Mineralogy and Characterization of Clay Mineral of West Lampung

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Abstract. Clay mineral resources were found in West Lampung Regency. Local citizen has been using clay for pottery and building materials. Optimization of mineral utilization is needed to increase the economic value of these mineral resources. The study of mineralogy and characterization was carried out to determine the possible uses of clay minerals. The study was conducted on 5 clay samples of different color using XRD, FTIR, TGA, and SEM analysis. The result shows natural clay minerals assemblages are kaolinite and halloysite. Thermal behaviors of the samples have a multi-stage decomposition with relatively stable intermediates. Kaolinite appears like pseudo-hexagonal platelets with various sizes and halloysite looks like a distinct tubular form in different sizes.

1. Introduction
Clay minerals refer to the minerals with less than 2 µm in diameter. Such size was obtained by using a petrography microscope to optically distinguish the smallest particle [1]. Clay minerals are abundant in Indonesia, making it a low-cost mineral resource to exploit. Compared with other raw materials, clay minerals are environmentally friendly raw materials [2]. The weathering process involves physical disaggregation and chemical decomposition converted native minerals into clay minerals [3]. The residual soil submerged by the Quaternary volcanic rock in a general mixture of clay, silt, and fine sand. Residual soils closely related to the weathering of volcanic rock deposits [4].

Indonesia is a tropical climate zone, under high intensity of sunlight, rainy season and humidity levels, so the chemical weathering process occurs rapidly. Clay deposits in Indonesia cover more than two-thirds of the area [4-5], and some are available in West Lampung Regency. Some examples of clay minerals are Kaolinite and halloysite. Kaolinite is an important industrial mineral such as ceramic pastes used for the production of certain types of porcelain, sanitary ware, earthenware, and stoneware. It can be used as paper coating clays, filler clays in several industries, for ceramics and refractory. Halloysite is becoming important with its tubular habit to use in nanotechnology applications for pharmaceuticals, remediation of land or polluted waters and so on.

Mineralogical and characterization research of natural clay is important to determine the utilization of clay mineral resources in West Lampung Regency. Previous studies have shown that clay has potentials use for bricks, tile making, solid fine earthenware and acid-resistant materials, and fire-resistant materials [6]. This research was conducted on clay samples which represent different physical colors, to determine its properties and constituent minerals for determining the utilization of clay resources.
1.1. Geological Setting

Based on the geological map of Kotaagung Sheet [7] and Baturaja Sheet [8], published by the Research and Development Center for Geology, Department of Energy and Minerals Resources, Indonesia, the research area is classified into three rock formations (Figure 1). There are Quaternary Volcanic Rock, Quaternary-Tertiary Pyroclastic Rock, and Tertiary Volcanic Rock [7-8]. Each of these groups is divided into several rock units [9], among others; Quaternary volcanic rocks (Qhvs) namely Sekincau volcanic rocks in the formation of andesite lava, volcanic breccias, tuffs with clay insertion containing charcoal, these units were good consolidated. These volcanic rocks are Pleistocene-Holocene aged.

Pyroclastic rocks are composed of Ranau Tuff (QTr) or Plio Pleistocene Liwa Tuff. Tertiary volcanic rocks (Tomh) are basaltic-andesitic volcanic rocks in the Hulusimpang Formation, which are in the Early Oligocene-Miocene age. The distribution of clay deposits (halloysite) is associated with weathering and/or hydrothermal alteration of Pliocene andesitic lava, andesitic breccias and Pleistocene pyroclastic deposits [10]. Post depositional alteration on intercalated pyroclastic tuff deposits results in dominant halloysite clay or mixed halloysite/kaolinite clay.

2. Methodology

Five samples of natural clay were collected from the West Lampung region. The samples were grouped based on their differences in physical color (Figure 2). They were prepared into grain sizes of <2 mm material.

The mineralogical composition was determined by X-ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM). XRD analyze trough XRD Maxima-7000 Shimadzu in The Research Center for Geotechnology Laboratory, while SEM analysis was carried out in The Research Unit for Clean Technology laboratory by using JEOL JSM-IT300LV SEM instrument in December 2019. XRD technique used to characterize the crystalline materials of the sample.
and determination of their structure. Each solid crystalline material possesses a unique characteristic X-ray powder pattern, and it can be used as a “fingerprint” for its identification [11]. Identification of clay minerals assemblages was conducted by comparing the peak intensity position (2θ) in the sample X-ray diffraction pattern with the peak position value of the diffraction intensity (2θ) standards contained in the Joint Committee for Powder Diffraction Standards [12]. SEM analysis observes the particles with high magnification in terms of understanding their morphology, texture, topography, etc [13]. SEM is one of the best instruments to recognize the micro fabric of soils and their microstructures, which constitute macro fabric.

![Figure 2](image)

**Figure 2.** Samples of natural clay from West Lampung Region, grouped by color difference

Fourier transforms infrared spectroscopy (FTIR) method was used to identify the organic materials and a small number of inorganic compounds. FTIR data were collected trough IRTracer-100 FTIR Spectrophotometer Shimadzu in The Research Center for Geotechnology Laboratory in September 2019. The FTIR techniques used to distinguish different types of clay minerals and to derive information concerning structure, composition and structural changes upon chemical modification of clay minerals. The instrument is the most informative technique for assessing mineralogy and crystalline chemistry from clay mineral samples [14].

Thermogravimetric Analysis (TGA) was carried out in The Research Center for Geotechnology Laboratory by using TGA analyzer Leco TGA-701 in September 2019. TGA was a quantitative measurement technique for analyzing the changes within the sample mass that experiences temperature changes in a controlled environment. The samples (4-7 mg) were placed in a platinum pan and heated up to 900°C at a rate of 10°C/min under nitrogen purge (30 mL/min). The TGA records mass changes due to dehydration, decomposition, and oxidation of the sample with time and temperature. Changes in mass over a certain temperature range give an indication of sample composition, including volatiles such as water and solvents, and indications of thermal stability.
3. Results and Discussion

3.1. X-Ray Diffraction

XRD analyses were performed on the fifth samples (Figure 3), X-Ray Diffraction pattern shows similar peaks value among the samples. The XRD pattern observe some absorption peaks at \(2\theta = 12.2^\circ, 20.2^\circ\) and \(35.2^\circ\) attributed to 7 Å Halloysite [15]. Diffraction peaks with intensity value 674, 384, 332, 364 and 318, (background counts are around 240 cps), at \(2\theta = 21.2^\circ, 24.9^\circ, 35.9^\circ, 36.8^\circ\) and \(38.6^\circ\) attributed to Kaolinite [16]. The clay mineral assemblages are composed of halloysite and kaolinite.

![XRD patterns of natural clay samples. Kao = kaolinite, Hall = halloysite, the horizontal axis, and the vertical axis (2\(\theta\) value 10\(^\circ\) to 60\(^\circ\), 240 cps) represent the intensity of the X-ray and the angle of the detector receives at 2\(\theta\).](image-url)

**Figure 3.** XRD patterns of natural clay samples. Kao = kaolinite, Hall = halloysite, the horizontal axis, and the vertical axis (2\(\theta\) value 10\(^\circ\) to 60\(^\circ\), 240 cps) represent the intensity of the X-ray and the angle of the detector receives at 2\(\theta\).
3.2. FTIR
Figure 4 shows the FTIR spectra from wave number 400 – 4000 cm\(^{-1}\) for each five clay samples. Based on the absorption of FTIR spectra, sharp peaks appear in wave number 3697, 3624, 1649, 1278, 1207, 1110, 935, 806, and 700 cm\(^{-1}\).

![FTIR spectra diagram](image)

**Figure 4.** FTIR diagrams of Clay Samples, the X-axis and Y-axis represent the infrared spectrum and the amount of infrared light absorbed or transmitted by the sample material.

Vibration bands from all samples show the similarity of the peak pattern of the IR spectrum. In the range of 400 – 1550 cm\(^{-1}\), there were five uptakes at band 700, 806, 935, 1110, 1207 and 1278 cm\(^{-1}\), show vibration Si-O-. There was also absorption in 1649 cm\(^{-1}\) among the wave number 1550 – 1650 cm\(^{-1}\), it attributes to absorption of the –OH buckling vibration trapped in the lattice crystal. The sharp peak between 2500 - 4000 uptake of 3697 and 3624 cm\(^{-1}\) indicates to absorption caused by a single OH bond. The peak of the uptake area 3697 cm\(^{-1}\) corresponded to the OH scratching vibrations of the structural OH groups [17].

3.3. TGA
The results of the TGA weight loss profile of the samples are shown in Figure 5. Weight loss began with an increasing temperature of 29° to 900°C. The first region showed mass degradation was very sharp between temperatures 29° to 100°C. Thermal reaction paths in the second region showed a gradual change of weight at 100° to 800°C. In the third region, mass loss was relatively stable above 800°C.

The TGA characterizes physical and chemical changes of materials with temperature by monitoring its mass change [18]. The weightloss (WL) calculated between 26°C and 900°C (peak heating temperatures) using the following formula [19-20]:

\[
\text{WL} = \frac{m_1 - m_2}{m_0}
\]
Md is the dry mass and Mf is the heated mass (at each final heating temperature).

\[
WL (\%) = \left(\frac{Md - Mf}{Md}\right) \times 100
\]  

(1)

Three regions selected in the thermogravimetric pattern for the samples (Figure 5). Weight loss in the first region attributed to physisorbed water, low molecular weight volatile compounds and trapped gases evolve. In the second region, the gradual change of weight at 100 to 800°C the mass loss is due to chemisorbed water and low molecular weight compounds like additives and volatile decomposition. In the third region, at temperature 800°C, the limit stability of the clay sample reaches above 800°C. It corresponded to the removal of organic clay residues and strengthening of interlayer anions and removal -OH group bonds. The thermogravimetric curve based on the Main Types of TGA Curve [21-22] was classified as type IV (Figure 6). It indicates a multi-stage decomposition with relatively stable intermediates.

**Figure 5.** TGA diagrams of natural clay samples, weight loss changes vs. temperature. The purple dotted line shows the three regions selected in the thermogravimetric pattern for the sample.
Figure 6. The main types of TGA curve (Duval, 1973 in Brown, 2001)

Figure 7. SEM image of natural clay from West Lampung region (a) EV 2, (b) EV 3, (c) S 8, (d) DS 9 and (e) S 10B
3.4 SEM
The Figure 7 is the micrograph's appearance of SEM analysis results of the natural clay samples. The micrograph image of the samples exhibits diverse microstructure and particle size of the constituent minerals. Some pseudo-hexagonal platelets in various sizes appear with an irregular edge (Exhibit in Figure 7a–e). A few particles contact each other, there is a little agglomerate phenomenon and some flakes are separated individually. While some minerals look like a distinct tubular form in different sizes. The presence of tubular minerals appears in Figure 7 (a, c and e).

The kaolinite crystals are predominantly elongated, rounded, and subrounded with a relatively lower proportion of hexagonal particles [23]. The halloysite generally has a fibrous, spheroidal or irregular morphology, and its fibers appear in electron micrographs to be tubular or scroll-like with elongation parallel to y [24]. The halloysite and kaolinite may occur together in nature because they formed under similar conditions in soils and weathered and hydrothermally rock alterations. These minerals have a similar structure, composition, and genesis [25]. The tubular form of halloysite becomes an important criterion to distinguish it from the other kaolin group minerals [26].

4. Conclusion
Based on the analysis of the samples by using SEM, XRD, FTIR, and TGA methods, natural clay minerals from West Lampung region composed as kaolinite and halloysite. Thermal behaviors of the samples have a multistage decomposition with relatively stable intermediates. Kaolinite appears like pseudo-hexagonal platelets with various size and halloysite looks like a distinct tubular form in different sizes.

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