Physical-chemistry of Nawangan’s phyrophyllite and its prospective as environmental friendly geopolymer materials

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Abstract. The chemical composition and thermal behaviour of Nawangan-phyrophyllite have been studied using XRF, powder XRD and FTIR. The fourier transformation infrared was applied to analyze the phyrophyllite after treating by calcinating at various temperature. Initial investigation has also been carried out by adding sodium hydroxide and potassium hydroxide to study the possibility of phyrophyllite as geopolymer materials. The phyrophyllite contains Si (57.7%), Al (16.7%), K (20.6%), Fe (2.47%) Ti (2.33%) and Cu (0.088%). Based on the XRD diffractogram, peaks at 2 theta (9°, 20°, 21°, 26°, 34°, 36° and 39°) were characteristic for phyrophyllite. While, infrared study showed that at 3630 cm⁻¹, 756 cm⁻¹ and 938 cm⁻¹ are responsible for phyrophyllite’s peaks. The hydroxyl bonded to alumina still existed under heating up to 400 °C and disappeared at 600 °C. It indicted that covalent bond of Al-OH was broken. By heating at 600 °C, the peak at 1021 cm⁻¹ splitted into two peaks, 990 cm⁻¹ and 1049 cm⁻¹. It may be due to the displacive transition. By adding NaOH 10 M, the peak intensity of Al-OH (3630 cm⁻¹) reduced to 17% but the peak intensity of Al=O (1661 cm⁻¹) incresed to 14% and the new peak (5%) emerged at 1387 cm⁻¹(O-Al-O). The most reactive phyrophyllite was obtained by adding KOH 5 M. The present of reactive functional groups (Al=O, O-Al-O and Al-OH) indicates that the local phyrophyllite has a good change as geopolymer materials.

1. Introduction
Phyrophyllite is one among a lot of minerals in Indonesia that has not been explored due to the limitation of its physical-chemistry properties. It is found at East Java, East Nusa Tenggara, Sumatera and West Java. Phyrophyllite in Nawangan–Pacitan East Java spreads out in about 37 ha [1,2].

It is categorized as methamorphic rock, which is the hardness of 1-2 mosh scale and in general, is isomorphous to tacle. Its structure is a dioctahedral alumina between two tetrahedral silicas, as shown in Figure 1.
Figure 1. The structure of phyropyllite [3]

It has a lamellar structure which the van der Waals bond connected between the tetrahedral SiO$_2$ layers and terminal hydroxyl bonded covalently to the octahedral alumina. Phyropyllite is classified as 2:1 aluminosilicate based on the Si:Al ratio. It is also can be applied as fire and heat resistance materials (refractory products), filler and adsorbent. Mutrofin and Anggraeni (2007) had reported that Phyropyllite taken from Sumbermanjing Malang Selatan-Indonesia work significantly as filler when it was applied to concrete [4,5]. Adding 15% phyropyllite of total concrete mixture increases the compression stress up to 42 % from the characteristic compression stress of concrete without phyropyllite (25 MPa). Phyropyllite as filler and fine aggregate added to asphalt was able to increase the stability of hot roller aspalt toward acid [5].

In this coming work, initial study is conducted to investigate the possibility of phyropyllite as geopolymer materials. According to Joseph Davidovits, there are five types of geopolymer materials based on the Si:Al ratio. They are: 20:1 < Si : Al < 35 : 1; Si : Al > 3 : 1 ; Si : Al = 3 :1; . Si : Al = 2 : 1 and Si : Al = 1 : 1. As the ratio of Si : Al of phyropyllite is 2:1, it has a possibility as a geopolymer material candidate and can be applied as cements, concrete and fire/heat resistance materials [6].

The term geopolymers is introduced as inorganic polymers chain or network consisting of aluminosilicate which is bonded covalently, low calcium content and heat or fire resistant. One of the benefits of geopolymer materials is its low calcium concentration that is greener chemistry when it is used as eco-green cement’s materials compared to the Portland cement that produces a big amount of CO$_2$ emission to the space.

2. Experimental details

2.1 Materials
Nawangan phyropyllite, NaOH AR (Sigma-Aldrich), KOH AR, KBr and aquadest.

2.2 Characterizations
The chemical composition of Nawangan-phyropyllite was analyzed using XRF PANanalytical Type Minipal 4, its phase or crystallinity was characterized using powder XRD PANalytical (PHILIPS) expert pro. Both analyses were done at Centre of Mineral Analysis, State University of Malang. While, the analysis for sodium oxide was carried out using AAS/AA6800 and the infrared study was performed using FTIR Shimadzu 8400 LS, using KBR powder, the number of scanning was 10 and the resolution was 4.0. Both analyses were done at analysis laboratory, Chemistry Department, Brawijaya University. Prior to use, phyropyllite ground to fit the size of 120 mesh. Heat treatment was performed by putting the mineral in the furnace (Carbolite) in various temperatures (200 °C, 400 °C, 600 °C and 800 °C) for 5 hours.

3. Result and Discussion
The chemical composition of Nawangan-phyropyllite analyzed using XRF is tabulated in Table 1 and the picture of phyropyllite are presented in Figure 2. The percentage of silica is the highest and the ratio of silica and alumina is 3:1, but it does not mean that the mineral is not phyropyllite. The present of quartz and kyanite are common in natural mineral. Iron oxide and titanium oxides are detected also and it supposes as hematite and rutile. Potassium oxide, vanadium oxide (karelianite) and copper oxide (cuprite) are found as impurities that fulfill the space in between the phyropyllite structure.

| Table 1. Chemical composition of Nawangan phyropyllite. |
|---------------------------------------------------------|
| The Elements   | Si    | Al    | K    | Fe   | Ti   | Cu  |
| % wt.          | 57.7  | 16.7  | 20.6 | 2.47 | 2.33 | 0.088 |
X-ray powder diffraction analysis is carried out for further characterization. Phyropyllite is amorphous which shows specific sharp peaks at 2θ (9°, 20°, 21°, 26°, 34°, 36° and 39°) based on the JCPDS data. There are 3 identified peaks responsible for phyropyllite with the significant intensity, that are at 2θ (9°, 21° and 26°) [7]. The present of quartz, rutile and hematite are also detected. The diffractogram of Nawangan-phyropyllite is exhibited in Figure 3.

Infrared study reveals that the characteristic peaks of phyropyllite are at 3630 cm\(^{-1}\), 756 cm\(^{-1}\) and 938 cm\(^{-1}\) that are attributable for \(-\text{OH}\) bond to alumina. While the peak at 1021 cm\(^{-1}\) is for Si-O/Al-O which is compatible with the peaks at 538 cm\(^{-1}\) and 477 cm\(^{-1}\). The spectrum of Nawangan- phyropyllite is displayed in Figure 3.
The effect of heat treatment onto Nawangan-phyrophyllite structure was studied by heating the mineral under various temperature, that is: 200 °C, 400 °C, 600 °C and 800 °C. It was heated for 5 hours. Hydroxyl group from water molecules which is shown by the peak at 3443 cm\(^{-1}\) disappears by heating at 200 °C. The peak at 3630 °C (Al-OH) still persist under heating up to 400 °C, but it disappears at 600 °C. At the temperature of 600 °C, the peak at 1021 cm\(^{-1}\) split into two peaks (1049 cm\(^{-1}\) and 992 cm\(^{-1}\)). It may be due to the displacive transition. The spectra of heated phyrophyllite is shown in Figure 4.

**Figure 4.** The spectra of phyrophyllite treated under heating at 200°C, 400°C, 600°C and 800°C

To study the possibility of Nawangan-phyrophyllite as geopolymer material, three treatment was applied by adding aquades, NaOH 10 M and NaOH 15 M to the phyrophyllite powder (120 mesh) with the ratio of 2:1 (phyrophyllite : solvent). Hydrolysis and condensation reaction involves which can produce three proposed new structure of phyrophyllite containing Al-OH, Al=O and Al-O-Al by virtue of inter- and intra-interaction of terminal OH. The reaction scheme is in Figure 5.

The infrared spectra of phyrophyllite (as reference) denoted as (p-r), phyrophyllite + aquades (p-a) , phyrophyllite + NaOH 5 M (p-n5), phyrophyllite + NaOH 10 M (p-n10)/15 M (p-n15) are shown in Figure 5. The infrared spectra of phyrophyllite treated with KOH 5M (p-k5), KOH 10 M (p-k10) and KOH 15 M (p-k15) are displayed in Figure 6.
Figure 5. The hyrolysis and condensation reaction of phyllonite

Figure 6. The spectra of phyllonite-aquades (p-a), phyllonite + NaOH 5 M (p-n5), phyllonite + NaOH 10 M (p-n10) and phyllonite + NaOH 15 M (p-n15)
Figure 7. The spectra of phyopyllite+aquades (p-a), phyopyllite + KOH 5M (p-k5), phyopyllite + KOH 10 M (p-k10) and phyopyllite + KOH 15 M (p-k15)

There is a new peak at 1638 cm\(^{-1}\) for the spectrum of p-a which supposes the peak for Al=O (8% of intensity) while the peak intensity of Al-OH (3630 cm\(^{-1}\)) reduces to 24% compared to p-r (33%). It shows that hydrolysis-condensation reaction occurs reactively in phyopyllite only by adding water. Alkaline treatment by adding NaOH 10 M shows a new peak at 1387 cm\(^{-1}\) (5% of intensity) that is proposed for Al-O-Al vibration. The peak intensity of Al-OH reduces to 17%, the peak intensity of Al=O rises to 14% and the peak intensity for Al-O-Al is 5%. Adding NaOH 15 M exhibits the peaks of Al-OH (22%), Al=O (5%) and Al-O-Al (30%). The most reactive Al is in oxidation state of V, it means that by adding NaOH 10 M, the most reactive product of geo-polymer is obtained. All the data are tabulated into Table 2. Based on the data tabulated in Table 3, the most reactive functional groups were obtained by adding KOH 5 M.

### Table 2. The effect of adding water and sodium hydroxide on the infrared spectra of phyopyllite

| Functional group | Intensity (%) | p-a | p-n5 | p-n10 | p-n15 |
|------------------|--------------|-----|------|-------|-------|
| Al-OH            | 33           | 24  | 18   | 17    | 22    |
| Al=O             | 3            | 8   | 14   | 15    | 5     |
| O-Al-O           | -            | -   | 2    | 5     | 30    |

### Table 3. The effect of adding water and potassium hydroxide on the infrared spectra of phyopyllite

| Functional group | Intensity (%) | p-a | p-k5 | p-k10 | p-k15 |
|------------------|--------------|-----|------|-------|-------|
| Al-OH            | 33           | 24  | 22   | 21    | 15    |
| Al=O             | 3            | 8   | 8    | 9     | 9     |
| O-Al-O           | -            | -   | 17   | 6     | 7     |
4. Conclusions
The physical chemistry of Indonesian’s phyropyllite are: It is composed of Si (57.7%), Al (16.7%), K (20.6%), Fe (2.47%), Ti (2.33) and Cu (0.088%), amorphous that has characteristic peak for phyropyllite at 2θ = 9°, 20°, 21°, 26°, 34°, 36° and 39°. Its characteristic peak of infrared are at 3630 cm⁻¹, 756 cm⁻¹ and 938 cm⁻¹, attributed to –OH bonded to alumina. By heating at 600 °C for 5 hours, the displace transition occur. It is just by adding water, the functional groups of phyropyllite change to the reactive and adding NaOH 10 M and KOH 5 M producing the most reactive sides of phyropyllite.

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