Synthesis and characterization of silica gel from Lapindo mud Sidoarjo

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Abstract. Silica gel was synthesized from Lapindo mud by the sol-gel process. XRF analysis confirmed that Lapindo mud contained silica (50%) which was major components, therefore Lapindo mud has great potential as a raw material for silica gel synthesis. Metal silicates commonly used as a precursor to prepare silica gel. A Lapindo mud was mixed with an alkaline solution, stirred and heated to prepare metal silicates. Hydrochloric acid was then slowly added to the metal silicates solution to obtain silica gel. The pH 4 selected as the optimum pH in the synthesis of silica gel. The purity of synthesized silica was determined by XRF and shown that silica purity by 100 mL sodium hydroxide 6 M (4 h, 80 °C) treatment was 63.25% with optimum yielded 32.3%. Whereas 12 M potassium hydroxide 200 mL (5 h, 90 °C) treatment could be produced better purity up to 77.71% with a yield of 39.72%.

1. Introduction

Lapindo Mudflow is in Porong District, Sidoarjo Regency, East Java (Figure 1). Mudflow has occurred almost 13 years and has caused a lot of losses, especially for residents. Mudflow is a burst of volcanic eruptions in the lowlands, with a flow of 180,000 m³/day, bursts erupting with a constant flow rate of 5000-10,000 m³/day for several months. Bursts were expected to have a flow rate of 100 m³/day in the next 26 years. The utilization of Lapindo mud is needed because of its abundant presence. The study on the utilization of Lapindo Mud has been carried out including as additional material in the manufacture of cement and bricks [1-4], geopolymer [5-7], lightweight concrete [8], pavement fillers [9], a catalyst at transesterification of oils waste [10]. Lapindo mud has also been used as an adsorbent for orange metal textile dyes [11], and adsorbents in ethanol purification [12].

According to Aristianto [13], the study on Lapindo Mud has stated that there was a content of volcanic material rich in minerals. Silica content in Lapindo mud reaches 53.03% and is the most abundant element compared to other compounds. This makes Lapindo mud potentially large enough to be used as a source of silica in Indonesia and is very likely to be used as one of the developments in the production of silica gel. Silica gel can be produced from sodium silicate solution by hydrothermal method with a sol-gel process [14]. Previous researchers have successfully synthesized silica gel through the sol-gel process with siliceous sand of southern Tunisia [15], synthesized silica nanoparticles from clay [16], and synthesized silica gel from Douiret sand (Southern Tunisia) [17]. Therefore, in this study...
Lapindo mud was used in the production of silica gel. Silica gel was an amorphous material with a high absorption capacity so that it has been widely used as an air humidity absorber in the storage of hygroscopic materials such as food products, medicines, bags, shoes, electronic equipment and so on. This work aimed to characterize a local material and to produce silica gel from Lapindo mud through a synthesis method with optimum reaction conditions to obtain high-quality silica gel. Characterization of synthesis silica gel using X-Ray Fluorescence analysis. The synthesized material will be used to adsorb air humidity with variations in humidity levels and contact time.

![Figure 1. Map of the location of Lapindo mud Sidoarjo, East Java.](image)

2. Materials and methods

2.1. Materials
Lapindo muds were collected from 2 Km from the explosion center. Commercially available distilled water, sodium hydroxide (NaOH), potassium hydroxide (KOH), and hydrochloric acid (HCl) were purchased from a local market.

2.2. Methods
Lapindo mud was cleaned from impurities. The mud was soaked in distilled water for 24 hours while dried at 110 °C. The subsequent dry mud has been pounded into powder. Mud compositions were determined by XRF. 20 grams of mud powders were put into the beaker glass and added alkaline solution while stirring with a magnetic stirrer for various concentration, hours and temperature. The mixture was filtered and the filtrate was slowly titrated with 12 M HCl at room temperature to pH 4 and white precipitate appeared. The suspension was left at room temperature for 24 hours, then filtered and washed with distilled water five times to remove impurities (Figure 2). The purity of silica was determined by XRF. Silica gel was characterized and calculated the yield. The yield of silica gel was determined from equation (1)

\[
\% \text{ yield} = \frac{m_2}{m_1}
\]  

(1)

Where,

\( m_1 \) = mass of Lapindo mud (g)

\( m_2 \) = mass of silica gel (g)
3. Results and discussion

The composition of Lapindo mud was determined by XRF and given in Table 1. The Lapindo mud contained Al₂O₃ 6%, CaO₂ 8.59 % and Fe₂O₃ 27.7% and SiO₂ 50% as major components, so it has the potential to be a source of silica. To produce silica-rich mud, Lapindo mud was soaked in distilled water followed thermally treated at 110 °C for 24 h to removed organic impurities. Synthesis of silica gel from Lapindo mud was carried out following this step, first, preparation of the metal-silicates solution and then destabilization of metal silicates solution by addition 12 M hydrochloric acid slowly under continuous stirring until the gel was obtained.

To produce silica gel, the Lapindo Mud was treated at 80 °C for (1-5) hours with 100 mL NaOH 6M. Experimental data presented in Table 2 shows an increasing trend in yields with an increase from 1 hour to 4 hours of reaction. Then reduced during 5 hours of reaction. The optimal time for the reaction is obtained at a reaction time of 4 hours, which is equal to 32.2%. The yield was obtained from the ratio of the percentage of silica obtained with the initial mass of the sample. The choice of optimum time could be important to determine the optimum reaction conditions in extracting silica from Lapindo mud.

The results of the silica gel synthesized with an treatment of 200 ml KOH (6, 8, 10, 12, and 14) M at 90 °C for (1, 2, 3, 4, 5) hours are shown in Table 3. An increasing trend yield with increasing concentrations from 6 to 14 M. The yield is higher with increasing KOH concentration used. At a concentration of 14 M, it shows a very large product. Transparent lumps of crystal appear that have not previously appeared in other reactions. It's suspected that the product was not pure. So that optimal results are obtained at a concentration of 12 M, which is as much as 27.3%. The results also show an

Figure 2. Preparative experimental flow chart for silica gel.
increasing trend with an increased reaction time from 1 to 5 hours. The most yield obtained at 5 hour reaction time which is 39.72%.

Table 1. Composition of Lapindo mud analized by XRF.

| Compound | Concentration (%) |
|----------|-------------------|
| SiO₂     | 50.00             |
| Al₂O₃    | 6.00              |
| SO₃      | 1.60              |
| K₂O      | 2.46              |
| CaO      | 8.59              |
| TiO₂     | 2.02              |
| V₂O₅     | 0.10              |
| MnO      | 0.44              |
| Fe₂O₃    | 27.70             |
| CuO      | 0.14              |
| ZnO      | 0.05              |
| Br       | 0.08              |
| Rb₂O     | 0.04              |
| SrO      | 0.49              |
| ZrO₂     | 0.10              |
| Re₂O₇    | 0.07              |

Table 2. Details of experiments synthesis product with NaOH treatment at various reaction times.

| Lapindo mud (g) | Sodium Hydroxide (M) | Time reaction (h) | Silica gel (g) | Yield (%) | Physical appearance of Silica gel |
|-----------------|----------------------|-------------------|----------------|-----------|----------------------------------|
| 20              | 6                    | 1                 | 4.1            | 20.5      | Fine crystalline                 |
| 20              | 6                    | 2                 | 3.6            | 18.0      | Fine crystalline                 |
| 20              | 6                    | 3                 | 6.4            | 32.1      | Fine crystalline                 |
| 20              | 6                    | 4                 | 6.4            | 32.2      | Fine crystalline                 |
| 20              | 6                    | 5                 | 4.3            | 21.4      | Fine crystalline                 |

Table 3. Details of experiments and synthesis product with KOH treatment.

| Lapindo mud (g) | Potassium Hydroxide (M) | Time reaction (h) | Silica gel (g) | Yield (%) | Physical appearance of silica gel |
|-----------------|-------------------------|-------------------|----------------|-----------|-----------------------------------|
| 20              | 6                       | 2                 | 0.6            | 3.1       | Fine crystalline                  |
| 20              | 8                       | 2                 | 0.7            | 3.6       | Fine crystalline                  |
| 20              | 10                      | 2                 | 0.8            | 3.8       | Fine crystalline                  |
| 20              | 12                      | 2                 | 5.5            | 27.3      | Fine crystalline + Transparent lumps of crystal |
| 20              | 14                      | 2                 | 24.6           | 123.1     | Fine crystalline                  |
| 20              | 12                      | 1                 | 2.6            | 13.06     | Fine crystalline                  |
| 20              | 12                      | 2                 | 2.9            | 14.59     | Fine crystalline                  |
| 20              | 12                      | 3                 | 4.0            | 19.79     | Fine crystalline                  |
| 20              | 12                      | 4                 | 2.7            | 13.36     | Fine crystalline                  |
| 20              | 12                      | 5                 | 7.9            | 39.72     | Fine crystalline                  |
Analysis of silica purity was carried out using X-Ray Fluorescence (XRF). The obtained gels were left to rest for 24 hours allowing water overfloats. The precipitates obtained from extracts were washed and filtrated first before XRF analysis to eliminate the chlorine, alkali, and salt, therefore, obtain an amorphous gel. Table 4 shows the component analysis after dissolving silica-rich mud in 6 M NaOH. Alumina presents as a major impurity component in product synthesis. While dissolving silica-rich mud in KOH has been able to remove all alumina in the component (Table 5).

**Table 4.** XRF analysis results of silica gel were synthesized by NaOH.

| Compound | Concentration (%) |
|----------|------------------|
| SiO₂     | 63.25            |
| Al₂O₃    | 31.80            |
| K₂O      | 0.48             |
| CaO      | 1.38             |
| TiO₂     | 0.16             |
| V₂O₅     | 0.17             |
| MnO      | 0.05             |
| Fe₂O₃    | 2.53             |
| CuO      | 0.15             |
| Br       | 0.04             |
| ZrO₂     | 0.01             |

**Table 5.** XRF analysis results of silica gel were synthesized by KOH.

| Compound | Concentration (%) |
|----------|------------------|
| SiO₂     | 77.71            |
| K₂O      | 20.81            |
| Fe₂O₃    | 0.71             |
| CuO      | 0.70             |
| ZrO₂     | 0.07             |

X-Ray Fluorescence analysis of silica gel produced with 14 M KOH showed mixed product which is fine crystalline and transparent lumps of crystal. The formation of transparent lumps of crystal is not silica but a high concentrations of alkaline oxides. So silica gel synthesis wasn't recommended using KOH with too high concentrations.

**Table 6.** XRF analysis results of Transparent lumps of crystal product were synthesized by KOH 14 M.

| Compound | Concentration (%) |
|----------|------------------|
| SiO₂     | 0.00             |
| K₂O      | 35.87            |
| CaO      | 57.53            |
| MnO      | 0.85             |
| Fe₂O₃    | 2.18             |
| CuO      | 1.45             |
| ZnO      | 0.78             |
| SrO      | 0.51             |
| Re₂O₇    | 0.83             |
A series of alkaline treatment and acid treatment processes were performed on Lapindo mud to lower alumina, iron, and calcium and increase the silica content. Figure 3 shows, the treatment of sodium hydroxide and acid addition causes an appreciable decrease in the amount of alumina, iron, and calcium were observed in silica-rich mud. SiO₂ content increased from 50.00% to 63.25% while Al₂O₃ increased to 31.80%, Fe₂O₃ decreased to 2.25% and CaO decreased to 13.8%. Better results demonstrated in the treatment process potassium hydroxide and the addition of acid. SiO₂ content increased from 50.00% to 77.71%, while Fe₂O₃ decreased to 0.71%, alumina and calcium were gone.

This research was conducted with a batch system. Na⁺ or K⁺ ion in alkaline solution extracts silica in mud which then comes out to form a slightly yellowish metal-silicates compound. This yellow is possible because there are still HCl contained in the solution. Acid conditioning to pH 4 was done by adding HCl 12 M gradually, so the solution slowly becomes cloudy to form a white precipitate. These precipitate indicate that silica gel has been formed. The choice of pH is based on the nature of silica which was insoluble in acidic conditions so that the condition was expected to precipitate silica to occur optimally. The reaction mechanism that occurs in the extraction process could be seen in equations 2 and 3.

\[ 2\text{ACH}_\text{(aq)} + \text{SiO}_2\text{(s)} \rightarrow 3\text{H}_2\text{O} \]
\[ 2\text{ACH}_\text{(aq)} + \text{SiO}_2\text{(s)} \rightarrow 2\text{ACH}_\text{(aq)} + \text{SiC}_\text{(s)} + \text{H}_2\text{O} \]

![Figure 3. The result of oxide component changes.](image)

The stages of silica gel formation through the sol-gel process include (a) hydrolysis and condensation, (b) gelation (sol-gel transition), (c) aging (growth gel), and (d) drying. This process begins with the formation of hydrosols, particles that coagulate and produce silica polymer growth. Hydrosol is usually formed at a low pH and if the washing stage is also carried out at a relatively low pH it will produce a product that has a high surface area (>700 m²/g) [18, 19]. Furthermore, if the hydrosol stops flowing like a liquid (gelation process) then this is referred to as a hydrogel. The interaction of acids with sodium silicate solution produces orthosilicate acid which is a product of hydrolysis. This substance is very unstable and easily condenses by itself forming colloidal polymers from silica sol. Further condensation of silica sol produces a gel form.

4. Conclusion
Based on experiments and characterizations that have been done, it could be concluded that Lapindo mud has a high silica content of 50% so that it has the potential as a source in the production of silica gel. Synthesis with a batch system using NaOH at 80 °C in 4 hours, the silica yield of 32.2% with purity
63.25% was obtained. For synthesis with KOH treatment optimally at 12 M at 90 °C in 5 hours, the silica yield of 39.73% with good purity up to 77.71%. The characterization of the natural raw material and synthetic silica gel indicate that Lapindo mud can be yield a very interesting silica gel product characterized by high purity.

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