Fabrication of Zeolite-Geopolymer Hybrid Bulk Materials Based on Laterite Soils Deposit Gowa Regency, South Sulawesi, Indonesia

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Abstract. In this study, zeolite-geopolymer hybrid bulk materials were fabricated by using laterite soils deposit Gowa regency, South Sulawesi, Indonesia as a precursor for possible heavy metal absorbent. Laterite soils was calcined at 750°C for 6 hours to transform it into the amorphous aluminosilicate phase. Zeolite-geopolymer materials were produced through alkali activation method with curing temperature around 70°C for 2 hours. There were two different oxide molar ratios of SiO₂/Al₂O₃ used to produce zeolite-geopolymer hybrid bulk materials and the specimens were designated as K1 and K2. The presence of zeolitic phase within geopolymer network was examined by using of XRD, FTIR, and SEM-EDS technique. The mechanical properties of the resulting material were studied by means of compressive and tensile strength. The results showed that Gowa laterite soil was successfully fabricated as zeolite-geopolymer hybrid bulk materials, and the type of zeolite coined with geopolymers were zeolite A in sample K1 and un-named zeolite in sample K2. The mechanical strengths of zeolite-geopolymers produced in this study were below to those of pure geopolymers.

1. Introduction
Laterite soil is commonly formed in tropical area through weathering processes which suitable for the formation of iron, aluminum and titanium oxides. These processes break down silicate minerals into clay minerals such as kaolinite and illite having a variety of physical properties [1]. An important feature of these soils is their capability of hardening upon exposure to wetting and drying. The hardening process is due to crystallization of continuous aggregates of iron oxide minerals followed by dehydration [2]. Despite the fact that laterites have been recognized as a potential source of aluminosilicates for inorganic polymers (geopolymers) synthesis, very little has been reported on the development of geopolymers from laterites [1]. In Indonesia, laterite soil deposits can be easily found, one of them is in Gowa regency, South Sulawesi which is considered as aluminosilicate minerals [3].

Geopolymers are inorganic polymeric materials with three dimensional Si-O-Al networks synthesized from aluminosilicates in high alkaline environment. Apart from having excellent early and long-term mechanical strength, geopolymers also have low shrinkage value, low density, good immobilization of heavy metals and excellent fire and chemical resistance [4]. As a porous material, the durability of geopolymers depends on the ability to withstand the intrusion of aggressive agents. The transport properties of a porous materials are influenced by the pore structure characteristics [5].
It has been recognized that geopolymer is a family of zeolite which is known to have good thermal and chemical stability. Zeolite can be used as membranes or catalytic materials which offer a wide range of operating conditions [6]. Inorganic membranes such as ceramics, metals, and glass show promising properties different from the organic ones. They can be backwashed frequently without damaging the separation layer. Inorganic membranes are highly resistant to cleaning chemicals, they can be sterilized and autoclaved repeatedly at 130–180 °C and can withstand temperature up to at least 500 °C [7]. Zeolite-geopolymer hybrid bulk materials can have a wide pore size distribution, since zeolites have high microporosity and geopolymers have mesopores [8].

Zeolites have attracted intensive research due to their potential applications such as separation membrane, catalytic membrane reactor, chemical sensor, electrode, opto-electronic device, low dielectric constant material for electrical insulator, protection or insulation layer or as host for the organization of functional guest molecules [9]. In this study, zeolite-geopolymer hybrid materials were fabricated using laterite deposit Gowa regency for possible application as heavy metal membrane. The amounts and species of zeolite, pore distribution of the resultant zeolite-geopolymer hybrid bulk were investigated.

2. Experimental

The soils from Gowa regency were clean, immersed in water for 24 hours, dried, grounded and sieved 200 mesh. The soils were dehydroxylated at 750 °C for 6 hours and grounded again by using ball milling at 200 rpm for 5 hours. Samples were synthesized by varying the molar ratio of SiO2/Al2O3, Na2O/SiO2, H2O/Na2O. The geopolymers paste was molded in accordance with the measurements requirement. All samples were cured at 70 °C for 2 hours and the resulting materials were stored in open air for 7 days before conducting any measurements.

The functional groups of the resulting sample were examined by using Fourier Transform Infra-Red (FTIR). Precise Fourier Transform Infrared Shimadzu was used in Laboratorium Instrumen Jurusan Kimia FMIPA ITS Surabaya. The sample was prepared by dissolving it in KBr with ratio 1: 600, then analyzed by FTIR.

X-ray diffraction (XRD) measurements were conducted to study the structure and phase of the resulting sample [10] by using XRD Rigaku MiniflexII with an acceleration voltage of 30 kV and a current of 15 mA. Phase analysis and mineralization of geopolymer were examined by using PDXL2. In this study, the measurements were performed in range of 10°-70° 2θ.

SEM characterization was used to study the structure and morphology of the laterite sample. Analysis of geopolymer morphology by using SEM Tescan Vega3SB coupled with Bruker Energy Dispersive Spectroscopy (EDS).

The mechanical properties of the resulting materials was characterized by means of compressive and tensile strength. The samples for compressive strength were cylindrical in shape with a diameter of 2.5 cm and height of 5 cm, whereas the samples for tensile strength measurements were rectangular in shape with a dimension of 12.0 x 2.5 x 1.5 cm in accordance with the requirement for three point bending tensile measurement.

3. Results and Discussions

The raw material for zeolite-geopolymer synthesis was in the form of aluminosilicate mineral obtained from the processing and dehydroxilation of laterites at 750 °C for 4 hours. Figure 1 shows the laterite soil from Gowa regency before and after dehydroxylation with grain size passed the 200 mesh sieve.
Figure 1. Laterite soils (A) before and (B) after dehydroxylation at 750°C about 6 hours.

The loss of water in the form of hydroxyl chain from the network of aluminosilicate changed the color of laterite before and after dehydroxylation as shown in figure 1. As a result, the structure of laterite changed from crystalline to amorphous phase. The red-brown color of laterite is also an indications of the high content of hematite (Fe₂O₃) phase. The chemical composition of laterite was examined by using SEM-EDS technique and the result is shown in table 1.

Table 1. Chemical compositions of laterite Gowa before and after dehydroxylation.

| Compound | Before | After |
|----------|--------|-------|
|          | Norm.Comp [wt.%] | C Error (3 sigma) [wt.%] | Norm.Comp [wt.%] | C Error (3 sigma) [wt.%] |
| Na₂O     | 0.69   | 0.17  | 0.89   | 0.18  |
| MgO      | 2.16   | 0.24  | 2.35   | 0.23  |
| Al₂O₃    | 33.85  | 1.79  | 35.72  | 1.67  |
| SiO₂     | 32.34  | 1.37  | 33.11  | 1.24  |
| SO₃      | 0.13   | 0.17  | -      | -     |
| TiO₂     | 2.03   | 1.31  | 1.98   | 1.06  |
| FeO      | 28.80  | 9.70  | 28.94  | 8.85  |

Table 1 shows that the molar oxide ratio of Al₂O₃ and SiO₂ of laterite Gowa is an excellent aluminosilicate mineral for Na-poly (ferro-sialate) type geopolymer production [3, 11]. Figure 2 showed the XRD structure and phase compositions of Gowa laterite before and after dehydroxylation at 750 °C for 6 hours.
Figure 2. The diffractogram of Gowa laterite before and after dehydroxylation with phase compositions.

Figure 3 shows the FTIR spectrum of laterite before and after dehydroxylation in the range of 400 – 4000 cm\(^{-1}\). The spectrum clearly showed the transformation of crystalline laterite into amorphous state. Figure 3(a) shows that the bands at 3622 and 3697 cm\(^{-1}\) were attributed to the OH stretching vibrations of inner-surface hydroxyl groups. The bands at 1629 and 3448 cm\(^{-1}\) were assigned as bending and stretching vibration of H–O–H, respectively.

Figure 3. FTIR spectrum of Gowa laterite (before and after dehydroxylation)

The stretching band of Si–O–Si was observed at 1039 cm\(^{-1}\). The band at 912 cm\(^{-1}\) indicated the presence of hematite, whereas quartz was observed at 794 cm\(^{-1}\). The band of Si–O was observed at 430, 470, 540, and 698 cm\(^{-1}\) confirmed the presence of kaolinite [12]. In this study, zeolite-geopolymer materials were prepared by using two different compositions, designated as K1 and K2. The oxide molar ratios of K1 and K2 are shown in table 2.
Table 2. The oxide molar ratios of samples K1 and K2

| Sample | SiO$_2$/Al$_2$O$_3$ | Na$_2$O/SiO$_2$ | H$_2$O/Na$_2$O |
|--------|------------------|----------------|----------------|
| K1     | 3                | 0.3            | 10             |
| K2     | 4                | 0.3            | 10             |

Figure 4 shows the zeolitic phase of the resulting geopolymers K1 and K2 based on XRD examinations. It can be seen that both samples contained high weight percentage of zeolite. Sample K1 was characterized by 70 wt. % of zeolite A (Na$_{12}$ Al$_{12}$ Si$_{12}$ O$_{48}$ (H$_2$O)$_{27}$) and sample K2 contained 90 wt.% of un-named zeolite (Na$_3$ Al$_3$ Si$_3$ O$_{12}$ (H$_2$O)$_2$). Other phase such as hematite and quartz were originated from raw laterite. The presence of analcime phase (Na (Al Si$_2$ O$_6$) (H$_2$O) was formed through alkali activation of kaolinite phase of laterite and become parts of geopolymer paste. These results suggested that the type of zeolite produced through geopolymerisation process of aluminosilicate minerals such as laterite soils depends on oxide molar ratios of SiO$_2$/Al$_2$O$_3$ keeping other molar ratios remains constant. This results are in line with those reported by [13] who synthesized zeolite X dan Y through geopolymerisation of metakaolin. The functional groups of zeolite-geopolymers based on FTIR measurements are shown in figure 5.

Figure 4. Diffractogram of K1 and K2 showing zeolitic phases

Figure 5. FTIR Spectrum of zeolite-Geopolymer for samples K1 and K2
The broad bands around 1650 and 3469 cm\(^{-1}\) were attributed as bending and stretching of water, respectively. The spectrum indicated that sample K2 contain more water than K1. The broad band at 456 and 1002 cm\(^{-1}\) were attributed to the zeolitic formation within the geopolymer network. The presence of band at 1407 cm\(^{-1}\) was due to unreacted parts of laterite during geopolymer synthesis [11].

The surface morphology of zeolite-geopolymer of K1 and K2 were examined by using by using SEM as shown in figure 6(a) and 6(b), respectively. The quality of SEM images of K1 and K2 are not the same due to the difference of SEM used during this study as the first machine for sample K1 was out of order.

![Figure 6. SEM image of Gowa laterite zeolite-geopolymer (a) K1 and (b) K2.](image)

The morphology of K1 and K2 shown in figure 6(a) and 6(b) clearly indicate the crystalline phase of zeolite on the surface of geopolymers. It can be seen, particularly for sample K1 the highly uniform shape of zeolite crystal with a length around 10 μm and wide about 1 μm. The pore structure and distribution have not been able to determined during the time of this study. The formation of zeolitic phase through geopolymerisation route has been subject to intensive research [13–16]. This type of material offer a potential as a new membrane reactor for methanol or alcohol production [17,18], or for molecular separation and adsorption [19].

It well known, however, that the presence of zeolitic phase within the network of geopolymer will reduced the overall mechanical strength of geopolymer [13]. Table 3 shows the compressive and tensile strength of sample K1 and K2 produced in this study.

**Table 3. The magnitude of compressive and tensile strength measurements**

| Sample | Compressive Strength (MPa) | Tensile Strength (MPa) |
|--------|-----------------------------|------------------------|
| K1     | 5.09                        | 3.30                   |
| K2     | 13.77                       | 4.93                   |

Table 3 showed that the magnitude of compressive and tensile strength of K1 and K2 were far below to those of most geopolymer produced from metakaolin or fly ash. It is clear that these materials are not suitable for structural applications which require high mechanical strength.
4. Conclusions
The results of this study showed that laterite soils deposit Gowa Regency, South Sulawesi, which contain high wt.% of hematite has been successfully synthesized as zeolite-geopolymer hybrid bulk material. The mineralogy of laterite soil before and after dehydroxylation was examined by means of SEM-EDS, XRD and FTIR suggesting that the material was suitable as geopolymer precursor. The variation of oxide molar ratio of SiO$_2$/Al$_2$O$_3$ produced zeolitic phase within geopolymer network which is suitable for various catalytic applications. The mechanical strength of zeolite-geopolymer hybrid bulk materials is low and not suitable for structural applications.

References
[1] Lemougna P. N et al 2017 Appl. Clay Sci. 148 109-117.
[2] Gualtieri. M. L et al 2015 Cem. and Conc. 67 259-270.
[3] Subaer et al 2017 MATEC Web Conf. 97
[4] Liew. Y. M et al 2017 Constr. and Build Mat. 156 9-18.
[5] Nguyen. Q. H. et al 2018 Constr. and Build Mat. 191 853-865.
[6] Dogan. H et al 2010 Vacuum 84 1123-1132.
[7] Caro. J et al 2010 Adv. in Nanoporous Mat. 1 1-96.
[8] Takeda. H et al 2013 Characterization of Zeolite in Zeolite-Geopolymer Hybrid Bulk Materials Derived from Kaolinitic Clays 6.
[9] Caro. J et al 2008 Micro. and Meso. Mat. 115 215-233.
[10] Subaer, “Pengantar Fisika Geopolimer” 2015.
[11] Obonyo E. et al 2014 Sustainability 6 5535-5553.
[12] Eisazadeh. A et al 2012 App. Clay Sci. 67-68 5-10.
[13] Subaer et al 2018 Sol. Stat. Phenom. 273 167-174
[14] Lee. N. K et al 2016 Micro. and Meso. Mat. 229 22-30.
[15] Arbel Haddad. M et al 2017 Journal of Nuclear Materials 493 168-179.
[16] Wang. H et al 2018 Engineering 4 406-415.
[17] Gorbe. J et al 2018 Separation and Purification Technology 200 164-168.
[18] Achiou. B et al 2018 Journal of Environmental Chemical Engineering 6 4429-4437.
[19] Abdelrasoul. A et al 2017 Micro. and Meso. Mat. 242 294-348.