Comparrative Analysis of Physiochemical Properties of Selected Clay Samples

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Abstract: Clay is an unconsolidated rock matter, with very fine grain which is plastic when wet and undergoes ceramic change to become hard and stony when heated. This research is aimed at carrying out physiochemical analysis of selected clay samples obtained from Bunza and Kalgo local government of Kebbi state. The samples were coded as A and B, The chemical composition of the clay samples was determine using X-ray fluoresce (XRF) method. While the physical properties were determine using American Society for Testing Material (ASTM) method. The physical properties tested include: porosity, linear shrinkage, cold crushing strength, thermal shock resistance. and loss on ignition. The results of the chemical analysis has showed that both the samples A and B contained Al_2O_3, SiO_2 and Fe_2O_3 as the major constituent with minor traces of K_2O, CaO, TiO_2, MnO, MgO, Na_2O and Cr_2O_3. The results of the physical test of the samples shows that an apparent porosity 29.46% and 22.95% respectively, which is within the range of the standard for the production of fire clay and siliceous clay. The results of thermal shock resistance is below the accepted value for both the samples A and B. The cold crushing strength values obtained for both samples A and B, were $100KN/M^2$ and $227KN/M^2$ which is below the specification for the manufacture of fireclay, siliceous fireclay and ceramic industries with the standard value of $15000KN/M^2$.Therefore the practical implication of these results is that, their use is restricted for line of cable slog pots only. It issimilarly observed that Tunga clay sample has more kaolinite than the other sample obtained from Diggi site in Kebbi state with 15.50% of alumina to 60.00% silica which could apparentlybe taken as ratio 1: 4 of Alumina to silica.

I. Introduction

The ceramic industries are the major users of clay. These industries consume about 70% of all clays marketed in crude or beneficiated form and those marketed only as finished products (Fakolujo *et al*, 2012). Clay is composed of silica (SiO_2), Alumina (Al_2O_3) and water (H_2O) plus appreciable concentration of oxides of iron, alkali and alkaline earth, and contains groups of crystalline substances known as clay minerals such as quartz, feldspar, and mica. These other minor oxides components (impurities) which occur in variable quantities are important as their presence impart some properties to clay which are of technical value. It is important to note that the amount of impurities allowable in clay depends o4n the purpose for example; when white wares are needed, coloring impurities such as Fe_2O_3 must not use (Abia-Bassey *et al*., 2006).

Local demands for ceramic products are very high considering the population yet the supply is met through importation. Nigeria currently spends about N5Bn annually on importing ceramics products (Pialy, 2009). Nigeria imports more than 50 containers of ceramics products daily into the country, in spite of the availability of both raw materials and human capacity for research, production and development of quality ceramics products of international standard and safety (Manukaji, 2013). Also, it is a worrisome fact that most of the imported ceramic wares are made with colors, glazes and body recipe that are not consumable and very dangerous to the human body. With the growing demand for ceramics wares such as dinner wares, sanitary wares, pottery wares, floor and wall tiles, ceiling fittings, spark plugs, Beryllium oxide ceramics, chemical and refractory porcelains, Electrical porcelain insulators, combustion chambers for engines and furnaces, decorative wares, etc. there is a need to quest for local peed stocks that could be utilize in Nigeria ceramic industries. When clay body is fired, after processing, the resulting physical properties usually determine their suitability for intended use. The chemical and mineralogical composition of the samples bears enormous influence on the physical characteristics (Abia-Bassey *et al.,* 2006).

Clay plays a predominant role in human life and their value is recognized in many economic branches, agriculture, civil engineering and environmental studies (Lee *et al.,* 2015). This is largely because of their wide-ranging properties, high resistance to atmospheric conditions, geochemical purity, and easy access to their deposits near the earth's surface and low price (Konta, 2014). In developed countries, industrial uses of clays have many applications such as coating and filler pigment for paper, filler for paint, rubber and plastics,

formulation additives in food, insecticides, cosmetics, pharmaceutics, fertilizers and soil correctors, and also as a major component in ceramics (Pialy, 2009). Clays are natural materials abundantly found and largely used by the prehistoric civilization to make household utilities. Presently, they are still used in the manufacturing of ceramic products such as bricks, porcelain, sanitary ware, floor and roofing tiles, also used in various industrial applications. As a basis of traditional and modern ceramic fabrication, raw material selection plays a vital role in the final product design. The final product is strongly influenced by chemical and mineralogical compositions and particle size distributions (Kitouni and Harabi, 2011).

Therefore, the knowledge of properties of the natural clay materials is of great interest since it provides useful information in the selection of more appropriate clay raw materials associated with industrial applications. Generally, clays contain different non-clay minerals as impurities besides major and minor clay minerals (Sousa and Holanda, 2011). The Maastrichtian clays in Bida Basin Nigeria were found to compare favorably with the plastic fire clays of St. Louis and Florida active kaolinite and if beneficiated was suitable as raw materials for ceramics, pharmaceuticals and paints (Ojo *et al.,* 2011).

Physio-chemical and mineralogical studies on alluvial clay sample obtained from the confluence of River Niger and Mimi River in Lokoja (Kogi state) showed that the sample had limited industrial potential because of the high salty organic contents. The chemical composition of the clay was however found to be suitable for making building blocks, traditional ceramic pots, and insulation bricks. The table1 and table2 below showed the physical properties and mineral composition of the samples.

Table 1 physical property of alluvial clay samples

S/NO	Sample Name	Bulk Density	Porosity %	C.C.S (Kcm^3)	Shrinkage	Slap R
A	Ikere	1.74 ± 0.11^d	31.44 ± 0.91^a	100 ± 6.21^c	5.0 ± 1.23^a	Good
B	Fagbolum	2.0 ± 0.15^a	20.69 ± 1.01^{bc}	`$140\pm6.44b$	2.0 ± 00^b	Good
C	Ishan	2.0 ± 0.02^{as}	19.10 ± 0.19^d	227 ± 12.9^a	1.5 ± 16^{bd}	Poor

(Lawal and Abdullahi, 2010).

Table 2: Mineral composition of some clay samples

Sample Location	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	L.O.I
Refractory Clay	46-62	258-39	0.4-2.7	0.2-1.0	0.2-1.0	8-18
Higher melting Clay	53-73	16-29	1-9	0.5-2.6	0.5-2.6	4-12
Ceramic	67.50	26.5	0.5-1.2	0.18-0.3	1.0-0.19	

(Lawal and Abdullahi, 2010)

II. Materials And Methods

Materials

The materials used in this study include;

Hoe; -This is simple Farm tool with metal bled on its head place on a wooden handed. Use for digging a clay sample.

Plate 1; Hoe   *Plate 2 plastic bottle*

Plastic bottle; - this are small plastic container, look like a beaker with plastic cover. Use for storage of sample.

Grinding Mortar and Pestle; - those are simple local machine used for grindings the clay sample and resizing of the grain.

| **Plate 3;** *Grinding mortar* | **Plate 4;** *Pestle* | **plate 5;** *Mesh* |

Mesh; - A structure made of connected strands of metal, fiber or other flexible/ductile material, with evenly spaced openings between them. Use for sieving the clay sample.

Samples: - Two different clay samples used for this research were collected from Bunza and Kalgo local government. In Bunza local Govt. Sample was collected from Tunga Dan Nufe fadama area, in Kalgo local Govt. the sample was collected from Diggi fadama area of kebbi state.
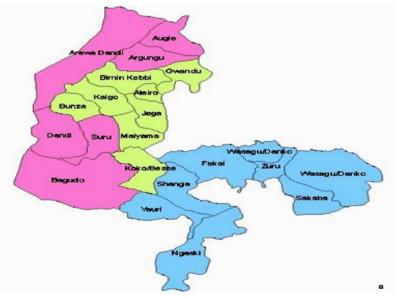

Plate 6 Regional map of Kebbi State. Source; retrieved from www.glooge.com, (2017)

Figure 1 Clay Site at Diggi

Figure 2 Clay Site at Tunga

III. Methodology

3.1 Sampling Method and Sample Preparation

The clay samples were collected from a hand digging of shallow holes which was dug for the purpose of this research in selected local government area of Kebbi state, Nigeria. The entire area is composed relatively of abundant deposits of this clay. The clay sample was collected at random from the dugout soil at the site between depths of about 2 meters to 5 meters. The clay had a slightly visible stratified arrangement of about 4cm to 9cm apart. Once collected the lumps was transported to Kebbi state university of science and technology Aliero, where the samples were crushed and thoroughly mixed by quartering and coning method in order to achieve a representative homogeneous samples. The clay samples were collected from five different locations on a particular area in order to have a good representation of the site. The two areas were used for the state in order to further give a wider sample spread for the state.

The samples from the five locations on an area were mixed properly and a representative sample from that area was produced using the cone and quartering system as recommended by the American Society of Testing Materials (ASTM) (Abubakar *et al,* 2014). The process involves mixing the samples and spreading them uniformly and equally into a rectangle. The rectangle is divided into four equal parts and two alternate portions were taken, then mixed properly and form into a cone. The cone was also divided into four equal parts while the alternate portion was further being taken. This process of mixing properly, spreading into rectangular shapes and cones and taking the alternate portions continued until a sizable quantity sufficient for the tests to be carried out is produce (Abubakar *et al.*, 2014).

3.2 Determination of Chemical Composition

The chemical composition of the clay samples was determined using the X-Ray Fluorescence (XRF) spectroscopy technique at the National Geosciences Research Laboratories Centre, Kaduna, Nigeria. This is popular technique applied for multi-element determination in wide variety of minerals. The samples were analyzed using a Mini Pal 4 version (PW 4030) compact energy dispersive X-ray spectrometer. The samples to be analyzed were weighing and ground to powder form using an agate mortar into a particle sizes within the range of 125μm and less. Pellets of 19mm in diameter were prepared by carefully mixing small portions of an organic liquid as binder (PVC dissolved in toluene) and pressed with a hydraulic press to 10 tons. Each of the pellets will be put in a plastic holder because there would be no interaction with the primary X-rays emerging from the X-ray tube window and the plastic holder. The holder and specimen were then loaded into the specimen chamber of the spectrometer and the instrument operated at 30kV and 1mA for 10mins. The primary X-rays would excite secondary emissions characteristic of the elements being analyses and the spectrum analyses to determine the concentration of the elements in the sample (Aliyu *et al.,* 2013).

3.3 Determination of Physical Properties

The physical properties of the clay samples to be determining include the following; - apparent porosity, loss on ignition, linear shrinkage, cold crushing strength and thermal shock resistance.

3.3.1 Determination of apparent porosity

The clay samples would be mould into bricks in cubical form (2.5×2.5×2.5 cm) and oven dry at 110±5⁰C until a constant weight (Wn) is obtain (with an accuracy of 0.1grams). The dry specimen was suspended in 300ml beaker containing distil water and boil at 100⁰c for two hour. It was allowed to cool down to room temperature and its new weight(s) will be determining (Ws). The specimen was removing from water and again re weigh in air to obtain (Ww) (Aliyu *et al.,* 2013).

Apparent porosity (p) will be determine using equation

$$P = Ww - Wd/(Ww - Ws) * 100 \qquad (1)$$

3.3.2 Determination of loss on ignition

Clay samples in percentage. Hence the loss on weight of each clay samples will be determined to be the difference in their weight before and after firing and consequently, the loss on ignition at firing temperature will be determine using equation below

$$LOI = \frac{W_1 - W_2}{W_1} * 100 \qquad (2)$$

Where; W_1= initial weight of clay sample before firing

W_2 = final weight of clay sample after firing (Al-Maireh, 2009).

3.3.3 Determination of Linear Shrinkage

The clay material is made into rectangular shapes of dimension 2.5×2.5×2.5cm in a mould and compacted under hydraulic pressure of 350KN/M². A slant line of length 10cm is inserting diagonally on each piece and record as (L_1). The test pieces are then place inside the furnace and fire up to 1000⁰C and line drawn across the diagonal axis of the pieces is measure to determine its final length (L_2) after firing. The linear shrinkage of the materials will be determined by giving equation (AL-Maireh, 2009).

$$Linear\ Shrinkage\% = l1 - \frac{l2}{l1} \times 100 \qquad (3)$$

3.3.4 Determination of cold crushing strength

Cold crushing strength is the amount of load that the clay material could withstand after it has been fire to a temperature of 1200⁰C. In determine of cold crushing strength (CCS) of the clay samples, cubical specimens are made from the clay samples, the dimensions of the test pieces will be taken before they are fire to the require temperature and allow to cool to the room temperature before the tests to be carry out. A card board sheet not exceeding 0.63cm in thickness is then place between the platen of the hydraulic press and the breaking faces of the test pieces which is place centrally on the platen. Hydraulic load will be applied on the test pieces, until the test pieces fail to support the load. The maximum record load is take as the crushing load. The CCS will be calculated using equation 4.0 (AL-Maireh, 2009).

$$CCS = load/Area \qquad (4)$$

3.3.5 Determination of Thermal Shock Resistance

Test pieces of clay samples bricks are thoroughly dry and place in the cold furnace and heat at the rate of 5⁰C/ min until the furnace temperature read 1200°C. This temperature is kept for 30 minutes after which the test pieces is remove with a pair of tong previously warm in the furnace for a short time. The test pieces are then place on cold firebricks in the environments free of draught and allow cooling down for about ten minutes. The test piece is then return to the furnace for a further 10 minutes. The cycle is repeat 30 times before thermal crack could occur (AL-Maireh, 2009).

IV. Results And Discussion

The particle size distribution for the clay samples was determined with aid sieved analysis and was found to be less than 250µm for all samples. This is indication that the clay grains were finer quality than fine sands in term of compactness and smoothness. The mean results for chemical and physical analysis of the samples are presented in tables 1,2, and 3..

Table 1 chemical composition of the samples

Samples Description	AL₂O₃	SiO₂	K₂O	CaO	TiO₂	MnO	Fe₂O₃	MgO	Na₂O	Cr₂O₃	L.O.I
DIGGI (A)	15.18	16.43	3.50	1.80	5.20	0.29	30.26	0.37	1.89	ND	18.06
TUNGA (B)	15.50	60.00	1.50	1.40	2.58	0.08	6.04	0.02	2.30	0.03	9.24

. It is observed that sample B as reported in the table 1is more kaolinite than samples A with 15.50% of alumina to 60.00% silica which could apparently take as ratio 1: 4 of Alumina to silica. This is agreeing with the standard as reported by (Sanni, 2005). The clay samples from the location outside the Samples B probably

contain higher impurities of mineral oxides and iron III which make them more plastic (Ball clay) than Tunga clay. Consequently, table 1 show that Samples B contains the least amount of iron III oxides (Fe_2O_3), which is 6.04%wt. than Diggi with 30.26% of Fe_2O_3 respectively.   Nevertheless, the proportion of elemental composition of iron in the clays determines the thermal conductivity potential of such materials. Hence (Sanni, 2005) Suggested that any fire clay to be use in refractory should have at least 30% Al_2O_3 and less than 1.8% Fe_2O_3. The proportion increases in the ratio of Al_2O_3 in the samples, will undoubtedly improve clay refractiness, whereas a progressive reduction in Fe_2O_3 content of the samples will perhaps lower their thermal conductivity in that order. This is probably suggesting why samples A would be regarded as having better insulating properties than the samples from other location. By implication therefore the thermal conductivity will be highest in B but least in A clay, Making A clay the material of choice. Other associated impurities in various clay samples include K_2O, CaO, TiO_2, MnO, MgO, Na_2O and Cr_2O_3 which are in various proportions by weight as shown in the table 1. But the impurities are less in Diggi clay. The loss on ignition of the clays (LOI) was determined as the percentage of moisture loss to ignition on firing the prepared clay samples. This is highest in Diggi clay with 18.06% and, but least in Tunga with 9.24% as shown in the table 1.

Table 2 physical properties of the samples

Samples Description	Apparent Porosity(%)	Bulk Density(g/cm3)	T.Shock Resistance(circle)	C.C.S (KN/M2)	Shrinkages (%)
Diggi	22.95	1.7	9	227	9.00
Tunga	29.46	1.91	7	100	4.11

Table 3 Required Standard physical properties of clay for industrial applications

Samples Description	Apparent Porosity (%)	Bulk Density(g/cm3)	T. Shock Resistance (circle)	C.C.S (KN/M2)	Shrinkages (%)
Fire Clay	20-30	2.3	20-30	15000	4-`10
Siliceous Fire Clay	23.7	2.0	1	15000	7-1`0
Ceramic	10-30	2.30	20-30	15000	
Refractory brick	10-30	2.30	20-30	15000	

Omowumi (2000)

The physical tests result of samples A and B show an apparent porosity of 29.46%, and 22.95% respectively, which is within a range of a standard for the production of fire clay and siliceous fire clay with 20-30% and 23.7% respectively Omowumi (2000) Except Sample A with apparent porosity 22.95% less than required for siliceous fireclay. Therefore, clay from sample B serves as a raw material for the production of fireclay and siliceous clay as reported by (Omowumi, 2000).

Their thermal shock resistance is below the accepted value of 20-30 circles as compared in table 3. The practical implication of this is that their use is restricted to lining of cables slag pots.

The linear shrinkage of the samples after drying and firing fall within the accepted value of 4-10% for fire clay samples B for siliceous fireclay. Higher shrinkage values may result in warping and cracking of the clay and this may cause loss of heat in the finished product.

The refractoriness or temperature reached for the samples was 1200^0c. This is lower than the recommended range for the manufacture of fireclay, siliceous fireclay and ceramic industries. This may be due to the low amount of Al_2O_3 obtained for all the samples. The cold crushing value obtained for both A and B was $100KN/M^2$ and $227KN/M^2$ which is below the specification for the manufacture of fireclay, siliceous fireclay and ceramic industries with standard value of $15000KN/M^2$

V. Conclusion

The results of the chemical analysis shows that the clay samples contain aluminum oxide (Al_2O_3), Silica oxide (SiO_2) and iron III oxide (Fe_2O_3) as the major constituents, with minor trace of K_2O, CaO, TiO_2, MnO, MgO, Na_2O, Cr_2O_3. The clay samples B has the high loss on ignition with value 18.06% it has the least impurities contain in the samples and A has least loss on ignition with value 9.24%. The cold crushing value obtained for both A and B was $100KN/M^2$ and $227KN/M^2$ which is below the specification for the manufacture of fireclay, siliceous fireclay and ceramic industries with standard value of $15000KN/M^2$. It is observed that sample B as reported in the table 1 is more kaolinite than a clay samples obtained from A with 15.50% of alumina to 60.00% silica which could apparently take as ratio 1: 4 of Alumina to silica. This is agreeing with the standard as reported by (Sanni, 2005). The practical implication of both samples is that their uses are restricted

to the line of cable slog pot. Also sample B can be use as a raw material in the production of modern pop, paint, fertilizer, medicine, paper e.t.c. because it contain higher amount of kaolinite that sample A.

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