MINERALOGICAL, PHYSICOCHEMICAL AND MORPHOLOGICAL CHARACTERIZATION OF OKPELLA CLAY

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Abstract: *Local clay mineral was mined from Okpella Town, Etsako Local Government Area of Edo State, Nigeria. Mineralogical characterization of the clay was carried out using X-ray diffraction analyzer. Chemical characterization of the clay was carried out using X-ray fluorescence analyzer and the pH analysis of the clay was carried out using pH meter. The mineralogical analysis revealed that the clay was majorly a dolomite mineral having 72% dolomite. The impurities present are 18% cristobalite, 4.1% garnet, 5% calcite and 1% quicklime. The pH analysis of the clay revealed that the clay was acidic having average pH value of 3.9. The pH determined for the 1:1, 1:2, 1:4, 1:8 and 1:10 samples were 3.61, 3.85, 3.85, 4.05 and 4.09, respectively.*

1. Introduction

Clay is a naturally occurring powder mineral formed by the weathering action of rocks, majorly granite feldspathic and igneous rocks [1]. Clay minerals are layered type hydrous aluminosilicates. Their chemical structures are made of layers of silica and alumina sheets stacked upon each other in a specific pattern. Particle size of clay mineral is in the range of 1 – 2 μm . Clay minerals are the major constituent of fine-grained sediments and rocks [2,3]. Clay minerals possess different classifications based on the number of alumina and silica sheets involved in their structural architecture. The major structural classifications of clay are the 1:1 and the 1:2 structural types. The structural classifications of clay determine their mineral categories which include kaolinite, montmorillonite, illite, vermiculite and chlorite [1]. Each of these classifications of clay possess their unique properties which make them preferable in some specific industrial applications where clay is needed. However, clay generally possess a set of excellent properties that make them suitable for a wide industrial and domestic applications. These properties include plasticity, chemical and temperature resistance, malleability, and complex composite formulations.

Clay is used in a variety of industrial applications such as including paper processing, cement manufacturing, chemical filtration, water treatment, cement manufacturing, paint processing, agricultural soil treatment, ceramic processing and building and road construction. [4, 5, 6]. Clay and other clay-like materials such as dolomite and limestone powder have been widely used as supplementary cementitious material (SCM) in the modern construction industry [7,8, 9].

Dolomites are subsurface cements and replacements that form below active phreatic zone reflux and mixing zones in permeable intervals flushed by warm to hot magnesium-enriched basinal and hydrothermal waters [10]. Dolomite is a natural mineral found in seabed and rock deposits among others. Dolomite chemical structure contains layers of carbonate separated by alternating layers of calcium and magnesium ions make up the ideal structure of stoichiometric dolomite [11, 12]. The mineral name got its origin as a name in honour of a French geologist Deodat Guy de Dolomieu [13]. Dolomite belongs to the flux and building minerals category and is used in the iron and steel and Ferro-alloys industries [14]. Dolomite is chemically represented as $\text{CaCO}_3 \cdot \text{MgCO}_3$ and it theoretically contains 54.35% of CaCO_3 and 45.65% of MgCO_3 [13, 14, 15]. Although, in nature dolomite does not occur in this precise proportion due to presence of impurities. Therefore, the rock having 40–45% MgCO_3 is commonly referred to as dolomite.

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This study is aimed at determining the mineralogical and chemical characteristics of Okpella clay so as to provide an informed insight on its economic viability in terms of determining its suitable industrial application.

2. Materials and methods

2.1. Materials

Okpella clay was collected from Okpella deposit, Etsako Local Government Area of Edo State, Nigeria. Equipment used include X-ray Diffraction machine (Model; Rigaku MiniFlex), scanning electron microscopy (Model; Phenom ProX), weighing balance and X-ray fluorescence machine (Model; SKYRAY-EDX3600B). Other apparatus and materials used include pH meter and glassware.

2.2. Methods

Sample to be analyzed was pulverized to powder size and pressed to make thin layer which was placed in a flat sample holder of the XRD machine. XRD scan was carried out at Bragg's angle range of 5° - 70° with a Bragg's angle interval of 0.026261 at 8.67 seconds per step. The X-ray tube was operated at 40 mA and 45 VA. X-ray fluorescence analysis was conducted using SKYRAY-EDX3600B. Scanning electron microscopy (SEM) was carried out using Phenom ProX Desktop SEM. Sample wafer was placed in the sample chamber of the SEM machine and the SEM gun was focused on a selected area of the sample at certain magnification. The electron gun shot a beam of high energy electrons on the focused area to generate a SEM micrograph of the sample. pH analysis was conducted by inserting the electrode of pH meter in clay-water mixture. Various samples of clay-water mixtures using 10 g constant weight of clay in varying weight of water to make 1:1, 1:2, 1:4, 1:8 and 1:10; wt%-wt% of clay-to-water were prepared and analyzed.

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows both the qualitative and quantitative XRD analysis of Okpella clay. The qualitative analysis present results of the Bragg's angle in degree against the intensity in count of the various mineral present in the clay. Analysis of the quantitative XRD revealed that Dolomite phase was identified at Bragg's angle values of 31.06° , 41.28° and 51.13° . Quartz (Cristobalite) phase was identified at Bragg's angle values of 21.66° and 69.11° . The peaks for Garnet phase were at Bragg's angle of 22.20° and 60.0° . The peaks for Calcite were at Bragg's angle of 29.63° and 45.04° . The peaks for Quicklime were at Bragg's angle of 33.6° and 37.33° . The quantitative XRD analysis shown as the pie chart in Figure 1 revealed quantities of the various minerals present in the clay. It could be observed that Dolomite, Quartz (Cristobalite), Garnet, Calcite and Quicklime were present at 72%, 18%, 4.1%, 5% and 1%, respectively.

Figure 1. X-ray Diffraction of Okpella clay

3.2. X-ray fluorescence analysis

Table 1 presents the XRF chemical composition analysis of Okpella clay. The SiO₂ content of the clay was 37.4 wt% and the Al₂O₃ content was 7.6 wt%. The silica-alumina content of the clay was high having value of 4.9. of 41.61%. Although the silica and alumina content of the clay were higher than values reported for pure dolomite [14], the silica-alumina ratio falls within reported values [14]. CaO was the highest metallic oxide having value of 42.6 wt%, this is consistent with report by other researchers [13,14]. The high CaO content further validates the XRD result showed that dolomite was the highest single-phase mineral present in Okpella clay. The other substantial metallic oxides compositions of the clay were MgO and Na₂O which were present at 7.5 and 3.8 wt%, respectively. The MgO which is also a key chemical constituent of dolomite was lower in the current study than 12.8 wt% reported by Pradeep et al., [14] for a pure dolomite. The substantial presence of Al₂O₃ was as a result of alumina presence in garnet while high SiO₂ was due to its presence in the cristobalite impurity. Other metallic oxides such as K₂O, Fe₂O₃, TiO₂, P₂O₅ and SrO were only present in trace quantities less than 0.3 wt%. Their presence could be attributed to the presence of associated impurities in the clay.

Table 1 X-ray fluorescence analysis of Okpalla clay

Metalic Oxide	wt%
CaO	42.6
SiO ₂	37.2
Al ₂ O ₃	7.6
MgO	7.5
Na ₂ O	3.8
SO ₃	0.3
K ₂ O	0.2
Fe ₂ O ₃	0.2
TiO ₂	0.1
La ₂ O ₃	0.1
P ₂ O ₅	0.1
SrO	0.1

3.3. pH analysis

Table 2 presents the pH analysis of Okpella clay. It could be observed that at the various water to clay ratio the pH was at acidic range having the lowest value of 3.61 at the 1:1 ratio sample. The pH value increased marginally with increase in the water content of the clay-water mixture. The highest value was recorded at 1:10 sample having pH value of 4.09. Using Equation (1) the average pH of the clay was determined as 3.9. The acidic pH of the clay suggested that the clay originated from weathering of igneous rock [16]. Also, the acidic pH was possibly due to presence of some acidic impurities which may be sulphate salt as the presence of 0.3 wt% of SO₃ was confirmed in the XRF result of the clay.

Table 2. pH analysis of Okpella clay at varying ratio of clay-water mix

Clay-water ratio	1:1	1:2	1:4	1:8	1:10
pH	3.61	3.85	3.85	4.05	4.09

$$\text{Average pH} = \frac{\sum \text{pH}}{n} = \frac{19.45}{5} = 3.9 \quad (1)$$

3.4. Scanning electron microscopy

Figures 2(A), 2(B), 2(C) and 2(D) show the SEM micrographs of Okpella clay at 300x, 500x, 1000x and 1500x magnifications, respectively. Analysis of the micrograph shows that the clay possessed dispersed morphology having tetrahedral crystal shape with some level of crystal defects. The average particle size was estimated to be 350 µm.

Figure 2. SEM image of Okpella clay at; (A) 300x magnification; (B) 500x magnification (C) 1000x magnification; (D) 1500x magnification

4. Conclusion

Mineralogical characterization of Okpella clay has shown that the clay is a dolomite mineral consisting of 72% dolomite. Other impurity phases present in the clay were cristobalite, garnet, calcite and quicklime, they were present by 18%, 4.1%, 5% and 1%, respectively. Chemical characterization of the clay further confirmed presence of dolomite as indicated by substantial content of CaO and MgO at 42.6 and 7.5 wt%, respectively. The XRF analysis further confirmed presence of cristobalite and quicklime as impurity phases present in the clay as indicated by the substantial SiO₂ and Na₂O content of 37.2 and 3.8 wt%, respectively. Although, Okpella clay was majorly a dolomite mineral it also contained some impurity minerals which were responsible for the its higher Al₂O₃ and SiO₂ content compared to reported values [14] for a pure dolomite. SEM Analysis of Okpella clay has shown that the clay possessed dispersed morphology having defective tetrahedral crystal shape. The pH determined for the 1:1, 1:2, 1:4, 1:8 and 1:10 clay-water mixture samples were 3.61, 3.85, 3.85, 4.05 and 4.09, respectively. The average pH of the clay was 3.9. The acidic pH of the clay suggested that the clay originated from weathering of igneous rock [16]. The acidic pH of the clay could also be due to presence of acidic salt impurity which was likely a sulphate salt as suggested by the XRF result which shows presence of 0.36 wt% SO₃. In view of the findings of this study Okpella dolomite is recommended as a good raw material for production of cement. The dolomite content can even be improved if beneficiation of the clay is carried out.

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