of the compressive strength of geopolymer. NaOH alkaline solution can produce higher compressive strength of geopolymers than that of KOH, from 65.28 MPa to 28.73 MPa [9]. Sodium hydroxide in an alkaline solution may activate Si and Al oxides in the geopolymerization process to form geopolymer-forming monomers [7]. Therefore, many studies use sodium hydroxide concentrations with a molarity of 8 M [7,10], 9 M [4], 10 M [7], and 14 M [6]. The best geopolymer can be produced from aluminosilicate if the ratios of SiO₂ and Al₂O₃ are from 3.3 to 4.5 [7].

These results also provide preliminary information that a modification of the ratio of SiO₂ and Al₂O₃ is important to do to elevate the mechanical properties. An alternative modification offered in this study is by substituting 20% fly ash into natural kaolin. In this present paper, we report the results of the characterization of basic materials, and the effect of the use of lower concentrations of NaOH than previous studies, on the compressive strength. Additionally, this study aimed to study the potential utilization of the low fly ash content as a geopolymer material.

2. Methods

Fly ash and naturally occurring kaolin clay were activated using alkaline solution. The fly ash was taken from the waste of Asam-asam coal combustion power plant and was categorized as class F based on ASTM C168. The kaolin clay was taken from Tatakan sub-district, South Kalimantan. The kaolin clay was calcined into metakaolin after calcining temperature determination by differential scanning calorimetry and thermogravimetric analysis (DSC-TGA). The alkali activation was prepared by mixing sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH) solutions. The sodium hydroxide molarities were controlled at 2M, 4M, and 5M since the molarities below 10 M provide good workability of the paste mixing during molds casting [11].

The resultant homogeneous mixtures were then fed into the mold and vibrated for 5 minutes to reduce the trapped air particles and dried for 1.5 h for geopolymerization. The curing process was done at 60 °C for 24 hours. Afterward, the series of samples were kept for 14, 21, and 28 days prior to further characterizations. The characterizations were conducted by X-ray fluorescence (XRF), X-ray diffraction (XRD) using Cu-K α wavelength and universal test machine (UTM) with ASTM C39 standard respectively for compositional analysis, crystalline phase investigation, and compressive strength measurement. Additionally, the porosity of the as prepared samples was determined using Archimedes method.

3. Results and Discussion

3.1. Kaolin Clay and Fly Ash XRD Patterns

The XRD profiles of the as-prepared samples are shown in Figure 1. Crystalline phase identification was conducted by means of the search-match method. The kaolin clay contains quartz-SiO₂ (JCPDS number 085-0504) and kaolinite-Al₂SiO₅(OH)₄ (JCPDS number 029-1448). The fly ash contains crystalline phase in the form of magnetite-Fe₃O₄ (JCPDS number 074-0748), quartz-SiO₂ (JCPDS number 085-0504), and dmitryivanovite-CaAl₂O₄ (JCPDS number 023-1036). The quartz-SiO₂, kaolinite-Al₂SiO₅(OH)₄, magnetite-Fe₃O₄, and dmitryivanovite-CaAl₂O₄ crystallize in hexagonal, triclinic structures, cubic spinel, and orthorhombic structures.

The XRD analysis was supported by XRF characterization, which resulted in the elemental unveiling within the samples. The XRF test revealed that Si (72.98%), Al (21.08%), Fe (2.33%), and K (1.08%) were found in the kaolin and the fly ash contained Si (15.49%), Al (15.49%), Fe (25.46%), and Ca (6.88%).

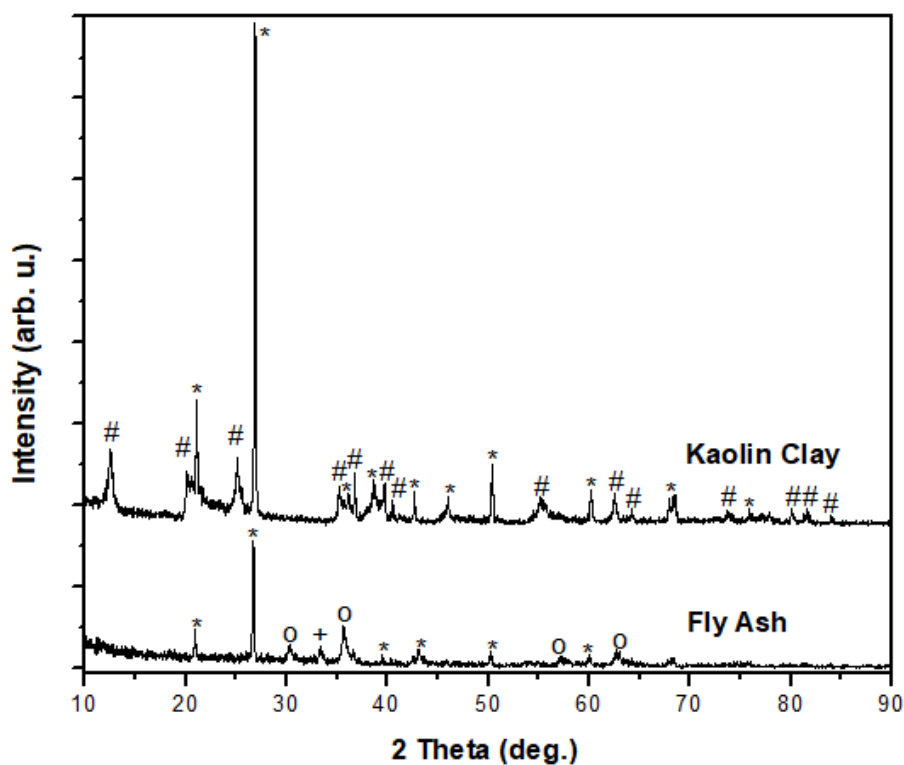


Figure 1. XRD Patterns of the kaolin clay and the fly ash. Note: #, *, o, and + Signs Respectively Represent Kaolinite, Quartz, Magnetite, and Dmitryivanovite Crystalline Phases.

3.2. Thermal Stability of Tatakan Kaolin Clay

The dehydroxylation temperature can be determined by the DSC-TGA curves, as depicted in Figure 2. It shows some thermal movements that occur in the kaolin sample from room temperature to 1200 °C. The thermodynamical phenomena include pre-dehydroxylation, dehydroxylation, endothermic, and exothermic. The pre-dehydroxylation was found at a temperature of 50 - 20 °C due to the little amount of water propagation. The dehydroxylations were detected from 430 °C to 650 °C indicated by the mass change up to 9.3%. This is the manifestation of the phase change from SiO₂·2Al₂O₃·H₂O to SiO₂·2Al₂O₃. The exothermic event occurred in the temperature range of 925 °C to 1100 °C, where in this process the crystalline phase such as spinel and mullite were formed. Again, the phase change was found at 650 °C due to the transition of kaolin to metakaolin. The kaolin can be completely transformed into metakaolin

at 750 °C and undergoes a dehydroxylation process. Therefore, 750 °C was then chosen as the calcination temperature of kaolin. Furthermore, the activity strength index depends on the dehydroxylation level and amorphous phase, which is at least 55%, to transform kaolin to pozzolanic metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) [14].

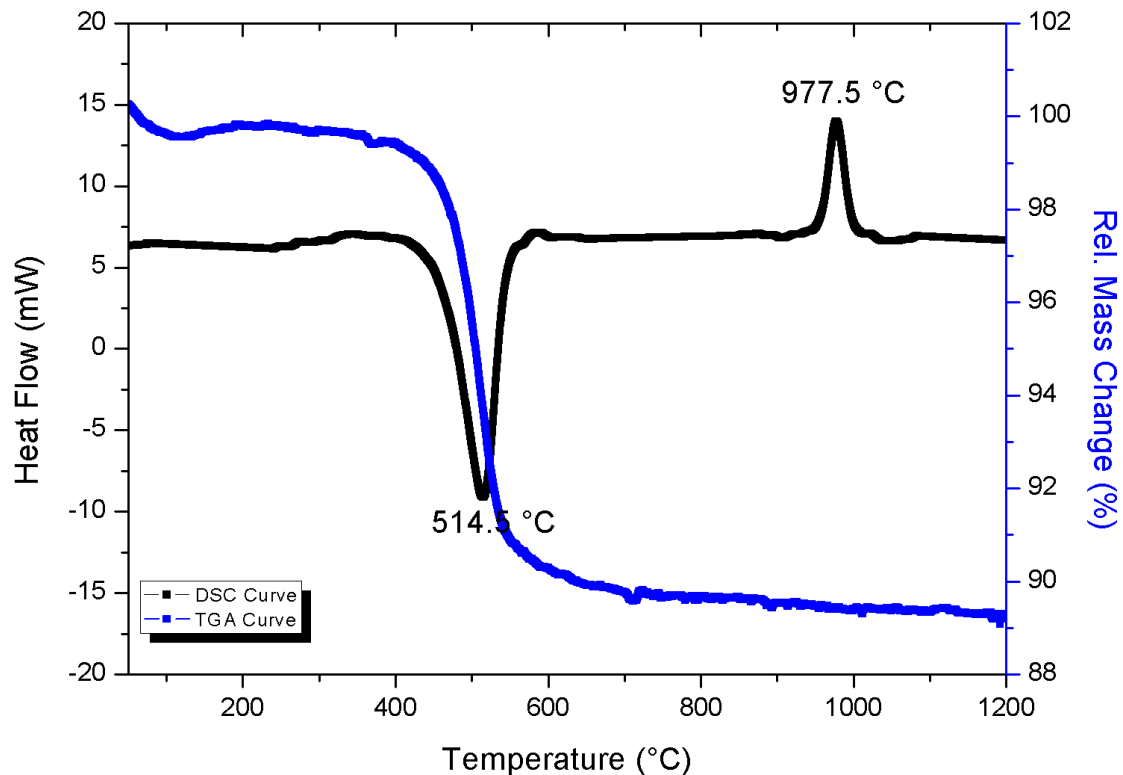


Figure 2. DSC-TGA Curves of kaolin clay from Tatakan, South Kalimantan, Indonesia.

3.3. Compressive Strength of Geopolymer Specimen

The compressive strength of the produced geopolymers with varying NaOH molarities are given in Figure 3a. The porosities as the function of setting time are drawn in Figure 3b. Clearly, the compressive strength increased as the alkali solution molarity increased. The setting time also plays an important role in raising the compressive strength. Through in-depth comparison with the porosity values, the mechanical behavior of the geopolymers obeys the rule of physics, i.e. compressive strength also depends on the porosity. When the porosity decreases, the compressive strength increases, and vice versa. Another study revealed that pure fly ash-based geopolymer with 14 M NaOH and 14-day setting time exhibited 30 MPa of compressive strength [6] that was lower than that in this study. Our geopolymer with the lower concentrations of NaOH, particularly with 5M NaOH, produced a higher compressive strength, i.e. 50 MPa, and when the setting time was doubled, the compressive strength was almost doubled, i.e. 92 MPa.

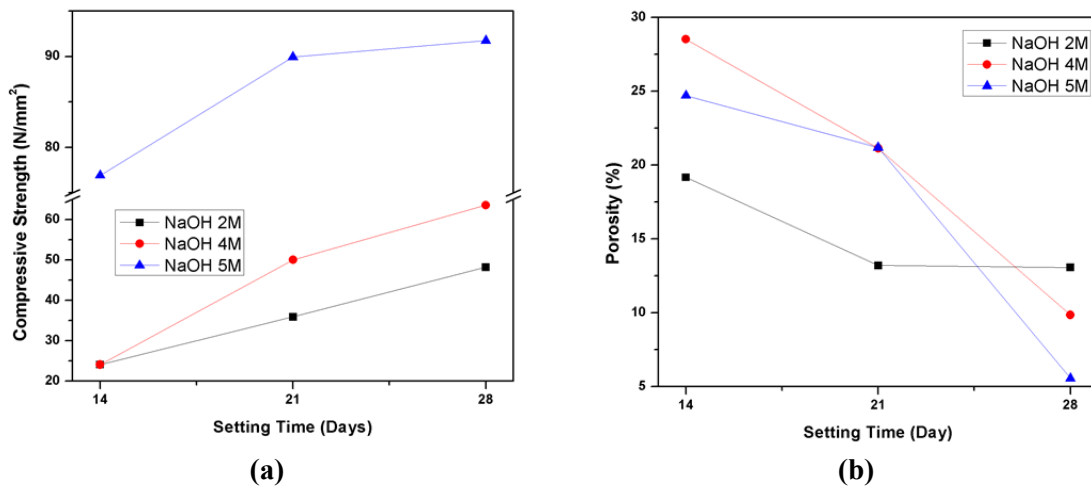


Figure 3. (a) Compressive strength and (b) porosity content of geopolymer with different concentration of NaOH and setting time.

NaOH is a source of hydroxide-based ions that can activate Al and Si atoms to form monomer and forces aluminosilicate to their Si^{4+} and Al^{3+} ions [12]. This alkali solution can enhance the mechanical strength of the geopolymer. This is due to the modeling of geopolymer-alkali solution formation (Figure 4.) [7], wherein with the lack of alkali solution within the geopolymer (Figure 4a) or excessive alkali solution (Figure 4c) will lead to relatively higher porosity than in the proportional alkali solution and geopolymer ratio (Figure 4b). That proportional ratio will maximize the mechanical characteristics of the geopolymer.

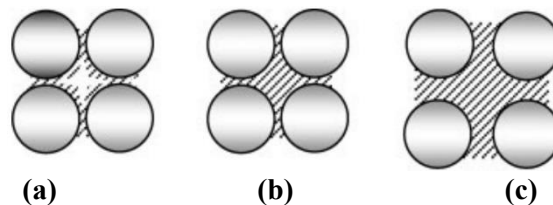


Figure 4. The Role of NaOH addition to aluminosilicate solubility (modified from [7]).

Sodium silicate, as an alkali solution, has oligomer-shaped silicate ions to polymerize with silica and alumina ions in a mixture of fly ash and metakaolin. Meanwhile, the sodium hydroxide solution, a provider of OH⁻ ions, enables the formation of monomers in an optimum manner. The geopolymerization reaction can continue even though the setting time has reached 28 days. The addition of sodium hydroxide increased the compressive strength. Thus, sodium hydroxide provided beneficial use for decomposing aluminosilicate in the fly ash and to release Si^{4+} and Al^{3+} ions [12].

Furthermore, the samples with 5 M sodium hydroxide performed a higher compressive strength than those of the other samples, even with a setting time of only 14 days. It is believed that the degree of homogeneity of the fly ash/metakaolin had reached the acceptable values for building the structure purposes. According to another reference, the strength of geopolymer depends on the amount of sodium hydroxide [7]. In addition, the high concentration of sodium hydroxide can accelerate the process of geopolymerization [11]. The pure fly ash, in general, contains unactivated silica. Addition of metakaolin to fly ash will, therefore, give a significant contribution to both mechanical strength and geopolymerization process [4]. In addition to the concentration factor of the alkali solution as a medium for forming the geopolymer monomer which affects the compressive strength of the resulted geopolymer material, the porosity contained in the sample also has a great effect. The porosity is produced by the trapped air bubbles in the sample which can be eliminated by a heating process [16-17].

4. Conclusion

Geopolymer from fly ash and natural kaolin clay from Tatakan, South Kalimantan, Indonesia has been successfully produced by the use of low concentration of alkali solution. The sodium hydroxide, as the alkali solution, plays a crucial role in enhancing the compressive strength and reducing the porosity. The largest compressive strength value was driven by 5 M sodium hydroxide, i.e. 91.6 MPa with the setting time of 28 days. In conclusion, the fly ash with the low content of NaOH can be used as geopolymer material with the addition of metakaolin.

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