Utilization of volcanic ashes for geopolymer based on alkaline activator and solid-liquid ratio

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Abstract. The volcanic ashes are an abundant natural resource in Indonesia, but they are still little is used optimally, such as geopolymer raw material. Geopolymers are a class of inorganic polymer that be able by the reaction of an aluminosilicate material with an alkaline solution. The research aims to investigate the synthesis of geopolymers using two types of volcanic ash (Mt. Merapi and Mt. Sinabung). The synthesis of geopolymer was carried out at variation of solid/liquid ratio at 65% : 35% and 70% : 30%, with two alkaline solutions (NaOH and KOH) under different alkaline concentration (8, 9, and 12 M). A multi-analytical approach is proposed: chemical (XRF) and spectroscopic (FT-IR) analyses. The Results showed that geopolymer is influenced by volcanic ash-type and SiO₂/Al₂O₃ ratio. Geopolymers are formed when volcanic ash of Sinabung mix with NaOH 10 NaOH with ratio of 65% : 35%, and the polymers are relatively stable. The FTIR spectra of the synthesized geopolymers showed broad absorbance bands, between wave 972-962 cm⁻¹ and 931-976 cm⁻¹ assigned to the internal vibrations of Si–O–Si, and Si–O–Al respectively. Both volcanic ash materials from the Merapi and Sinabung volcanoes can be utilized for making geopolymer, suitable for both engineering and agriculture applications.

1. Introduction

Geopolymers are a class of inorganic polymers prepared by chemical reactions of alkaline solutions and aluminosilicate material [1]. Geopolymers have attracted the attention of researchers for several years due to they are environmental friendly materials [2]. The geopolymerization process influenced by the chemical and mineralogical composition of aluminosilicate raw materials, particle size distribution and specific surface area of the raw material, curing temperature, the composition of alkaline solution, and liquid to solid ratio [3].

The use of raw materials commonly for the synthesis of geopolymer was kaolinite, metakaolin, and fly ash [4-6]. Volcanic ash is one of aluminosilicate-type whose percentage in Al₂O₃ and SiO₂ can allow their utilization in the synthesis of geopolymers [7]. Among the materials of aluminosilicate for synthesis geopolymer, volcanic ash has used as raw materials for polymers [7-9]. On the other hand, volcanic ash is one of more efficient material, because of low CO₂ emission and good physical and mechanical properties for geopolymer materials [10].

Indonesia is an active volcanic region with over 100 volcanoes [11], i.e., Mount Merapi in Central Java and Mount Sinabung in North Sumatera. Their volcanic activities generate vast deposits of
volcanic ash. The eruption of Mt. Merapi in 2010 resulted in volcanic deposits around $1.5 \times 10^8 \text{ m}^3$ [12], while volcanic deposits of Mt. Sinabung were approximately $3 \times 10^8 \text{ m}^3$ [13]. [14] reported that some characteristics of these volcanic ash can be considered as pozzolan material, due to their high silica (49.33% - 61.13% SiO$_2$) and alumina (15.93% - 17.78% Al$_2$O$_3$) content. Hence, volcanic ashes can allow readily soluble in alkali to produce geopolymers. Nevertheless, the little amount of this raw material is used for the production of geopolymers. The possibility of utilization of volcanic ash for the synthesis of effective geopolymers could be of economic importance for countries with vast deposits of this raw material.

The objective of this work is to investigate the synthesis of geopolymers using two types of volcanic ash (Mt. Merapi and Mt. Sinabung) as source material and second to study the properties of geopolymers with solid/liquid ratio, molar ratio, and alkaline types. The products were characterized by Infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Material
Volcanic ashes were collected from the volcanic deposit of Indonesia (Mount Merapi and Sinabung). Mount Merapi is at Central Java about 30 km north of Yogyakarta city located 7° 32.5’ S and 110° 26.5’ E, and having a height of 2986 m. While Mount Sinabung is located in Karo District, North Sumatera, geographically on 3° 10’ 16.7” N and 98° 23’ 24.66” E and altitude 2,460 m.

The volcanic ashes were dried at 105° C for 72 hours, and ground order to have a fine powder of <200 µm. Their chemical composition was determined by X-ray fluorescence. The alkaline solution used alkaline hydroxide (NaOH and KOH), followed by the addition of sodium silicate (Na$_2$SiO$_3$).

2.2. Geopolymer synthesis
The synthesis of geopolymer was conducted at the variation of solid-liquid ratio 65:35, 70:30 and molarity of NaOH/KOH; 8, 9 and 10 M. The solid consists of volcanic ash and Al$_2$O$_3$. This volcanic ashes between Mt. Merapi and Mt Sinabung have a higher SiO$_2$/Al$_2$O$_3$ molar ratio [14], then the need for the addition of reactive aluminum such as Al$_2$O$_3$. Geopolymer pastes were obtained by mixing alkaline solution with volcanic ashes (Figure 1).

Alkaline solution (NaOH and KOH) was prepared using NaOH pellet with distilled water. The solution was stored for 24 hours. Alkali solution was prepared by mixing sodium silicate (Na$_2$SiO$_3$) with NaOH or KOH solution. The volcanic ashes and Al$_2$O$_3$ as the starting material, was mixed with alkali solution. The paste was then poured into 4 x 4 x 4 cm$^3$ and then vibrated for 5 min to remove air bubbles during pouring. After casting, the samples were cured at 70° C for 7 days. Before curing the samples in oven at 70° C, they were first cured in open air at ambient temperature for 30 min to avoid cracks due to rapid water evaporation. Then, the geomaterial formation of geopolymer was used FTIR spectroscopy.
3. Results and discussion

3.1. Geopolymer structure

Total chemical properties (Table 1) of volcanic ash showed that the SiO$_2$ / Al$_2$O$_3$ molar ratio is 5.26 for volcanic ash of Mt. Sinabung (Vsg) and 5.84 for volcanic ash of Mt. Merapi (Vmr) [14]. These values are content basic from raw material of geopolymer. After geopolymer volcanic ash is formed, the change in the ratio of SiO$_2$ / Al$_2$O$_3$ becomes 3.88 for Vsg 65/30 NaOH 10, and 3.66 for Vmr 65/30 NaOH 10. It showed that geopolymer have occurred optimally [15, 16] reported that the optimum value geopolymers was reported to vary from 3.3 to 4.5.

The type of volcanic ash influenced the formation of geopolymers (Figure 2). Geopolymer had cavities caused by volcanic glass content contained in the volcanic ash mineral. Volcanic glass content will result in the cavity [17]. While the hardening time influenced CaO content in the raw material. The higher the CaO content, the faster the geopolymer hardening time. Mt. Merapi (CaO; 6.22%) very quickly hardens with a curing time of 2 days at 70°C, while Mt. Sinabung (CaO; 5.87%) which requires more curing time for 4 days at 70°C. However, high CaO content affected the fragility and strength of geopolymers [18]. Geopolymer, which has high CaO content will easily crack, such as Vmr.

The use of the ratio of solid and liquid 65:35 produced better geopolymers compared to 70:30. The high comparison of liquid and solid caused the more unreactive of geopolymerization reaction. Hence, its resulted in concrete solids with low density but high porosity [5]. The alkaline molarity (NaOH and KOH) affects geopolymers, the optimum conditions of geopolymer were obtained at 10 M NaOH and 10 M KOH. Geopolymer with NaOH solution as activator has better geopolymer than geopolymer with KOH solution as an activator [19].

Figure 1. Schematic illustration of geopolymer preparation process.

Figure 2. Geopolymer (a) Vsg 65/35 NaOH 10, (b)Vmr 65/35 KOH 10, (c)Vsg 70/30 NaOH 10, (d)Vmr 70/30 KOH 10
Table 1. Total chemical composition of volcanic ash and geopolymer

| Sample  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | SO$_3$ | P$_2$O$_5$ | MnO | ZnO | Cl | TiO$_2$ | SiO$_2$/Al$_2$O$_3$ |
|---------|---------|-------------|-------------|-----|-----|--------|--------|-----------|-----|-----|----|---------|-------------------|
| Vsg$^a$ | 49.33   | 15.93       | 6.48        | 5.87| 0.79| 1.54   | 17.63  | 0.06      | 0.03| 0.06| 0.63| 5.26    |                   |
| Vsg1$^b$| 52.80   | 13.76       | 5.96        | 7.25| 3.67| 2.83   | 10.84  | 0.77      | 0.05| 0.83| 0.05| 0.53    | 3.88              |
| Vmr$^c$ | 59.65   | 19.06       | 4.41        | 7.23| 1.48| 2.75   | 3.17   | 1.05      | 0.12| 0.01| 0.15| 5.84    |                   |
| Vmr1$^d$| 53.77   | 14.99       | 5.96        | 9.76| 4.28| 4.80   | 2.57   | 1.15      | 0.16| 0.95| 0.12| 0.61    | 3.65              |

$^a$ Vsg (volcanic ash of Sinabung).
$^b$ Vsg1 (geopolymer of Vsg 65/35 NaOH 10M)
$^c$ Vmr (Volcanic ash of Merapi)
$^d$ Vmr1 (geopolymer of Vmr 65/35 NaOH 10M)

3.2. FTIR spectra

The infrared spectra of volcanic ashes and geopolymers presented in Figure 3 and 4. FTIR spectra of the geopolymer are characterized by the main absorption bands around 800 - 1200 cm$^{-1}$ region. This main feature refered asymmetric stretching vibrations of Si (Al)-O which indicated the formation of the amorphous aluminosilicate gel phase. The broad absorption band at 1026 cm$^{-1}$ for volcanic ash of Merapi (Figure 4) and 993 cm$^{-1}$ to volcanic ash of Sinabung (Figure 3) which is ascribed to the stretching vibrations of Si-O-Al/Si [20] clearly shifts to lower waves in geopolymers. The switch of the main band in volcanic ash of Mt. Merapi (1026 cm$^{-1}$), and Mt Sinabung (993 cm$^{-1}$) to lower wave 972 - 962 cm$^{-1}$ and 931 - 976 cm$^{-1}$ as a result of alkaline activation is an indication of the geopolymerization reaction, respectively [8, 10]. It is also observed that FTIR main band systematically switches to lower wave with concomitant increase in band intensity as molaritas alkali activator ratio increases in the system [21].

The absorption of sharp peak around 1600 cm$^{-1}$ and 2985 - 3321 cm$^{-1}$ are assigned to stretching (-OH) and bending (H-O-H) vibrations of bound water molecules [22], which gives evidence of adsorbed water in the geopolymers. The absorption bands between 1400 - 1500 cm$^{-1}$ are attributed to stretching vibrations of O-C-O bond indicating the presence of sodium bicarbonate that is suggested to occur due to the atmospheric carbonation [23]. The presence of sodium carbonate may disrupt the polymerization process. It was showed by solid/liquid (65:35) less steep compared to (70:30).

Figure 3 and 4, showed band of KOH solution higher than NaOH for geopolymer products. Geopolymers with KOH as activator has rather lower strength than geopolymer with NaOH solution as an activator. The difference between KOH and NaOH is due to ionic size where Na$^+$ is having smaller ionic size compares to K$^+$. Na$^+$ will be more active thus will enhance the dissolution process of aluminosilicate minerals [19].

4. Conclusions

The geopolymer of volcanic ash depends mainly on SiO$_2$/Al$_2$O$_3$ molar ratio and chemical composition from raw material. The results obtained showed that the strength of geopolymers increases with increasing amount of amorphous phase and decreases with increasing SiO$_2$/Al$_2$O$_3$ molar ratio of the amorphous phase. Geopolymerization phase increases with alkali solution, i.e., NaOH. However, it decreases with KOH. Geopolymers with very good and successfully prepared from Vsg 65/35 NaOH 10 formed geopolymers that are relatively stable.
Figure 3. FTIR spectra of Volcanic ash of Mt.Sinabung prepared geopolymer

Figure 4. FTIR spectra of Volcanic ash of Mt.Merapi prepared geopolymer

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