EVALUATION AND CHARACTERIZATION OF GAKEM AND ABOUCHICHE CLAY SAMPLES IN BEKWARRA LGA OF CROSS RIVER STATE FOR USE AS REFRACTORY MATERIALS

F. A. Ovat[1,*], D. E. Ewa[2] and E. A. Egbe[3]

[1] DEPT. OF MECHANICAL ENGR., CROSS RIVER UNIVERSITY OF TECHNOLOGY, CALABAR, CROSS RIVER STATE, NIGERIA.
[2] DEPT. OF CIVIL ENGINEERING, CROSS RIVER UNIVERSITY OF TECHNOLOGY, CALABAR, CROSS RIVER STATE, NIGERIA.
[3] CROSS RIVER STATE COMMUNITY AND SOCIAL DEVELOPMENT AGENCY, CALABAR, CROSS RIVER STATE, NIGERIA.
E-mail addresses: [1] *fraijoe@yahoo.com,* [2] *desmondewa4sky@gmalil.com,* [3] *egbesonandy@yahoo.com*

ABSTRACT

The characterization of some clay as refractory materials for furnace lining has become relevant to find solutions to the cost involved in the purchase and importation of these refractory materials. This work investigated the refractory properties of clay samples for their suitability for use in the industries. Clay samples were collected from Gakem and Abouchiche areas and analysed for physical and chemical properties to determine the suitability of the clays as refractory materials. The results showed cold crushing strength (21.46MN/m^2), thermal shock resistance(27 cycles), bulk density(3.52g/cm^3), linear shrinkage(3.80%), apparent porosity(28.84%) and permeability(80%) for Gakem; and cold cold crushing strength (18.40MN/m^2), thermal shock resistance(25 cycles), bulk density(2.81g/cm^3), linear shrinkage(3.70%), apparent porosity(25.86%) and permeability(77%) for Abouchiche respectively. The chemical compositions of these clay samples were also investigated. The results showed that the samples fall under Aluminosilicate type of clay because of their high values of Aluminium Oxide and Silicon Oxide. Tests showed that clay from these areas can be used to produce refractory materials that can withstand a furnace temperature of about 1600℃.

Keywords: refractory, clay, Gachem, Abouchiche, Bekwara, materials

1. INTRODUCTION

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 [1]. According to them, refractory materials are materials capable of withstanding high temperatures, and that high quality refractory materials resist high temperature fluctuations between 1000℃ and 1500℃ and are also good thermal and electrical insulators.

It was observed by[2]that, the raw materials for the production of various types of refractory materials are kaolinite ($Al_2Si_2O_5(OH)_4$, Chromites ($FeCr_2O_4$), Magnesite ($MgCO_3$) and various types of clays. He also noted that other additives such as sawdust, graphite and some binders are available locally.

The author of [3] studied the characteristics of Nigerian clays and established that Otukpo clay can withstand a furnace temperature of about 1710℃ which compared favorably with imported refractories. [4] in his research on the characterization and evaluation of refractory properties of some clay deposits in Southwest Nigeria, reported that clays displayed reasonable refractory properties that compared favorably with standard values and recommended a blend of some clays for furnace lining. Meanwhile, [5] investigated the moulding properties of locally available clays for casting operations and observed that the Barkinladi and Alkaleri clay samples were suitable for construction of furnaces and their linings.

For chemical composition, refractories constitute either single or multi-component inorganic compounds with non-metallic elements [6]. They are classified as acid refractories, basic refractories and/or neutral refractories. The Acid refractories are a set of

refractories used where slag and atmosphere are acidic. They cannot be used under basic conditions [2].

It was noted by [7] that, the main raw materials used for the production of these acid refractories are silica, ZrO_2 and alumino-silicate; typical refractories are fire clay, quartz and silica. Basic refractories are produced from a composition of dead-burnt magnesite, dolomite, and chrome ore. Investigation by [8] on the applications of various refractories showed that magnesite, chrome combinations have good resistance to chemical action of basic slag, have good mechanical strength and volume stability at high temperatures. Chrome-magnesite refractories used for side walls of soaking pits, magnesite with varying amounts of carbon has excellent resistance to chemical attack by steel-making slag.

In their physical forms refractory materials are either bricks or monolithic. Shaped refractories are in the form of bricks of some standard dimensions [9]. Special shapes with required dimensions are hand-molded and are used for particular kilns and furnaces. Ramming refractories are in loose dry form with graded particle size and are often mixed with water for use. Investigation by [10] revealed that castable refractory materials contain binders such as aluminate cement which imparts hydraulic setting properties when mixed with water; the materials are installed by casting and are also known as refracting concretes. Research by [11]on the analysis and characterization of Nyikangbe clay deposit that, mortars are finely ground refractory materials which become plastic when mixed with water and are used to fill gaps created by a deformed shell, and to make walls gas-tight to forestall slag penetration.

The available literature is scanty on the investigation of Gakem and Abouchiche clays, it has become necessary to carry out such investigations to ascertain the suitability of clay deposit in these locations for their refractory properties.

2. MATERIALS AND METHODS
2.1 Sample Collection
Clay samples were collected from different locations of Gakem and Abouchiche of Bekwarra Local Government Area in the Northern Senatorial district of Cross River State. The samples were randomly collected from different points at a depth of 50cm and about 25m apart in a triangular manner.

2.2 SAMPLE PREPARATION
The samples of about 3 kg were collected and air-dried for five (5) days. Samples were then finely ground to achieve homogeneity of the particles sizes. The ground samples were sieved with a mesh of about1.13µm. The ground and sieved samples were mixed with some

quantity of water to a pastry form. It was moulded (70x50x 50mm) into bricks and compacted with a hydraulic press according to ISO standards [17]. 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.

3. PHYSICAL ANALYSIS
3.1 Cold crushing Strength
Test pieces measuring 75mm by 50mm by 50mm were prepared and are-dried for 24 hours and were transferred to a furnace and heated for 6 hours and at a temperature of 1600^0C. After the heating process they were removed from the furnace and allowed to cool down to room temperature and each piece was in turn placed in a crusher. Load was applied axially and continually until the test piece failed. The procedure was repeated for other test pieces. The respective loads at which each test piece failed were recorded. The cold crushing strength (CCS) was calculated [1] using:

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

In (1), A is the Area of specimen (mm^2) and P is the Load applied (N)

3.2 Thermal Shock Resistance
75mm × 50mm×50mm test pieces were inserted in a furnace maintained at 1600^0C for a period of about 10 minutes. The samples were removed and allowed to cool in a dessicator for 10 minutes and then returned back to the furnace (which is still at 1600^0C) for another 10 minutes. The process was repeated until the pieces were deformed when a small force is applied. The number of heating and cooling cycles for each of the specimen was recorded. 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 locations were recorded in Table 1.

3.3 Linear Shrinkage
The samples were prepared and their original lengths of 75mm recorded. They were dried in the air for 24 hours and then dried in an oven at 110^0C for 24 hours and were then transferred to a furnace maintained at 1600^0C and heated for a period of 6 hours. They were then brought out by means of a pair of tongs and allowed to cool in a dessicator. The samples were measured after heating and their linear shrinkage values determined [2] using:

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

Here, L_D is the dried or original length $=75$mm, and L_F is the Fired length

3.4 Bulk Density

Bulk density was determined by air-drying for 24 hours, thereafter the test pieces were then put in an oven and dried at a temperature of 110^0C 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 thereafter transferred to a beaker and heated for 40 minutes and cooled and the soaked weight was recorded. Water was put in another beaker and each of the test pieces in turn suspended in the water so that their suspended weights were recorded. The equation for calculating bulk density is given by [1] as:

$$\text{Bulk Density} = \frac{D\rho w}{W - S} \qquad (3)$$

In (3), D is the Dried weight, ρw is the Density of water, W is the soaked weight and S is the suspended weight.

3.5 Apparent Porosity

Test pieces from the different locations were prepared and allowed to dry in air for about 24 hours before transferring them to the oven and drying for another 24 hours at 110^0C. They were thereafter transferred to a furnace and fired to a temperature of 1600^0C, the samples were removed by pair of tongs and allowed to cool in open air before weighing them in a dessicator and noted the dry weight (D_w). 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, and then weighed in the dessicator so that their soaked weights (S_w) were noted. Also, by means of beaker placed on a balance, the specimens were weighed suspended in water and the suspended weight (W) was taken. The apparent porosity for each location was determined from [2] as:

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

Here S_w is the Soaked weight, D_W is the dried weight, and W is the suspended weight

3.6 Permeability

Different samples were prepared and air-dried for 24 hours and thereafter oven dried at 120^0C for 12 hours. Two thousand cubic centimeter 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, and noted. The time taken for the 2000 cm^3 of air to pass through the specimen was recorded. The respective permeabilities were calculated from [2] using:

$$\text{Permeability number}, P_n = \frac{Vh}{APt} \qquad (5)$$

In (5), P_n is the permeability number, V is the Volume of air, cm^3, h is the height of specimen, cm A is the Cross sectional area of specimen, cm^2, P is the pressure of air in cm of water, N/cm^2 and t is the time, minutes

Modulus of Rupture (MOR): Different test pieces of clay bar, 75mm $\times$ 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 1600^0C 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 7.0 span and MOR was calculated from the expression [13] as follows:

$$\text{MOR} = \frac{3PL}{2bh} \qquad (6)$$

Here P is the Breaking Load in kgf, L is the Distance between support, b is the Breath and h is the Height

3.7 Modulus of plasticity (MOP)

The molded clay was deformed by dropping onto it from a fixed height of a flat-headed plunger of known weight. The distance traveled was read from the graduated scale. The modulus of plasticity (MOP) for the clay sample was obtained from [14] as:

$$\text{MOP} = \frac{\text{Original Height}}{\text{Deformed Height}} \qquad (7)$$

Also, the percentage making moisture for the clay samples were obtained from [14 as:

$$\% \, Making \, Moisture = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Net Weight}} \qquad (8)$$

4. CHEMICAL ANALYSIS

The Chemical Analysis of the clay samples was done using X-Ray Fluorescence Spectrometer (XRFS). The technique was used to determine the concentrations of elements present in the various samples. The samples were ground and sieved to produce 75μm particle sizes. Thereafter, 2grams of the sieved samples were mixed with 5grams of lithium tetra borate binder ($Li_2 B_4 O_7$) anhydrous solution that acts as a bonding agent. It was then pressed to a pellet in a mould and then dried in oven at 120°C for 20 minutes to remove the absorbed moisture and kept in a desicator. The spectrometer was turned on and allowed to warm up to stabilize the optics and x-ray tube. The samples were placed in the machine and the elemental concentrations present in the samples

were displayed on the monitor. The result of the analysis is as given in Table 2.

5. RESULTS AND DISCUSSION

The results obtained from the various tests carried out in chapter three are presented in Table 1 and Table 2. The tests revealed that, while most of the results agree with previous research, others are at variance.

Table 1: Physical Properties of the tested clays from Cross River State

Properties	Gakem	Abouchiche
Cold Crushing Strength (MN/m^2)	21.46	18.40
Thermal shock Resistance (Cycles)	27	25
Linear Shrinkage (%)	3.80	3.70
Bulk Density (g/ cm^3)	3.52	2.81
Apparent Porosity (%)	28.84	25.86
Permeability (%)	80	77
Modulus of Rupture (Kgf/cm^2)	47.21	45.0
Modulus of plasticity (Kgf/cm^3)	30.5	3.60

Table 2: Chemical Composition of clay samples at 1600ºC

Elements/compound	Gakem	Abuochiche
Al_2SO_3	29.09	30.65
SiO_2	56.44	58.09
MgO	0.14	0.11
CaO	0.12	0.19
Fe_2O_3	2.56	2.9
K_2O	2.19	0.98
Cl	0.026	0.018
Co	0.035	0.017
MnO	0.00	0.047
Cr_2O_3	0.06	0.048
Na_2O	1.249	0.373
Ni	0.045	0.079
Cu	0.044	0.027
P_2O_5	0.053	0.049
SO_3	0.025	0.029
Sr	0.00	0.020
TiO_2	0.897	1.513
Zr	0.03	0.106

5. DISCUSSION

5. 1 Linear shrinkage

The linear shrinkage is an indicator of the firing efficiency of the clay samples. However, [5] pointed out that lower values were more desirable as this means the clay is less susceptible to volume change. That means the

values obtained from Gakem and Abouchiche having shrinkages of 3.80%, 3.70%respectively will make for very good refractory materials. These values compete favourably with those obtained by [16] in his investigation.

5.2 Bulk density

The bulk density is a measure of the weight of a given volume of refractory and is often considered in conjunction with porosity. Gakem had the highest values of bulk density of 3.52g/cm^{3}compared to that of Abouchiche. However, these values showed that these clays are good when compared with values obtained from Gur and Yamarkumi clays (2.06-2.11 g/cm^3), Plateau and Bauchi clays (1.94-2.04 g/cm^3), as respectively reported by [5] and [15].

5.3 Apparent Porosity

The values for Gakem and Abouchiche fall within the internationally accepted range of 20-30% as was noted by [2].

5.4Thermal Shock Resistance

The thermal shock resistance determines the ability of the material to withstand repeated heating and cooling cycles. Gakem withstood thermal value of 27 cycles which makes them suitable for long term refractory use as these measure their longevity which in turn could result to cost saving due to minimal replacement. Also Abouchiche, having 25cycles each fall within the accepted range. These values are within the range recommended by [15] for refractory materials

5.5 Cold Crushing Strength

This is a measure of the ability of the clay to withstand abrasion and loading. Values that are recommended are above 18MN/m² and the areas investigated, Gakem and Abouchiche, have all met the standard, in other regions, [1] reported 26.5 MN/m² for Nsu clay, while [4], reported 18.065 MN/m² and 16.620MN/m² for Nyikangbe and Beji clays. However, the values of cold crushing strength for Gakem and Abouchiche are 21.46 MN/m² and 18.46 MN/m² respectively. This implies that, the clay samples from these locations have acceptable cold crushing strength values.

5.6 Permeability

Permeability is the measure of the ability of the clays to prevent gases and liquids from penetrating the walls. The permeability numbers of all the samples fall within the standard range of 25-90% as given by [2] Refractories under the influence of liquids and gases should be impervious, as this will help to eliminate leakage of gases

and penetration of liquids through the walls of the furnace [12].

5.7 Chemical Composition

The results obtained from the chemical analysis of clay samples from Gakem and Abouchiche shows that for Gakem alumina (29.09%), silica (56.44%) and Abouchiche samples contained alumina (30.65%), silica (58.09%). Other elements such as MgO, CaO, Fe_2O_3 and K_2O for Gakem were 0.14% 0.12%, 2.56% and 2.09% respectively. Those for Abouchiche were 0.11%, 0.19%, 2.90% and 0.9% for MgO, CaO, Fe_2O_3 and K_2O respectively. The degree of refractoriness increases with alumina content, while the presence of alkali and their earth metals oxides is in low concentration lowers its fusion temperature and also accounts for relatively high refractoriness [13]. The clay samples from Gakem and Abouchiche satisfies the above conditions by virture of their chemical compositions interms of elemental values. The presence of Fe_2O_3 contributed to the reddish colour of both clay samples from grey. This colour changed after the firing process when carbonaceous materials and the iron began to oxidize [14].The proportion of elemental composition of iron in clays determines the thermal conductivity potential of such materials any fire clays to be used in refractories should have at least 30% Alumina and less than 1.8% Iron (III) Oxide. However, with the use of the XRFS equipment for the chemical analysis, other compounds and elements were found to exist in the samples tested but in very low percentages as shown in Table 2.

6. CONCLUSION

Despite vast amounts of clay deposits in the country, we are yet to set up any refractory industry for the production of locally made refractories products. Nigeria depends till now, on the importation of these refractories for use in its manufacturing industries and refractory products. The uncertainty faced by the manufacturing industries and the decrease in economic growth, self-imposed on the nation's economy has necessitated the need to source for local raw materials. This study has shown that Gakem and Abouchiche clay samples have good refractory properties, hence they can be used as refractory materials. In addition to refractory materials these clays proved their applications to other areas such as ceramics, high melting clays, tiles, colored vaze and even porcelain.

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