Physicochemical Properties and Temperature Variation Characteristics of Ituku Clay Deposit for Industrial Uses

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Abstract– **The industrial potential of Ituku clay deposit was investigated by determining its physicochemical properties as well as the firing temperature variation characteristics. The clay was obtained from Ituku in Agwu local government area of Enugu State Nigeria. The oxide analysis of Ituku clay showed silica (53.01%) and alumina (18.71%) as major constituent as well as other metal oxides in smaller amounts. The presence of appreciable amounts of alkali oxides of 2.85, 1.93 and 2.48% for CaO, K_2O and Na_2O respectively reduced the refractory properties of the clay. High Fe_2O_3 concentration of 7.03% impacted a reddish colour to Ituku clay after firing. The clay showed high modulus of plasticity of 1.57 which indicated a good workability making it easily moldable into shape. With increase in firing temperature of Ituku clay from 900 to 1200^{0}C an increase in linear shrinkage, total shrinkage, bulk density and modulus of rupture was observed while a decrease in the apparent density, water absorption and apparent density was obtained. The clay had refractoriness of up to 1200^0 but at higher firing temperatures signs of failure were observed. This study showed that Ituku clay could be utilized in the manufacture of ceramics, refractory bricks, tiles and pottery thereby reducing over dependency on import of clay minerals into the country.**

Keywords– **Ituku Clay, Firing Temperature, Modulus of Rupture, Refractoriness and Industrial Use**

I. INTRODUCTION

Clay can be referred to a complex aluminosilicate compound containing attached water molecules, obtained from the chemical and mechanical disintegration of rocks [1]. It has the tendency to acquire plasticity once mixed with a little amount of water [2]. Clays are broadly classified into swelling and non-swelling clays, examples are smectites and kaolinites respectively. The kaolinites usually have one silica and one alumina unit stacked in alternating fashion (1:1 lattice type), only the external surfaces determine their colloidal properties as no ion or water molecules can get into adjacent layers. Kaolinites usually possess less cohesion, swelling and plasticity compared to other clay minerals due to its relatively larger particle sizes and smaller surface area [3]. Kaolin which a very important industrial mineral is refined from kaolinte, its physical properties as well as chemical composition helps to determine its uses for industrial purposes. Kaolin could be utilized in the manufacture of paints, plastic, ink pigment, adhesives, porcelain, dinner wares, tiles and cosmetics, just to mention a few. An example of the swelling clay under the smectite classification is bentonite, they are hydrated aluminosilicates composed predominantly of montmorillonite. They are composed of a three-tier structure with alumina silica sheets sandwiched between tetrahedral silica units [3]. Bentonite clays are used in drilling mud, as bleaching agents in cooking oil industries and lubricating oil recycling, as a catalyst, absorber, and filler. It is also used in foundry sand bond in iron and steel foundries and in iron ore pelletizing in metallurgy. Clay minerals in general have a broad range of industrial uses in ceramics porcelain, dinner wares, glasses, refractory bricks, burnt bricks, tiles, rubber, paper and paint industry [4].

Clay has some properties useful in it classification such as the colour, strength, plasticity, shrinkage, water absorption, apparent porosity, apparent density and bulk density. The percentage of mineral oxides in a clay determines the area of application of the clay; to be used in bricks, porcelain, tiles, paper or paints etc, while the amount of the alkali metal oxides determine the applicability in the making of ceramic products [2]. The presence of these minor oxide impurities occurring in variable amounts in clays tends to impart some properties to the clay which are of technical value, thereby making clays to have different properties and thus application from another. Nigeria has a large number of industries which utilizes clay materials for production for the benefit of the country. In this regard so many researchers have over the years characterized the vast amount of clay deposits present in Nigeria to determine their suitability for industrial purposes [5]-[9]. However, there are high local demands for ceramic products due to the high population, yet the bulk of clay utilized in the industries are imported from Japan, United Kingdom and the United States of America [10]. This is discouraging due to the abundance of clay deposits present in Nigeria which could be utilized rather than been imported. Consequently despite the characterization of many clay deposits in Nigeria by researcher to determine their industrial suitability, the potentials of most of the clay deposits have not been investigated. This study therefore characterizes Ituku clay deposit which is present in abundant amount in Agwu Local Government Area (LGA) Enugu state Nigeria in order to determine its industrial suitability and uses. The chemical and physical properties of ituku clay deposit as well as the temperature variation characteristics were determined and analyzed.

II. MATERIALS AND METHODS

A) Sample preparation and Molding

Ituku clay was collected by random sampling at different points in Ituku, Agwu LGA, Enugu state, Nigeria. The samples were taken at a depth of 1.55 m and mixed properly to obtain a homogenous mixture. Thereafter, the collected clay was put in excess water in a plastic container and stirred vigorously to ensure proper mixing. The mixture was then filtered through a 0.425 mm mesh sieve to get rid of unwanted particles and plant materials. The filtrate was allowed to settle, after which excess water was decanted off. The clay was sundried and oven dried at 100 ^{0}C for 3 hr, pulverized and passes through a mesh sieve of size 0.18 mm. 2.0 kg of the clay was weighed and mixed with appropriate amount of water to make it plastic for the molding process.

The clay was then molded into three types of shapes using metallic moulds and the application of lubricants to the surface of the moulds to prevent the test pieces from sticking to the surface. The first shape is cylindrical with a width of 3.5cm and height 3cm, the second is a rectangular piece with length 8cm, width 4cm and height 1.5cm, while the third has a long rectangular shape with length 9.5cm, width 2cm and height 1.5cm [11].

B) Physical Analysis

The making moisture was determined by weighing the cylindrical test pieces immediately after molding and recorded as the wet weight, *Wo*. The test pieces air-dried for 24 hr and then dried in an oven at 105^{0}C until a constant weight was recorded. After drying the test pieces were weighed and the dried weight recorded as *Wi*. The making moisture was then calculated.

$$\text{Making Moisture (\%)} = 100[Wo-Wi]/Wo$$

The relative plasticity was obtained by the use of the cylindrical test pieces. The original height, *Ho* of the test pieces were determined by the venier caliper by taking the average of three sides. Afterwards, a manual plastometer machine was used to deform the test pieces. The deformation height, *Hi* was recorded taking the average of three sides. The relative plasticity was then calculated [11]:

$$\text{Relative Plasticity} = Ho/Hi$$

The Modulus of Rupture (MOR) was determined as follows: five long rectangular test pieces were made and air dried for 7 days after which they were oven dried at 105^{0}C until a constant weight was obtained. Four of the pieces were fired to their respective temperatures of 800, 900, 100 and 1100^{0}C in a laboratory kiln (Fulham Pottery). The electrical transversal strength machine was used to determine the breaking load, P (Kg). A vernier caliper was used to determine the distance between support L (cm) of the transversal machine. The height, H (cm) and the width, B (cm) of the broken pieces were determined and the average value obtained from the two broken parts was recorded. The modulus of rupture was then calculated [10]:

$$\text{Modulus of Rupture } (KgF/cm^2) = 3PL/2BH^2$$

Immediately after molding of the rectangular test pieces, a vernier caliper was used to insert a 5m mark on each; this was recorded as the original length *Lo* (cm). The test pieces were then air dried for 7days and then dried in an oven at 105^{0}C until a constant weight was obtained. The shrinkage from the 5cm mark was then determined and recorded as the dried length, *Ld* (cm). Afterwards, four of the dried samples were fired to their respective temperatures of 800, 900, 1000 and 1100^{0}C each temperature corresponding to a particular test piece. The shrinkage of the test pieces from the 5cm mark were then determined and recorded as the fired length, *Lf* (cm). The shrinkage was then calculated [12]:

$$\text{Dry Shrinkage (\%)} = 100[Lo - Ld]/Lo$$

$$\text{Linear Shrinkage (\%)} = 100[Ld - Lf]/ Ld$$

$$\text{Total Shrinkage (\%)} = 100[Lo - Lf]/ Lo$$

The test pieces obtained after firing were then weighed and the weight recorded as dry weight, *M1* (g). Thereafter, the test pieces were soaked in water for one hour, then removed, cleaned and weighed immediately and recorded as soaked weight, *M2* (g). The water of adsorption was then calculated:

$$\text{Water Absorption (\%)} = 100\,[M2 - M1]/ M1$$

After the procedure described above was completed. The suspended weight of the test pieces were then determined by the use of a lever balance and recorded as *M3* (g). The apparent porosity, apparent density and bulk density were then calculated:

$$\text{Apparent Porosity (\%)} = 100\,[M2- M1]/ [M2 - M3]$$

$$\text{Apparent Density } (g/cm^3) = M1/[M1 - M3]$$

$$\text{Bulk Density } (g/cm^3) = M1/[M2 - M3]$$

The Loss on Ignition (LOI) was determined as follows: The weight of an empty porcelain crucible was determined and recorded as W_1, 2 g of the dried pulverized clay was added and the weight of the crucible + clay was determined, W_2 (g). The sample was then ignited in the laboratory kiln at 1200 ^{0}C.

After, the cooling of the sample the weight of the crucible + sample after ignition was determined, W_3 (g). The loss on Ignition was then calculated:

$$Loss\ on\ Ignition\ (LOI) = 100[W_2 - W_3] / [W_2 - W_1]$$

C) Chemical Analysis

0.2 g of the clay was weighed into a beaker and 10ml of aqua regia (HCl + HNO_3 in the ratio 3:1 respectively) was added and digested in a hot plate in a fume cupboard. 10 mL of Hydrofluoric acid was also added to aid the digestion process. After digestion 30 mL of de-ionized water was added and the mixture filtered through a filter paper into a 250 mL volumetric flask and made up to the meniscus mark with de-ionized water. The sample was then analyzed for the elemental composition by the use of the Atomic Absorption spectrophotometer (AAS) (Buck scientific model 210 VGP). The concentration of metal oxide in the clay was expressed in mg/L. The percentage composition of the elements in the clay was calculated from the equation:

$$\%\ Composition = 100CV/M$$

Where C (mg/L) is the elemental composition obtained from the AAS, V (L) is the volume of the volumetric flask in which the digested solution was diluted and M (mg) is the mass of sample diluted [13].

III. RESULTS AND DISCUSSION

Table I: Physicochemical properties of Ituku clay deposit

Parameters	Value
Al_2O_3 (%)	18.71
SiO_2 (%)	53.01
Fe_2O_3 (%)	7.03
CaO (%)	2.85
K_2O (%)	1.93
Na_2O (%)	2.48
MgO (%)	0.92
MnO (%)	0.44
LOI (%)	12.30
Colour before firing	Grayish brown
Colour after firing	Reddish brown
Refractoriness (^{O}C)	1200
Modulus of Plasticity	1.57
Making moisture (%)	19.83
wet-dry shrinkage (%)	3.2

A) Physicochemical characterization

Table I shows the physicochemical properties of ituku clay. It was observed as expected that silica and alumina form the major constituent of the clay while other minerals are present in minute amounts as impurities. The silica content was below the standard requirement for the manufacture of ceramics (>60.5%), glass (80-90%) but within the standard requirement for manufacture of refractory bricks (>51.7%) and high melting clays (53-73%) [14]. It was also higher than that required for the manufacture of paper (45.0-45.8%) and paint (45.3-47.9%) [15]. The concentration of alumina in ituku clay was within the standard required for high melting clays (16-29%) and glass (12-17%) but lower than that required for ceramics (>26.5%), Refractory bricks (25-44%), paper (33.5-36.1%) and paint (37.9-38.4%) [14], [15]. The low alumina content of ituku clay suggests the low refractory properties of the clay [3]. The iron content of ituku clay of 7.03% was within the requirement for the manufacture of high melting clays (1-9%) but above that for ceramics (0.5-1.2%), refractory bricks (0.5-2.4%), glass (2-3%) and below that for paper production (13.4-13.7%) [3]. The presence of Fe_2O_3 was responsible for the reddish-brown colouration obtained after firing of ituku clay (Table 1) which makes it unsuitable for white wares [16]. Also, the presence of high iron content usually affects the refractoriness of the clay [10]. The presence of alkali oxides in reasonable amounts in ituku clay acts as mild fluxes by combining with the oxides of silica and alumina on firing to form eutectics and so reduce the vitrificaion temperature and refractoriness [17]. Ituku clay is therefore expected to have moderate refractory properties. Similar result has been reported [11]. The Loss on Ignition (LOI) of ituku clay was within the standard requirement for the manufacture of refractory bricks (8-18%), ceramics (>8.18%), and high melting clays (5-14%) [15]. Ituku clay had moderate refractoriness (Table 1) and did not show any sign of failure at 1200^0C but displayed signs of failure at higher temperatures. The low refractoriness is due to the presence of considerable amount of alkali oxides, low alumina content and high iron content as stated earlier; indicating that ituku clay did not met the standard classification for refractory materials (1580-1750^0C). Similar results have been reported with Ezzodo clay [11] and Adiabo clay deposits [12].

B) Effect of Firing Temperature

The physical properties of ituku clay obtained at different firing temperatures of 900 to 1200^0C are given in Figs 1-7. The result for the effect of firing temperature on the linear shrinkage of Ituku clay is shown in Fig 1. An increase in linear shrinkage from 7.7 to 9.86% with increase in firing temperature was observed. The increase was as a result of the removal of volatile components and absorbed water in the clay with temperature which resulted in sintering and compression of the clay body. The moderate shrinkage characteristics of the clay is desirable because high shrinkage values may result in warping and cracking of the clay and this may result in loss of heat and create an undesired finished product [11]. Also, the linear shrinkage of ituku clay (7.70 - 9.86%) was within the standard range of 4-10% required for fireclays and 7-10% for aluminosilicates and kaolinites [3]. This result was different from that obtained in the characterization of Ezzodo clay [11] and suggests that ituku clay may be from a kaolinite origin.

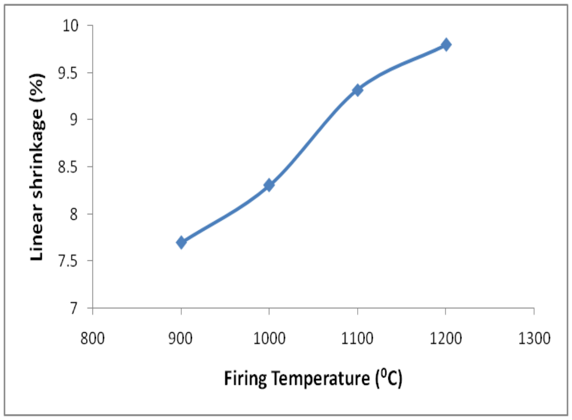

Fig. 1: Effect of firing temperature on the linear shrinkage of ituku clay

An increase in the total shrinkage from 9.60 to 12.2% with increase in firing temperature was observed as shown in Fig. 2. The dry-fired shrinkage (Table I) and the total shrinkage are less important than the linear shrinkage in products manufacture since they are largely affected by the making moisture of the clay body. Therefore the making moisture of 19.83% is related to the dry-fired and total shrinkage values obtained in this study, which would vary if the amount of water added during molding is altered.

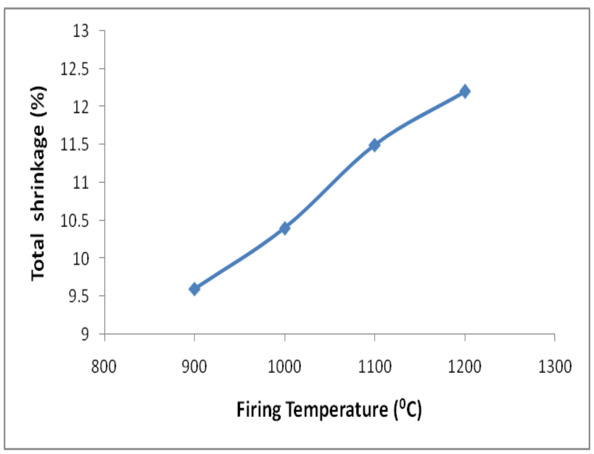

Fig. 2: Effect of firing temperature on the total shrinkage of ituku clay

The variation in apparent porosity of ituku clay with firing temperature is shown in Fig. 3. It was observed that a decrease in the apparent porosity from 25.41 to 19.23% with increase in firing temperature was recorded. The decrease is attributed to an increase in shrinkage with temperature which resulted to the closure of the pores. This implies that as the temperature is increased less water would be able to penetrate the resulting clay product due to decrease in porosity. Consequently a resulting decrease in the water absorption tendency with temperature is expected. The apparent porosity was within the standard for manufacture of fire bricks (20-80%) and fireclay (20-30%) [18]. The application of glaze help to reduce porosity in the final product when desired in manufacturing processes.

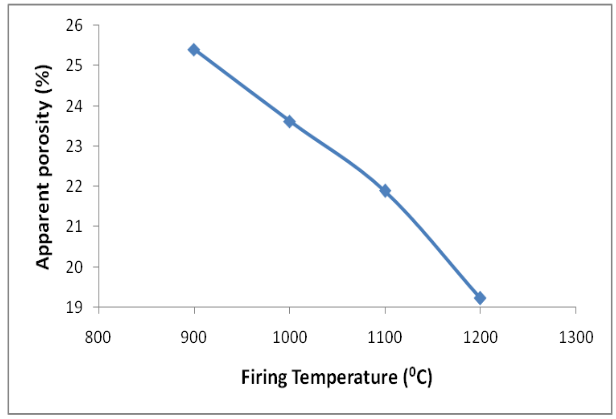

Fig. 3: Effect of firing temperature on the apparent porosity of ituku clay

The result of variation of water of absorption of Ituku clay with firing temperature is illustrated in Fig.4. A decrease in the water absorption from 14.81 to 10.21% with increase in firing temperature of ituku clay was obtained. This result corroborates the expectation that as a result of decrease in porosity with temperature a corresponding decrease in water absorption should occur. This decrease is attributed to an increase in shrinkage and decrease in porosity of the clay with increase in firing temperature [13].

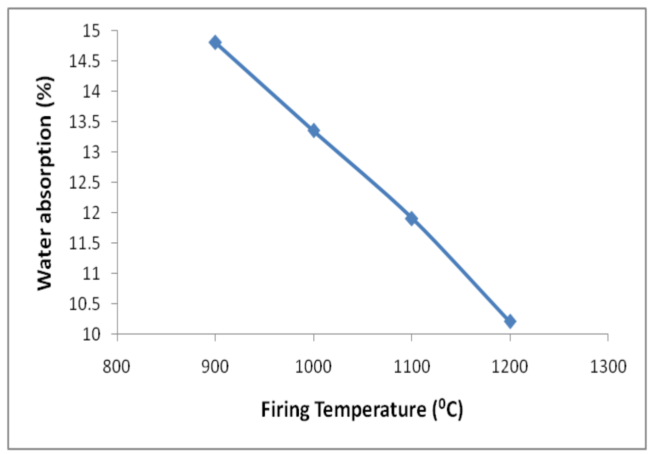

Fig. 4: Effect of firing temperature on the water absorption of ituku clay

The result for the effect of firing temperature on the apparent density of ituku clay is shown in Fig.5. It was observed that a decrease in the apparent density from 2.33 to 2.22 g/cm^3 of the clay with increase in firing temperature was obtained. Similar results have been reported [11], [13]. An opposite result was observed with the bulk density as shown in Fig.6 were an increase from 1.71 to 1.79 g/cm^3 with increase in firing temperature was recorded. This implies that the clay became more compact and dense as the shrinkage increased and thus is expected to have a progressive increase in strength of the clay body [12]. The bulk density of ituku clay was within the acceptable standard of 1.7 - 2.1g/cm^3 for building and fireclays [19].

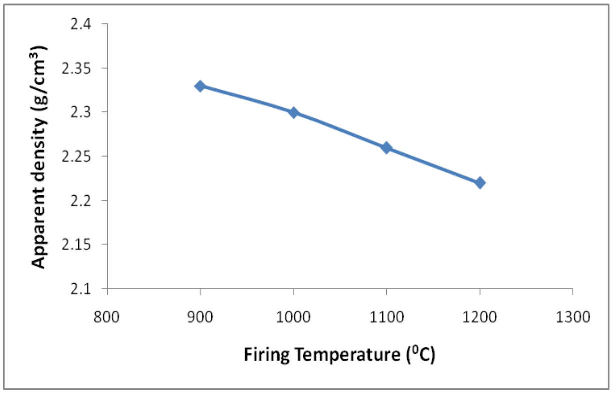

Fig. 5: Effect of firing temperature on the apparent density of ituku clay

The effect of firing temperature on the Modulus of Rupture (MOR) of ituku clay is shown in Fig. 7. It was observed that an increase in MOR from 32.41 to 41.22 kgF/cm^2 with increase in firing temperature was obtained. This increase is attributed to the increase in bulk density, sintering and vitrification of the clay body with temperature increase. The increase is also due to bond formation in the glassy phase of the body; also the alkali metal oxide fluxes in the clay body combine to form some considerably low temperature melting compounds, which increased the strength of the body on cooling [10]. The MOR of ituku clay was within the standard acceptable wide range of 1.4 to 105 kgF/cm^2 for manufacture of any clay product [10', [12]. Furthermore, the relative plasticity of ituku clay was 1.57 as shown in Table 1. This is higher than the values reported for adiabo clay (1.33) [12] and ezzodo clay (1.35) [11]. The higher value is desirable and indicates a good workability of ituku clay enabling it to be moulded easily into shape.

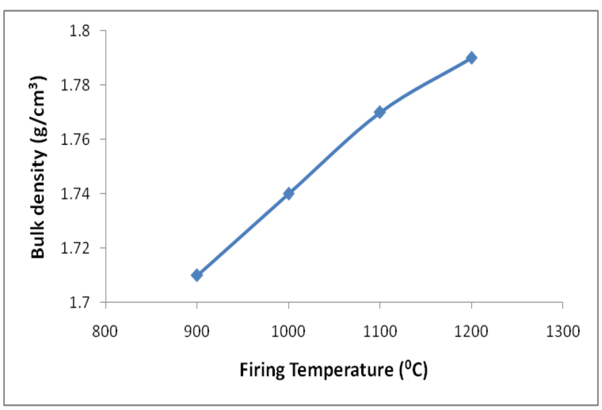

Fig. 6: Effect of firing temperature on the bulk density of ituku clay

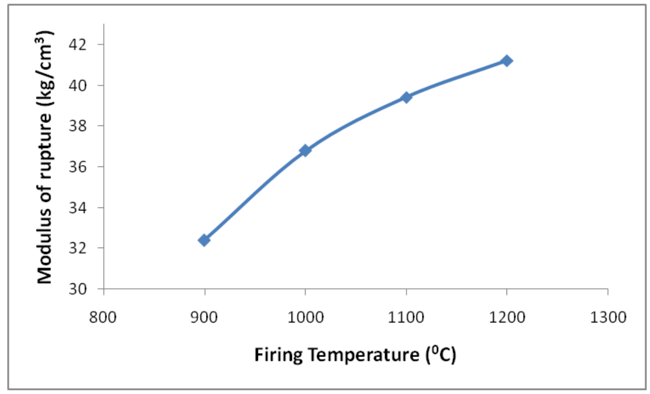

Fig. 7: Effect of firing temperature on the modulus of rupture of ituku clay

VI. CONCLUSION

The result for the characterization of ituku clay indicated the presence of several metal oxides which influences the suitability of the material for industrial purposes. The high plasticity suggested the use of Ituku clay as additives for short clay. The presence of appreciable amounts of alkali oxides, and iron oxide and low alumina reduced the application of ituku clay in refractory although it can still be utilized as an additive for such purposes. However, the clay could be applied in the manufacture of ceramics, refractory bricks, tiles and pottery products.

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