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RESEARCH ARTICLE

An Investigation on Refractory Clays Properties for Application in Metallurgical Industries in Nigeria

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Abstract

With the present yearning towards industrialization of the nation which has seen the emergence of various metallurgical industries, the need for refractory materials therefore is no doubt of paramount importance and necessity. Items produced from refractoriness include firebricks, crucibles, chimneys and electric insulators etc. The results of the investigation carried out on the refractory properties of clay samples obtained from three different locations in Niger state of Nigeria are presented. The properties obtained include among others, refractories of about 1400°C, cold crushing strength (4.820-14.30MN/M²), bulk density (1.0-2.94g/CM³) and linear fine shrinkage (2.17-4.30%).

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Introduction

Refractories are materials of construction capable of withstanding high temperatures and maintaining their physical properties in a furnace environment when in contact with corrosive slags, liquid metals and gases. They are widely used in most high-temperature manufacturing processes such as copper and aluminium smelting, glass and ceramic manufacture, cement and ore processing, petroleum refining and petrochemicals manufacture. However, iron and steel making account for almost two-thirds of all refractories used and it is in this industry where many refractory developments have occurred. The primary responsibilities of refractories are to keep the particular high-temperature process in operational a minimum operating cost and to control the consumption of energy required grain usually without chemical additives and develop strength only after heating to high temperatures, when ceramic bond is formed.

Refractory insulating materials are often used in high-temperature applications to reduce heat losses and save fuel. They may have the form of insulating brick, refractory fiber board or blanket, or special vacuum cast shapes. High-temperature ceramic coatings are seldom used in refractory applications, since typically the refractory is too rapidly consumed or worn away in use. However, in certain

applications, the life of a refractory metal or ceramic part may be extended by applying a high-density refractory material to the surface by flame or plasma spraying. Such coatings are typically limited to special applications and would not be used in conventional furnaces Muhammadu M. M. (1998).

The most important aspects of a refractory material are that it must be able to provide necessary thermal properties, support metallic windings (for electrical resistance furnaces), and capable of holding solid or liquid metal without entering into any undesirable chemical reaction with them. Refractory supplies to industries in Nigeria are tight and sometimes delivery promises are often extended well beyond twelve months from placement of orders. With the changing competitive structure of the import-export trade and quantitative restrictions on importation created by government policies, tight supplies of refractory materials threaten the future growth of industries in Nigeria. Therefore, the development of local refractory clay materials for the production industries in Niger is justified by the needs to meet the technology requirements of the country according Muhammadu (1998). A material is refractory in nature if it has a very high melting point in addition to its physical, chemical mechanical and thermal properties that make it suitable for use in furnaces, kilns, reactors and other high temperature vessels as reported by Solomon M. E., (2002). In his

investigation concluded that the properties of refractory clay samples from Onibode, Ara-Ekity, Ibamajo and Ijoko compare favourable with imported fire clay refractories. Hassan and Adewara (1993) found that Onibode refractory clays are suitable for the production of refractory bricks for furnace building. Research work by Akomolafe L.E., et al (2011) revealed that kaoline clays from kankara, Jos and Oshiele are of the residual variety suitable for paper, paint and pharmaceutical manufacture. Loto and Ndaliman (1991) in their research finding concluded that Igbokoda refractory clay has good binding properties for synthetic moulding sand.

Chester et al (1975) worked on the structural properties of clays at high temperatures. The clays were found to be kaolinitic in nature with the colour ranging from earthy brownish to red lateritic. Research work carried out by Aderibigbe and Chukwuogo (1984) revealed that the basic constituents of the clays from Nsu, Ukpok, Ozubulu, Enugu, Onibode, Orun, Oshiele, Ifon, Okpeke, Werrom, SabonGida, Alkaleri, Kankara and Giro in Nigeria were alumina (Al_2O_3) and silica (SiO_2). In general, the alumina contents were found to vary between 19.30% for Ozubulu clay and 39.30% for Onibode clay while the silica contents were over 40% in all the samples except that of SabonGida. Loto and Akeju (1994) carried out investigation on the effects of additives such as sodium carbonate, cassava flour and coal dust on Igbokoda clay. It was discovered that the additive increased the green and dry compression strengths, green hardness, permeability, green and dry shear strength, collapsibility and toughness of the synthetic moulding sand. The improved durability properties were contributed by the additives bonding property of cassava flour and fine coal dust. It also contributed to the change in the chemistry of the clay due to the sodium ion from the sodium carbonate addition. It was clearly observed that, the general durability/performance of the tested clay in synthetic moulding sand sample forms was controlled by the heat effect due to the very high liquid-metal temperature during casting. The high casting temperature caused loss absorbed moisture from the surface of the plates and also from between the Si-O layer, loss of lattice or constitutional water and that all these affected adversely the bonding characteristics of the synthetic moulding sand Aniyi J. A., (1985).

While, Adegbuyi and Uhomobhi (2007) worked on the foundry properties of backing sand. Orumwese (2002), investigated the foundry sand qualities of Clay is equally less expensive than other binders like bentonite and sodium silicate moulding material. The abundance of these two materials in Nigeria necessitates the current investigation into their

properties for foundry use. The utilization of 100% local materials is bound to bring down cost to weight ratio of castings. Investigations have been carried out on some of the natural sand deposits across the country. In some of the earlier works, Sheidi and Ajuwa (2008) investigated the moulding properties of Bacita river sand for moulding properties. Abolarin et al. (2006) investigated the moulding properties of Erusu and Ire clays for casting operations, synthetic moulding sand mixtures prepared from indigenous sand and clays of different plasticity using Enugu sand, Enugu fire clays and Ukpok clay. In other works, Muhammadu M. M., (1998) studied bulk density variation on the compression strength of clay/sodium silicate-bonded moulding clay. Omotoyinbo and Oluwole (2008) examined the working properties of some clay deposits in Ekiti State, Nigeria, specifically Ara, Isan, and Awo clays and concluded that Ara clay is most suitable for production of crucibles, and furnace lining for nonferrous metals processing, such as Aluminium, Lead and Bronze.

2.0 Compositions

Most industrial refractories are composed of metal oxides or of carbon, graphite or silicon carbide. Other newer refractory materials such as carbides, nitrides, borides and suicides are generally used only for special applications, because of economic considerations. The most commonly used refractory oxides are SiO_2 , Al_2O_3 , MgO , CaO , Cr_2O_3 and ZrO_2 . Those refractories containing SiO_2 or ZrO_2 are referred to as acid, those with MgO or CaO as basic, and those with Al_2O_3 or Cr_2O_3 as neutral. This is an old notation and, while not strictly true chemically, is very helpful in discussing the reactions of high-temperature slags in contact with refractories. For example, magnesia or lime reacts with silica at a temperature far below the melting point of either. Accordingly, in the application of refractory materials, care should be taken to make sure that the refractory compositions used in contact with one another do not react at a temperature below the expected service application temperature (see Table 1).

The most common refractories are made from materials which occur in nature but, with the trend higher service temperatures in many applications, these of chemically processed or high-purity oxides has increased. Examples are high-purity alumina made by the Bayer process; high-purity magnesia made by the precipitation of magnesium hydroxide or by calcining magnesium chloride, and chemically processed zirconia.

2.1 Materials

Approximately 70% of all refractories used by industry are in the form of bricks, which are preformed shapes such as straights, soaps, splits, arches, wedges, keys, skews, jambs or other special and frequently patented shapes. Formed bricks may be chemically bonded with an additive to give strength at room temperature, or they may be burned or fired at elevated temperatures to develop the desired physical properties. The remaining 30% of the refractories used take the form of monolithic materials; that is, castables, gunning mixes, plastics and ramming mixes. These materials are placed directly in the furnace to form a refractory lining that is fired in situ (Muhammadu, M. M. 1998).

The clay samples used in this research work were collected from Bosso, Doko and Lapai locations in Niger State of Nigeria.

2.2 Properties and Testing

The significant properties of any refractory, including its high-temperature strength, depend on its mineral makeup, the particle-size distribution of the minerals, and the way these materials react to high temperatures and furnace environments. Particles varying in size from 6 mm to less than 74 constitute the unfired refractories. Upon firing, the finer particles form a ceramic bond between the larger particles. The fired refractory consists of bonded crystalline mineral particles and glass or smaller crystalline particles, depending largely on the composition of the refractories. In the case of fireclay and high-alumina refractories, elongated mullite crystals tend to interlace and form relatively strong bonds at temperatures approaching their melting point. When the bond in the refractory is glassy in nature, the brick has good strength at lower temperatures. If at furnace temperatures the glass has a low viscosity, however, it will soften and the refractory will deform under load. When choosing a refractory for a particular application, a variety of physical properties must be considered but, for control purposes or purchasing specifications, bulk density, apparent porosity and strength at room temperature are often used.

2.3 Linear Shrinkage

Linear shrinkage represents the permanent change that the refractory shapes undergo on heating or after reheating under a given set of conditions. Even, if a brick is capable of withstanding normal loading at operating it can cause serious problem due to permanent shrinkage. Thus, a soft fired silica brick

may grow by several percentages linear due to the conversion of individual quartz to cristobalite or tridymite. Furthermore, growth can be due to other causes, for example, internal gas pressure in a pyroplastic mass. Green bricks were pressed in a box of size 100mm x 80mm x 50mm and the shrinkage properties of the pressed bricks were measured in the green state compared with the fire dimensions.

The linear shrinkage of the refractory materials was measured using a calibrated metal rule and determined by using the relationship below according to Chester (1975).

Percentage drying shrinkage = $[(\text{Wet length} - \text{fired length}) / \text{Wet length}] \times 100$ 2.1

Also, percentage firing shrinkage = $[(\text{Dry length} - \text{Fired length}) / \text{dry length}] \times 100$ 2.2

2.4 Specific Gravity

Specific gravity test is useful for the determination of the particle size distribution of any powdered material. Specific gravity is defined as the ratio of the mass of the material to the mass of a quantity of water at 4°C which has a volume equal to the solid volume at the temperature of measurement.

The procedure adopted for the determination of the specific gravity was by using the specific gravity bottle method for each sample and the relation.

Specific gravity = $[(w_2 - w_1) / (w_4 - w_1) - (w_3 - w_1)] \times 100$ 2.3

Where: w_1 = weight of the empty bottle, w_2 = weight of the bottle and sample, w_3 = weight of the bottle, sample and liquid and w_4 = weight of the bottle completely filled with liquid.

2.5 Bulk Density

Bulk density is the weight per unit volume of the refractory including the volume of open pore space. It is one of the factors responsible for the overall weight coming upon the foundation of a refractory structure which limits the size of a furnace. Foundations of the structures from non-porous refractory materials are stronger than those built from porous materials to bear the heavy load coming on it. Bulk density was determined by direct volume measurement method. A test specimen was cut from the core of the refractory shape with the help of a cut-off wheel. Adhering particles were wiped off from test specimen. The dry weight and saturated weight of the test specimen was then determined using the relation by Chester (1975).

Bulk density = $w_a / (w_a - w_b)$ 2.4

Where w_a = weight of dry test piece, w_b = weight of test piece soaked with suspended in the immersion.

2.6 Apparent Porosity

Porosity is a measure of the volumes of all pores present in a material. The pores may be open or close. Open pores are generally interconnected with each other by channels thereby making the material permeable to liquids or gases. Close pores may be enclosed within individual particles or may form isolated spaces within the matrix of the body so that the material is permeable to liquid or gas, despite its high porosity, called also the effective, expressed as the percentage of the volume of open pores with respect to the exterior volume of the material under consideration. True porosity represents the volume of both open and close pores in the volume of the volume of the body. Porous refractorines have high permeability, poor heat conductivity, low strength and less sensitivity to temperature fluctuation. The apparent porosity heat conductivity, low strength and less sensitivity fluctuation. The apparent porosity is calculated using the relation by Chester (1975).

$$\text{Apparent porosity, } P_a = \left[\frac{(W_c - W_a)}{(W_c - W_b)} \right] \times 100 \quad 2.5$$

W_a and W_b are as defined in equation

Where W_c = weight of the test piece soaked with the immersion liquid and suspended in air.

2.7 Permeability

Permeability is the measure of the rate at which a fluid will pass through porous materials. Refractories which come directly under the influence of gases and liquids should be impervious. This will eliminate the leakage of gases and penetration of liquids through the walls of the furnace. The permeability is affected by the sizes of the pores, their uniform distribution, the internal surface area, and capillary effects.

The methods of measurement involved water from a constant head supply, which flowed into the cylinder and displaced air which passed through the test piece at a pressure indicated by a water manometer. The water flowed first into an internal perforated metal tube which eliminated ripples on the water surface when the flow was drop wise. The volume of air displaced in a measured time is indicated on a water level tube at the side of the cylinder. The

permeability number is calculated using the formula by Chester (1975).

$$\text{Permeability number, } P_n = \frac{V \times h}{t \times A \times P} \quad 2.6$$

Where V = volume of air passed through the test piece, h = height of test piece, t = time of flow, A = surface area of test piece and P = pressure head under which the air passed.

2.8 Cold crushing strength

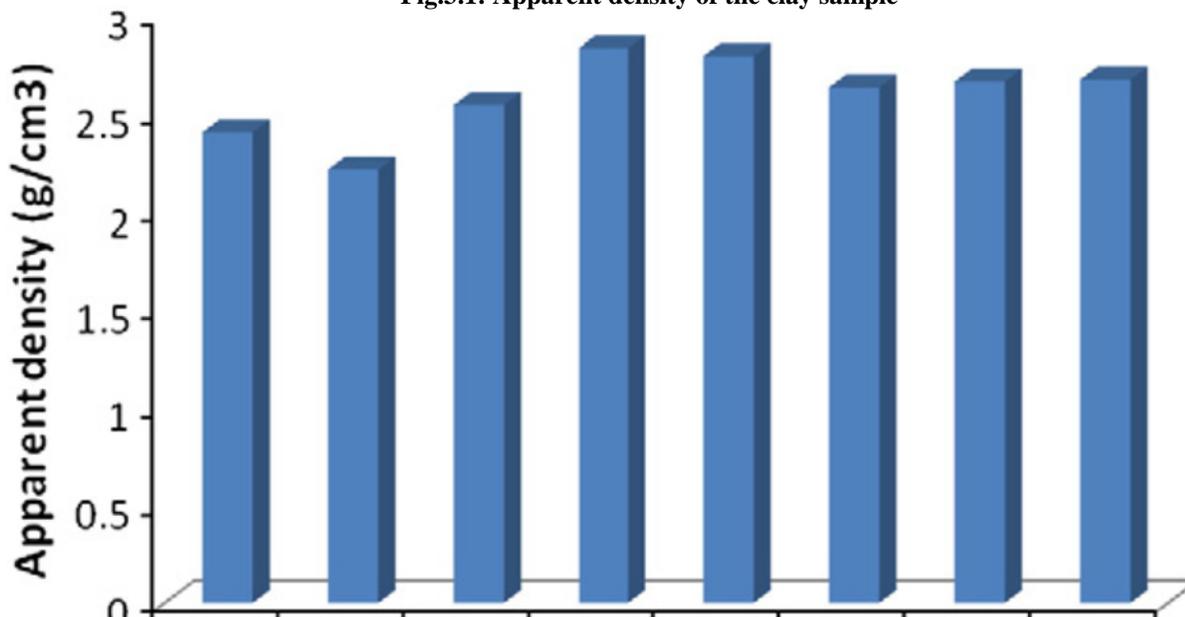
Cold crushing strength is the ability of the clay materials to withstand abrasion and loading without damaging or crumbling into powdered form. Standard bricks measuring 76.2mm cube were tested for strength under universal strength testing machine. The strength values both in the directions and normal to the directions of forming of the bricks were recorded in table 3.2.

2.9 Refractoriness

A pyramidal shape of perpendicular height 40mm with a triangular base 15mm was cut from the body of the brick and prepared as the test piece as indicated by Chester (1983). The test piece was mounted so that the edge perpendicular to its base is vertical. Pyrometric cones were cemented to the plaque, in such a way as to surround the test pieces. The arrangement was placed in the furnace. The temperature was raised at the rate of 10°C/min up to the value of 1200°C where the rate was reduced to 5°C. This was continued until the tip of the test cone has bent over with the base, where the plaque was removed from the furnace and examined after cooling.

3.0 Results and Discussion

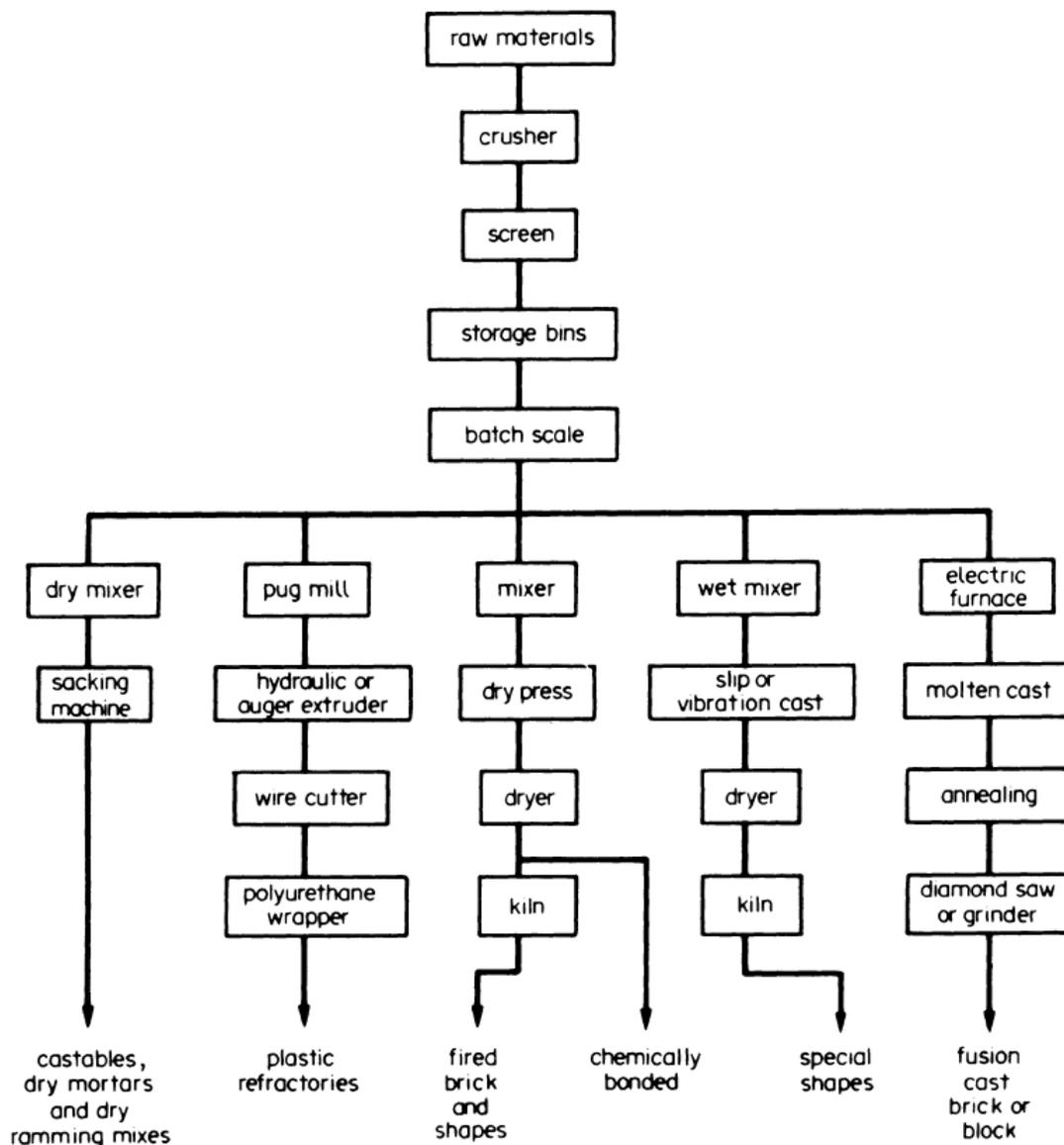
Tables 3.1 and 3.2 show the chemical composition and physical properties of the clays respectively. From Table 3.1, it can be deduced that the clay belonged to the group of Alumino silicate refractories. When compared with a typical fireclay, they can be further classified as a medium alumina fireclay as reported by Carrol D., (1978).

Fig.3.1: Apparent density of the clay sample**Table 3.1 Chemical Composition of the Clay Sample**

Main constituents %	Typical fireclay	Bosso	Doko	Lapai
Al ₂ O ₃	36.10	37.65	33.12	35.77
SiO ₂	56.80	46.22	45.66	51.10
Fe ₂ O ₂	3.40	2.90	--	--
CaO + MgO	1.10	0.70	--	--
K ₂ O + Na ₂	1.20	2.10	--	--
T ₂ O ₂	1.40	0.90	--	--
L01	--	14.09	14.01	11.74

Table 3.2 Some Properties of the Samples.

Properties	Typical fireclay	Bosso	Doko	Lapai
Linear Shrinkage (%)	0.35	4.36	2.17	2.17
Specific Gravity	2.30	2.30	2.79	2.40
Bulk Density (g/cm ³)	1.97	2.06	2.94	1.27
Apparent Porosity (%)	22.10	18.89	40.69	21.81
Permeability Number	--	0.20	0.46	0.23
Cold Crushing Strength (MN.m ³)				
a. Direction of Forming	22.20	5.70	9.89	20.00
b. Normal to Forming Direction	--	4.82	8.70	
Refractoriness (°c)	1,690	1,400	1,400	1,400

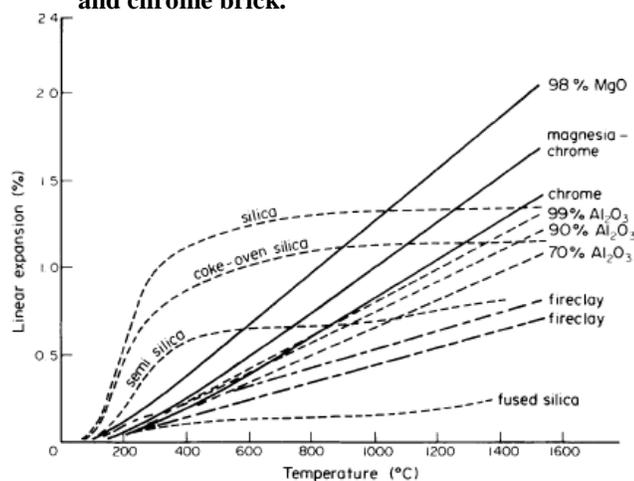
Fig.3.2: Schematic of the processes used in the manufacture of refractory products

The type and proportion of potassium, sodium, calcium, barium, iron, and titanium ions and associated oxides like Fe_2O_3 and TiO_2 are responsible for impurity, colour, sintering and melting behaviour. Potassium and calcium ions act as fluxing agents that lower the melting and fusion point by several hundreds of degrees centigrade. The shrinkage by firing was between 0.5 and 9.6% for samples with 70% and 60% glass frit addition, and 1.1% for 50% glass frit addition. The samples with 1–11% shrinkage values were comparable with the values for white wares.

3.1 Linear Shrinkage

From Table 3.2, it can be seen that the firing shrinkages of Doko and Lapai clay are the same (2.17%) and less than of Bossoclay (4.36%). However, both values are higher than that of the medium alumina fireclay recorded by Dryden (1982) as seen in the fifth column of Table 3.2.

Depending on the type of application, the shrinkage value can be reduced the moisture content of the clay through oven drying before firing.

Fig.3.3: Linear thermal expansion of magnesia and chrome brick.

3.2 Specific Gravity

The specific gravity values of the various clay samples are 2.30, 2.40 and 2.79 respectively in agreement with the findings of Muhammadu (1998).

3.3 Bulk Density

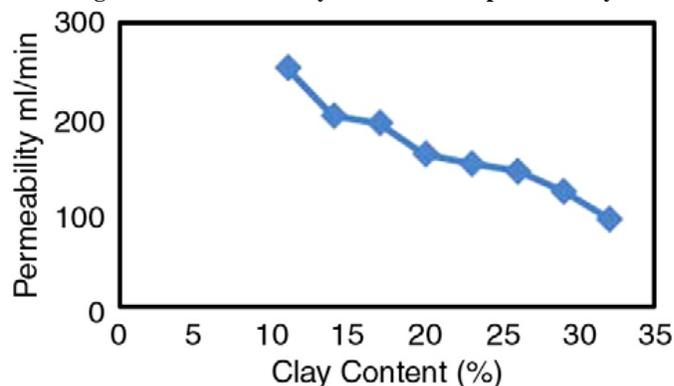
The highest amount of bulk density attainable is from Doko sample with a value 2.94g/cm^3 . On the average, all the value are within the acceptable limits compared to the value of 1.97g/cm^2 of the fireclay according to Chester (1975).

3.4 Apparent Porosity

The apparent porosity of Doko sample is the highest of the three samples. With the value of 40.69%, it is likely to be a poor heat conductor, and of low strength. It can be used for insulating purposes as indicated in the findings of Ndaliman (1999). The low strength can be improved upon by increasing the firing intensity.

3.5 Permeability

The permeability numbers for the sample are low. The highest of them is that of Doko clay samples as shown on Table 3.2. Since there is correlation between porosity and permeability as concluded by Muhammadu M. M., (1998), Doko clay being more porous is expected to be moderate permeability. Others would therefore have poor resistance to the penetration of molten metal, and flue gases.

Fig.3.4: The effect of clay content on the permeability.

3.6 Cold Crushing Strength

The Lapaiclay possesses the highest value of cold crushing strength. This alone compared favorably with the firebrick according to the findings of Dryden (1982) and those of Indian firebricks as recorded by Chesti (1986) as shown in Table 3.2.

3.7 Refractoriness

The softening point of the samples is expected to be more than 1400°C since this is the capacity of the furnace used during the investigation. Although initial cracks developed at this temperature, the tip of the test piece has to bend over to the base at this point.

3.8 Chemical Composition

This is another factor which indicates how well a refractory material will stand up under certain conditions. For example, in fireclay and high-alumina refractories as the alumina-silica ratio increases, the refractoriness usually increases. In addition, the presence of certain impurities or accessory oxides, such as soda, potash, lime and iron oxide, which promote the formation of low-melting glasses tends to reduce the refractoriness. Chemical composition can also be used to predict the extent of corrosion—the destruction of refractory surfaces by the chemical action of external agencies. Acid refractories, for example, contain a substantial amount of silica which will react chemically with basic refractories, basic slags or basic fluxes.

4.0 Conclusion

At alumina contents below 20%, the clay/glass frit mixtures were classified as refractory materials, at contents above 20%, as plastic clays. Samples with 50% frit had the highest cold crushing strength, with 80% frit being the lowest strength. The sintering

temperatures were 1025–1400°C. The materials can, therefore, be used for production of ceramics like earthenware, sanitaryware, table wares, and vitrified tiles.

The shrinkage values were low; this reduces the risk of defects such as warping and cracking...

Hence, the results of the tests revealed that the clay samples obtained from different locations could be used for refractory purposes such as furnace bricks and lining.

Further investigations on the refractoriness under load, the use of additives to improve upon the current properties, and purification of the chemical composition is currently being pursued. Individual entrepreneurs, and government are therefore being called upon to support such efforts both morally and financially.

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