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Extraction and Characterization of Silicon Dioxide from Volcanic Ash of Mount Sinabung, Indonesia: A Preliminary Study

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ABSTRACT

The study was conducted on the extraction of volcanic ash from Mount Sinabung through the co-precipitation method to recover silicon dioxide (SiO_2). The X-ray fluorescence (XRF) analysis showed that the SiO_2 content in volcanic ash was 48.5%, and after extraction, it was 99.1%. The morphology shown by scanning electron microscope (SEM) indicated that SiO_2 looks cleaner and tends to be the same size compared to the volcanic ash sample. The average particle size of volcanic ash and extracted SiO_2 were 32.28571 ± 2.51259 and 12.97521 ± 0.60657 µm, respectively. The X-ray diffractometer (XRD) analysis showed that the crystal structure of the volcanic ash sample was quartz, maghemite, and cristobalite. Besides, the extracted SiO_2 had an amorphous quartz crystal structure. The test conducted using Fourier transform infrared (FTIR) resulted in the absorption of 1095.57 cm^{-1} and 798.53 cm^{-1} for the Si–O–Si and Si–OH groups which were the groups of siloxanes and silanols, respectively.

Keywords: volcanic ash, characterization, electron microscopy, Mount Sinabung, particle size distribution.

INTRODUCTION

Mount Sinabung is one of the active volcanoes in Indonesia which spewed hot clouds in mid-September 2013. The hot cloud conditions reached a temperature of 700ºC and a distance of 4,500 meters which caused many villages around Mount Sinabung to be covered in thick volcanic ash for several months. During the eruption, people's livelihoods were disrupted by the explosive eruption of Mount Sinabung, which released much material in the form of volcanic ash and sand thrown as far as 5 km from the summit. Explosive eruptions involve the volcanoes which expel their materials into the air with a powerful eruption. These materials are in the form of clastic materials such as bombs (large lumps of rock), lapilli (small rocks such as gravel), and volcanic sand or ash.

Mount Sinabung ash is the ash produced from the eruption of Mount Sinabung, which replaces the properties and functions of cement after being mixed with additional chemicals. If the ash is used as an additive, it will make the concrete easier to mix, denser to water, more resistant to chemical factors, and reduce the expansion of concrete due to the alkaline silicate reaction process in the concrete mixture (Wijaya, 2018).

The abundance of volcanic ash material resulting from the eruption of Mount Sinabung is an interesting case to study. According to the tests that have been done using atomic absorption spectrophotometry (AAS), it was shown that the volcanic ash from Mount Sinabung contains 78.3% of SiO_2, 2.91% of Fe_2O_3, 4.56% of Al_2O_3, 1.07% of MgO, 4.84% of CaO and 0.46% of Na_2O. Silicon dioxide (SiO_2) is one of the most

abundant compounds in the volcanic ash of Mount Sinabung that have the potential to be used in a variety of needs. One of the ways to obtain high-purity of SiO_2 involves extracting these compounds from the natural sample using the co-precipitation method (Hasanah et al., 2021).

The potential of natural resources as a source of silica has been widely studied and known. As one of the abundant metal oxides in volcanic ash, silica can be used as a primary material for synthesizing silica gel through the formation of alkaline silicate precursors. Sodium silicate can be converted into silica gel by condensation and hydrolysis using solvents, both polar and non-polar. By extracting silica in an alkaline state, sodium silicate will be formed. Sodium silicate will undergo a polymerization process to form silica gel at several different conditions of pH and solvent. Silica gel is one of the silica-based materials with broad uses, such as in the ceramic industry or special applications in the chemical field. Silica gel has a significant molecular weight and absorbs much water, which will cause the formation of a spongy solid (Maulida et al., 2017).

Silica, which consists of silicon and oxygen, can be obtained from mineral, vegetable, and crystalline silica synthesis. Mineral silica is a compound that is commonly found in mining or excavation materials in the form of quartz sand, granite, and feldspar (Gonçalves & Bergmann, 2007). Silica is naturally found in crystalline and amorphous forms. Crystalline silica exists in three primary forms: quartz, tridymite, and cristobalite. The three general forms of crystalline silica are considered based on their stability to high-temperature increases. Each of the three forms mentioned before exhibits a change at high and low temperatures, where the structure is only slightly altered by a simple change in the orientation of the SiO_2, which is tetrahedral relative to each other. The changes in shape at high temperatures have higher symmetry or smaller unit cells than at low temperatures (Purba, 2018).

The use of silica is extensive in the commercial industry. Quartz sand is the primary raw material in glass, ceramic, foundry, cement, tile, and silicon carbide abrasives (sandblasting). On the basis of the explanation above, the extraction and characterization of SiO_2 gained from the volcanic ash of Mount Sinabung require investigation. This is a preliminary study supporting the further research on water treatment that will be conducted.

METHODS

This study uses a qualitative descriptive method that explains the results of the research procedure. The materials used in this study were the volcanic ash from Mount Sinabung. The technique used in this research involved the use of instruments in the laboratory such as scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), and X-ray fluorescence (XRF).

The analysis technique goes through several stages of the process, each requiring the tools mentioned earlier. The procedure in this study consisted of two main steps: extraction and characterization of SiO_2 from the volcanic ash sample. The sample was sieved with a 230-mesh sieve to homogenize the size. The volcanic ash that has been sifted was taken in the amount of 50 grams, soaked with HCl, and filtered. The sample was then washed and dried using an oven. After that, it was dissolved with 500 mL of NaOH and heated for 120 minutes, then filtered. The filtrate was tested gravimetrically. In this step, the filtered sample was sodium silica solution. Then, 8 M of HCl was dropped into the solution to form a white gel until pH of 7. Finally, the silica gel was deposited for 24 hours.

RESULTS AND DISCUSSION

The silicon dioxide (SiO_2) obtained from volcanic ash was characterized using several analytical instruments: SEM, FTIR, XRD, and XRF. The purposes of each instrument were as follows: (1) SEM was used to determine the morphology; (2) FTIR was applied to obtain the data about the functional groups; (3) XRD was used to describe the phase; and (4) XRF was applied to obtain the content information of oxide compounds. All of the instruments were applied to the volcanic sample before and after extraction.

Morphology analysis

Figure 1 shows morphological differences of the volcanic ash sample and the extracted SiO_2. The volcanic ash particles look more random than ordinary ash particles. The shape looks sharper and jagged. This was caused by the enormous gas pressure from the magma extrusion process at Mount Sinabung (Latif et al., 2016). Those shapes

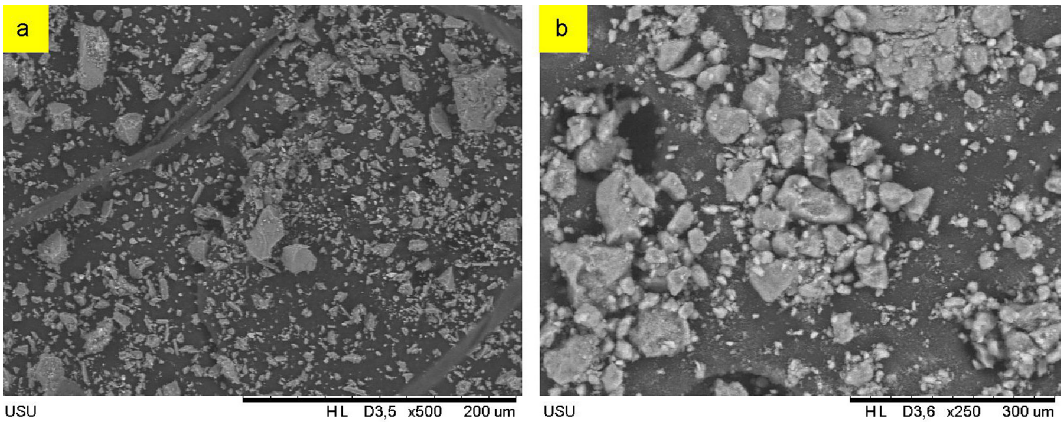

Figure 1. The morphology of (a) the volcanic ash of Mout Sinabung and (b) the extracted SiO_2

of volcanic ash must be dangerous if inhaled, because they can cause lungs infection and eyes irritation (Sinuhaji, 2014). Moreover, the pores formed in the extracted SiO_2 were also observed.

The SiO_2 obtained from volcanic ash extraction was subjected to SEM analysis. The morphology of SiO_2 looks cleaner, and the size tends to be the same. Using the *Image J* software as shown in Figure 2, the size of the volcanic ash particles and SiO_2 from the extraction of volcanic ash can be measured. The average particle size of volcanic ash and the extracted SiO_2 are 32.28571 ± 2.51259 and 12.97521 ± 0.60657 µm, respectively.

FTIR characterization

The absorption band of about 921 cm^{-1} on the volcanic ash spectra and 950 cm^{-1} on the extracted SiO_2 are related to the stretching vibration of the Si–O–Al bond (Alraddadi & Assaedi, 2020).

The appearance of stretching and bending vibration of the O–H group is due to the presence of water molecules and silanol groups (Si–OH) which are still contained, both in the volcanic ash before and after extraction (Liu et al., 2019; Utari et al., 2020).

On the basis of Table 1, the formation of sodium silicate (Na_2SiO_3), which indicates the presence of the Si–OH group, gives absorption at wavenumbers of 787 cm^{-1} and 802 cm^{-1}. The reaction mechanism for the formation of Na_2SiO_3, as shown in Figure 4, begins with the excitation of hydroxyl ion (–OH) in the silicon. In this reaction, one oxygen atom is released and forms SiO_2OH^- which is unstable. SiO_2OH^- undergoes the release of hydrogen atoms (dehydrogenation) to form SiO_3^{2-} and bonds with hydroxyl ions (O–H) to form water molecules (H_2O). Na^+ from

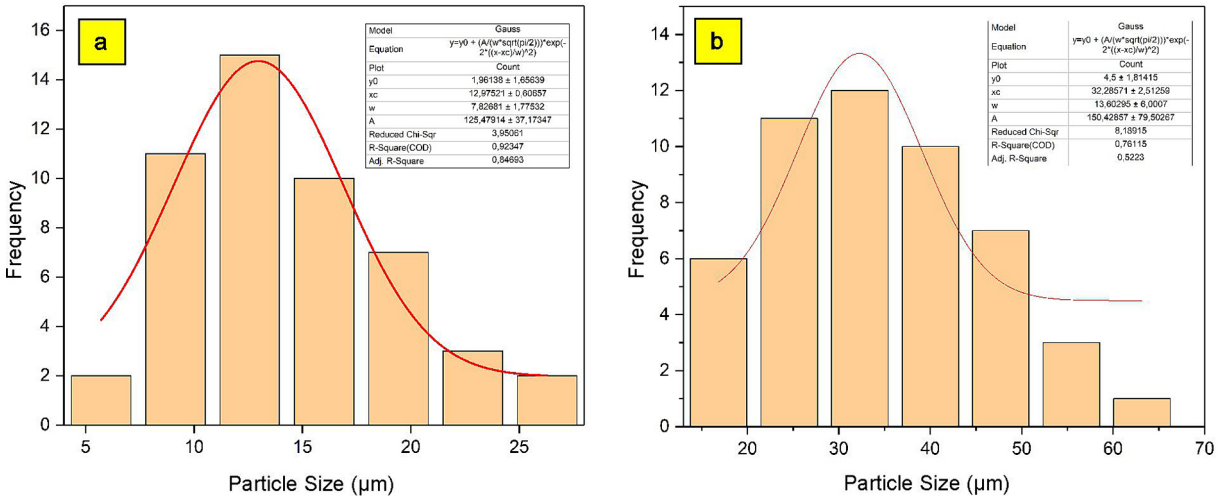

Figure 2. Particle size distribution of (a) volcanic ash sample from Mount Sinabung and (b) the extracted SiO_2

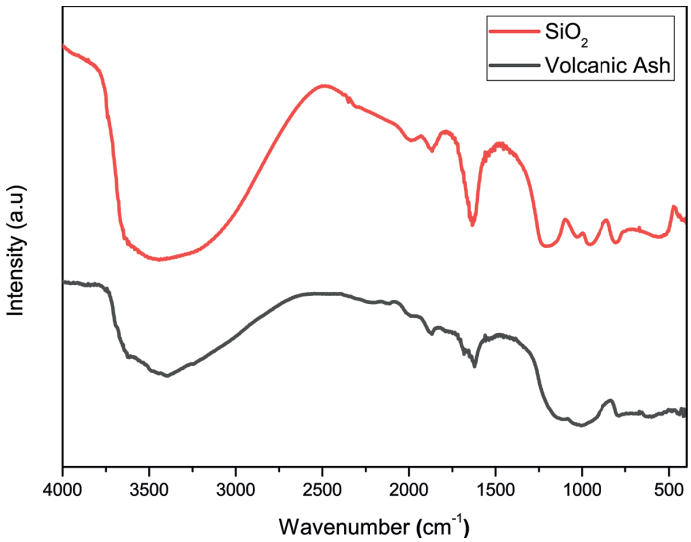

Figure 3. FTIR spectra of volcanic ash and SiO_2

Table 1. Functional groups interpretation of volcanic ash sample (before and after extraction)

Functional groups	Wavenumber (cm^{-1})	
	Before extraction	After extraction
O–H (stretching)	3396	3451
O–H (bending)	1622	1632
Si–O–Si (stretching)	1008	1030
Si–O–Al (stretching)	921	950
Si–OH (stretching)	787	802
Si–O (stretching)	545	555

sodium hydroxide (NaOH) and SiO_3^{2-} anions will form Na_2SiO_3.

The absorption peaks at 1008 and 1030 cm^{-1} are associated to the functional groups of Si–O–Si, which are siloxane groups. The absorption peaks of 545 and 555 cm^{-1} are attributed to the Si–O functional group of the siloxy. The reaction mechanism for the formation of SiO_2 is shown in Figure 5. Si–O and Si–O–Si functional groups were formed when hydrochloric acid (HCl) was dropped into Na_2SiO_3 to produce SiO_2 and form Si–O–Si functional groups (Caroles, 2019). During the process, Na^+ will bind with Cl^- to form NaCl salts which are dissolved in water and leave an $Si(OH)_4$ precipitate. The addition of acid causes the O–H group to detach and form a siloxane bond. The more acid added, the more siloxane bonds formed, which finally resulted in silica gel formation. The silica gel formed was washed until neutral using distilled water to remove the remaining acid and salt. The silica gel was then dried to obtain solid SiO_2.

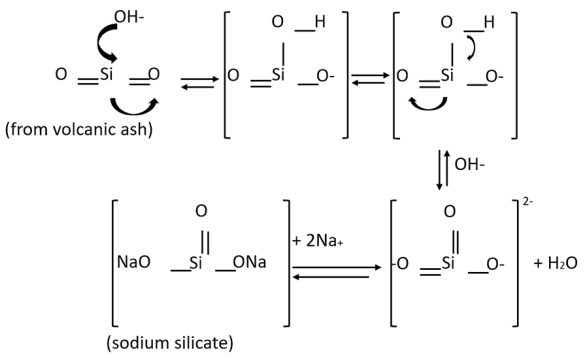

Figure 4. The reaction mechanism in the formation of sodium silicate (Na_2SiO_3)

XRD analysis

The results of XRD analysis are featured using the *Match2* software as a diffractogram. There are three crystal structures observed using XRD, specifically quartz (SiO_2), maghemite (Fe_2O_3), and cristobalite (SiO_2) so that Mount Sinabung volcanic ash can be asserted as a polycrystalline material.

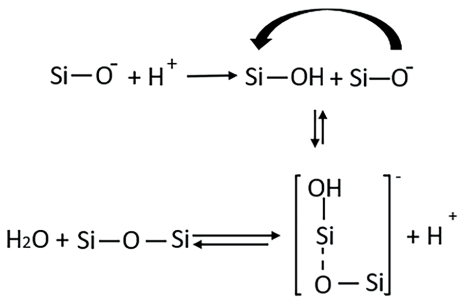

Figure 5. The reaction mechanism of SiO_2 formation

Figure 6 shows the diffractogram that was analyzed using the *Match2* software. Quartz crystal structure according to COD:9012602 has a trigonal crystal system with lattice parameters of a=4.7050 and c=5.2500. Quartz is identified at angles of 2θ=21.84º, 27.68º, and 42.20º with Miller indices of (110), (011), and (111) (Tian et al., 2020). In turn, the maghemite structure, according to COD:9006317, has a cubic crystal system with lattice parameters of a=8.3300. Maghemite is identified at angles of 2θ=23.58º, 30.58º, and 35.58º with Miller indices of (201), (202), and (311) (Lemougna et al., 2011). According to COD:9009685, the crystal structure of cristobalite has a tetragonal crystal system with lattice parameters of a=4.9570 and c=6.8903. Cristobalite is identified at an angle of 2θ=31.42º with Miller index of (012). The emergence of the crystal structure of quartz and cristobalite is due to the temperature difference in the magma body of Mount Sinabung. The high-temperature forms the cristobalite structure, and the lower one forms the quartz structure. The three crystal structures appeared according to the XRF analysis, which represent SiO_2 and Fe_2O_3 as the highest content in the volcanic ash sample.

The XRD test results for SiO_2 from the extraction of volcanic ash showed amorphous properties (Amin et al., 2016). This can be seen from the peak that is wide and not sharp. Figure 7 shows the crystal structure of SiO_2 as quartz. The quartz crystal structure according to COD:9012605 has a trigonal crystal system with lattice parameters of a=4.5350 and c=5.1700. Quartz is identified at an angle of 2θ=22.74º with a Miller index of (100). The absence of other crystal peaks indicates the purity of the SiO_2 obtained from volcanic ash extraction (Dubey et al., 2015).

XRF analysis

XRF is an instrument used to characterize the content of metallic elements and metal oxides in the samples. There was a color change in the sample before and after extraction. Before extraction, the volcanic ash sample was gray, and after extraction, the volcanic ash of Mount Sinabung turned white.

Table 2 shows the volcanic ash content with SiO_2 as the most abundant (48.5%). It indicates that the volcanic ash from Mount Sinabung is a raw material that can be used to yield SiO_2. A chemical process was carried out using the co-precipitation method to obtain SiO_2. This is a consecutive method to obtain metal deposits and remove impurities from the material. The following is the reaction that occurs in the volcanic ash sample during the extraction using the co-precipitation method:

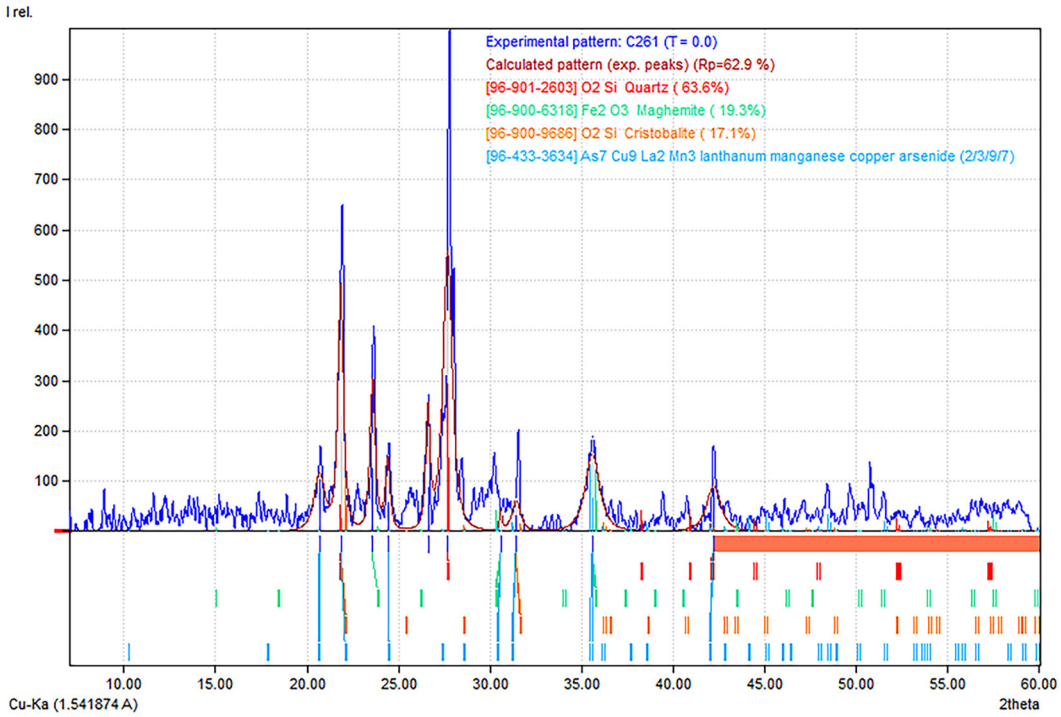

Figure 6. Diffractogram of volcanic ash processed using the *Match2* software

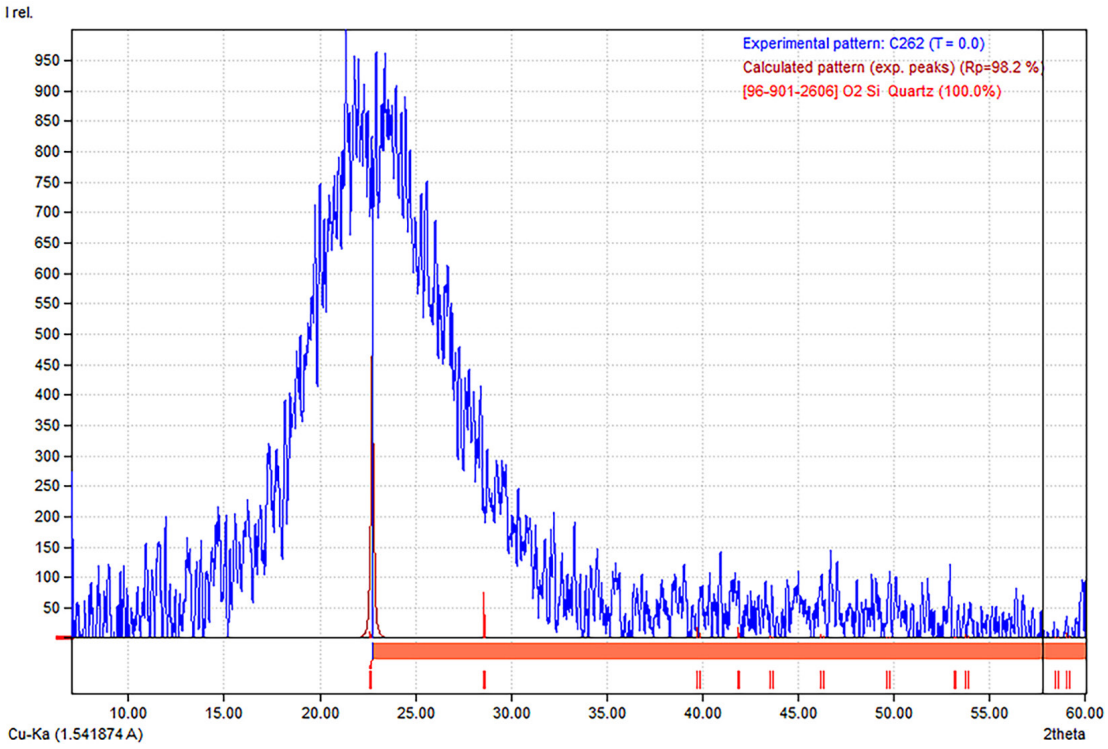

Figure 7. Diffractogram of the extracted SiO_2 from volcanic ash processed using the *Match2* software

Table 2. Compositions of the volcanic ash sample from Mount Sinabung

Compounds	%
SiO_2	48.5
Fe_2O_3	15.5
Al_2O_3	12
CaO	11.1
SO_3	6.7
K_2O	2.71
MoO_3	1.7
TiO_2	1.25
SrO	0.21
MnO	0.17
Re_2O_7	0.1
BaO	0.06
V_2O_5	0.056
CuO	0.051
Cr_2O_3	0.042
ZnO	0.008

$$SiO_{2(s)}\ (\text{volcanic ash}) + NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(aq)} \quad (1)$$

$$Na_2SiO_{3(aq)} + H_2O_{(aq)} + 2HCl_{(aq)} \rightarrow Si(OH)_{4(aq)} + 2NaCl_{(aq)} \quad (2)$$

$$Si(OH)_{4(aq)} \rightarrow SiO_{2(s)} + H_2O_{(aq)} \quad (3)$$

HCl solution performs as a precipitation agent. SiO_2 compounds are easily soluble in alkaline solutions and precipitate in acidic solutions. Therefore, to gently extract the SiO_2 compound from the volcanic ash, an alkaline solvent such as NaOH solution was used. Following that, an acid solution of HCl was used to form deposit. The deposit was dried in an oven to free SiO_2 from water (Agung M et al., 2013). The addition of HCl solution is intended to dissolve the metal oxide compounds contained in the volcanic ash to reduce and eliminate the metal oxide content (Naufal et al., 2013).

On the basis of Table 3, it was known that the SiO_2 level increased while other oxides decreased after the extraction process. The value of the SiO_2 content is found to be 99.1%. Hence, it can be concluded that the co-precipitation method is reliable to recover SiO_2 and remove other metal oxides or impurities from volcanic ash samples.

CONCLUSIONS

This study found that XRF could give the information about the SiO_2 content in volcanic ash samples before and after extraction, the values of which were 48.5% and 99.1%, respectively. This means that the co-precipitation method was

Table 3. Compositions of volcanic ash after extraction

Compounds	%
SiO_2	99.1
Fe_2O_3	0.357
CaO	0.35
TiO_2	0.069
Cr_2O_3	0.025
NiO	0.006
Eu_2O_3	0.069
Yb_2O_3	0.03
CuO	0.031

successful in extracting SiO_2. In addition, the characterization by other instruments shows that the volcanic ash sample is a polycrystalline material, as shown by the XRD results. Meanwhile, the characterization results using FTIR can explain the reaction mechanism about the formation of SiO_2 during the extraction process. The particle size distribution was described using SEM, both before and after the extraction of the volcanic ash sample, with values of 32.28571 ± 2.51259 and 12.97521 ± 0.60657 μm, respectively.

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