ASSESSMENT OF THE INDUSTRIAL POTENTIALS OF SOME NIGERIAN KAOLINITIC CLAY DEPOSITS

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ABSTRACT

Nigeria has appreciable level of distribution of industries engaged in metal and process industries. Therefore the need for raw materials to support their growth has become necessary. In this research clay samples from Cross River State (Idere and Ito) were characterized. Linear shrinkage, apparent porosity, cold crushing strength, drying and firing, bulk density as physical properties and chemical compositions were determined. The results of the physical and chemical properties of both Idere and Ito clay samples showed that, these clays can be used for brick making, floor tiles and stoneware. This is based on the comparable values obtained most of which agrees with internationally acceptable values such as; thermal shock resistance 21 cycles for Ito, cold crushing strength 13.33MN/m^2 for Idere, apparent porosity of 29.41% for Idere and 27.27% for Ito, permeability of 88% for Idere and 67% for Ito and linear shrinkage value of 9.20% and 7.73% for Idere and Ito respectively. The chemical values are also in agreement with standard values.

Keywords: Cross River State, Southern Senatorial District, Physical and Chemical Properties, Aluminum Oxide, Silicon Oxide, Clay, Nigeria.

INTRODUCTION

Clay deposits have been identified in many regions in Nigeria though with differing properties probably owing to geological differences. Furthermore several studies have been done on clay soils around Nigeria. They include Mayo-Belwa in Adamawa (Kefas et al., 2007), Kachia, Kafanchan, Wusasa in Kaduna (Manukaji,2013);Sheda, Abaji and Karimu in Abuja (Manukaji,2013); Olokoro, Ukpor, Otamiri and Nsu in South eastern Nigeria (Nwoye, 2010), Abakiliki in Ebonyi (Nweke et al.,2007) and Ugbegun clay deposit in Edo central Nigeria (Ogbebor et al.,2010) amongst others .

Clay materials are basically divided into three groups; Those that contain mainly Kaolinites which are white, grayish-white or slightly colored becoming darker and plastic when moistened with water (Lopez-Galindo et al., 2007 and Nwoye, 2010).The second group are those that contain mainly Montmorillonite and the third group of clays are the intermediate product of disintegration of mica into kaolin (Nwoye, 2010). Ceramic products behavior depends greatly on the composition, grain size, grain distribution, grain structure and pores (Arisa, 1997).

In addition, Nwoye (2003) has shown that grain size and distribution of clays tend to have effect on their physical properties and technological properties such as binding ability, shrinkage and plasticity. Furthermore shrinkage has been related to rupture in fired clay increased while there is decrease in porosity (Bergaya et al, 2006 and Nwoye, 2008). The chemical constituents of clay help to ascertain their usage. The presence of Fe_2O_3, MgO,

CaO, Na_2O (mineral oxide) in clay sample determines its uses in bricks, floors tiles and paper making (Kefas et al, 2007). While the presence of Na_2O, K_2O and CaO (Alkali metal oxides) help to indicate refractory potential hence making clays suitable for ceramic products. Clay has also being applied in pharmacy and cosmetics though such clay materials have variable composition (Lopez-Galindo, 2007).

LITERATURE REVIEW

Refractory materials are made from clay and are a set of materials that retain their strengths at high temperatures. They are non-metallic materials having those physical and chemical properties that make them applicable to structures or as components of systems that are exposed to high temperature applications. A material is refractory if it has a very high melting point in addition to its physical and chemical properties that makes it suitable for use in kilns, furnaces, reactors and other high temperature vessels (Ameh and Obasi, 2012). According to them, refractory materials are materials capable of withstanding high temperatures, and that high quality refractory materials resist high temperature fluctuations between 1000°C and 1500°C and are also good thermal and electrical insulators.

Omowumi (2001) stated that the raw materials for the production of various types of refractory materials are kaolinite ($Al_2O_3.2SO_2.2H_2O$), Chromites ($FeCr_2O_3$), Magnesite ($MgCO_3$) etc. He also noted that other additives such as sawdust, graphite and some binders are available locally. Nnuka and Enejor (2010) studied the characteristics of Nigerian clays and discovered that the Otukpo clay can withstand a furnace temperature of about 1710°C which compared favorably with imported refractories. Amuda (2005), in an earlier research on the characterization and evaluation of refractory properties of some clay deposits in Southwest Nigeria, reported that the clays displayed reasonable refractory properties that compared favorably with standard values and recommended a blend of these clays for furnace lining. Meanwhile, Abolarin et al (2006) determined the moulding properties of locally available clays for casting operations and discovered that the Barkinladi and Alkaleri clay samples were suitable for construction of furnaces and furnace lining.

From the findings of Kure (2011), on the analysis and characterization of some selected North-west clay deposits showed that the clays could be used for production of ceramic, basic refractory, mortar lining, kilns and also as refractory bricks for furnace lining.

Some organic molecules can be intercalated as 'guest molecules' between the layers of kaolin. The reaction provides a simple method for distinguishing between halloysite, dehydrated halloysite and kaolin (Range et al., 1970. Differentiation between different types of kaolin is based on the maximum degree of reaction, (1.m, with some selected guest compounds. The value of (1. is taken from the intensity of the (001) reflections of kaolin and the intercalation compound. The maximum degree of reaction is not always 100% (am = I) even after very long reaction times, as this depends on the type of kaolin.

Weiss and co-workers concluded that kaolins in general are mixtures of different types of kaolinites with different chemical reactivity. Using dimethylsulfoxide (or hydrazine) and urea as guest molecules, three types were distinguished
(i) a highly reactive type A which reacts with a large number of guest molecules;
(ii) type B with low, but detectable, reactivity;
(iii) type C, which is unable to form intercalation compounds.

The experimental procedure is very simple: the maximum degree of reaction of a kaolin with dimethylsulfoxide (or hydrazine) and urea (concentrated aqueous solution) is measured. The ratio of types A, B and C in the kaolin specimen is calculated from am with dimethylsulfoxide (or hydrazine) (am, DMSO) and urea (am, urea)(Table I). Kaolins with high proportions of type A are China clays. Ball clays are kaolins with larger amounts of type B. High contents of type C characterize flint clays and fire clays (Range et al., 1970

Refractoriness is one of the properties of refractory materials and is the property at which a refractory will deform under its own load (Gupta, 2008). The refractoriness of a clay sample is directly related to its softening temperature and is expressed as its Pyrometric Cone Equivalent (PCE). The pyrometric cone equivalent is the number which represents the softening temperature of a refractory specimen of standard dimension. The refractory should exhibit strength which is the resistance of the refractory to compressive loads, tension and shear stresses. In taller furnaces, the refractory has to support a heavy load; hence strength under the combined effects of temperature and load, that is, refractoriness under load is important (Ogbebor et al., 2010 and Manukaji, 2013).

METHODOLOGY

Sample Collection

Clay samples were collected from different locations of Idere and Ito in the Southern Senatorial District of Cross River State. The samples were randomly collected from different points at a depth of 500mm.

Sample Preparation

The samples of about 3kg were collected and air-dried for five (5) days. Samples were then finely crushed to achieve homogeneity of the particles sizes. The ground samples were sieved with a mesh of 1.13µm. The ground and sieved samples were mixed with some quantity of water to a pastry state. The pastry sample was moulded (70x50x 50mm) into bricks and compacted with a hydraulic press according to ISO standards. The different clay samples were subjected to both physical and chemical tests. The equipment used during the test included Son Holland-Telex 59388 Furnace, Oven, Navigator N3B110 Ohaus Electronic weighing machine, crusher, bell jar, dessicator, X-ray Spectrometer. These equipment can be found in the laboratory of Bao Yao Huan Jian Iron and Steel Company, Export Processing Zone (EPZ) Calabar, Cross River State-Nigeria.

Physical Analysis

Cold crushing strength: Test pieces measuring 75x50x50mm were prepared and air-dried for 24 hours after which they were transferred to a furnace and heated for a period of 6 hours and at a temperature of 1600^{o}C. After the heating process, samples were removed and allowed to cool at room temperature and each piece was placed in a crusher (Amsler Type Crusher). During test, the pressure adding surface was adequately aligned to the centre of the spherical seat of the equipment. Load was applied axially and continually until the test piece fractured. The procedure was repeated for other test pieces. The respective loads at which each test piece fractured were recorded. The cold crushing strength (CCS) was calculated from equation (1)

$$CCS = \frac{P}{A} \quad \ldots\ldots\ldots\ldots (1)$$

Where A = Area of test specimen

P = Applied load

Thermal shock resistance: 75 × 50 ×50mm test pieces were inserted into the furnace maintained at 1600°C for about 10 minutes. They were removed and allowed to cool in a dessicator for 10 minutes and then returned back to the furnace (at 1600°C) for another 10 minutes.The process was repeated until the pieces were comfortably deformed when a small force was applied. The number of heating and cooling cycles for each of the specimen was recorded. As the thermal shock resistance is the number of heating and cooling cycles needed to cause crack on the samples, the values obtained for the various samples were recorded.

Linear shrinkage: The test samples were prepared and their original lengths of 75mm recorded. They were dried in air for 24 hours and in the oven at 110°C for 24 hours. They were transferred to the furnace, maintained at 1600°C and heated for a period of 6 hours. The samples were then brought out and allowed to cool in a dessicator. Measurements were taken for the various samples before and after heating to determine their dimensional changes. The linear shrinkage was determined using equation (2).

$$\text{Linear Shrinkage} = \frac{L_D - L_F}{L_D} \times 100 \quad \ldots\ldots\ldots \quad (2)$$

Where L_D = Dried or original length =75mm,
L_F = Fired length

Bulk density: The samples were prepared and air dried for 24 hours, the test pieces were put in an oven dried at a temperature of 110°C for 6 hours. They were allowed to cool and weighed by means of weighing balance and their dried weights (D) recorded in turn. They were transferred to a beaker and heated for 40 minutes and then cooled, the soaked weight was recorded. Water was put in another beaker and each of the test pieces suspended in the water so that their suspended weights were recorded. The equation for calculating bulk density is given by equation (3).

$$\text{Bulk Density} = \frac{D\rho_W}{W-S} \quad \ldots\ldots\ldots \quad (3)$$

WhereD = Dried weight
ρ_w = Density of water
W = soaked weight
S = suspended weight

Apparent porosity: Test samples from these different locations were prepared and allowed to dry in air for a period of 24 hours. There were transferred into the oven and dried for additional 24 hours at 110°C. They were transferred to a furnace and fired to a temperature of 1600°C, after which they were removed by pair of tongs and allowed to cool in open air before weighing them in a dessicator and the dry weight(D_W) recorded. Bubbles were observed as the pores in the samples were filled with water. The bubbles were made to escape through periodic agitation and after about 40 minutes. The soaked weight(S_W) were measured. Also, by using a beaker placed on the balance, the specimens were weighed suspended in water and the suspended weight (W) was taken. The apparent porosity for each location was determined from equation (4)

$$\text{Apparent porosity} = \frac{S_W - D_W}{S_W - W} \times 100 \quad \ldots\ldots\ldots \quad (4)$$

Where S_w = Soaked weight
D_W = dried weight
W = suspended weight

Permeability: Test samples were prepared and allowed to air dry for 24 hours and thereafter oven dried at 120°C for 12 hours. 2000cm^3 of air held in a bell jar was forced to pass through the specimen. At this time, air entering the specimen was equal to that leaving the specimen. The pressure difference was read by a manometer. Also, the time taken for the 2000cm^3 of air to pass through the specimen was recorded. The respective permeabilities were calculated using equation (5).

Permeability number, $P_n = \frac{Vh}{APt}$ …….. (5)

Where P_n = permeability number
v = Volume of air, cm^3
h = height of specimen, cm
A = Cross sectional area of specimen, cm^2
P = pressure of air in cm of water, N/cm^2
t = time, minutes

Modulus of rupture (MOR): Different test pieces of clay bar, 75 × 50x50mm dimension were prepared, the dry samples were moistened and mixed to a workable state .The wedged samples was cast in wooden mold, coated with thin film of machine engine oil. The bars were (temperature marked) then charged into an electric furnace separately along with American standard pyrometric cones of refractoriness 1600°C and fired for approximately ten hours, removed from the furnace and allowed to cool. Each batch of bars were broken at the center bending on a Denison strength testing machine at 35mm span and MOR was calculated from the expression below;

$$MOR = \frac{3PL}{2bh}$$

Where p = Breaking Load in kgf,
L = Distance between support,
b = Breath
h = Height.

Modulus of plasticity (MOP): The molded clay was deformed by dropping on it from a fixed height of a flat-headed plunger of known weight. The distance traveled was observed and read from the graduated scale. The modulus of plasticity (MOP) for the clay sample was calculated from the expression below

$$MOP = \frac{OriginalHeight}{DeformedHeight}$$

Tthe percentage making moisture for the clay samples were obtained from the following expression: % Making Moisture = $\frac{WetWeight - DryWeight}{NetWeight}$

Loss of Ignition: Loss of ignition was determined by weighing. Thirty gramme of pulverized sample was emptied into a clean dry platinum crucible using an analytical balance (Model PM4000). The sample was placed in an oven at a temperature of 700°C for 4 hours to obtain the loss on ignition. This process was repeated until a constant weight was reached for the samples using the formula;

$$\mathbf{LOI} = \frac{WeightLoss}{Weightofsample} x100$$

Chemical Analysis

The Chemical Analysis of the clay samples was carried out using of X-ray Fluorescence Spectrometer (XRFS). The technique was used to determine the concentrations of differents

elements present in the various samples. The samples were ground and sieved to produce 75µm particle sizes. Two grams of the sieved sample was mixed with 5grams of lithium tetra borate binder ($Li_2B_4O_7$) anhydrous solution that acted as a fluxing agent. It was then pressed to a pellet in a mould and dried in oven at 120°C for 20 minutes to remove the absorbed moisture and then kept inside a desicator. The spectrometer was turned on and allowed for some time to stabilize the optics and X-ray tube. The samples were placed in turn into the machine and the elemental concentrations present in the samples were displayed on a monitor. The result of the analysis is shown in Table 2.0.

RESULTS

The results obtained from the various tests carried are presented in Table 1.0 and Table 2.0

Table 1.0: Physical Properties of the tested clays from Cross River State

PROPERTIES	IDERE	ITO
Cold Crushing Strength (MN/m²)	13.33	11.74
Thermal shock Resistance (Cycles)	18	21
Linear Shrinkage (%)	9.2	7.73
Bulk Density (g/ cm³)	2.53	1.73
Apparent Porosity (%)	29.41	27.27
Permeability (%)	88	67
Modulus of rupture KgF/cm²	48.1	46
Modulus of plasticity KgF/cm³	3	3.32

Table 2.0: Chemical Composition of clay samples

CHEMICAL COMPOSITION	LOCATION	
	IDERE	ITO
Al_2SO_3	15.56	18.11
SiO_2	43.76	46.41
MgO	0.15	0.12
CaO	0.19	0.03
Fe_2O_3	11.92	10.28
K_2O	1.8	0.79
Cl	0.025	0.028
Co	0.08	0.036
MnO	0.104	0.05
Cr_2O_3	0.037	0.045
Na_2O	0.604	0.255

Ni	0.06	0.075
Cu	0.135	0.046
P_2O_5	0.047	0.059
SO_3	0.06	0.12
Sr	0.016	0.008
TiO_2	1.566	1.044
Zr	0.030	0.06

DISCUSSION

The physical and chemical properties of Idere and Ito clays were independently analysed using standard techniques.

Table 1 shows the physical properties of the clays from Idere and Ito. From the table, the bulk density for Idere and Ito are 2.53 and 1.73g/cm^3 respectively. The result of the linear shrinkage test shows that Idere recorded a higher value of 9.20% while Ito has a value of 7.73%. This shows that the clay deposits from these two locations are within acceptable standard values of bricks materials (Singer and Singer, 1971).

The shrinkage property of the clay is also important because it is the factor that determines the clay suitability for brick production. The values for Idere and Ito are shown in Table 1.
Apparent porosity for both clays were also determined and the recorded values were 29.41 and 27.27% for Idere and Ito respectively. These values show that the clay from Idere source has higher water absorption capacity than that of Ito. This is important because the water absorption capacity of clay has a bearing relationship on the drying behavior of the clay.
The thermal shock resistance for Idere and Ito are as shown in the Table 1.0, the acceptable range of cycle for good clay is between 25-30 cycles.

The colour of both clays was observed to be grey, however changes occurred from the grey to red when they were heated to a temperature of 1600ºC. This was due to the fact that both clays from Idere and Ito have ferrous values of 11.92 and 10.28% respectively ((Rhodes, 1973). The presence of ferrous iron influenced the colour of the fired samples resulting to changes from ferrous to ferric compound. The colour variation makes it suitable for manufacture of flower ports and stoneware.

For cold crushing strength, the values of cold crushing strength obtain are shown in Table 1, the Idere and Ito shows lower values compared to the recommended values of 18MN/m^2. The consequences of this low value will be poor cold crushing strength which will render them unsuitable for slag and flux Transportation.

The values of permeability for Idere and Ito clays are presented in Table 1:0. Given the acceptable range of 25-90%, Idere and Ito clays are good clays based on their values.
Table 2 shows the result of chemical analysis carried out on the clays of Idere and Ito, the silica content of Ito clay is higher in value than that of Idere caly, with values of 46.41% and 43.76% respectively.

These values shows that both clays exist as quartz which also suggest that they can be used for tha production of floor tiles (Haruna, David and Timothy, 2007). The silica in both clays exist in free form and as a compound due to the presence of other elements like Al2O3 in mix state to form Kaolin(formula for Kaolin) in the feldspar group (Johari, 2011).

The presence of Silica and Alumina in these clys depicts that they could be used for floor tiles production (Bergaya, 2006). The Silica presence can also make the clay a raw material for brick production.

From literature, the low values of K_2O, Na_2O, MgO and CaO for Idere (K_2O=1.90%; Na_2O=0.602%; MgO=0.15% and CaO=0.19%) and Ito (K_2O=0.79%; Na_2O=0.257; MgO=0.12% and CaO=0.03%) clays shows that they can be used for the production of refractory materials.

The loss of ignition for both clay materials were also determined, Idere showed a value of 84.2% while Ito recorded a value of 81.92%. both values indicated that, there was rentention of about 15.8% of water for Idere clay and 18.02% for Ito clay after heating for three hours at a temperature of 700ºC. This implies that increase in the heating time will reduce the moisture content while the clays physical properties will be retained due to their established parameters.

CONCLUSION

Idere and Ito clays were characterized using standard techniques. It was found that clays from both locations have moderate modulus of plasticity of 3.00kgF/cm^2 for Idere and 3.32 kgF/cm^2 for Ito, linear shrinkage of 9.20% for Idere and 7.73% for Ito, these values are within acceptable standard range for industrial clays. The clays when fired up to 1600ºC changed colour from grey to red. The values obtained from the characterization of these clays in the red colour upon heating shows that there can be suitable for flowerpots, floor tiles refractory materials and binders.

REFERENCES

Abolarin, M. S., Olugboji, O. A. and Ugwuoke, I. C. (2006). Determination of Moulding properties of Locally Available Clays for Casting Operations. Assumption University Journal of Technology, Thailand, vol. 9, No 4. January 2006, pp.238-242.

Ameh, E. M. and Obasi, N. W. (2012). Effect of rice husk on insulating bricks produced with Nafuta and Nsu clays. Global Journal of Engineering and Technology, 2(4), 661-668.

Amuda, M.O.H., Lawal, G.I. and Majolagbe, F.O. (2005). Characterization of Some South West Clay Deposits. NSE Technical Transactions, 40, 13-23.

Arisa, U.S. (1997) Effect of initial particle size and size distribution on physical and mechanical properties of some Nigeria clays sinistered at 1200^{o}C. A thesis report

Bergaya, F., Theng,B.K.G. and Lagaly, G. (2006) Handbook of Clay Science, Elsevier Publications, 1St edition:.289-309

Gupta, O. P. (2008). Elements of Fuels, Furnaces and Refractories. 5th edition, second reprint, Khanna Publishers, New Delhi – 110006.

Haruna, M. K., David O. P., and Timothy, M. C. Characterization of Mayo-Belwa Clay. Leonardo Electronic Journal of Practices and Technologies. 2007, 11 123-130.

Irabor, P. S. (2002). Physical and Chemical Investigation on some Nigerian kaoline clays for use in the ceramic and allied industries. Nigerian J.Eng. Res. Dev.. 1(1): 54-59.

Johari,I .,Said S., Jaya,R.P., and Bakar, B.H.A (2011) Chemical and Physical properties of fired clay brick at different type of Rice Husk ash. International conference on environment science and Engineering, Singapore. 8.

Kefas,H.M., Patrick,O.D., and Chiroma, M.T (2007) Characterization of Mayo-Belwa clay. Leonardo electron journal of practices and technologies.11:123-130

Kure, M. N. (2011).Analysis and characterization of some selected North west clay deposits. Research report NO.32. Federal Institute of industrial research, Oshodi, Lagos, pp.808.

Lopez-Galindo, C. Viseras and Cerezo, P. (2007). Compositional, Technical and Safety speciation of clay to be used a pharmaceutical and cosmetic products. Applied clay sciences. 36:51-63.

Nnuka, E.E. and Enejor,C (2010) Characterisation of Nahuta clay for industrial and commercial applications. Nigerian journal of Engineering and materials. 2(3)9-12.

Nwoye, I.C. (2010) Effect of water- steam transition temperature on the evaporation of clay during oven drying of clay. New York Science Journal.3(4):33-38.

Nwoye, I.C. (2003) Investigating the influence of particle size and size distribution on the physical and mechanical properties of ceramic materials. Project report, 6-22

Nwoye, I.C. (2008). Effect of porosity on the shrinkage behavior of Ukpor and Nsu clays. Journal Engineering applied science. 3(1, 2):27-30.

Manukaji, J. U. (2013). Chemical and mechanical characterization of clay samples from Kaduna state. International Journal of Engineering of Research and applications 3(2):1-5.

Ogbebor,O.J., Okiemien, F.E and Uzoma, M.O (2010) Characterisation of Ugbegun clay deposit.1(2): 22-23.

Oluwole, O. O. (2008). A Comparative study on the refractory properties of selected clays in North central Nigeria. Material Science and Engineering Department, Obafemi Awolowo University, Ille-Ife, Nigeria.

Omowumi, O. J. (2001). Characterization of some Nigerian clay as refractory materials for furnace lining. Mineral Raw Materials Department, Federal Institute of Industrial research, Ikeja, Lagos, Nigeria.

Onyemaobi, O. O. (2002). Mineral Resources Exploitation, Processing and Utilization – A Sine Qua Non for Nigeria's Metallurgical Industrial Development Inaugural Lecture Series 5 of FUTO, Owerri: FUTO Press. pp48 J T , 10 (3): 159-162.

Range K. J., Range, A. and Weiss, A. (1970) . Fire-clay type kaolinite or fire-clay mineral? Experimental classification of kaolinite-halloysite minerals. Proc, Int. Clay Con]. Tokyo, 1, 3 13.

Rhodes D., Clay and Glazes for the Porter, Revised Edition, Chilton Book Company Rednor, Pensylvania, A&C London, pp. 6-23, 1973.

Singer F., Singer S. S., Industrial Ceramics, Chapman and Hall Ltd., London, pp. 20-51, 1971.