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SUITABILITY OF EHA-NDIAGU CLAYS FOR THE PRODUCTION OF LABORATORY CRUCIBLES

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Abstract

Eha-ndiagu clay was investigated for application in the production of laboratory crucibles. Chemical and physical characterization of the clays were carried out. The physical properties such as linear shrinkage, apparent porosity, water absorption, apparent density, bulk density, flexural strength, and refractoriness were investigated. The results obtained showed that Eha-ndiagu clay has low refractoriness, (1150^{0}C). Beyond 1150^{0}C, visible cracks were observed in the body which limits the utilization of Eha-ndiagu clay at higher temperature. The chemical characterization gave values for Fe_2O_3 above 1.7% which accounted for the brownish colour of the fired sample of this clay. The presence of fluxing oxides in the clay made it unsuitable for refractory applications. However the results showed that the clay is suitable for ceramics such as earthware and building bricks. And more so, for the clay to be used for production of laboratory crucible the clay must be modified with some non-plastic inorganic material such as silica and feldspar.

Keywords: Suitability, Eha-Ndiagu, Clays, Production, Laboratory Crucibles

Introduction

A crucible is a ceramic container capable of withstanding extreme temperature. The cover is designed to prevent heat escaping from the crucible itself. Modern crucibles come in a range of materials forms, including graphite, platinum and other inert heat resistant metals. Basically these containers can be made from pretty such materials that are capable of withstanding high temperatures for a prolonged period of time without losing its mechanical properties.

Crucibles are used for many purposes, and are particularly common amongst chemicals for the chemicals analysis of various substances. They are usually found in laboratories where various chemicals compounds are heated, but can also be used to determine the ash content of burnable samples such as coal wood, and animal bones. In general reaction mixture are heated in crucibles and purpose –built custom tongs must be used to handle the scorching hot materials contained in them. They are often considered dangerous because of their ability to cause fatal burns, and so it's of vital importance that they are used with great care and caution at all times, preferably under the supervision of a trained scientist.

The use of the crucible has changed quite dramatically over hundreds and using the two objects for alloy production and the people of the medieval era using them to smelt and other copper alloys such as lead.

More so, a crucible is a cup-shaped piece of laboratory equipment used to hold chemical compounds in small qualities when heating them to very extremely high temperatures. They are very durables and resist temperatures to over 1600^0c.

Usually, they are made of clay, and can also be made of any materials with a higher temperature resistance than the substances they are designed to hold. Typically, a crucible will be placed into a furnace and, after the melting; the liquid metal is taken out of the furnace and poured into the mold. Some furnaces are designed in such a way that they have an embedded crucible and are tilted for when the metal is poured out. Typically they are made of high temperature – resistant materials, usually porcelain but other metals such as nickel and zirconium have been used. The lids tend to be loose-fitting to allow gases to escape during heating of a sample inside. Crucibles and their lids can come in high form and low form shapes and in various sizes. Small size crucibles and their covers that are made of porcelain are relatively inexpensive and so sometimes disposed of after use in very precise quantitative chemical analysis.

Crucibles are used in: (i) Chemical analysis (ii) Ash content determination etc.

Crucibles are glazed on inner and outer surfaces except for outside bottom and rim.

Aim and Objectives of this work are:

Investigation of the suitability of Eha-Ndiagu clay for production of laboratory crucibles in order to curtail the rate of importation of crucibles and to carry out physical and chemical characterization of Eha-Ndiagu clay and production of laboratory crucibles from the aforementioned clay deposits.

MATERIALS AND METHODS

SPECIMEN PREPARATION

In order to produce the material with optimum characteristics, finding the appropriate processing procedure that enables high homogeneity in powder mixture is very important [27]. First, the dry components of the clay sample were mixed, and then deflocculant containing water was added and mixed for 4 min. After moulding, all samples were cured for 24 hours at room temperature, dried at 110°C for 24 hours, sintered at various temperatures of 900, 1000 1100 and 1200°C, cooled to room temperature inside the furnace.

MOLDING OF THE TEST PIECES

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 shapes are cylindrical with a width of 3.5cm and height 3cm, the second is a rectangular test piece and another which has a long rectangular shape with 9.5cm width 2cm and height 1.5cm.

PHYSICAL PROPERTIES

Density, apparent porosity and water absorption of clay samples were determined by water immersion method according (ICS 81.080 SRPS B.D8.302) on the three specimens of cube shape with 40 mm edge length for each sintering temperature.

WATER ABSORPTION

Water absorption measured the maturity of a fired clay body. The rectangular bars test pieces of dimension 8cm x 4.1cm x 2.1cm were used for this study according to British standard EN (1991). The test pieces fired to the various temperatures were weighed to the nearest cm. The fired test pieces were then boiled for 2hrs and then allowed to cool. The surface of the bar (test pieces) were dried with a dry towel and weighed again. The % water adsorption was computed using the equation

$$water\ absorption = \frac{saturated\ weight - dry\ weight}{dry\ weight}\ x\ 100$$

POROSITY AND DENSITY

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 M_3 (g).

The apparent porosity, apparent density and bulk density were then calculated (Akwilapo and Wiik, 2003).

$$Apparent\ Porosity\ (\%) = \frac{(m_2 - m_1)\ \times 100}{(m_2 - m_3)}$$

$$Apparent\ Density = \frac{(m_1)}{(m_1 - m_3)}$$

$$Bulk\ Density\ = \frac{(m_1)}{(m_2 - m_3)}$$

MECHANICAL CHARACTERISTICS

Flexural strengths of the samples treated at different sintering temperatures were determined by classic method of destructive testing following standard laboratory procedures ICS 81.080 SRPS B. D8 307, respectively.

REFRACTORINESS

The rectangular test pieces moulded from the sample using calculated amount of water to achieve plasticity were dried and fired to temperature beginning from 900^{0}C in a muffle furnace fitted with a digital pyrometer. Heating was performed at temperatures ranging from 900^{0}C-1300^{0}C.The corresponding test pieces were then analyzed to see the refractoriness of the clay.

Pyrometric cones (Orton standard pyrometric cones) designed to deform at 1000, 1250, 1300 and 1350^{0}C were used in accordance with the ASTM standard.

Temperature was raised at 10^{0}C/min as was programmed in the digital pyrometer fitted to the kiln. The kiln had a maximum temperature of 1350^{0}C and the test pieces did show sign of failure and deformation, meaning that the clay sample was not refractory. For the clay to be utilized in refractory applications, the composition needed to be modified.

MODULUS OF PLASTICITY

Cylindrical test pieces of dimension 3.7cm x 3.3cm were molded and used for this test. The distance of drop was 10.05cm high. The heights before deformation of the various molded test pieces were noted before deformation. The plastometer drop had a mass of 777.5g with a drop height in the range 10cm – 10.20cm. The deformation was performed in triplicate and the average result was taken to represent the deformation height from where the modulus of plasticity was computed. The plastic modulus and water of plasticity were computed using the equation below.

$$Plastic\ Modulus = \frac{Hi}{Hf}$$

Where Hi= Initial height of test piece before deformation and Hf = final height of test piece after deformation.

TRIAXIAL FLEXURAL STRENGTH TEST

The modulus of rupture/transversal strength machine fitted with a salter scale was used. The test pieces of dimension 10.2cm x 1.5cm x 2.1cm were used for this test and were supported on the ends of three cylindrical rods arranged in an equilateral triangle form and a load electrically applied by the rupture machine until it failed. The test was performed in triplicate and the average was used as the triaxial flexural strength of the clay body. 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, which is 7cm. 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 (Akwilapo and Wiik, 2003).

$$Modulus\ of\ Rupture\left(\frac{Kg}{cm2}\right) = 3PL/2BH^2$$

LINEAR SHRINKAGE

The rectangular bar test pieces of dimension 8.0cm x 4.1cm x 2.1cm were moulded and a mark of 5cm apart was made at their centers. The green samples were allowed to dry at room temperature while the others were dried at room temperature and then fried to the corresponding temperatures intended for them in a kiln. After drying at room temperature, they were again dried in an oven at 110^0C to constant weight. The drying shrinkage was determined using the equation.

The shrinkage was then calculated (Lynne et al, 1980).

$$Wet - Dry\ Shrinkage(\%) = (\frac{Lo - Ld}{Lo} x\ 100$$

$$Linear\ Shrinkage(\%) = (\frac{Ld - Lf}{Ld} x\ 100$$

$$Total\ Shrinkage(\%) = (\frac{Lo - Lf}{Lo} x\ 100$$

PRESSING MOISTURE

The cylindrical test pieces made for modulus of plasticity were used for this test. They were used as a representative batch of the pressed test pieces and weighed as soon as they were molded (W_1). They were then oven dried at 110^oc for 24hrs, cool in a desiccator for 30mins and then weighed again (W_2).

The test was carried out in triplicate and the pressing moisture/making moisture was computed as:

$$M.C = \frac{(w_1 - w_2) \text{ x } 100}{w_1}$$

Where M.C = Making moisture content; W_1 = Weight of sample before drying; and W_2 = Weight of sample after drying at 110^0C.

LOSS ON IGNITION (LOI)

This test measures the organic combustible matter present as impurities. This impurities leads to gas evolution and reduces the refractoriness of clay. 50g of oven – dried clay after cooling in a desiccator, was measured into a clean flat surface porcelain crucible of known mass (M_1). The crucible and its content was placed in a muffle furnace and incinerated to a temperature of 800^0c. The crucible and its content were then put back into a desiccator to cool. After cooling, the incinerated crucible and the clay content were then weighed again to constant weight (M_3). The loss on ignition was then computed using the equation below:

$$Loss\ of\ ignition\ (\%) = \frac{(m_2 - m_3) \times 100}{(m_2 - m_1)}$$

Where; M_1 = Mass of crucible, M_2 = Mass of crucible + sample before heating, and M_3 = Mass of crucible + sample after heating.

CHEMICAL ANALYSIS

0.5g of the day sample was weighed into a beaker and 10ml of aqua-regia (HCl + HNO_3) in the ratio 3:1 was added and digested 5ml of Hydrofluoric acid, HF, was also added to aid the digestion process. After digestion 30ml of de-ionized water was added and the mixture filtered through a filter paper into a 250ml volumetric flask and made up to the meniscus mark with de-ionized water. The samples were then analyzed for the elemental composition by the use of the atomic absorption spectrophotometer. The concentration of the metal oxides in the day was expressed in mg/g.

SLIP CASTING

The process of slip-casting, as applied to the production of clay ware (laboratory crucible), is simple in principle. The “Slip”, which is an aqueous suspension of the clay mixture, is poured into a plaster of paris mold where it gradually solidifies by absorption by the plaster of water from the slip. The solidified casting is subsequently removed from the mold and is dried and fired.

Low temperature laboratory crucible produced as an aggregate with the maximum particle size of 180µm, and the matrix composed of fine fractions of orthoclase (Feldspar-k) being the source of reactive Alumina, silica to confer the strength, reduce the plasticity of the clay and increase thermal resistance and reduce thermal shock of the crucible.

Composition of recipe used:

(i) Aggregate (clay) – 60%, (ii) Modifiers, Silica –24% Feldspar –15%, (iii) Admixture – 1%

20wt.% of water was mixed with the recipe for slip casting and deflocculated with sodium silicate as the admixture.

Casting Process:

To form a crucible, the slip was poured into the plaster mold rapidly to ensure homogeneity. The plaster immediately began to absorb water from the slip, and a film of solidified material formed on the walls. The liquid level within the mold was maintained by additions of slip until the film of solidified material reached the desired thickness. The mold was then inverted and the residual slip was poured out.

The time required forming a crucible with a wall thickness of 2 or 3mm usually was about 1 minute, but this varied with the consistency and acidity of the slip and with the condition of the plaster mold. The crucible, therefore, was allowed to remain in the mold for further drying by absorption of water by the plaster. After about 2 hours the inner surface was dry and firm to the touch and shrinkage cracks began to appear at the junction of the top of the crucible and the wall of the mold. The casting then could be removed from the mold, particularly if the mold was gently tapped before it was inverted. The crucibles at this stage were somewhat plastic but were strong enough to be removed from the mold without collapsing. They were air-dried for about 24 hours and then were heated slowly for another 24 hours during which the temperature rose to about 110^0C. Drying in this manner did not appreciably affect the dimensions of the crucible, but subsequent firing to 900^0C – 1200^0C was accompanied by a linear shrinkage of about 8.8 percent. The density and shrinkage of the crucible increased, and the porosity decreased, with increasing temperature of firing; but a maximum temperature of 1300^0C was used in the work, primarily to provide a safe margin for subsequent use of the crucibles at about temperature of 1200^0C.

RESULTS AND DISCUSSION

Table 1: SUMMARY OF PHYSICAL ANALYSIS OF THE CLAY.

Parameter	**Green**	**900 (^{0}C)**	**1000 (^{0}C)**	**1100 (^{0}C)**	**1200 (^{0}C)**
Linear Shrinkage(cm)		2.05	3.6	6.9	8.8
Apparent Porosity(%)		26.33	25.80	5.63	5.56
Water Absorption(%)		15.16	14.49	2.9	2.86
Apparent Density(g/cm^3)		2.36	2.34	2.06	2.06
Bulk Density(g/cm^3)	*-	1.74	1.75	1.94	1.94
Modulus of Rupture (kgF/cm^2)		18.01	31.61	45.29	51.87
Modulus of plasticity	1.28				
Making Moisture (%)	32.90				

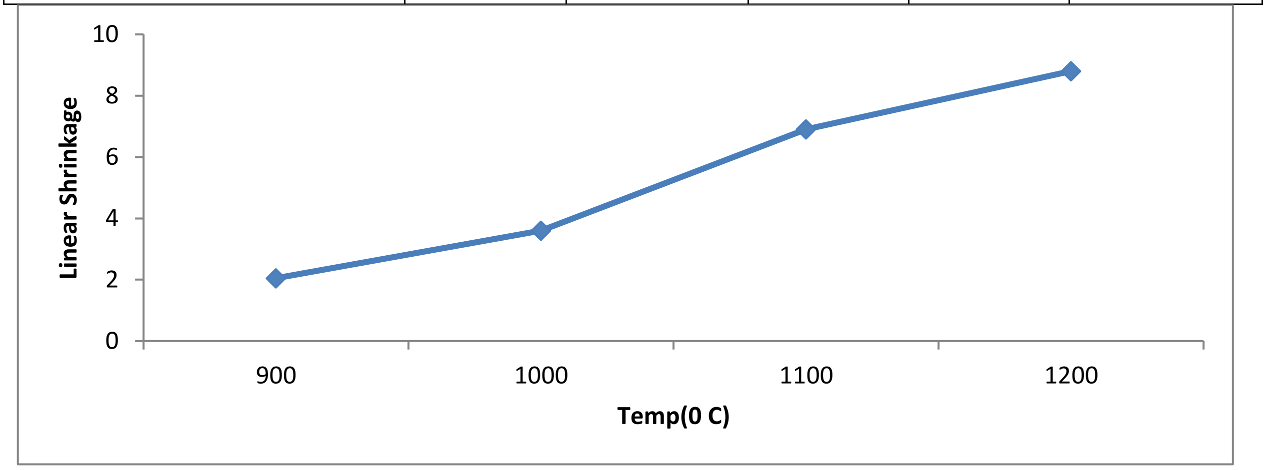

FIGURE 1: A GRAPH OF LINEAR SHRINKAGE AGAINST TEMPERATURE(^{0}C)

This is an indicator of the firing efficiency of the clay samples. The values reported by Musa & Aliyu (2011) for Tatiko and Beji clays were 1.41 % and 1.20 %, Omowumi (2001) quoted a recommended range of 4-10% for fireclays and Abolarin *et al* (2004) pointed out that lower values were more desirable as this means the clay is less susceptible to volume change. The clay however has a comparatively high linear shrinkage value (8.8% at 1200^{0}C) but falls within the range for normal kaolin ($Al_2O_3.2SiO_2.2H_2O$) which is between 7 and 10 %. This means that the clay must be processed so as to dry slowly in order to minimise any deformation or damage to finished articles. The linear shrinkage (Dry – Fired) was increasing with increase in temperature for the unmodified clay as shown in figure 1.

Shrinkage of 8.8cm at 1200^{0}C is regarded as being within the internationally accepted range for refractory clays. Chester (1973) recommended a linear shrinkage range of 7-10 %

for refractory clays; therefore, the clay can be classed, based on this range, as refractory clays

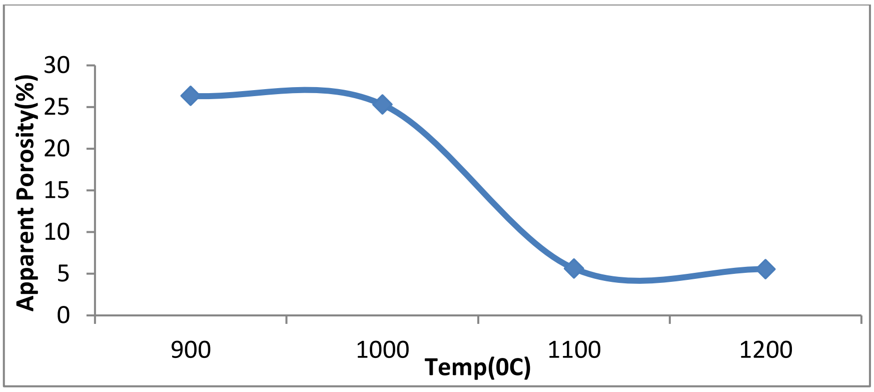

Figure 2: A Graph of Apparent Porosity against Temperature (^{0}C)

Figure 2 shows the variation in porosity with changes in temperature. At 1200^{0}C, porosity was 5.56% as shown in table 1. Porosity was however decreasing with increase in temperature. porosity of 5.56% found not to be within internationally defined standard of 15-25% (Mazen, 2009). These make the clay unsuitable for usage as fire bricks for insulation. The low percentage of apparent porosity enhances the entrapping of gases in the material during operation.

This will adversely affect the life span of the refractory material when in operation (Gupta, 2008).The values may be increased with addition of fine grain of additives, such as, saw dust or rice husk.

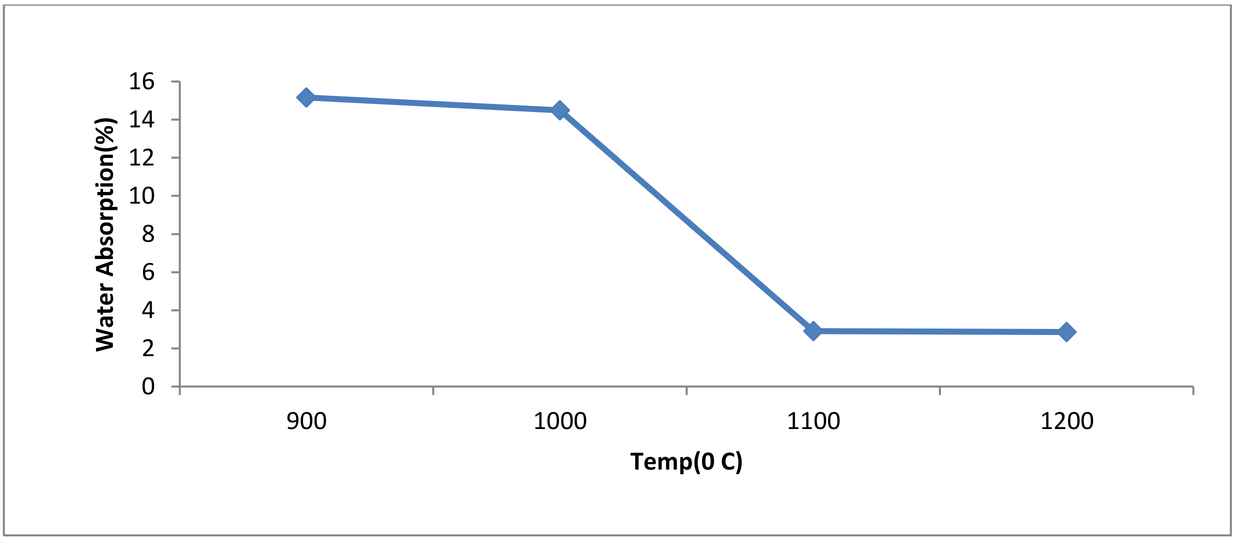

Figure 3: A Graph of Water Absorption(%) Against Temperature(^{0}C)

Water absorption for the clay tends to decrease with increase in temperature as shown in figure 3. A value of 2.86% at 1200^{0}C (table 1) . The water absorption of the clay samples fall within the recommended value of 2.6-2.9% according to Chester (1973).

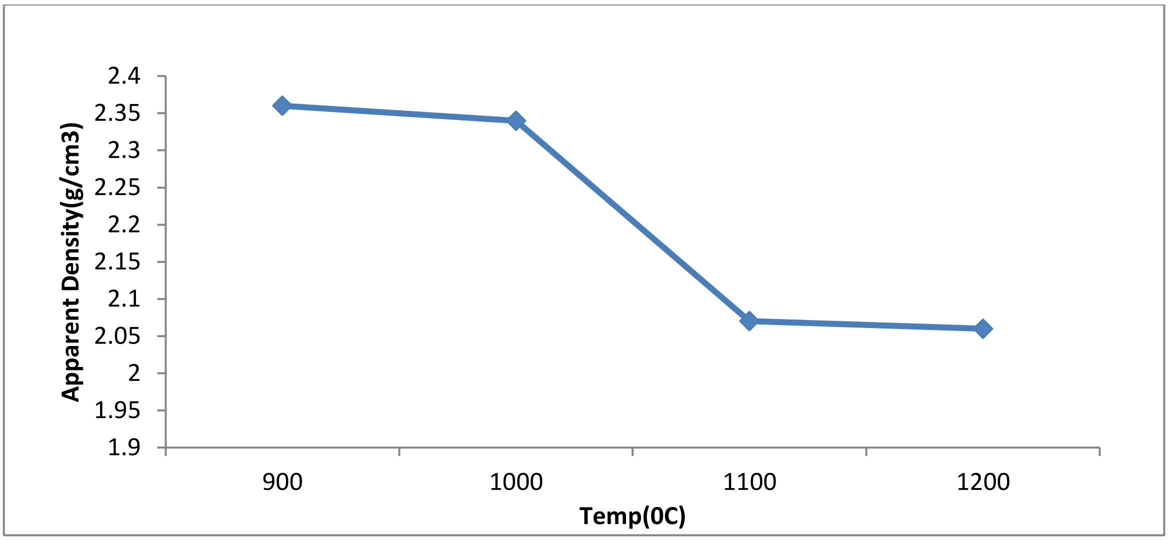

Figure 4: A Graph of Apparent Density (g/cm^3) Against Temperature (^{0}C)

In the Apparent density (A.D), the volume of closed pores is also included so it's always more than the Bulk density. It is the mass divided by its apparent volume. The range of apparent density for the unmodified clay at the various temperatures is shown in table 1. From figure 4, A.D decreased with increase in temperature from 900^{O}C to 1200^{O}C. The range at this temperature (1250^{O}C) was found to be within the range of 2.3 – 3.5g/cm3 being the internationally accepted standard range [Abuh *et al.,* 2014; Ryan, 1978; Manukaji, 2013). With increase in temperature, the particles are forced together to occupy the pores/spaces created by the eviction of pore water, entrapped gasses, organics and other thermally unstable non fusible components of the matrix(Abuh *et al.,* 2017). As the spaces are closed up and particles forced together, the A.D will decrease. This compaction will impact on the bulk density which will increase with decrease in A.D.

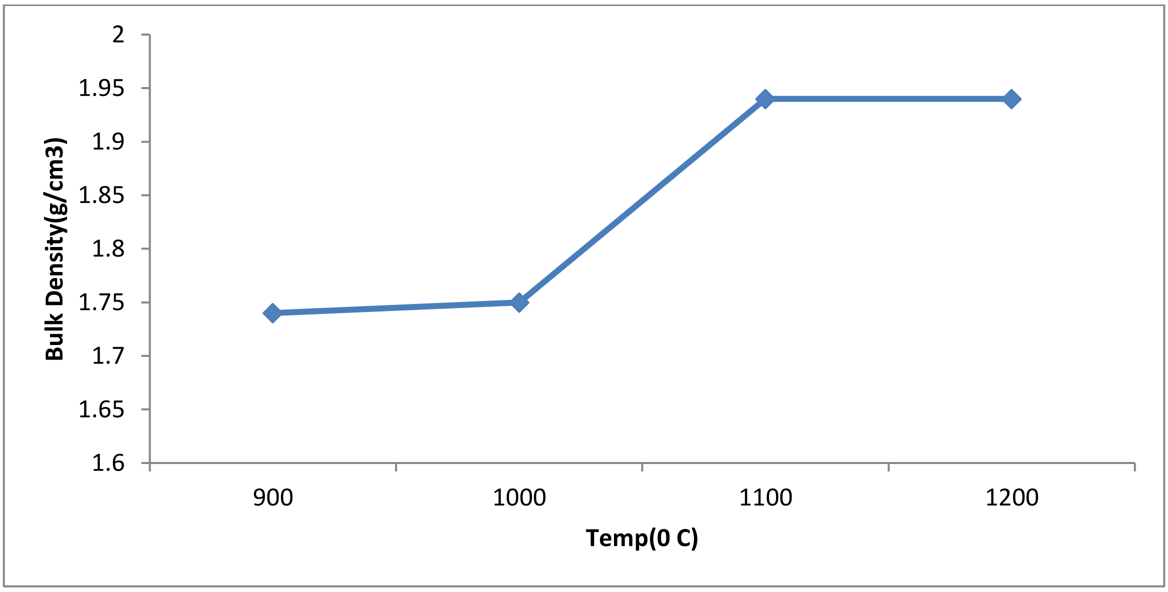

Figure 5: A Graph of Bulk Density (g/cm^3) Against Temperature(^{0}C)

For the most part, bulk density varies with the volume concentration of the open and close pore space. To a certain extent however, it is also related to the mineral composition of the clay. Mazen (2009) observed that the specific gravity of bricks varies indirectly with Al_2O_3 content in the raw materials. Onyeji (2010) noted the correlation between bulk density, linear shrinkage and apparent porosity and stated that the denser clays are less porous and less likely to shrink.

The bulk density measures the weight per volume. B.D increases with compaction. The Soils with bulk density > 1.6g/cm^3 are too compacted to support root growth. Figure 5 shows the B.D of the unmodified clay under study. The increase in B.D with increase in temperature may be due to increase in compaction and availability of free silica which densifies on interaction with fluxing oxides forming a glass phase that seals up the pores. High bulk density is not desirable in building bricks and construction applications. This is why the search for light weight materials without compromised mechanical properties is high today(Abuh etal, 2017)

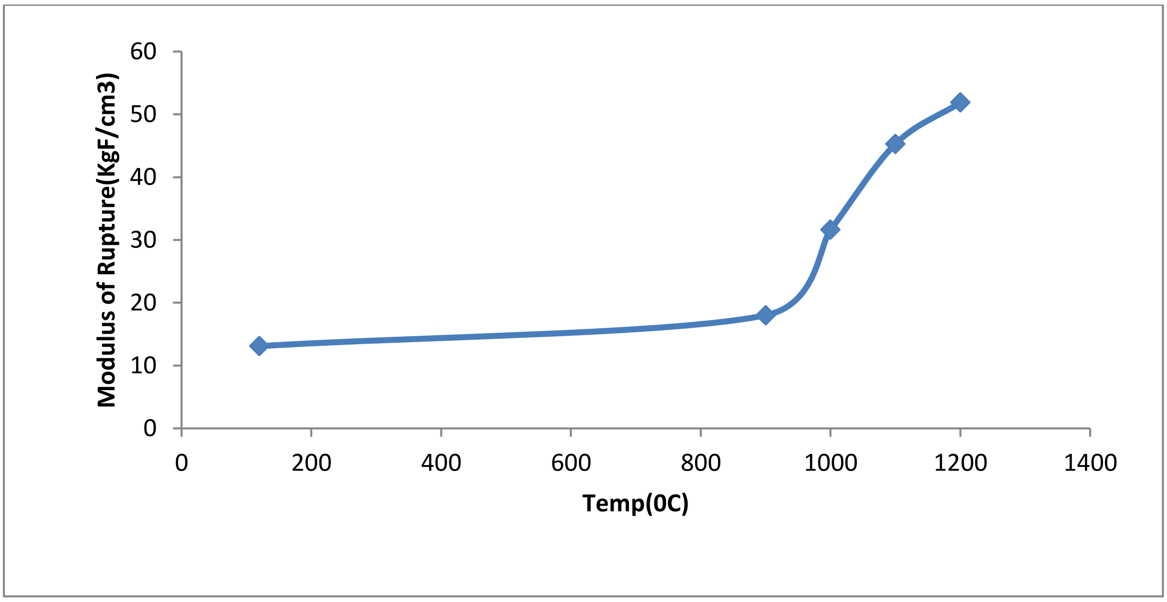

Fig 6: A Graph of sheer Strength Against Temperature (^{0}C)

The tri-axial flexural strength of the clay with increase in temperature is shown in figure 6. The sheer strength increased with increase in temperature. However, the values for the temperature range of 1000^{0}c - 1200^{0}c were > 31.61KgF/cm2 which shows a very strong clay. The breaking load for the clay within the experimental temperature range of 1000^{0}C - 1200^{0}C was greater than 12kg indicative of the high shear strength of the sample. M.O.R measure of the ability of clays to withstand abrasion and loading.

Refractoriness

Refractoriness refers to a material's ability to withstand high firing temperatures without deterioration of their physical and mechanical properties. The clay withstood up to 1150^0C thereby exhibiting poor refractoriness and therefore cannot be directly applied for high refractory application. The celebrated Nsu clay has refractoriness which was theoretically determined to be 1683^oC by Ameh & Obasi (2009) using Shuen's formula. For Tatiko and Beji clays, Musa & Aliyu (2011) reported values of 1300 and 1350 ^{0}C respectively. These are much lower than the recommended range of $1500\text{-}1700^0$C for fire clay refractories as quoted by Yami & Umaru (2007) who went further to attribute the low values to high silica content and as such, their use is restricted to non ferrous metals processing with melting points below 1400^0 C**.**

Tab 2.0 CHEMICAL ANALYSIS OF EHA-NDIAGU CLAY

Oxides	Fe_2O_3	MgO	K_2O	MnO	CaO	Na_2O	Al_2O_3	SiO_2
Concentration(%)	2.9	2.72	Nil	0.02	1.73	0.05	31.04	52.26

The colour of the clay deposit varied from grey to red on firing. This is due to the content of iron oxide of 2.9%. The ferrous oxide impacted a red colour on the fired sample due to conversion from ferrous to ferric compound. The colour variation is considered usable for the manufacture of flowerpot and earthenware (Rhodes, 1973). The composition of Fe_20_3 that is less than 1.7% indicates that the clay will usually burn white on firing while that above 1.7% will tend to change colour of the products to brownish or ruby-red depending on the percentages involved (singer *et al.*, 1993; Gupta, 2008).The result for chemical analysis in table 2.0 shows a high silica content ($SiO_2 > 45.6\%$) which must likely mean that Eha-ndiagu clay exist as quartz and comparing the result to that obtained for clays, suggest its use as source of silica for the production of floor tiles and ceramics (Nwajugu and Aneke, 2001). The percentages alkali oxides (CaO, K_2 and Na_2O) are low and this explains the weak plasticity characteristics of the clay. (Nnuka and Enejor, 2001). High percentage of CaO and Mg0 increases the shrinkage value of the materials but the value here would aid the bonding effect of the system as it was low (Gupta, 2008). The alkali oxides (flux) and low aluminum content made the clay unfit for refractory production.

CONCLUSION

From the results obtained, it is indicated that;

1. Since the clay fired red, the presence of fluxing oxides responsible for the colour change would make the clay unsuitable for high refractory applications.

2. The low value of porosity exhibited by the clay would encourage the entrapment of gases which would crack the material if used for refractory purposes without the body being modified.
3. For refractory utilization of the clay, especially for laboratory crucibles, very fine particle sizes (passing 180µm) of feldspar and silica must be added.
4. The values obtained for the clay suggested that the clay can be used for production of ceramic wares such as flower vase, building brick and floor tiles etc.

REFERENCES

Abolarin, M.S. O.A. Olugboji, (2004) "Experimental investigation on local refractory materials for Furnace Construction." Proc. Of 5th Ann. Eng. Conf., Federal University of Technology: Minna, Nigeria. Pg. 82-85

Abuh, M.A, N. Abia bassey, T.C. Udeinya, H.U. Nwannewuihe, A.A. Abong, and K.G. Akpomie. (2014) ''Industrial potentials of Adiabo Clay in Calbar Municipal of Cross River state, South- South Nigeria." Pacific Jounral of Science and Technology. 15(1): Pg. 63-75

Adondu A.S. (1988), Indigenous Refractory raw-materials base for Nigerian steel industry journal of Nigerian soceity of Chemical Engineers (NSCHE), (7): 2. Pg. 322-327

Ameh, E.M; & Obasi, N .L (2009). Effect of rice husk on insulating bricks produced with Nafuta and Nsu clays. Global Jour. Of Engg. & Tech, 2 (3), pg 661-668

Borode, J.O, O.O Onyemobi and J. Omotoyinbo. (2000). Suitability of nigerian Clays as refractory raw materials Nigerian journal of engineering Management Pg. 3.14-18

Chester J.H. (1973), refractories production and properties, the Iron and steel instituties, London, Pg. 4-13, 295-315

Grimshaw, R.W. (1971), the Chemistry of Clays and allied ceramic materials 3rd Edition ernest benn limited Pg. 801-802

Gupta, O.P. (2008) 'Elements of Fuels furnance and Refractories" 5th Edition, second Reprientkhanna publishers, New Delhi-110006 JMME Pg. 55-62

Manukaji, J.U. (2013). " Industrial potential of some Clay deposits in kogi state, North central Nigeria". American Journal of Engineering Research.2 (4) Pg. 33-38

Mazen, N.A. (2009) production of fire clay refractory bricks from local materials. European Journal of Scientific Research, 26 (3), Pg. 386-392

Musa, U; M A; Mohammed I. A; Sadiq M.M.A (July 2012). comparative study on the refractory properties of selected clays in North central Nigeria. Academic research International, Vol.3.

Manukaji, J.U. (2013), Industrial Potential of some Clay Deposits in Kogi State, North Central Nigeria. American Journal of Engineering Research, 2(4) Pg 33 –38

Nnuka E. E; Enejor C; (2001), Characterization on Nafuta Clay For Industrial and Commercial Applications, Nigerian Journal of engineering and materials, 2(3), Pg. 9-12 .

Nwajugu C. O; Aneke I.E; (2001) Characterization of Ukpor Clay Deposit, Journal of Nigerian society of Chemical Engineering 5(1), Pg. 1-3

Omouwmi, O.J. (2000). Characterization of some Nigerian clays as refractory materials for furace lining. Nigerian Journal of Engineering management.

Onyeji, L.I. (2000) Analysis and Characterization of Nyikangbe Clay, Chanchaga L.G.A. Niger State.