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PHYSICO-CHEMICAL AND MINERALOGICAL PROPERTIES OF A CLAY MINERAL DEPOSIT IN GEHEKU, KOGI STATE, NIGERIA

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Abstract

The physico-chemical and mineralogical properties of a clay mineral deposit in Geheku, Kogi State, Nigeria were assessed. The results of the study revealed that the deposit consisted of phyllosilicate minerals- Illite, montmorillonite, kaolinite, halloysite, almandine; other minerals present were quartz and ramsdellite. The clay minerals exhibited good swelling property, medium plasticity, good thermal shock resistance and apparent porosity; it had refractoriness below 1200 °C. The properties of the clay reflected the combined properties of the constituent clay and non-clay minerals which recommends it for a variety of applications which requires the blend of property though the working temperature must be below 1200 °C. The clay mineral deposit colours were influenced by the minerals almadine and ramsdellite.

Key words: phyllosillicates, swelling, plasticity, porosity, thermal property

Introduction

Clay refers to a naturally occurring material composed primarily of fine-grained minerals with particle size less than 2 microns. When mixed with water, it becomes plastic and can be moulded into any shape and will harden when dried or fired [1, 2]. It consists mainly of hydrous aluminosilicate minerals arranged in well-defined octahedral and tetrahedral geometry which results in closely packed layers or sheets [3, 4]. It is classified structurally as (1:1) if the clay is made up of single units of silica tetrahedral and alumina octahedral respectively, (2:1) if, there are two silica tetrahedral units in which an octahedral alumina unit is sandwiched between the silica sheets [5]. In addition, it also contains other materials such as oxides of alkali and alkaline earth metals, silicate minerals and non-aluminosilicates such as shale and argillaceous materials which influence the properties and end use of the clay [6]. On account of the differences in the behaviour of clays when they absorb water, they are also loosely classified as expanding (montmorillonite which swells to several times its original size on absorption of water) and non-expanding (kaolinite) [7]. Clays have several applications in construction, agriculture, paper, pharmaceutical, ceramic, petroleum industries etc. [8, 4, 9]. Nigeria has large proven reserve deposits of clay minerals which are estimated to be several billions of tonnes [10], a large number of these deposits are yet to be characterized [11, 12]. In the light of the prevailing dwindling revenue from crude oil which has been the main stay of the Nigerian economy and the macroeconomic instability, unemployment and other social economic disruption it has caused [13, 14], it has become imperative to intensify efforts at diversification of the economy by adding value to the vast clay mineral resources in Nigeria. This study therefore, is an attempt to evaluate the physico-chemical and mineralogical properties of a clay mineral deposit in Geheku in Kogi State, Nigeria.

Materials and Methods

Sampling

The samples were collected on profile basis in the study site in Geheku, Kogi State, Nigeria between latitudes N 8˚19′26″ and longitude E

6˚52′47″. The profiles were determined by colour variation [15]. A minimum of fifteen (l5) samples were collected per depth. The samples were labelled, and air-dried in the laboratory.

The physical properties of the clay minerals such as moisture content, loss on ignition, Atterberg limits, linear shrinkage, refractoriness, thermal shock resistance, bulk density were carried out in accordance with British Standard [16]. Triplicate determinations were carried out in all the test

Moisture content determination

The moisture content was determined on dry weight basis.

The clay sample (5.0 g) was oven dried at a temperature of 105-110 ^{O}C, cooled in a desiccator and weighed in an analytical balance. This was repeated until a constant weight was attained. The loss in weight was computed and expressed in terms of percentage.

$$\%\ \text{Moisture content} = \frac{Loss\ in\ weight\ (g)}{weight\ of\ sample\ (g)} \text{ x } 100 \quad \text{…….(1)}$$

Loss of ignition

The clay sample (5.0 g) was heated in a muffle furnace at 400 ^{o}C for 4 hours after which it was cooled in a desiccator and weighed. The difference in weight gave the loss on ignition. This was expressed in percentage terms.

$$\%\ \text{Loss of ignition} = \frac{Loss\ in\ weight\ (g)}{weight\ of\ sample\ (g)} \text{ x } 100\text{... (2)}$$

Atterberg limits determination

Liquid Limit

The air-dried clay samples (120.0 g) which had been filtered through 425 microns sieve, were mixed with distilled water in a mixing disc to form uniform paste. This was subjected to standard procedure and from the flow curve obtained, the moisture content corresponding to 25 drops (blows) was read, which represented the liquid limit. Triplicate determinations were carried out and the average value obtained was approximated to the nearest whole number.

Plastic Limit (PL) and Plasticity Index (PI)

The sieved clay sample (15.0 g) was wetted with water until it became plastic. The mix was rolled on a glass plate with the hand into thread of about 1.3 mm in diameter until the thread showed sign of crumbling. The rolled clay was weighed and placed in an oven for 24 hours after which the moisture content was determined. This process was repeated three times and the average %moisture content was determined. The values obtained were recorded as plastic limit to the nearest whole number. The plasticity index was then calculated as the difference between % Liquid limit and the % plastic limit.

Linear shrinkage

The sieved clay sample was wetted by addition of water and then placed in a shrinkage mould of dimension 140mm by 12.5 mm and the top smoothened with the aid of a spatula. The mould was placed in an oven set at a temperature range of 105-110^{o} C for 24 hours. It was allowed to cool to room temperature after which the length of the oven-dried sample was measured and recorded. The difference in length was recorded, the % linear shrinkage was determined. Triplicate determinations were made. The average value approximated to the nearest whole number was used

$$\text{Linear shrinkage }\ \% = \frac{change\ in\ length}{original\ length} \text{ x } 100\text{..(3)}$$

Bulk density

The test pieces were prepared and air-dried for 24 hours, the clay samples were oven dried at 110^{o} C for 24 hours, heated to 1100^{o} C, cooled in a desiccator and weighed to nearest 0.001 g (**D**), after which the specimens were transferred to a beaker filled with water and heated for 30 minutes to assist in releasing trapped air. The specimen was cooled and soaked weight (**W**) taken. The specimen was then suspended in water using a beaker placed on a balance and suspended weight (**S**) was taken, the bulk density was calculated from equation below;

Bulk Density $= \frac{D}{W-S} \times \rho$ (g/cm^3)….(4)

Where D = Dried weight
W = Soaked weight
S = Suspended weight
ρ = Density of water

Permeability to air

Test samples were prepared to specification of 5.08 cm diameter and 5.08 cm height from a standard rammer. The test pieces were air-dried for 24 hours and then dried at 110 °C for 12 hours in an oven. 2000 cm^3 of water was allowed to pass through the sample from the jar containing water. The time taken for 2000 cm^3 of water to displace equal volume of air through the test piece was recorded. The pressure difference between the surfaces was measured by a manometer. Permeability was calculated from the equation below:

$$P_A = \frac{V \times h}{A \times p \times t} \text{……(5)}$$

Where P_A = Permeability number

V = Volume of air
H = Height of specimen
A = Cross sectional area of specimen
P = Pressure of air in cm^3 of water
t = Time in minutes

Apparent porosity

Disk samples were prepared and air dried for 24 hours. The samples were then oven dried at 110^o C, thereafter fired at 1100^o C, cooled and then transferred into desiccator and weighed to the nearest 0.001 g (D). The specimen was then transferred into a 250 ml beaker in an empty vacuum desiccator; water was then introduced into the beaker until the test place was completely immersed. The specimen was allowed to soak in boiled water for 30minutes being agitated from time to time to assist in releasing trapped air bubbles. The specimen was transferred into a desiccator to cool. The soaked weight (W) was taken. The specimen was then weighed, suspended in water using a beaker placed on a digital weighing balance and this gave suspended weight (S). The apparent porosity was calculated using the equation below; triplicate determinations were made and the average value taken which was approximated to the nearest whole number.

Apparent porosity $= \frac{W-D}{W-S} \times 100$…. (6)

Where W= Soaked weight
D= Dried weight
S= Suspended weight

Refractoriness (pyometric cone equipment)

Test cone was prepared by mixing each clay sample aggregate with sufficient quantity of water to make the clay become plastic and moulded by hand into a cone shape. The test piece was mounted on a refractory plague. The plague was then put inside the furnace, and the temperature was raised at a rate of 100^o C per minute. The test was continued until the tip of the test cone had bent over level with the base. The plague bearing the test piece was removed and the test cone examined when cooled to room temperature under microscope

Thermal shock resistance (TSR)

Test pieces measuring 50 mm by 75 mm were prepared. The pieces were inserted in a furnace, which had been maintained at temperature of 900 °C. This temperature was maintained for 10 minutes. The specimens were removed with a pair of tong from the furnace one after the other and then cooled for 10 minutes on firebrick. The specimens were returned to the furnace for a further 10 minutes. The process was continued until the test pieces were readily pulled apart. The number of heating and cooling (cycles) for each specimen were recorded.

Chemical Assay: The chemical compositions of the mineral deposit were determined on dry samples obtained by taking some quantity of the test sample, heated to 105-110 °C for one hour to remove moisture, cooled in a desiccator and thereafter kept in a sealed container. The clay sample (1.0 g) was weighed into a beaker and digested in Aqua-regia (HCl:.HNO_3, (3:1)) The determination of the chemical components of the samples were carried out using Atomic Absorption Spectrophotometer (Bulk Scientific 210 VGP) for Fe, Al, Mg, Mn and flame Photometer (Model Sherwood 410) for Na and K as described by Young [17] and the total silica content was determined by the standard method [18].The quantity of the elements present were expressed as percentage of their respective oxides

Mineralogical Analysis. The samples were pulverized to fine particles (≤ 2 µm) and were subjected to X-ray diffraction using GBC Enhanced Mini Material Analyzer (EMMA) X-ray Diffractometer with Cu, Kα radiation source. The generator operating conditions were 40KV and 5SmA. The d-values obtained were compared with the standard X-ray powder diffraction file published by the Joint Committee on Powder Diffraction (J.C.P.D.) [19] for the identification of the different mineral species and Pei-Yuan [20].

Results and Discussion

Table 1: The Chemical Assay of Geheku Clay Mineral Deposit

	Layer 1	Layer2
Colour	Light yellow	Grey
Moisture %	0.800 ±0 .15	1.00 ± 0.09
L.O.I. %	3.400± 0.260	5.200 ± 0.16
SiO_2 %	10.93 ± 1.27	12.130 ± 1.77
Al_2O_3%	8.330 ± 1.24	6.670 ± 0.98
Fe_2O_3 %	0.830 ± 0.31	0.670 ± 0.07
K_2O %	0.340 ± 0.021	0.570 ± 0.012
Na_2O %	0.874 ± 0.007	0.872 ± 0.011
MgO %	0.020 ±0.005	0.032 ± 0.003
CaO %	0.061 ± 0.004	0.03± 0.001
MnO_2 %	0.046± 0.006	0.118± 0.004

Table 2: The Physical Properties of Geheku Clay Mineral Deposit

	Layer 1	Layer 2
Liquid limit %	55	48
Plastic limit %	30	29
Plastic index %	25	19
Linear shrinkage %	12	10
Apparent porosity	20	30
Air permeability	80	78
Bulk density g/cm^3	2.42	2.45
Thermal shock resistance (cycles)	30	30
Refractoriness	<1200˚C	<1200˚C

Table 3: Results of the Mineralogical Assay of Geheku Clay Mineral Deposit

Minerals	d-value
Illite $K_{0.7}Al_{2.1}(SiAl)_4O_{10}(OH)_2$	4.49, 3.35, 2.54
Almandine $Fe_3Al_2(SiO4)_3$	2.57, 1.54, 1.66
Halloysite $A1_2Si_2O_5(OH)_{4..}2H_20$	10.0, 3.35, 2.54
Montmorillonite $(Na\ Ca)_{0.33}(AlMg)_2Si_4O_{10}OH_2.nH_2O$	15.0, 4.50, 1.50
Kaolinite $Al_2Si_2O_5(OH)_4$	7.17, 3.58, 1.49
Ramsdellite MnO_2	1.66, 2.55, 1.47
Quartz SiO_2	3.34, 4.26, 1.82

The results of the chemical, physical and mineralogical analyses of the Geheku clay mineral deposits are presented in tables 1, 2 and 3 respectively. The chemical composition of the clay mineral deposit indicates that it is made up of aluminosillicate mineral [21]. The clay mineral illite which is non-expanding [22] was detected. The clay mineral almandine an iron alumina garnet of deep red colouration which could be held accountable for the colour of the deposit [23] was detected. The montmorillionite clay mineral which is an expanding clay mineral certainly influenced the swelling characteristics of the mineral deposit [24]. The Kaolinite mineral with low swelling and shrinking characteristics was present. The associated low linear shrinkage and high thermal resistance of the clay mineral deposit have been influenced by the presence of this mineral [25, 26]. Halloysite is a weathering product formed by the hydrothermal alteration of aluminosilicate minerals. It can occur intermixed with kaolinite, dickite and montmorillonite and it is (1:1) kaolinite type clay. Thus, its presence, also enhanced the thermal properties of the clay mineral [5]. The presence of quartz reduced the plasticity, shrinkage and refractoriness of the clay [27, 28]. The presence of ramsdellite a manganese mineral is a major source of colouration which is known to lower apparent porosity [27]. The value of the liquid limit (average of 52%) indicates that the clay has good swelling properties [22]. The value of plastic index (19-25%) showed that the clay mineral deposit falls within the medium plastic clay based on classification in terms of Atterberg Plastic Index (API) (15-30%) based on the classification of the clay minerals [29]. The linear shrinkage of the deposit which was between (10-12%) was slightly above the recommended limit (4-10%) for refractory clays [26] but this has been described as non-critical [15]. The values of the apparent porosity were within the acceptable limit for refractory clays (20-30) [30]. The thermal shock resistance of the clay met the standard set for refractory clays [31]. The air permeability of the clay mineral deposit was within the recommended standard (25-90) [8]. The bulk density values (2.42-2.45g/cm^3) exceeded the internationally permissible limit (1.7-2.1 g/cm^3) for fireclays [32]. The clay mineral had refractoriness below 1200 ^{o}C which means that they cannot withstand very high temperature operations.

Conclusion

The clay mineral deposit at Geheku has been evaluated. The results showed that mineralogically, it consisted of a mixture of montmorillonite (an expanding clay) and other non-expanding clay minerals such as kaolinite, illite and halloysite. The presence of almandine and ramsdellite accounted for the colouration of the clay minerals. The combined effect of the mix of these minerals resulted in the clay mineral having good swelling properties, good thermal shock resistance but low refractoriness. It can be applied in various industries which require a combination of the above properties in which the operating temperature is below 1200^{0}c

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