Characteristics and utilization of clay minerals in Kuwu Mud Volcano, Kradenan District, Grobogan Regency, Central Java Province

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Abstract. The benefits of clay minerals are currently numerous. Therefore, this study aims to determine clay minerals' characteristics in the mud material recommended for use, especially in the ceramic and cosmetic industry. This research is located in Bledug Kuwu, in Kuwu Village, Kradenan District, Grobogan Regency, Central Java Province. Bledug Kuwu produces mudflows composed of gravel, sand, silt, plastic clay, and water. Field observations and sampling were carried out on any differences in the morphology of the existing mud volcanoes, namely inactive craters and active griffins, with an average area of about 0.8–5 meters of mud material distribution. Samples were prepared to analyze X-ray diffraction (XRD), cation exchange capacity (CEC), pH, grain size distribution, plasticity test, swelling test, shrinkage limit test, and specific gravity. The results of the analysis show that the dominant clay minerals were smectite, followed by kaolinite and illite minerals, with dominant clay to silt grain sizes, plasticity levels of 24.78% to 55.48%, swelling percentage of 7.8% to 12.5%, with shrinkage limits of 9.36% to 14.83%, specific gravity values of 2.50–2.84, cation exchange capacity (CEC) values of 9.96–20.47 meq/100g, and the pH value shows the numbers 8.01–8.40. These characteristics can be recommended to use clay minerals as raw material for cosmetics and ceramics.

1. Introduction
Mud volcanism is a unique phenomenon. The periodic eruptions of large quantities of gases (mainly hydrocarbons) included rock fragments ranging in size from small to several meter blocks. The eruptive products accumulate near volcanic cone vents and craters. The size of a volcanic cone depends on the frequency of eruptions and the eruptive material's character [1]. Mud volcanoes have long been known in Indonesia. There are several active mud volcanoes, including Bledug Kuwu, Bledug Medang, Bledug Kesongo in Central Java Province [2]. Bledug Kuwu is a mud volcano phenomenon located in Kuwu Village, Kradenan District, Grobogan Regency (Figure 1). This 45-hectare area is unique and is one of the mainstay tourist attractions in Grobogan Regency. The mud is composed of gravel, sand, silt, plastic clay, and water. The material originates from the clay facies of the Pucangan Formation or the Pleistocene Lidah Formation from a depth of 750 to 1900 meters [3]. According to Ibrahim et al. [4], the mud volcano formed millions of years ago (5 million years) can upward to the surface until now due to tectonic pressure. Bledug Kuwu Mud Volcano lies on the active mud volcano that stretches from Purwodadi, Cepu, Bojonegoro to Porong.

Research on mud volcanoes in Indonesia has been widely carried out by researchers such as [5,6,7,8,9]. The research includes a discussion of the dynamics of mud volcano movement, the
characteristics of swelling and shrinkage in clay minerals, physicochemical properties of clay minerals in mud volcanoes, identification of mud volcano properties and their utilization, geological conditions, and characteristics of clay minerals in mud volcanoes. These studies took data from several fields, i.e., active mud volcano complexes such as the Kradenan Mud Volcano Complex, Cengklik mud volcano, and Sidoarjo mud volcano. In 2016, Utama researched the implications of the constituent materials' characteristics and the mud's viscosity value on the morphological formation of the Kesongo Mud Volcano in Blora Regency, Central Java Province [10]. This study aims to determine the mud material's mineralogical and physical characteristics in the Bledug Kuwu mud volcano (Figure 1) and determine the possible utilization of clay minerals that have economic value in various industrial fields, especially cosmetics and ceramics.

![Figure 1](image-url) The research location is Bledug Kuwu mud volcano, Kradenan District, Grobogan Regency, Central Java Province. Map of Java Island and map of mud volcano locations (adapted from Google Maps).

2. Geological setting
The research area is located in the central part of Java Island. It is included in the Randublatung Zone, elongated depression or valley between the Kendeng Hills and Rembang Hills. According to Van Bemmelen, the Randublatung Depression was formed as a subsidence area, part of a regional isostasy equilibrium when the Rembang Hills and Kendeng Hills experienced tectonic uplift at the end of the Tertiary [2]. Stratigraphically, the Randublatung Zone has rock sequences such as those that develop in the Rembang Zone and Kendeng Zone. The stratigraphic order of the Randublatung Zone, according to Datun et al. [11], is the Tawun Formation, Ngrayong Formation, Wonocolo Formation, Ledok Formation, Mundu Formation, Selorejo Formation, and Tambakromo Formation. The anticline folding pattern in the Randublatung Zone still follows the Kendeng Zone fold pattern. This shows that
the negative isostasy process is not the main factor in forming the Randublatung Zone. There are also compressive tectonic factors in the formation of the zone, as happened in the Kendeng Zone [12].

3. Methods
The research location is in Kuwu Mud Volcano, Kuwu Village, Kradenan District, Grobogan Regency, Central Java Province, the Kradenan Mud Volcano Complex (KMVK) in the Randublatung Depression Zone. This research uses grain size distribution analysis methods, X-Ray Diffraction (XRD) analysis, plasticity test, swelling test, shrinkage test, specific gravity analysis, cation exchange capacity (CEC) analysis and pH analysis. The interpretation of X-ray diffraction data was based on [13,14].

4. Results
4.1. Field data
Based on the field observations, there are two morphological types of mud volcano in the study area, i.e., active craters and active gryphons (Figure 2). The data of each morphology can be seen in the Table 1.

| Sample code | Coordinate | Morphology Type | Length (m) | Width (m) | Height (m) | Spread of Mud Materials |
|-------------|------------|----------------|------------|-----------|------------|------------------------|
|             | X          | Y              |            |           |            | Length (m) | Width (m) |
| STA 1       | 513317     | 9213218        | Active crater | 3         | 2          | -          | 4 | 4 |
| STA 2       | 513425     | 9213223        | Active crater | 5         | 5          | -          | 5 | 5 |
| STA 3       | 513509     | 9213247        | Active gryphon | 1.5       | 0.8        | 0.2        | 0.3 | 0.1 |
| STA 4       | 513572     | 9213291        | Active crater | 5         | 2          | 1          | 6 | 3 |
| STA 5       | 513546     | 9213178        | Active crater | 0.5       | 0.7        | 0.5        | 0.8 | 0.9 |
| STA 6       | 513496     | 9213313        | Active gryphon | 1         | 1.5        | 0.5        | 2 | 2.5 |

4.2. Laboratory analysis results
4.2.1. Physical properties of mud material
The dominant grain size distribution of mud material ranges from clay to silt size, with a plasticity level of 24.78% to 55.48%, a swelling percentage of 7.8% to 12.5%, with a shrinkage limit of 9.36% to 14.83 %, and the value of specific gravity are 2.50–2.84. The chemical characteristics of clay minerals produce a Cation Exchange Capacity (CEC) value of 9.96–20.47 meq/100g and a pH value of 8.01–8.40.

4.2.2. Mineralogical characteristics of mud material
Clay minerals characteristics were based on the results of X-ray Diffraction (XRD) analysis (Figures 3–4). XRD analysis using both random powder and clay oriented was carried out on 4 selected samples, namely KW-01, KW-02, KW-03, and KW-04. The results of XRD analysis showed that the mud samples at Kuwu Mud Volcano consisted of clay minerals and non-clay minerals. Clay minerals have a greater abundance than that non-clay minerals. The clay mineral with the greatest abundance is smectite, followed by kaolinite and illite minerals. The non-clay minerals that appear are halite, calcite, quartz, and plagioclase minerals (Figure 3).
Figure 2. Map of the morphological distribution in the Kuwu Mud Volcano.

Figure 3. Mineral identification from XRD results for all four samples based on random oriented measurement.
Figure 4. X-ray diffractogram of selected mud samples from the Kuwu Mud Volcano measured by clay treatment (air-dried, ethylene glycol, and heated 550°C).

Smectite is a clay mineral that is dominant in all mud samples. In the bulk analysis, smectite minerals will appear at peak \( d \) \(15.05–16.70\) Å (\(2\theta = 5.28–5.78\)°). In the clay treatment by air-dried, ethylene glycol and heated 550°C, smectite appeared at peak \( d \) 17.72–18.79 Å (\(2\theta = 4.99–4.60\)°); \( d \) 2.81–2.82 Å (\(2\theta = 31.60–30.30\)°); \( d \) 3.03–5.03 Å (\(2\theta = 29.3–17.5\)°). Besides, smectite has characteristics that when treated with ethylene glycol, the peak will shift from the air-dried treatment that has been done before. When it is heated to 550°C, the smectite peak will shift, or possibly even the peak will disappear (Figure 4).

Kaolinite is a clay mineral with the second largest percentage of all mud samples. In the bulk analysis, kaolinite minerals will appear at the \( d \) peak of 7.14–7.17 Å (\(2\theta = 12.38–12.31\)°). In the clay treatment by air-dried, ethylene glycol and heated 550°C, kaolinite appeared at peak \( d \) 7.26–7.34 Å (\(2\theta = 12.15–12.02\)°); \( d \) 3.58–3.60 Å (\(2\theta = 24.90–24.80\)°). Also, kaolinite has characteristics that when treated with ethylene glycol, the peak will not change from the air-dried treatment that has been done before. When it is heated at 550°C, the peak kaolinite will disappear completely.
Ilite is a clay mineral with the lowest percentage in the entire mud sample. In the bulk analysis, illite mineral will appear at peak $d = 9.04–10.99$ Å ($2\theta = 9.76–8.03^\circ$). In the clay treatment by air-dried, ethylene glycol and heated 550°C, illite appeared at peak $d = 10.15–10.78$ Å ($2\theta = 8.85–8.20^\circ$); $d = 5.02–5.11$ Å ($2\theta = 17.50–17.02^\circ$); $d = 3.25–3.36$ Å ($2\theta = 27.3–26.5^\circ$). Also, illite has characteristics when treated with ethylene glycol, so the peak will not change from the air-dried treatment that has been done before; even when given heated 550°C, the peak mineral illite remains the same.

5. Discussion

5.1. Morphological distribution on the Kuwu Mud Volcano

The main morphology of the Kuwu Mud Volcano area is in the form of active gryphons and active crater holes with varying dimensions spread widely and unevenly. The large gryphons and main crater holes are located in the central and western parts of the Kuwu Mud Volcano manifestation area. Based on field observations, it can be seen that there are two types of mud volcano morphology in this area, namely in the form of active craters and active gryphons. The active eruption has resulted in a more gentle or flat morphological distribution in the west of the Bleduk Kuwu area.

5.2. Clay mineral utilization recommendations

Based on the analysis results, it can be seen that the mineralogical characteristics, physical properties, and chemical properties of clay minerals contained in the mud samples in the Kuwu Mud Volcano area, so that clay minerals can be recommended as raw materials in making cosmetics according to the specifications.

The comparison of physical and chemical characterization shown in the table shows that the mud samples from the Kuwu Mud Volcano contain predominantly clay minerals of the kaolinite type, which can be recommended as raw materials in making cosmetics, especially powder cosmetics (Table 2). However, there is a significant comparison between CEC values (Table 3). According to standard specifications, in the clay samples from Kuwu Mud Volcano with CEC values, the use of clay minerals for cosmetics is extensive. The research must be specific to only one type of mineral. Apart from the cosmetic industry, it turns out that the clay minerals in the mud samples in the Kuwu Mud Volcano area can also be recommended in the manufacture of ceramic raw materials according to the right specifications (Table 4 & 5).

| Physical Properties | Remarks |
|---------------------|---------|
| Grain size distribution | Clay–silt |
| Plasticity Index (PI) | 24.78 – 55.48% |
| Swelling | 7.8 – 12.5% |
| Shrinkage Limit | 9.36 – 14.83% |
| Specific gravity | 2.50 – 2.84 |

Table 2. Comparison of physical characteristics of clay in Kuwu Mud Volcano with standard specifications for making cosmetics in the form of powder.
according to the specification standard. The use of clay minerals for this ceramic is extensive, and the research must be specific to only one type of mineral. Therefore, the CEC and pH values will result in reactions between the bonds between the clay mineral structures, which will later affect the ceramic formation process's strength.

Table 3. Comparison of chemical characteristics of clay in Kuwu Mud Volcano with standard specifications for making cosmetics in the form of powder.

| Chemical Properties            | Remarks                  |
|-------------------------------|--------------------------|
| Kuwu Mud Volcano samples      |                          |
| Cation Exchange Capacity (CEC)| 9.96 – 20.47 meq/100g   |
| pH                            | 8.01 – 8.40              |
| Standard Specification (Source: ClearOFF™ Minerals – Natural Mineral Solutions [15]) | |
| Cation Exchange Capacity (CEC)| 74 – 90 meq/100g         |
| pH                            | 6 – 10.8                 |

Table 4. Comparison of physical characteristics of clay in Kuwu Mud Volcano with standard specifications for making ceramics.

| Physical Properties | Remarks |
|---------------------|---------|
| Kuwu Mud Volcano samples |         |
| Grain size distribution | Clay–silt |
| Plasticity Index (PI) | 24.78 – 55.48% |
| Swelling             | 7.8 – 12.5%  |
| Shrinkage Limit      | 9.36 – 14.83% |
| Specific gravity     | 2.50 – 2.84  |
| Standard Specification [16] |        |
| Grain size distribution | Clay–silt |
| Plasticity Index (PI) | 35 – 45%    |
| Swelling             | 10 – 30%    |
| Shrinkage Limit      | 3.36 – 10%  |
| Specific gravity     | 1.75 – 2.95  |

Table 5. Comparison of chemical characteristics of clay in Kuwu Mud Volcano with standard specifications for making ceramics.

| Chemical Properties            | Remarks                  |
|-------------------------------|--------------------------|
| Kuwu Mud Volcano samples      |                          |
| Cation Exchange Capacity (CEC)| 9.96 – 20.47 meq/100g   |
| pH                            | 8.01 – 8.40              |
| Standard Specification [16]   |                          |
| Cation Exchange Capacity (CEC)| 3.73 – 5.97 meq/100g    |
| pH                            | 9 – 9.1                  |

6. Conclusions
Based on the results of the data exposure and discussion described in the previous sections, the conclusions that can be drawn for this research are as follows:

1. The characteristics of clay mineralogy in the Kuwu Mud Volcano area are predominantly smectite-type clay minerals followed by kaolinite and illite minerals. For physical characteristics, the dominant grain size distribution from clay to silt size, with a plasticity level of 24.78% to 55.48%, a swelling percentage of 7.8% to 12.5%, with a shrinkage limit of 9.36% to 14.83. % and the value of specific gravity are 2.50–2.84. The chemical characteristics of clay minerals produce a Cation Exchange Capacity (CEC) value of 9.96–20.47 meq/100g and a pH value of 8.01–8.40.

2. Through the analysis and processing of data on mineralogical characteristics, physical and chemical properties of the previous clay minerals, it is recommended that the use of clay minerals
in the Kuwu Mud Volcano area in the industrial sector, namely as a raw material for making cosmetics, especially powder and for making pottery-type ceramics.

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