The potential use of volcanic deposits for geopolymer materials

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Abstract. Volcanic deposits are abundant in the vicinity of an active and inactive volcano. They are produced from the cooling of magma during explosive volcanic eruptions. They have varying physical properties and can range in size from sub-millimetric ash up to boulder size. As Indonesia is considered as an active volcanic region, volcanic materials are abundant but they are still unexploited to full capacity such as geopolymer raw material. Geopolymers are generally understood as alkali-activated aluminosilicates. They may be considered as an inorganic two-component system which consists of: [1] a reactive solid source of SiO₂ and Al₂O₃, and [2] an alkaline activation solution. The aim of the research is to identify the chemical and mineralogical properties of Merapi and Mt. Sinabung volcanic ashes as the raw material of geopolymers. Results showed that Mt. Merapi contained amorphous volcanic glass and crystalline [feldspar] minerals with 61.13% SiO₂; 17.78% Al₂O₃; 3.47% Fe₂O₃; 6.22% CaO. Mount Sinabung deposit contains amorphous volcanic glass also and crystalline [feldspar] minerals with an oxide content of 49.33% SiO₂; 15.93% Al₂O₃; 6.48% Fe₂O₃; 5.87% CaO. The high content of silica and alumina in this material showed that it was pozzolan material which can be synthesized to geopolymers. The molar ratio of SiO₂/Al₂O₃ was high, Merapi is 5.84 and Sinabung is 5.26.

1. Introduction
Volcanic deposits are produced from cooling magma during explosive volcanic eruptions [1]. They have varying physical properties and can range in size from sub-millimetric ash up to boulder size [2]. A fine solid material of volcanic deposits that are below 2 mm in diameter is called volcanic ash [3]. It can be found in an active and inactive volcano.

Indonesia has active and inactive volcanoes, more than 30% of the world's active volcanoes are in Indonesia, which is around 129 volcanoes [4]. Meanwhile, many volcanoes in Indonesia will result in a higher eruption which produces abundant volcanic deposits. The volume of volcanic deposits in 2010 eruption of Mount Merapi has estimated 1.5 x 10⁸ m³ with the thickness of tephra layer was from 2.5 cm to 10 cm [5], while a volcanic deposit of Mount Sinabung was approximately 3 x 10⁸ m³ with thickness was <10m to 20 m [6].

The composition of volcanic ash depends upon the chemistry of the source magma [7]. Most volcanic ashes contain the main components of silica and alumina, that it presents pozzolanic activity [8]. The volcanic ash of Mount Merapi contained 61.55% SiO₂ and 15.85% Al₂O₃ [9], while Mount
Sinabung contains 74.3% SiO2; 3.3% Al2O3 [10]. Hence, volcanic ashes are an aluminosilicate natural resource that can economically and environmentally benefit [11]. Nowadays, volcanic ash has been used as a soil ameliorant, cement and concretes, ceramic materials, adsorbent [8, 12-14]. Compared to the abundant amount, but volcanic ashes are still unexploited to full capacity [7, 15, 16]. Due to their pozzolanic nature, volcanic deposits will be easier to be applied and be more attractive for engineering that will produce new materials [17], they can be used in agriculture and non-agriculture. One of the new material from volcanic deposits is geopolymer [15, 18, 19, 20]. Geopolymers are a new class of three-dimensional inorganic polymer obtained by reaction of an aluminosilicate material with an alkaline solution [21]. The synthesis of geopolymers requires two components, namely a reactive solid source of aluminosilicates and alkaline solution [22]. The reactivity of volcanic ashes as a raw geopolymer material is affected by the chemical and mineralogical composition, the particle size distribution and the amount of the amorphous phase [11]. Geopolymers will be reactive if they consist of amorphous or non-crystalline minerals. Non-crystalline minerals in volcanic ash are volcanic glass and are found in quite high amounts to reach 25% in Mount Talang volcanic ash [23], and 60% are found in Mount Merapi volcanic ash [9]. Volcanic ashes as a raw material for geopolymers have drawn more attention in the past decades since it does not require high temperatures in processing compared to other sources of aluminosilicate [15]. This research aimed to identify the chemical and mineralogical properties of Mt. Merapi and Mt. Sinabung volcanic ashes as the raw material of geopolymers.

2. Materials and methods

2.1. Study area

The samples of volcanic ash were collected from Mt. Merapi and Mt. Sinabung. Mount Sinabung volcano is located in Karo District, North Sumatera Province, Indonesia [Figure 1], geographically on 3° 10’ 16.7” N and 98° 23’ 24.66” E, the summit is approximately 2,460 m above sea level [asl]. It is a stratovolcano that has been estimated for 400 years inactive, therefore it is categorized as B type of volcano [24]. It turned into type A when it erupted on August 27, 2010, with the type of eruption classified as phreatic [25], and it has been in continuous eruption in 2013, 2015, 2016, 2018.

Mount Merapi is at Central Java [7° 32.5’ S and 110° 26.5’ E] about 30 km north of Yogyakarta city, Indonesia [Figure 1], having a height of 2986 m above the sea level. Geologically, Merapi is a basaltic-andesite volcano formed due to subduction between the Australian oceanic plate and the Eurasian continental plate [26]. The volcano is a large Quaternary stratovolcano composed of volcanic materials deposits such as pyroclastic flow, lava, basaltic andesite tephra [27]. The volume of pyroclastic material in the 2010 eruption of Mt Merapi was estimated to be 1.5 x 10^8 m^3 with the thickness was from 2.5 cm to 10 cm [5].

2.2. Volcanic ash sampling

The volcanic ash from Mount Merapi was collected about 8 km west of the volcano when erupted in 2006 and 2010. They widely distributed in the west to the south area of the volcano having a thickness of about 20 cm. While volcanic ash from Mount Sinabung was taken in January 2017. It was derived from the eruption in 2010, 2013, 2014, and 2016. The samples were taken by a scope until a layer of the soil was found. They were air-dried ground and passed through a 2 mm sieve before chemical and mineralogical analyses.
2.3. Morphology, chemical and mineralogical characteristics analysis of volcanic ash
The color identification is used by the matching method using Munsell Soil Color Chart. The pH of the volcanic ash was determined potential metrically in both deionized water \([H_2O]\) and 1 M potassium chloride \([KCl]\) with a glass electrode in a 1: 2,5 solid/solution mixture. The CEC and exchangeable cations were extracted with 1 M \(\text{NH}_4\text{OAc}\) at pH 7. The phosphor was determined with the Bray II method and extracted with HCl 25%.

The elemental chemical composition of volcanic ash was determined using the X-ray fluorescence spectroscopy [XRF] tool brand PANalytical Epsilon 3. Mineralogical analyses of the volcanic ash were conducted using an X-ray diffractometer [XRD]. The XRD analysis was performed with a PANalytical XPERT-PRO00000000011130968 type. In this apparatus, the Cu Kα [wavelength \(\alpha_1 = 1.54060\) and \(\alpha_2 = 1.54443\) ] radiation, operating at 40 kV and 40 mA start angle \([\text{°}2\theta] = 10,0181\) and end angle \([\text{°}2\theta] = 99.9781\), and scanned from 3 to 45°/min range. Then, data processing used a High Score Plus software.

3. Results and Discussion

3.1. Morphology and chemical properties of volcanic ash
The morphological and chemical characteristics of the ash from Mount Merapi and Mount Sinabung are summarized in Table 1. Volcanic Ash from Mount Merapi had a different color from Mount Sinabung. The color of the volcanic ash was light gray [10 YR 7/1] for volcanic ash of Mt. Merapi, and gray [2.5 YR 5/1] for volcanic ash of Mt. Sinabung. The gray color of volcanic ash was caused by
rhyolite, decide, and andesite composition that it is a high concentration of non-colored glass and low content of mafic mineral [28]. The color of samples can be used to identify the mineral content of materials. The color of both volcanic samples indicated the presence of colorless minerals, such as feldspar and quartz [29].

### Table 1. Chemical properties of the volcanic ash

| Parameter                        | Mt. Merapi    | Mt. Sinabung  |
|----------------------------------|---------------|---------------|
| Color                            | 10 YR 7/1     | 2.5 YR 5/1   |
| pH KCl                           | 4.78          | 3.37          |
| pH H2O                           | 5.12          | 3.46          |
| P Bray 2 [mg kg\(^{-1}\)]       | 3.53          | 1.38          |
| P HCl 25% [mg kg\(^{-1}\)]      | 63.10         | 76.50         |
| CEC [cmol kg\(^{-1}\)]          | 0.47          | 0.40          |
| Exchangeable cations             |               |               |
| Exchangeable K [cmol kg\(^{-1}\)] | 0.45    | 0.51          |
| Exchangeable Ca [cmol kg\(^{-1}\)] | 0.74    | 0.87          |
| Exchangeable Mg [cmol kg\(^{-1}\)] | 1.11    | 1.37          |
| Exchangeable Na [cmol kg\(^{-1}\)] | 0.31    | 0.35          |
| Base Saturation [%]              | 552.96        | 767.32        |

Table 1 shows that the accumulated volcanic ash of Mt. Merapi and Sinabung had low pH with acid to very acid criteria. The pH values of the fresh volcanic ash were mostly acidic [5, 23]. The acidity is produced during a volcanic eruption from sulphuric content on volcanic ash surfaces that release protons. It shows in Table 2 that Mt. Merapi had a lower pH than Mt. Sinabung. The CEC of the accumulated volcanic ash of Mt. Merapi and Mt. Sinabung was considered very low [0.47 cmol kg\(^{-1}\) and 0.40 cmol kg\(^{-1}\), respectively]. These values had similarities with the CEC of Mt. Talang which had low value at 5.75 cmol kg\(^{-1}\) [30]. Exchangeable cation composition was similar for all volcanic ash samples and showed the following distribution trends: Mg > Ca > K > Na. The available volcanic ash phosphate content, extracted by Bray 2, was considered very low. The P available of volcanic ash from Mount Merapi tended to be higher than Sinabung volcanic ash about 155 %. The source of phosphate in volcanic ash was apatite mineral. The dissolution rate of apatite increased with decreasing pH. The potential phosphate, extracted with HCl 25%, was very high. Generally, the potential phosphate of the volcanic ash was considered very high, it was up to 68.02 mg kg\(^{-1}\) from Mt. Talang [30].

#### 3.2. Total chemical composition of volcanic ash

Table 2 lists the total chemical composition of all volcanic ash which was determined using the X-ray fluorescence [XRF] analysis. All of the samples primarily consisted of SiO\(_2\) and Al2O3 on its framework mineral and lots of elements-bearing minerals, such as Fe, Ca, Mg, K, S, Ca, and P. The composition of volcanic ash depended upon the chemistry of the source magma [7]. All volcanic ash samples were dominated by silica [49.33%-61.13%] which can be considered as andesite to basaltic andesitic [32].

The minerals that possibly present in this material were feldspars [Figure 2], ferromagnesian minerals [usually pyroxene or amphibole] and no quartz [28]. Hence, the volcanic ash was a
moderately gray color. Among volcanic ash samples, the accumulated volcanic ash of Mt.Sinabung contained very high sulfur. The calcium oxide $[\text{CaO}]$ found in the three studied ash was greater than the alkaline elements $[\text{K}_2\text{O}$ and $\text{Na}_2\text{O}]$. The greater contents of CaO is believed to be a result of greater plagioclase feldspar [labradorite] content, and the volcanic ash was considered to have basaltic andesitic composition [30].

Total chemical properties of volcanic ash of Merapi and Sinabung showed that the intended pozzolan materials which had a high content of SiO$_2$ and Al$_2$O$_3$. The content of SiO$_2$ and Al$_2$O$_3$ in volcanic ash is needed to form Si-O-Al chains in geopolymers. Therefore, the materials are potential for geopolymer syntheses. The ratio of SiO$_2$/Al$_2$O$_3$ molecule in Sinabung volcanic ash was 5.26, while Merapi was 5.84. These values are suitable for geopolymer synthesis, which are considered as basic ingredients and are contained in the intervals of geopolymer synthesis [7].

| Oxides   | Sample [%] | Mt. Sinabung | Mt. Merapi |
|----------|------------|--------------|------------|
| SiO$_2$  | 49.33      | 61.13        |            |
| Al$_2$O$_3$ | 15.93      | 17.78        |            |
| Fe$_2$O$_3$ | 6.48       | 3.47         |            |
| CaO      | 5.87       | 6.22         |            |
| MgO      | 0.79       | 1.69         |            |
| K$_2$O   | 1.54       | 2.94         |            |
| SO$_3$   | 17.63      | 4.99         |            |
| P$_2$O$_5$ | 1.32       | 0.80         |            |
| MnO      | 0.05       | 0.10         |            |
| ZnO      | 0.03       | 0.01         |            |
| Ag$_2$O  | 0.18       | 0.19         |            |
| TiO$_2$  | 0.63       | 0.43         |            |

The optimal value of the ratio SiO$_2$/ Al$_2$O$_3$ for geopolymers varies from 3.3 - 4.5 [32]. Comparison to another raw material geopolymer such as metakaolin and fly ash, volcanic ash materials generally has a higher SiO$_2$/Al$_2$O$_3$ molar ratio. Table 2 shows that volcanic ash of Mount Merapi would be less reactive as a raw of material geopolymer than Mount Sinabung, due to its higher silica content. The higher SiO$_2$/Al$_2$O$_3$ molar ratio in these samples need a high concentration of alkali [33]. Some studies reported that the addition of reactive aluminum can be useful for reactivity of volcanic ash such as calcium aluminum or aluminum hydroxide [34, 35]. Calcium oxide content was reported to affect the process of geopolymer synthesis [20, 35]. The higher CaO make the faster of the hardening time of geopolymer. On the other hand, the greater content CaO in volcanic ash from Mount Merapi than Sinabung may allow lower setting time in the Merapi geopolymers.

3.3. Mineralogical properties of volcanic ash

X-ray diffraction analysis is known based on the reaction of crystalline minerals. The XRD pattern of volcanic ash is illustrated in Figures 2 and 3. The mineralogical composition of volcanic ash of Mount Merapi and Mt. Sinabung had similarities between these samples. The main crystalline mineral content was feldspar. The feldspar is silicates mineral group. Silicates mineral is known as an important group of minerals, almost 40% of the common minerals in an igneous rock are silicates group. Based on the basic structure, feldspar is known as tectosilicates minerals. The previous studies had shown that Mount Merapi mineralogical composition consisted of feldspar, quartz, cristobalite [5], [36].
Feldspar is known that its structures are composed of corner-sharing AlO$_4$ and SiO$_4$ tetrahedra. Their framework could accommodate K$^+$, Na$^+$, Ca$_2^+$ and occasionally large cations. Feldspars were identified by the prominent peaks at 0.318, 0.319, 0.365, 0.376, 0.406, and 0.404 nm, which resulted from microscopic observation.

The diffractogram pattern obtained in X [angle 2 Theta = 2θ] between 15-35° shows that volcanic ash consisted of amorphous mineral structures. Amorphous minerals in volcanic ash were volcanic glass and were found in quite high amounts to reach 25% in Mt. Talang [23], and 60% were in Mt. Merapi [9]. Amorphous minerals in ash greatly affected geopolymer reactivity, high volcanic ash reactivity if there was a higher amorphous mineral content [18]. The Geopolymer synthesis was also influenced by mineral composition [33].

![Figure 2. XRD pattern volcanic ash of Mt. Merapi](image1)

![Figure 3. XRD pattern volcanic ash Mt. Sinabung](image2)


4. Conclusions
Mt. Merapi and Mt. Sinabung volcanic ash had macronutrient elements, such as K, Mg, Ca and P, which caused the volcanic ash to have great potential to agriculture. Then, volcanic ashes were a pozzolan material. Therefore, this material was potential for the synthesis of geopolymer materials. The ratio of \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) molecules in Sinabung volcanic ash was 5.26, while in Merapi was 5.84. and then, they had high amorphous minerals and crystalline minerals [feldspar].

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