Physico-Mechanical Properties of Geopolymer Based on Laterite Deposit Sidrap, South Sulawesi

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Abstract. Laterite soil deposit Sidrap, South Sulawesi, has been used as a raw material in the production of Na-Poly (sialate-siloxo) geopolymers. The main objective of this study is to investigate the physicomchanical properties of the resulting geopolymers synthesized from laterite Sidrap. Geopolymers were produced through the alkali-activation method of dehydroxylated laterite. Dehydroxylation was performed by using high-temperature furnace at 750°C for 4 hours. The resulting geopolymers were characterized based on X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR) and Scanning Electron Microscopy (SEM) in order to examine their mineralogy and microstructure properties. The physimchanical properties of geopolymer were examined through compressive and flexural strength. It was found that geopolymer based on Sidrap laterite exhibited good and high mechanical strength which make them suitable for various structural applications.

Keywords: geopolymer, laterite, physicomchanical properties

1. Introduction
Laterite or laterite soils is a basic material used a long time ago for civil constructions such as road, buildings, and dam. The term of laterite comes from Latin word “later” which loosely means brick. The genesis of laterite consists of intensive and longtime weathering of tropical rocks, enriched with iron and aluminum elements followed by the reduction of silica content and enhancing its solubility in alkaline solution. The color of laterite ranges from brownish to reddish indicating the presence of iron oxide which makes laterite chemically written as $\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. This chemical formula shows that the content of kaolinite clay in the matrix of laterite which rich with $\text{Al}^{3+}$ has been replacing by $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$ [1][2]. Laterite soils are categorized as aluminosilicate minerals, abundantly available in tropical areas like Indonesia. The substitute of $\text{Al}^{3+}$ by $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$ in laterite has attracted a lot of attention to studying the possibility of this material for geopolimerization [2]–[5].

Geopolymer is an advanced material of inorganic polymer form of $\text{SiO}_4$ and $\text{AlO}_4$ tetrahedra connected by oxygen bridge and electrically balanced by the presence of cations, such as $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$. The raw materials for geopolymer production are aluminosilicates minerals such as metakaolin and fly ash which generally contains a small amount of iron oxide. Since laterite soils are aluminosilicate enrich with $\text{Fe}_2\text{O}_3$ or hematite, it is important to study the geopimlerization of this material and characterized its physimechanical properties. A number of studies on laterite or Fe-
enrichment geopolymer have been reported, however more studies need to be conducted since the chemical compositions of laterite are different from one site to another [3][5]–[8]. In this study, laterite from Sidrap Regency, South Sulawesi, Indonesia was used as a raw materials for geopolymer production. The extracted laterite was dehydroxylated at 750°C for 4 hours similar to those of kaolin. This mechanism was adopted to ensure the structural change of laterite from crystalline to amorphous after dehydroxylation took place. It is well known that amorphous aluminosilicate is highly reactive in the alkaline environment [9][10].

2. Experimental

The raw material of laterite was cleaned, immersed in tap water for 24 hours followed by vigorous stir. The laterite solution was then separated by gravimetric method until a very fine solution of laterite was obtained. The laterite was then dried inside a low-temperature oven at 100°C for 24 hours. Dried laterite was blended for 3 hours and sieved using 200 mesh sieve in order to achieve its particle size less than 100 µm. The extracted laterite was then dehydroxylated at 750°C for 4 hours to ensure the transformation from crystalline to amorphous state. The extracted and dehydroxylated laterite were subjected to several characterizations including X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR), and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). These characterizations were intended to gain information about mineralogy and physical-chemistry properties of laterite.

Laterite based geopolymers were synthesized by using the alkaline activation method by calculating the weight of Al₂O₃, SiO₂, Fe₂O₃ available. The molar ratio of the starting materials (including NaOH and Na₂O.3SiO₂) were adjusted to attain SiO₂: Al₂O₃ = 1.5, 1.75 and 2.0 referred to as K1 K2 and K3 compositions. The molar ratio of Na₂O:SiO₂ = 0.3 and H₂O:Na₂O = 10 were kept constant for all compositions. Geopolymer paste was produced by mixing dehydroxylated laterite with sodium silicate solution, stir until the homogenous mixture was achieve. The mixture was then poured into a plastic mold, sealed and cured at 70°C for 2 hours. The resulting geopolymers were kept in open air for 28 days before any measurement was conducted. The microstructure geopolymers were examined by using XRD and SEM-EDS, and their mechanical strengths were measured through compressive and three bending point flexural strength measurements.

3. Results and discussion

3.1 Characterization of laterite

The photograph of laterite used in this study as extracted and after the dehydroxylation process at 750°C for 4 hours took place is shown in Figure 1. Dehydroxylation process changes the color of laterite to become more reddish due to the loss of (OH⁻) from the bulk of the material.

Figure 1. Laterite (i) as extracted, and (ii) dehydroxylated at 750°C for 4 hours
The number of water molecules lost from the network of aluminosilicate mineral due to dehydroxylation process at temperature 750°C was about 14wt% [9]. The lost of water molecules was detected by the FTIR study (Figure 2) which showing a significant change in the vibration bands between 400 to 4000 cm\(^{-1}\). The FTIR spectrum shown in Figure 2 can be divided into several regions of wave numbers [5][8] namely:

- Bands higher than 1600 cm\(^{-1}\) are attributed to the bands of water molecules. The strong band at 3424 cm\(^{-1}\) is (OH)\(^{-}\) stretching and 1639 cm\(^{-1}\) is bending of (OH)\(^{-}\).
- Strong bands between 970 – 1100 cm\(^{-1}\) are vibration asymmetric stretching of Si – O – Si, and it is the backbone of the geopolymer network. The strong bond at 796 are attributed to Fe – O – Al, and band at 692 cm\(^{-1}\) are stretching and deformation of Fe – O and Si – O [5].
- Bands between 550 – 750 cm\(^{-1}\) are the vibration of symmetric stretching of Si – O – Si and Si – O – Al.
- Bands between 460 – 510 cm\(^{-1}\) are attributed to the vibration bending of Si – O – Si and O – Si – O.

![Figure 2. FTIR spectra of as extracted and dehydroxylated laterite](image)

The elemental compositions of dehydroxylated laterite were examined by using XRF and tabulated in Table 1. The calculation of the oxide molar ratio of the starting materials for geopolymerisation normally based on the XRF or EDS result.

![Table 1. XRF result of dehydroxylated laterite](table)

| Compound | m/m%   | Standard Error | Element | m/m%   | Standard Error |
|----------|--------|----------------|---------|--------|----------------|
| SiO\(_2\) | 64.48  | 0.76           | Si      | 30.14  | 0.36           |
| Al\(_2\)O\(_3\) | 19.01 | 0.92           | Al      | 10.06  | 0.49           |
| Fe\(_2\)O\(_3\) | 13.74 | 0.18           | Fe      | 9.61   | 0.13           |
| TiO\(_2\) | 1.82   | 0.07           | Ti      | 1.09   | 0.04           |
| K\(_2\)O | 0.630  | 0.031          | K       | 0.523  | 0.026          |
| MnO     | 0.123  | 0.028          | Mn      | 0.095  | 0.022          |
| CaO     | 0.100  | 0.039          | Ca      | 0.072  | 0.028          |
| ZrO\(_2\) | 0.0404 | 0.0038        | Zr      | 0.0299 | 0.0028        |
| Nb\(_2\)O\(_5\) | 0.0124 | 0.0012       | Nb      | 0.0087 | 0.0008        |
| MoO\(_3\) | 0.0087 | 0.0018       | Mo      | 0.0058 | 0.0012        |
| ZnO     | 0.0086 | 0.0043        | Zn      | 0.0069 | 0.0034        |
The main oxides of geopolymer synthesis are the availability of certain molars of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ in metakaolin. Table 1 shows that the molar oxide ratio of (SiO$_2$)/(Al$_2$O$_3$ + Fe$_2$O$_3$) is about 2 and this value is ideal for producing high quality of Na-Poly (sialate-silixo) type geopolymer [9]. The molar oxide of Fe$_2$O$_3$ in dehydroxylated laterite is about 13.74 wt% which is much higher than those in metakaolin and fly ash [11][12]. Other oxides with a smaller weight percentage such as TiO$_2$, K$_2$O, MnO$_2$ do not play an important role in the synthesis of geopolymer.

The morphology of laterite used in this study as well as its chemical compositions were examined by using SEM-EDS as shown in Figure 3. It can be seen that the shape and the particle size of laterite are not homogenous and also rich with smaller particles quartz and Fe$_2$O$_3$.

![Figure 3. SEM images of laterite (A) before (B) after dehydroxylated](image)

The elemental and oxides compositions of dehydroxylated laterite on Figure 3 based on SEM-EDS results are shown in Table 2. It can be seen that the weight percentage of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ are closely similar to those in Table 1.

| Element | unn. C norm. C Atom. C Compound norm. Comp. C Error (3 Sigma) |
|---------|---------------------------------------------------------------|
| Sodium  | 0.29 0.52 0.47 Na2O 0.70 0.16                               |
| Magnesium | 0.45 0.80 0.69 MgO 1.33 0.17                             |
| Aluminium | 10.15 17.96 14.03 Al2O3 33.93 1.55                      |
| Silicon  | 14.10 24.95 18.73 SiO2 53.37 1.09                         |
| Potassium | 0.26 0.46 0.25 K2O 0.56 0.12                            |
| Titanium | 0.50 0.88 0.39 TiO2 1.46 0.14                           |
| Iron    | 3.80 6.73 2.54 FeO 8.65 0.43                            |
| Oxygen  | 26.97 47.71 62.89 FeO 8.65 0.43                         |

Total: 56.53 100.00 100.00

3.2 Characterization of geopolymer products

Figure 4 (a) shows the examples of geopolymer paste and (b) geopolymer mortar which contain 40wt% of α-quartz produced in this study. The inclusion of α-quartz was intended for further study about the ability of geopolymer to bind aggregate.
Geopolymers produced in this study were synthesized in three different compositions by adjusting the molar ratio of SiO$_2$/Al$_2$O$_3$ from 1.50, 1.75 and 2.00 designated as K1, K2, and K3, keeping the ratio of Na$_2$O/Na$_2$O and H$_2$O/Na$_2$O constant at 0.3 and 10, respectively. The structure and phase of the resulting geopolymers paste were examined by means of XRD in the range of 10 – 70º 2θ.

Phase determination of laterite geopolymer showed that K1 sample comprised of 42 wt% of Sodium Aluminum Silicate Hydrate (Na$_3$Al$_3$Si$_3$O$_{12}$·2H$_2$O) and 56 wt% of quartz and about 2 wt% of Fe$_2$O$_3$. The K2 sample consists of 43 wt% of quartz and 57 wt% of Trisodium tecto-trialumotrisilicate (Na$_3$Al$_3$Si$_3$O$_{12}$ (H$_2$O)) 1.8). Sample K3 consists of 59 wt% of quartz and 41 wt% of Trisodium tecto-trialumotrisilicate. The significant change of phase in sample K1 was caused by the addition of more sodium silicate than sample K2. The presence of Fe$_2$O$_3$ in sample K1 and K2 was too small to be registered by the PDXL2 software used for phase determination.

The morphology of geopolymers K2 is shown in Figure 6 along with its EDS spectrum. The surface of the sample still contains a lot of unreacted laterite particles, pores, and cracks. The presence of quartz is also clearly visible and act like aggregate on the matrix of geopolymer. The presence of pores on the surface or bulk of geopolymer occurred due to the loss of water reaction when the sample was cured at 70ºC for 2 hours.
Figure 6. SEM image and EDS spectra of laterite geopolymer K1

Table 3. EDS result on the surface of laterite geopolymer K1

| Element | uncorr. C norm. C Atom. C Compound norm. Comp. C Error (3 Sigma) | wt.% | wt.% |
|---------|---------------------------------------------------------------|------|------|
| Sodium  | 8.57                                                        | 9.78 | 8.88 | Na₂O | 13.18 | 1.77 |
| Magnesium | 0.68                                                    | 0.77 | 0.66 | MgO  | 1.28  | 0.21 |
| Aluminium | 11.28                                                   | 12.86| 9.96 | Al₂O₃| 24.30 | 1.71 |
| Silicon  | 21.82                                                      | 24.89| 18.51| SiO₂ | 53.24 | 2.88 |
| Chlorine | 0.08                                                       | 0.10 | 0.06 |                  | 0.10  | 0.10 |
| Potassium | 0.33                                                      | 0.38 | 0.20 | K₂O  | 0.45  | 0.12 |
| Titanium | 0.64                                                       | 0.73 | 0.32 | TiO₂ | 1.21  | 0.16 |
| Iron     | 4.26                                                       | 4.85 | 1.82 | FeO  | 6.25  | 0.48 |
| Oxygen   | 40.03                                                      | 45.65| 59.60|      | 0.00  | 14.16 |

Total: 87.68 100.00 100.00

The EDS result on the surface of laterite geopolymer shows that the weight percentage of SiO₂ is much higher than the calculated composition. This is due to the presence of α-quartz in the raw material of laterite which did not react with an alkaline solution.

Figure 7 shows the SEM image of laterite geopolymer K2 together with the EDS spectrum. The machine used to examine this sample is different from those used for sample K1, and hence the quality of the image, as well as the graph of EDS, are also slightly different. The morphology of the sample surface is more homogeneous as the unreacted laterite particles have been decreased significantly. The presence of quartz particles is still visible on the surface of the sample. The weight percentage of SiO₂ on the sample is also approximately similar to the calculated composition as shown in Table 3.

Figure 7. SEM image and EDS spectrum of laterite geopolymer K2
Table 4. EDS result on the surface of laterite geopolymer K2

| El  | AN  | Series | un. C | norm. C | Atom. C | Error |
|-----|-----|--------|-------|---------|---------|-------|
|     |     |        | [wt.%] | [wt.%]  | [at.%]  |       |
| O   | 8   | K-series | 50.37 | 55.33   | 68.48   | 15.7  |
| Si  | 14  | K-series | 17.73 | 19.48   | 13.73   | 0.8   |
| Al  | 13  | K-series | 9.81  | 10.78   | 7.91    | 0.5   |
| Na  | 11  | K-series | 8.34  | 9.16    | 7.89    | 0.6   |
| Fe  | 26  | K-series | 3.87  | 4.25    | 1.51    | 0.1   |
| Ti  | 22  | K-series | 0.48  | 0.53    | 0.22    | 0.0   |
| K   | 19  | K-series | 0.38  | 0.42    | 0.21    | 0.0   |
| Mg  | 12  | K-series | 0.05  | 0.06    | 0.05    | 0.0   |

Total: 91.04 100.00 100.00

The mechanical strength of laterite geopolymer produced was examined by means of compressive strength measurement and three bending points flexural measurement. The measurement compressive strength was conducted on cylindrical samples 5.0 cm in height and 2.5 cm in diameter by a Universal Testing Machine with pressure increment of 100 kg.s⁻¹. The flexural strength was measured on samples with a length of 12.0 cm, 2.5 cm in width and 1.0 cm height. The results of both measurements are shown in Figure 8.

Figure 8. The compressive and flexural strength of laterite geopolymers

The results showed that both compressive and flexural strength of laterite geopolymers were influenced by the chemical composition of the starting material, namely the ratio of SiO₂/Al₂O₃ since Na₂O:SiO₂ and H₂O:Na₂O are kept constant. Samples LS K2 with SiO₂/Al₂O₃ = 1.75 showing the highest compressive and flexural strength after 28 days. The influence of Si:Al ratio in the network of geopolymer on the mechanical strength has been well-established[1][9][13]. The magnitude of the compressive and flexural strength of the resulting geopolymer are categorized high suggesting that laterite Sidrap is a good alternative for high-quality geopolymer.

4. Conclusion

Based on the results of this study it can be concluded that laterite Sidrap is a good starting material for geopolymer production. The chemical compositions of laterite Sidrap contain excellent molar oxide ratio (SiO₂/Al₂O₃+Fe₂O₃) as a raw material for geopolymer type Na-Poly (sialate-siloxy). The microstructure, as well as physical mechanics of the resulting laterite geopolymer, is strongly influenced by the ratio of a molar oxide of SiO₂ and Al₂O₃. The results of compressive and flexural strength measurements of the resulting materials suggest that laterite of Sidrap Regency is excellent raw material for geopolymer.
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