



Research Article

Effect of Stirring Time on Sodium Silicate Synthesis from Mount Kelud Volcanic AshIsna Nurhidayati^{1,2}, Endang Tri Wahyuni^{2*}, Nurul Hidayat Aprilita², Sarwendah Ratnawati Hermanto³¹ Department of Analytical Chemistry, Politeknik AKA Bogor, Jl. Pangeran Sogiri No. 283, Tanah Baru, Bogor Utara, Kota Bogor, Jawa Barat, Indonesia, 16154² Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara Bulaksumur 21, Yogyakarta, Indonesia, 55281³ Politeknik Negeri Ketapang, Jl. Rangka Sentap – Dalong, Kabupaten Ketapang, Kalimantan Barat, 78813**ARTICLE INFO****ABSTRACT****Article History**

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This study synthesized sodium silicate from the volcanic ash of Mount Kelud with various stirring times in the sodium silicate synthesis process. Synthesis of sodium silicate was carried out by alkaline extraction at low temperatures. This method was based on the solubility of silica under alkaline conditions. The dissolution of silica (SiO_2) in the volcanic ash of Mount Kelud was extracted using NaOH solution to form sodium silicate (Na_2SiO_3). The effect of stirring time on dissolved silica concentration was conducted with variation times of 0.5; 1; 1.5; 2; 2.5; 3, and 4 h using AAS (Atomic Absorption Spectrometry). The amount of dissolved silica increased sharply with the longer stirring time; however, the dissolution of silica was slow for a stirring time of more than 2.5 hours. The optimum of dissolved silica (SiO_2) was 19.82% at a stirring time of 2.5 h. The concentration of dissolved silica was very low because of semicrystalline silica and aluminium oxide in volcanic ash.

Keywords: volcanic ash, silica, sodium silicate, stirring time

1. Introduction

As an archipelagic state situated at the meeting point of three tectonic plates (Eurasian, Indo- Australian, and Pacific plates), the continuous movement of the plates makes Indonesia prone to natural disasters, such as tectonic earthquakes, volcanic earthquakes, and tsunamis. Moreover, Indonesia is one of the countries located in the ring of fire and has many active volcanoes. Lava flows, the release of gases, tephra, and ashfall from volcanoes can endanger humans. Volcanic eruption leads to huge losses of property, crop, plantation, and water sources damage. The disaster can cause fatalities, mainly the residents living alongside volcanoes.

Mount Kelud is an active volcano located on the border of Kediri, Blitar, and Malang Regencies in East Java Province, which produces explosive eruptions [1]. The volcanic materials of Mount Kelud eruption on February 13, 2014, thrown to other areas outside East Java. This eruption is the largest eruption of Mount Kelud that occurred in the 21st century [2]. Lava flows and material released from Mount Kelud in 2014 had caused volcanic ash rain in several places outside East Java, such as in Solo and Yogyakarta [3]. The volcanic ash carried by the wind and reached Yogyakarta caused pollution of water sources, disturbed vision, and health problems.

Many studies have been conducted regarding the impact of volcanic eruptions on the agricultural and fisheries sectors. However, research related to the utilization of Mount Kelud's volcanic ash has not been studied intensively. In general, ash or material from volcanic eruptions, such as Mount Kelud, contains oxides of several metal elements, such as Si, Al, Fe, Ca, Mg, Na, K, and P [4, 5, 6]. The volcanic ash's silica oxide (SiO_2) content, such as sodium silicate (Na_2SiO_3), makes it a potential alternative for making silica-based products. Silica can be derived from precursors, such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). The use of TEOS and TMOS precursors is considered relatively expensive

[7, 8]. Those alkyl orthosilicates are the most commonly used silica source. Because TEOS and TMOS are flammable materials and have difficulties handling and storage, it needs to explore alternative sources of silica [9]. Apart from synthetic results, silica oxide can also be obtained from volcanic ash with a relatively high concentration. In the previous report, the volcanic ash of Mount Kelud has silica oxide of 55.19% [10].

Volcanic ash expelled abundantly from the earth's bowels during volcanic eruptions. The high levels of silicate oxide in the volcanic ash of Mount Kelud make it a potential source of silica oxide. Sodium silicate is also known as an alternative silica source [11, 12, 13]. Commercial preparation of sodium silicate solutions can be achieved by reacting SiO₂-containing material such as quartz sand with carbonates or sulfates of alkali metals at temperatures exceeding 1300°C, with subsequent dissolution in the water below 200°C for several hours [14]. This synthesis route is energy-intensive and generates carbon dioxide and sulfur trioxide emissions that must be managed [15]. Therefore, developing a simple and low-energy method for the production of sodium silicate solutions is needed. This paper demonstrated silicon extraction for the production of sodium silicate solution as a silica oxide source.

2. Materials and Methods

2.1. Materials

This study used the volcanic ash of Mount Kelud eruption on February 13, 2014 carried by the wind and reached Pogung Kidul, Sinduadi, Mlati, Sleman, Yogyakarta. Some chemicals used are HCl 37% p.a (Merck), NaOH p.a (Merck), Whatman 42 filter paper (Merck), and universal indicators (Merck).

2.2. Volcanic Ash Characterization

The characterization of volcanic ash to determine the chemical and mineral compositions was conducted using XRF and XRD spectroscopy. X-ray spectroscopy was performed by an X-ray diffractometer (XRD) of Shimadzu type 6000X, while fluorescence spectroscopy was carried out by the Bruker S2 Ranger Spectrophotometer.

2.3. Volcanic Ash Preparation

Volcanic ash was washed by soaking and decantation. Afterward, the ash was dried under the sun. The dried ash was crushed and then sieved with a 250 mesh sieve to obtain volcanic ash with a homogeneous size.

2.4. Synthesis of Sodium Silicate

Sodium silicate synthesis was conducted by stirring 5 grams of volcanic ash with 30 mL of 6 M HCl solution for 2 hours. This step aims to remove elements as impurities from the solid waste material. The ash was filtered using filter paper, and the residue was washed with distilled water until it became neutral, then dried in the oven. The dried ash was added with 30 mL of 5 M NaOH solution. The mixture was heated up to $\pm 95^{\circ}\text{C}$, and stirred with varying stirring times, namely for 0.5; 1; 1.5; 2; 2.5; 3 and 4 hours. The purpose of this step is to extract silica in the volcanic ash as a sodium silicate solution. The cooled sodium silicate solution was filtered off to separate from the solid. The filtrate was put into a plastic bottle, then analyzed using an atomic absorption spectrophotometer (AAS) to determine its Si content.

2.5. Determination of Silica Concentration

The silica in the sodium silicate solution was analyzed by AAS (the Perkin Elmer brand type 3110). Sodium silicate solution with various stirring times was diluted into 50 mL of volumetric flask. The standard curve is made by diluting Si standard solution at a concentration of 0, 20, 40, 60,80, and 100 ppm. The concentration of Si was calculated by its absorbance on the corresponding standard curve. According to Proust's Law, the concentration of silica (SiO₂) was calculated by the ratio of molecular weight.

3. Result and Discussion

3.1. Analysis of Mount Kelud Volcanic Ash

The analysis was conducted to determine the chemical and mineral composition of the volcanic ash of Mount Kelud by using XRF and XRD methods, respectively. The results of XRF analysis was shown in **Table 1**, which indicated that the metal oxides of the volcanic ash of Mount Kelud was dominated by silica (SiO₂) of 56.29%, followed by Al₂O₃ and Fe₂O₃. The diffraction pattern of the volcanic ash of Mount Kelud was shown in **Figure 1**. Sharp peaks were apparent at various angles of 2 θ with various intensities. The 2 θ sample data were converted into d values according to Bragg's law. Identification was carried out by comparing d samples with d standards as presented in **Table 2**. It can be seen that the main mineral content of the volcanic ash of Mount Kelud was silica (SiO₂), Al₂O₃ and Fe₂O₃. These results was supported

by the XRF analysis (**Table 1**). The volcanic ash of Mount Kelud containing a high silica composition makes it a potential alternative raw material for the manufacture of several silica-based compounds, such as silica gel and sodium silicate [16].

Table 1. The Composition of Volcanic Ash Oxides of Mount Kelud

No	Oxide Compounds	Composition (%)
1	SiO ₂	56.29
2	Al ₂ O ₃	15.65
3	Fe ₂ O ₃	10.90
4	CaO	9.91
5	MgO	2.49
6	K ₂ O	1.56
7	TiO ₂	1.01
8	P ₂ O ₅	0.66
9	SO ₃	0.49
10	Cl	0.44

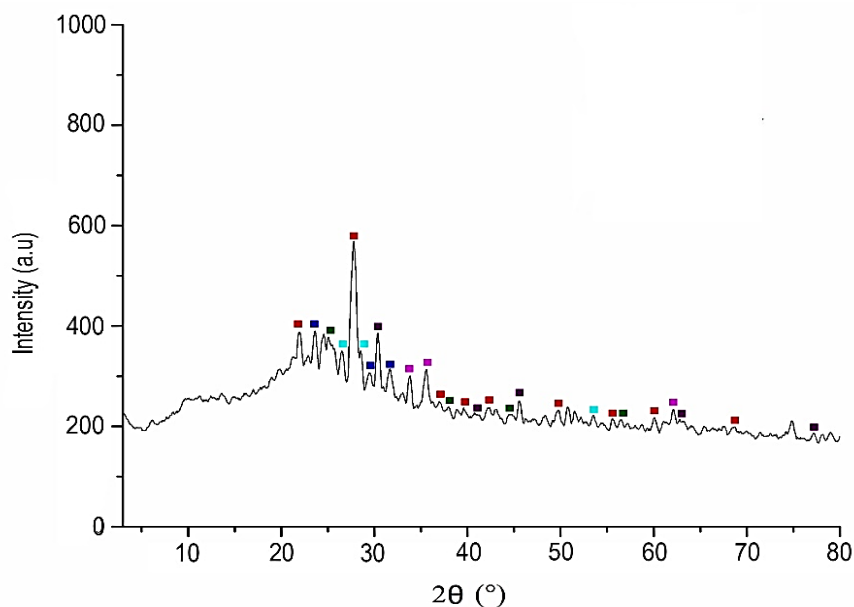


Figure 1. Diffractogram of Mount Kelud's volcanic ash : SiO₂ quartz (■), SiO₂ stishovite (■), SiO₂ coesite (■), SiO₂ christobalite (■), Al₂O₃ diaspore (■), Fe₂O₃ hematite (■)

3.2. Sodium Silicate Solution Preparation

The aim of washing of volcanic ash using 6 M HCl solution is to dissolve other oxides besides silica (SiO₂). The dissolution reaction of metal oxides with HCl is shown in **Equation 1, 2, and 3** [17].



The preparation of sodium silicate has been carried out by several previous researchers. Sodium silicate as a source of silica (SiO₂) can be obtained from rice husk ash by dissolving rice husk ash with NaOH [18, 19]. According to **Equation 4**, dissolution of silica from rice husk ash with NaOH produces sodium silicate (Na₂SiO₃) [20, 21].



In the preparation, silica in the volcanic ash was dissolved using NaOH solution with heating and stirring. This method was referred to Kalapathy et al. with modification [22]. The dissolving of silica with NaOH solution was influenced by several factors, such as NaOH concentration, extraction time, and solid/solution ratio [23]. Therefore, this study analyzed the effect of stirring time on the amount of dissolved silica.

The aims of stirring were to homogenize the solution and regulate silica extraction in volcanic ash by NaOH. The stirring range was carried out with time variations of 0.5-2.5 h. The effect of stirring on silica dissolution can be seen in **Figure 2**. It showed that the longer the stirring time, the greater of silica solubility. However, the solubility of silica was very slow for the stirring time of more than 2.5 h. Based on the experiment, the optimal stirring time was at 2.5 h with silica (SiO₂) solubility of 19.82%.

Table 2. Types of Volcanic Ash Crystals of Mount Kelud

2θ Sample (deg)	d Sample (Å)	d Standard (Å)	Standard Crystal Types
21.200	4.1875	4.26	SiO ₂ quartz (JCPDS 5-0490)
27.743	3.212	3.343	
49.647	1.834	1.817	
60.015	1.540	1.541	
30.365	2.941	2.959	SiO ₂ stishovite (JCPDS 15-26)
45.565	1.989	1.981	
62.76	1.479	1.478	
25.640	3.471	3.43	SiO ₂ coesite (JCPDS 14-654)
28.480	3.131	3.09	
53.455	1.712	1.71	
21.860	4.062	4.05	SiO ₂ cristobalite (JCPDS 11-695)
29.426	3.032	3.14	
31.620	2.826	2.841	
Widened peak 20-30			
			SiO ₂ amorf
22.860	3.887	3.99	β-Al ₂ O ₃ ·H ₂ O (diaspore) (JCPDS 5-355)
38.800	2.315	2.317	
44.665	2.027	2.077	
33.772	2.651	2.69	Fe ₂ O ₃ (hematite) (JCPDS 13-534)
35.505	2.526	2.51	
62.07	1.494	1.484	

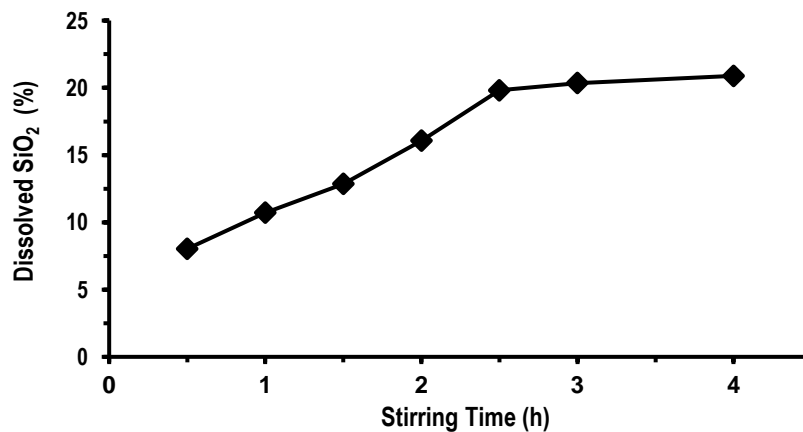


Figure 2. Effect of stirring time on the amount of dissolved silica

The solubility of silica occurred because of the reaction between NaOH and silica (SiO₂) in volcanic ash to make sodium silicate solution (Na₂SiO₃). Stirring time showed the reaction time between silica and NaOH. The increase in stirring time caused an increase in the reaction time between SiO₂ in volcanic ash and NaOH, resulting in a larger amount of silica solubility. For a stirring time of more than 2.5 hours, the amount of dissolved silica was relatively high enough. It was followed by reducing the contact between NaOH and silica and causing the amount of soluble silica to be relatively constant. Based on these data, the optimal stirring time was 2.5 h.

The amount of dissolved silica was relatively small, and it might cause silica in the volcanic ash in semi-crystalline form (**Figure 1**), making it difficult to extract. Amorphous silica in various conditions is more reactive than crystalline silica. Aluminium oxide (Al₂O₃) in volcanic ash also dissolved in the NaOH to form impure sodium silicate. Low dissolved silica could be caused by impure sodium silicate.

4. Conclusion

Mount Kelud volcanic ash can be used to manufacture silica-based materials, such as sodium silicate. The synthesis of sodium silicate from the volcanic ash using the alkaline extraction method was considered more economical because it did not require high temperatures. The results showed that stirring time influenced the silica extraction. The longer the stirring time, the longer the reaction between silica in volcanic ash and NaOH, which results in a greater amount of dissolved silica. Crystalline silica in volcanic ash caused the dissolved silica to be relatively low. Based on the experiment, the optimum stirring was at 2.5 hours with dissolve silica (SiO_2) of 19.82%.

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