Dissolution of quartz sand in sodium hydroxide solution for producing amorphous precipitated silica

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Abstract. This research studied the dissolution of quartz sand in sodium hydroxide solution as an effort to form silica precipitate. The dissolution process was carried out using the leaching method directly at atmospheric pressure. The process variables in this study included the concentration of sodium hydroxide solution, temperature, dissolution time, and stirring rate. The four process variables had a positive influence to enhance silica precipitate formation. The result showed that the extraction rate was still low even though the SiO₂ concentration in the starting material was very high. Temperature provided the most significant influence among other process variables. The result exhibited that silica precipitate content was 13.6% obtained in the optimum condition at a temperature of 90 °C with a stirring speed of 800 rpm using a 7.5 M of sodium hydroxide solution.

1. Introduction
Silica is an important oxide which is abundant, about 60% of the earth's crust layer contains silica both as silica itself and in the form of silicates with metal oxides. This material is commonly found as beach sand or river banks, desert sand, silica rock, and other minerals [1]. Silica is widely used as a raw material for the glass, ceramic, cement, sandblasting industries, as well as supporting materials for the metal casting, oil and mining industries, and refractory bricks [2]. Along with the development of technology, silica, especially in the form of amorphous and furthermore the size of the nanocrystal, can be applied to the polymer composite amplifier industry, electronic devices, bitumen, insulators, catalysts, enzyme encapsulation, batteries, etc [3].

In general, silica processing can be carried out using an alkaline fusion method at a temperature over 1000 °C with the addition of sodium carbonate through the roasting stage to form sodium silicate, dissolving sodium silicate into the water, silica deposition using acid [3,4]. Other sources of silica can be obtained from biomass materials such as rice husks or bagasse. The processing method for this biomass material, in general, is direct dissolution using base [5] or acid solutions [6]. The processing of silica from non-biomass material using a base dilution method has been carried out by several researchers before. Riyas et al. reported that 80% of pure precipitated silica can be obtained by reacting desert sand and NaOH at 150 °C for 45 minutes in an open system [4]. Conversion obtained
is still quite low considering the NaOH used as many as 2 stoichiometry based on the weight of quartz sand. Munasir et al. comparing the results of SiO$_2$ nanopowder obtained using the 5-7 M NaOH dissolution method directly at 90 °C for 2 hours, with the base roasting method using NaOH at a temperature of 500 °C [2]. The study did not explain the percentage of extraction from each method used.

This research will study the extraction of silica from quartz sand using the dissolution method with sodium hydroxide. Factors that influence the formation of sodium silicate will be analyzed based on the amount of quartz sand residue after dissolution.

2. Experimental

The raw material used as a source of silica for this research was quartz sand from Sukabumi Indonesia. Other ingredients were NaOH and HCl 37% from Merck, and deionized water. Figure 1 shows a flow diagram of the experimental process carried out. Quartz sand was first dried in an oven at a temperature of 110 °C for 8 hours, crushed with a disk mill, then sieved until a particle size of -200 mesh is obtained. (<74 µm). Quartz sand was then analyzed using XRF and XRD to determine the chemical composition and crystal structure respectively. The dissolution process was carried out using a sodium hydroxide solution in a glass beaker equipped with a magnetic stirrer, a thermometer to determine the temperature of the process, and a plastic wrapping cover to prevent the solvent evaporation. The heat source during the dissolution process was obtained from the hot plate. A certain amount of sodium hydroxide was dissolved in aquademin. The solution was then heated to a certain temperature. After the process temperature had been reached, a certain amount of quartz sand was put into the hot sodium hydroxide solution and the process temperature was kept stable at a process condition determined by ±5 °C intolerance.

After the dissolution process was carried out over a while, the solution was filtered to separate the insoluble material. The residue obtained was washed several times then dried in an oven at 110 °C for 4 hours and weighed to determine the extraction of silica from quartz sand. The filtrate was stored in a volume flask with a certain volume and then precipitated as precipitated silica by titrating sodium silicate solution using concentrated HCl dropwise while stirring with a magnetic stirrer to reach pH = 3. The precipitate formed was filtered, washed repeatedly until the pH of the washing water was near the neutral condition, then dried in an oven at 110 °C for 24 hours and weighed. The precipitated silica products formed were analyzed using XRF and XRD as well as the quartz sand raw material. XRD analysis (X-ray diffractometer) using Shimadzu XRD 7000 Maxima-X with Cu-ka radiation in the range of 2θ 10-80 °, while the elemental composition was analyzed using XRF (X-ray fluorescence) S2 Puma Bruker.
3. Results and Discussions

3.1. Characterization of quartz sand

The chemical composition based on the results of the XRF analysis is shown in Table 1. SiO$_2$ is the dominant oxide component in quartz sand samples. Most impurities in the form of Al$_2$O$_3$ are only 4.69%, and other impurities such as MgO, K$_2$O, Fe$_2$O$_3$, Cr$_2$O$_3$, CaO, P$_2$O$_5$, and TiO$_2$ are in small amounts, each under 1% with a total of about 1.6%. The XRD analysis results of the quartz sand samples used in this study are shown in graph Figure 2. The diffraction pattern in Figure 2 indicates that the quartz sand samples are dominated by the crystalline quartz phase with the highest peaks at 2$\Theta$ of 26.6, 20.8, and 59.9$^\circ$ (3.34, 4.26, and 1.54Å) based on PDF2 data 46-1045, according to previous research by Trabelsi et al.[7] dan Sdiri et al.[8].

| Component | Cl  | MgO | Al$_2$O$_3$ | SiO$_2$ | P$_2$O$_5$ | SO$_3$ | K$_2$O | TiO$_2$ | MnO | Fe$_2$O$_3$ | Cr$_2$O$_3$ | CaO |
|-----------|-----|-----|-------------|--------|------------|-------|--------|--------|-----|-------------|------------|-----|
| Raw Quartz Sand | 0.025 | 0.27 | 4.69 | 93.7 | 0.011 | 0.042 | 0.41 | 0.091 | 0.011 | 0.64 | 0.067 | 0.031 |

Figure 1. Flowchart of the experiment
3.2. Effect of sodium hydroxide concentration

Figure 3 shows the effect of different concentrations of sodium hydroxide solution (6.25 - 7.5 M) on the dissolution of quartz sand to sodium silicate. The dissolution process was carried out at a temperature of 90 °C for 3 hours with a stirring speed of 300 rpm and a solid : liquid ratio of 2 : 10 (wt/v). From the experimental results, it can be seen that the concentration of sodium hydroxide solution has a positive effect on silica solubility. The higher the concentration of sodium hydroxide solution, the higher the silica dissolved as sodium silicate [9]. A sodium hydroxide concentration of 6.25 M is equivalent to 1 stoichiometry for the calculation of reactions on a SiO₂ basis in the quartz sand sample used. But this amount has not been able to dissolve the silica contained in quartz sand even when the concentration of sodium hydroxide solution used exceeds the stoichiometric requirements. The process of dissolving silica is strongly influenced by the bond configuration between Si and O. Therefore it is very different from amorphous silica. Quartz, the most stable silica phase, is very difficult to dissolve in sodium hydroxide solution [9]. The stability of quartz sand can be shown in diffractogram Figure 2 where quartz has a very high intensity with a sharp peak [10]. Peak width due to crystallite size varies inversely with crystallite size, as the crystallite size gets smaller, the peak gets broader. The highest extraction rate that can be obtained from this dissolution process is 10.9%.
3.3. Effect of dissolution temperature
In general, the temperature is very influential in a chemical reaction. To find out the level of dissolving silica in a sodium hydroxide solution, the reaction temperature is varied from 70 to 90 °C. The dissolution process was carried out for 3 hours with a stirring speed of 300 rpm and a solid:liquid ratio of 2:10 wt/v. The results are as seen in Figure 4. The increase in temperature gives a significant influence on the level of silica solubility. The highest extraction rate of 11% was obtained in the dissolution process with a temperature of 90 °C. The heating of the reaction aims to increase the occurrence of collisions between molecules in the solution so that it can accelerate the dissolution process. The higher the temperature, the viscosity of sodium hydroxide solution decreases. This facilitates mass transfer between quartz sand and its solvent material thereby accelerating the silica dissolution reaction [11].

3.4. Effect of dissolution time
The effect of quartz sand dissolution time on an atmospheric dissolution system was carried out using a 7.5 M sodium hydroxide solution. The dissolution time varies from 1 to 5 hours. The dissolution temperature is kept constant at 90 °C, the stirring speed is 300 rpm, the solid : liquid ratio is 2 : 10 wt/v. From the experimental results shown in Figure 5, it is known that the dissolution time also has a positive
The longer the dissolution time, the more silica is dissolved into sodium silicate. Dissolving time up to 5 hours can dissolve as much silica as 12.2%.

![Figure 5. Effect of dissolution time](image)

3.5. Effect of stirring speed

Stirring speed in a chemical reaction process, in general, will be able to increase the reaction rate. In addition to accelerating contact between the reacting substances and reducing deposition, this stirring can also help distribute temperature during the extraction process.

In this reaction of dissolving quartz sand with a 7.5 M sodium hydroxide solution, the stirring speed is varied from 300 to 800 rpm. Other operating conditions are temperature 90 °C, solid:liquid ratio 2:10 wt/v. As we can see from Figure 6, the stirring speed can increase the percentage of silica extraction even though increasing the extraction rate is not so significant with higher stirring speed. The possibility that occurred in the dissolution reaction of quartz sand with sodium hydroxide solution in this study is that the reaction is controlled by chemical control so that the stirring speed does not significantly influence the percent of silica extraction [12,13]. However, stirring speeds up to 800 rpm is capable of providing a percentage of silica extraction of 14%. This is quite different from the results of the study of Mufakhir et al in the process of leaching silica from ferronickel slag material which states the opposite result, that the rate of silica dissolution decreases with increasing stirring speed due to reaction controlled by diffusion through the product layer [14].

![Figure 6. Effect of stirring speed](image)
3.6. Characterization of silica precipitate

XRF analysis of precipitate silica products obtained from the deposition process in the form of white powder with SiO\textsubscript{2} content of 96.4% with Al\textsubscript{2}O\textsubscript{3} main impurities of 2.56%. As shown in Figure 7, XRD diffractogram of a precipitated silica sample, the broadening of the peak centered at a 2\theta angle between 20-30° indicates that formed precipitated silica has an amorphous phase [15][16][17], and no crystalline phase was detected indicating that the washing process was effective in releasing precipitated silica from sodium chloride [16].

![Diffractogram of silica precipitate](image)

Figure 7. Diffractogram of silica precipitate

4. Conclusion

From the overall operating condition factors studied in the process of dissolving quartz sand in sodium hydroxide solution, it can be concluded that temperature, time, concentration of sodium hydroxide, and stirring speed have a positive influence on the level of silica solubility of quartz sand. The process of dissolving silica from quartz sand with sodium hydroxide solution is quite difficult to do under atmospheric conditions due to the stability of the SiO\textsubscript{2} phase in the quartz sand. Extra time may be needed, but the process will be ineffective. The highest extraction rate was obtained under the operating conditions of dissolving quartz sand with a 7.5M sodium hydroxide solution at 90 °C for 3 hours and a stirring speed of 800 rpm. From the dissolution process can be obtained amorphous precipitate silica with purity ±96%.

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