Synthesis of Sodium Silicate from Rice Husk Ash as an Activator to Produce Epoxy-Geopolymer Cement

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Abstract. Rice husk ash (RHA), a byproduct of the rice industry, is the primary source of amorphous silica for producing sodium silicate solutions to replace standard commercial sodium silicate in geopolymer mixture design. The effect of various concentrations of NaOH used as an activator to produce epoxy-geopolymer cement was studied. Three initial concentrations of NaOH were used (8, 10, and 12M) to examine the optimum dissolution and formation of silica oligomers that can function as the activator during the geopolymerization. The result indicated the increase of NaOH concentration raises the silica yield strength. The silica yield found was 65.84%, 70.53% and 72.06% on NaOH use of 8, 10, 12 M, respectively. IR-spectra results showed silica functional groups and the sodium silicate were successfully synthesized. The IR spectra indicated the appearance of hydroxyl bonds, which strengthen the geopolymer matrix. SEM results showed the C-S-H and N-A-S-H bonds in the geopolymer. With 10M NaOH, the compressive strength of the geopolymer cement paste was optimal at 27.53 MPa. Thus, Rice husk ash (RHA) is feasible to be used as an activator in high calcium fly ash-based epoxy geopolymer cement.

Keywords: sodium silicate, rice husk ash, activator, geopolymer, cement

1. Introduction.

The commercial sodium silicate production uses calcination of sodium silicate carbonate (Na₂CO₃) and quartz (SiO₂) at 1400 to 1500°C and produces CO₂ [1-3]. Sodium silicate is produced with high energy and results in CO₂ waste, so it is not environmentally friendly. The potential of global warming on the use of commercial sodium silicate can be reduced by utilizing agricultural waste, rice husks.
The world rice husk ash (RHA) production is millions of tons per year [3]; with its availability, this material is suitable for use as a silica producer, which is used to produce standard concrete, high-quality concrete, and even geopolymer [4]. The utilization of silica from rice husk ash (RHA) is related to its amorphous nature and allows chemical transformation. Silica in rice husk ash is the X-ray amorphous; it has a very fine size, very porous, and chemically reactive. The usage of rice husk ash into sodium silicate as an alkaline solution in geopolymers has been carried out by [5-7] and from bagasse [8]. The results showed that agricultural waste is suitable for making sodium silicate to produce geopolymers. Utilization of sodium silicate from rice husk ash as an activator can make the geopolymer have good mechanical properties.

To develop the use of value-added products from agricultural waste and reduce the enormous environmental impact, this research aims to synthesize sodium silicate from rice husk ash to become an activator in geopolymer cement paste. It replaces commercial sodium silicate as a solution for recycling agricultural waste. Sodium silicate from rice husk ash is seen as a viable solution to optimize geopolymer sustainability. This research utilizes amorphous silica solubility from rice husk ash in a high alkaline solution (geopolymerization solution) to become a more environmentally friendly sustainable agricultural activator.

2. Material and methods

2.1. Materials

Rice husk ash was taken from a community-owned rice factory in Aceh Besar District. It has white in color. The primary material used in the manufacture of geopolymers is fly ash. This study used fly ash high calcium from the Nagan Raya Steam Power Plant (PLTU), Aceh, Indonesia. The alkaline solution used was Merck brand NaOH. It has a purity of 98% and Na$_2$SiO$_3$, which was synthesized from rice husk ash. The epoxy resin used was the type of epoxy mortar that was commercially obtained in Indonesia. The chemical composition of rice husk ash and fly ash is shown in Table 1.

| Materials         | Chemical composition (%) | SiO$_2$ | Fe$_2$O$_3$ | CaO | MnO | K$_2$O | SO$_3$ | Cl | Ag$_2$O | Al$_2$O$_3$ | TiO$_2$ | Yb$_2$O$_3$ |
|-------------------|--------------------------|---------|-------------|-----|-----|--------|--------|----|---------|-------------|---------|-------------|
| Rice husk ash     |                          | 93.27   | 0.15        | 1.03| 0.17| 3.41   | 0.26   | 0.35| 0.10    | N/A         | N/A     | N/A         |
| Fly ash           |                          | 21.07   | 27.23       | 32.58| 0.44| 1.17   | 5.69   | 0.22| 0.23    | 9.65        | 1.68    | 0.06        |

2.2. Preparation of sodium silicate solutions

The rice husk ashes were first sifted through 200 mesh to achieve uniformity in size. Furthermore, NaOH 8, 10, 12M was dissolved with water according to the required concentration. Rice husk ash was weighed 100 grams and dissolved in a 600 ml NaOH solution according to the molarity of the variables on the research. The ratio of rice husk ash and NaOH solution was 1:20 (b/v). This material was refluxed for 1 hour at 90 °C. The solution was filtered and stored at room temperature. Samples were coded N-8, N-10, and N-12 according to the NaOH concentration. The complete making process of sodium silicate, as shown in Figure 1.

2.3. Preparation of pasta epoxy-geopolymer

The process of making geopolymer paste was carried out by preparing materials, as shown in Table 2. NaOH solution was made with a concentration of 10 Molar and mixed with Na$_2$SiO$_3$, which has been synthesized from rice husk ash and settled for 24 hours so that the solution was completely mixed into an alkaline solution. Fly ash is mixed with an alkaline solution and stirred for 20 minutes. The epoxy resin is mixed after the geopolymerization process was complete. The next process was molding and curing. The paste was put into a 5x5x5cm cube mold and treated at room temperature. Samples were coded GP$_{7,28,56}$-N8, GP$_{7,28,56}$-N10, and GP$_{7,28,56}$-N12. After three days, the paste was removed from the mold and tested for 7, 28, and 56 days.
Fig. 1. Preparation process of sodium silicate from rice husk ash

Table 2. Mix proportion of geopolymer pastes

| Specimens           | Amounts (g) |   |   |   |   |   |
|---------------------|-------------|---|---|---|---|---|
|                     | Fly ash     | NaOH | Na₂SiO₃ | Water | Epoxy | Na₂SiO₃/NaOH |
| GP7-N8, GP29-N8, GP56-N8 | 99          | 14  | 35 | 35 | 37 | 2.5        |
| GP7-N10, GP28-N10, GP56-N10 | 99          | 14  | 35 | 35 | 37 | 2.5        |
| GP7-N12, GP28-N12, GP56-N12 | 99          | 14  | 35 | 35 | 37 | 2.5        |

2.4. Testing procedures

The scanning electron microscope (SEM, EVOMA 15, ZEISS, Germany) was used to observe rice husk ash and geopolymer pastes’ microstructure. To characterize the functional groups, change of geopolymer pastes, the Fourier-transform infrared spectroscopy (FTIR, IRPrestige-21 Shimadzu, Japan) was used. After the test object was 28 days old, the geopolymer paste sample was crushed and sieved on a 200-mesh filter around 75-μm for FTIR testing. FTIR absorption spectra were read in the range 4,000-450 cm⁻¹. Spectra were recorded at a resolution of 4 cm⁻¹ at one time of scanning and a speed of 0.2 cm/s, which was then analyzed by Spectrum software. The rectangular specimen (50 cm x 50 cm x 50 cm) was used to measure the compressive testing at a crosshead speed of 400 N/s as per ASTM C109 by using the Technotest concrete testing machine. The results were presented at test ages of 7, 28, and 56 days. Three tests were carried out of each datum.

3. Result and discussions

3.1. Yield silica of sodium silicate

The silica content is seen to rise with the increase of NaOH concentration. In the treatment with the additional increasing concentrations of 8, 10, 12 M NaOH, the silica yield of sodium silicate continued to increase to 65.84, 70.53, and 72.06% respectively. The silica yield increased by 9.44%. The complete yield value generated is as in Table 3 and Figure 2.

Table 3. Yield silica concentration

| Sample (RHA) | Silica content | Silica content after treatments (%) | Yield (%) |
|-------------|----------------|-------------------------------------|-----------|
| N8          | 93.27          | 61.41                               | 65.84     |
| N10         | 93.27          | 65.78                               | 70.53     |
| N12         | 93.27          | 67.21                               | 72.06     |
3.2. Chemical bonding analysis

The FTIR spectra of the sodium silicate obtained were analyzed to see the changes in functional groups due to the addition of NaOH concentration in the manufacturing process. Figure 3 shows the spectrum and peak intensity at 3259.7 and 2850.79 cm\(^{-1}\), which shows the hydrogen bonds, namely O-H and C-H. This bond proved that with increasing NaOH concentration, the intensity of the hydrogen bonds formed also increased. The formation of hydrogen bonds was caused by breaking the degradation of the amorphous portion of the rice husk ash. At this stage, there was also an increase in silica yield.

The peak intensity at 721.38 cm\(^{-1}\) showed that Si-O-Si bond, which is the main component of sodium silicate. Si-O-Si intensity was spread at 414.70 to 721.38 cm\(^{-1}\) and this occurred in all sodium silicate products. The functional group analysis showed that sodium silicate had been successfully synthesized and suitable for use as an activator in geopolymers.

3.3. Compressive strength evaluation

a) The effect of NaOH concentration on the compressive strength

Different concentrations of NaOH will produce different silica yields in sodium silicate production. This concentration will ultimately affect the strength of the geopolymer paste [9]. In Figure 4, an increase in the compressive strength of the geopolymer paste occurred at a 10 M NaOH concentration. This increase occurred due to an increase in the yield value of silica. However, the addition of NaOH concentration to 12 M did not provide a significant increase in compressive strength. This can be understood because NaOH's increasing concentration in sodium silicate makes this solution become concentrated and difficult to agglomerate with fly ash. The more concentrated the solution, the less fly
ash dissolved, which affected the geopolymer paste's density. The optimum NaOH concentration at 10M will produce sodium silicate, which easily dissolves fly ash into a geopolymer matrix so that the resulting compressive strength is maximum.

![Compressive strength of geopolymer paste with various NaOH concentrations in sodium silicate](image)

**Fig. 4.** Compressive strength of geopolymer paste with various NaOH concentrations in sodium silicate

### b) The effect of treatment period on the compressive strength

Figure 5 shows that the longer the treatment period or the age of the geopolymer paste, the more increase in the compressive strength. At the age of 7 days, the difference in NaOH concentration did not show a significant difference in compressive strength. But at the age of 28 days, there was a significant difference in compressive strength at the 10 M NaOH concentration, where the compressive strength increased to 23.80 MPa, while the 8 and 12M NaOH concentrations did not show any significant differences. At the age of 56 days, the concentrations of 8 and 12 M also did not show any difference, only at a concentration of 10M was seen to continue increasing. This is because the longer the treatment period, the more C-S-H gel in the geopolymer paste was formed. This gel is very important in increasing the compressive strength of the paste.

![Average compressive strength of geopolymer paste with various NaOH concentrations in sodium silicate](image)

**Figure 5.** Average compressive strength of geopolymer paste with various NaOH concentrations in sodium silicate

### c) Relation of NaOH concentration in sodium silicate to yield and compressive strength

NaOH concentration and yield have shown a directly proportional relationship. The increase in NaOH concentration increased the yield. The silica yield was shown to continue to increase from 65.84 to 72.06%. However, the compressive strength of the geopolymer paste did not occur. The compressive strength was shown to increase at 10M NaOH concentration by 27.53 MPa while at 12 M, the compressive strength decreased to 23.89 MPa. Figure 6 showed that the increase in yield did
not affect the increase in compressive strength. This explained that a lot of silica is not dispersed in the formation of geopolymer bonds and does not play a role in producing hydroxyl (OH) bonds at a 12M NaOH concentration. The fewer hydroxyl bonds present, the less the matrix's ability to bind with the epoxy resin. Schematically, the geopolymer bond formed is depicted in Figure 7.

![Graph showing relationship between NaOH concentration, yield, and compressive strength of geopolymer](image)

**Fig. 6.** Relationship between NaOH concentration, yield, and compressive strength of geopolymer

![Diagram showing geopolymer and epoxy resin interaction](image)

**Fig. 7.** Schematic diagram of the interaction between geopolymer (left-right) and epoxy resin (center) matrices via hydroxyl (OH) bonds [10].

d) **Microstructure observations**

The EDS results showed that Si, Al, Na, Ca, and O were the dominant elements identified in the geopolymer mixture. The dissolution of silica and alumina in the binder substance played a crucial role in forming the geopolymer system [11-13]. The increase in compressive strength at the initial age was due to the rapid dissolution of alumina, which was higher than silica in the initial age of geopolymerization. In the next process, silica played a role in increasing the compressive strength [14]. Poor bonding between fly ash and the activator causing cracking was observed, resulting in weak matrix formation and low compressive strength [15, 16]. The geopolymer matrix appeared to be a denser structure due to the formation of the compounds' strength development, C–S–H and N–A–S–H gels. The C-S-H gel appears to have become solid; this was because the sodium silicate and NaOH have dissolved and bonded the Si and Al in the fly ash, plus the hydroxyl bonds contributed by the epoxy. Small gaps that appeared on the surface will weaken the structure in the future with a decrease in the compressive strength of the geopolymer concrete [17-18]. Cracks may appear during the curing process due to the evaporation of water and the contraction of the samples [19, 20].
4. Conclusions

Based on the results of this study, the following conclusions could be drawn.

a. SEM and EDS results on geopolymer paste with 10M sodium silicate activator showed the formation of calcium silicate hydrate C-S-H and sodium aluminosilicate hydrate (N-A-S-H). The C-S-H compound appeared to have solidified, this was because the sodium silicate has dissolved and bond the Si and Al in the fly ash, plus the hydroxyl bonds which is contributed by the epoxy.

b. Silica yield was seen to continue to increase from 65.84, 70.53 to 72.06%, along with the addition of NaOH concentrations from 8, 10, and 12 M. Compressive strength was shown to increase at 10M NaOH concentration by 27.53 MPa while at 12 M compressive strength drops to 23.89 MPa. This decrease occurs because many silica were not dispersed in the formation of geopolymer bonds and did not play a role in producing hydroxyl (OH) bonds.

c. The increase of NaOH concentration in sodium silicate made the solution concentrated and difficult to agglomerate with fly ash. This condition affected the density of the geopolymer paste, which ultimately affects its compressive strength. The optimum NaOH concentration at 10M will produce sodium silicate, which easily dissolves fly ash into a geopolymer matrix.

d. The spectrum and peak intensity at 3259.7 and 2850.79 cm\(^{-1}\) indicated hydrogen bonds, namely OH and CH, at the intensity of 721.38 cm\(^{-1}\) indicated Si-O-Si bonds, which were the main component of sodium silicate, besides that it was also seen the presence of Si-O-Si intensity was spread at intensities from 414.70 to 721.38 cm\(^{-1}\). From the IR-spectra analysis, it can be seen that sodium silicate has been successfully synthesized and was suitable for use as an activator in geopolymers.

Acknowledgments

The authors acknowledge the financial supports received from the Ministry of Research and Technology/National Research and Innovation Agency for the PKPT (Higher Education Cooperation Research) scheme No. Contract 193/SP2H/LT/DRPM/2020 and Institute for Higher Education Services (LLDIKTI-13) Contract number 121/LL13/AMD/AKA/LT/2020.

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