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Effects of Grog Additions on Some Refractory Properties of Raw (Abusoro) Kaolin Clay Deposit for Furnace Lining

A. O. Aluko[1*] and C. O. Ikubuwaje[1]

[1]Mineral and Petroleum Resources Engineering Department, The Federal Polytechnic Ado Ekiti, Nigeria.

Authors' contributions

This work was carried out in collaboration between both authors. Author AOA designed the study, carried out data acquisition, wrote the protocol, wrote the first draft of the manuscript and managed the literature searches and data analysis. Author COI carried out data acquisition, proof read the original manuscript and managed the analyses of the study. Both authors read and approved the final manuscript.

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ABSTRACT

The influence of the weight of grog on some refractory properties of raw Abusoro clay samples found in Abusoro Village, Ondo State, Nigeria was evaluated. These samples were presented for refractory tests (apparent porosity, linear shrinkage, refractoriness, bulk density and cold crushing strength). The weights of the grog were varied from 20-40 wt. % in the blend. The chemical and microstructural examinations of the untreated alumino-silicate Abusoro clay samples indicated that they are abundant in silica, SiO_2 (62.74wt. %) and alumina, Al_2O_3 (31.42wt. %). Other minor compounds found are Fe_2O_3 (1.43%), K_2O (0.30%) with no trace amounts of MgO (0.00); therefore, they are regarded as alumino-silicate. Particular observation is made on MgO with zero amounts and the total of K_2O + Na_2O + MgO which are less than 2% in the clay samples. These results signify that the clay possesses high viability for manufacturing of refractory bricks, pulp and paper, ceramics, fertilizers, paint and cement. The performance evaluations of the refractory bricks measured indicated acceptable and satisfactory results vis-à-vis standard refractory properties for

**Corresponding author: E-mail: alayrehoboth@gmail.com;*

refractory fireclay bricks. However, the apparent porosity (43.2%) and CCS (21.21MPa) obtained for Abusoro clay sample at 30% weight of grog may as well be suitable for insulating refractory applications. The high apparent porosity could be an indication of high content of silicon oxide in the raw clay.

Keywords: Refractory bricks; alumino-silicate; grog; abusoro; X-Ray diffractometer.

1. INTRODUCTION

Clay can be referred to as an earthy material composed mainly of layered systems of fine-grained minerals, which exhibit the characteristic of plasticity at suitable water content but turns completely hard when fired [1]. Clay is also fashioned from the chemical weathering processes on earth's crust and, this contributes approximately two-fifth of the fine grained sedimentary rocks (mud rocks) such as mudstones, resulting into diverse sort of clay materials [2].

Generally, clay minerals are three groups namely kaolin, montmorillite and illite. The kaolin institution comprises clay minerals like kaolinite, nacrite, hallosite and dickite; such kind of clay mineral composed of one layer of silica and alumina each. Its formation usually occurs beneath acidic conditions and weathers greatly to produce an adjustment, hydrothermally, given rising to feldspars and different allumino-sillicates [3]. Al_2O_3. $2SiO_2$. $2H_2O$ (39%Al_2O_3, 46%SiO_2 and 14%H_2O) is the chemical formula of kaolinite and its structure possesses strong binding forces between the layers which resist expansion when moistened [3, 4].

The clay minerals from the chemical weathering of silicate minerals (layered) are usually found in shales. They are stable and are of essential soil additives in cool and dry or temperate climatic situation and function as "chemical sponges" which preserve water and dissolved plant nutrient washed from other minerals.

Kaolin clay is refractory materials that are mostly non-metallic minerals and can bear great amount of temperature and pressure exerted on it such as thermal shock, chemical attack and high load at elevated temperature [5]. Omotoyinbo and Oluwole, [6] described refractories as materials which withstand high temperature without deforming or breaking. The formation of clay minerals is dependent on both the physical and chemical situations of the immediate weathering surroundings, nature of the starting substances and effects of environmental elements [7]. Moreover, the applicability of clay in a specific industry depends on the functionality and nature of the content of clay mineral(s). The characteristics of a clay mineral, on the other hand, rely largely on its internal shape and chemical composition [8, 9].

The inner linings of furnace made of kaolin clay exposed to elevated temperature are referred to as dense refractory bricks and as a result, they are in contact with the furnace materials. These furnace materials may consist of metal slag, fluidized and corrosive (acidic) particles. It is in the light of this that grog is introduced to the refractory clay brick blend to improve the shrinkage, decrease density, provides stability, enhances the drying overall performance and fired abrasion resistance in uses. This study is geared toward evaluating the effect of the weight of grog on the performance indices (properties) of refractory bricks utilizing the raw Abusoro clay as potential kaolin clay materials.

2. MATERIALS AND METHODOLOGY

2.1 Geology of the Study Area

The study area (Abusoro clays) is located in Southern Senatorial district Ondo State of Nigeria, precisely around latitude 06°37.718′, and longitudes 004°36.718′ with an elevation of 180. The humid tropical climate has high mean annual temperature of $30^{o}C$ and an annual average rainfall of 1500 mm^3. The area is sited in the south-western sector of the Nigerian Basement Complex as shown in Fig. 1. The geology of Nigeria is dominated by sedimentary and crystalline basement complex formations that can be found all over the country in virtually equal proportions [10, 11]. The sediment is mainly upper cretaceous to recent in age while the basement complex rocks are thought to be Precambrian.

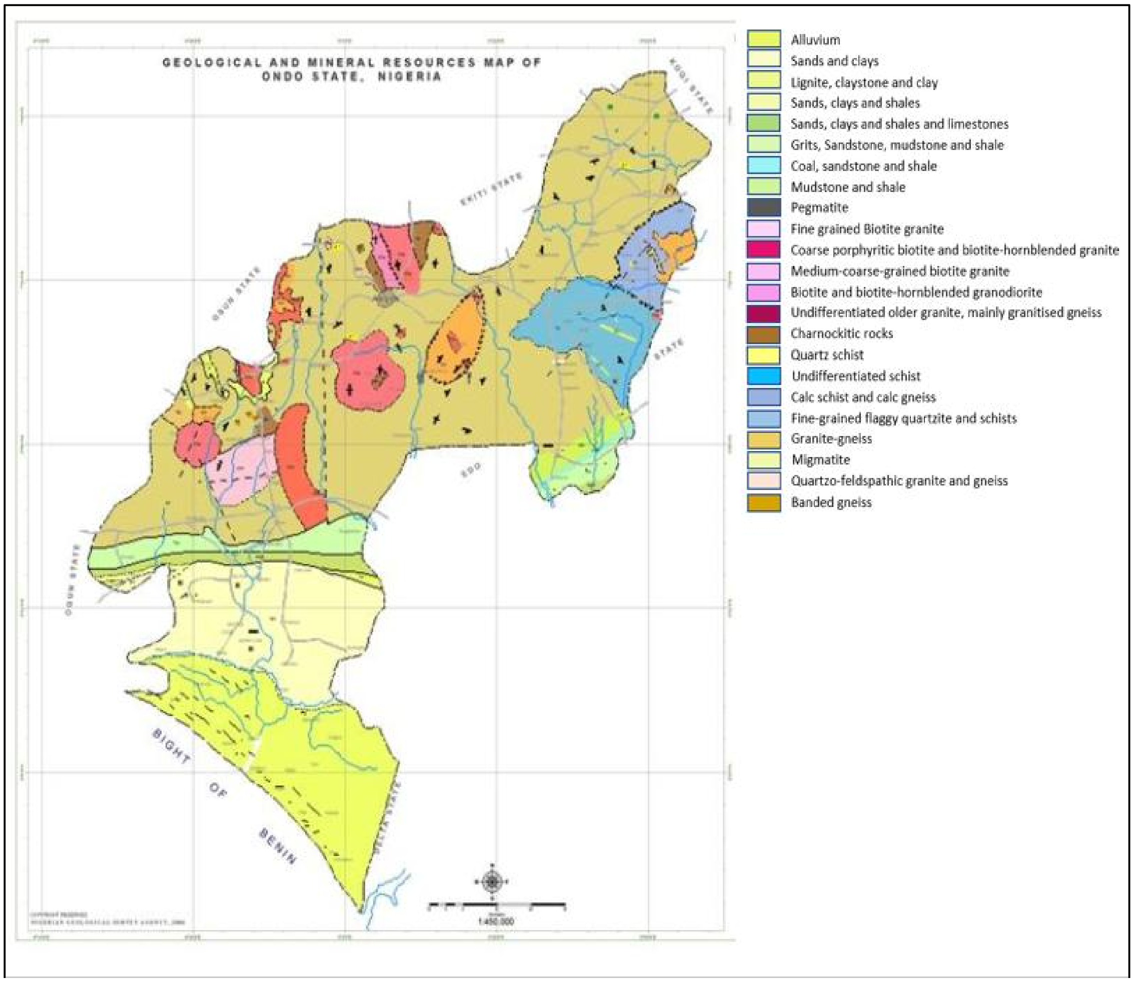

Fig. 1. The Geological Map of Ondo State (Adapted from NGSA, 2006)

2.2 Sample Collection and Preparation

The raw kaolin clay samples used for the experimental work were obtained from Abusoro clay deposits in Ondo State. The grog sample was prepared from the raw Abusoro clay using muffle furnace at the Strength of Materials Laboratory, Mechanical & Mechatronics Engineering Department, Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria. The chemical analysis of the clay sample was determined by utilizing X-ray Fluorescence spectrometer (XRF) at Nano Centre, University of Johannesburg, South Africa. The phase identification (mineralogy) of the raw Abusuro clay was characterized by utilizing X– ray Diffraction (XRD) analyzer at Chemistry department, University of Johannesburg, South Africa.

The extracted kaolin clay was soaked in water for 72hrs and dried in open air for 168 hrs. The dried clay was then crushed and ground using jaw crusher and ball mill respectively to allow particle size homogeneity. The grog also is known as calcine was obtained by firing some quantity of the Abusoro kaolin clay samples at a temperature of 1000°C within 1 hour. The calcined clay was allowed to cool, and thereafter it was ground with a pan mill and sieved with mesh 100 (<150µm) in order to produce the mandatory size. The test specimens of refractory bricks were formed by mixing freshly sieved kaolin clay with various percentage weight of grog in 20%, 30% and 40% respectively. The clay mixture was found to be plastic at 14% water content; allowed to be hardened for 24hrs; for the purpose of a workable mix. It is then pressed manually in a wooden brick mould of diameter 4cm and height of 1.5cm.The mould bricks were air-dried for 168hrs, and thereafter, oven-dried for 24hrs at 110°C to remove any moisture left in the bricks. The fired bricks were then evaluated for bulk density, linear shrinkage on firing, apparent porosity, compressive strength and refractoriness in accordance with the American Society for Testing and Materials.

2.2.1 Apparent porosity

The weights of the oven-dried specimens were taken and recorded (D). The specimen was then suspended in a vessel of boiling water for 15 minutes, after which they were transferred to cold water for half an hour, and the weight of the specimen soaked in water was taken and recorded as S. Thereafter, the weight of the soaked specimens in the air was taken and recorded (W) (i.e., specimens in air, including the moisture in its open pores).

The apparent porosity was calculated using the formula [12]:

$$Apparent\ porosity, A_p = \frac{W-D}{W-S} * 100 \qquad (1)$$

Where,

A_p= apparent porosity
W= weight of soaked specimen in air (including the moisture in its pores)
S= weight of fired suspended specimen (in water)
D= weight of fired specimen in air

2.2.2 Bulk density

The oven-dried specimens were weighed in air and the weights were recorded as D. Each of the samples was transferred to a beaker of water and they were heated for 40 minutes to release any trapped air. After which they were allowed to cool. Thereafter, the specimens were soaked in water, and the soaked specimens were weighed and their weights were also recorded as W. The specimens were subsequently suspended in water and the suspended weights were measured as S. The bulk density was determined based on the expression [13].

$$Bulk\ density = \frac{D}{W-S} \qquad (2)$$

Where,

D= weight of fired specimen in air (oven-dried sample)
W= weight of soaked specimen (in air)
S= weight of fired suspended specimen (in water)

2.3 Linear Shrinkage on Firing

The samples dimensions were taken before and after firing to the temperature of 1000°C to determine the linear shrinkage. The differences in dimensions were used to compute the linear shrinkage. The % averages of drying, firing and total shrinkage respectively were then calculated according to the expression [14].

$$\%\ average\ drying\ shrinkage = \frac{O-D}{O} \qquad (3)$$

$$\%\ average\ firing\ shrinkage = \frac{D-F}{F} \qquad (4)$$

$$\%\ average\ total\ shrinkage = \frac{O-F}{O} \qquad (5)$$

Where,

O, D, and F are the original length, the dried length and the fired length respectively.

2.4 Refractoriness

Refractoriness is referred to as the capacity of a refractory material to bear high temperature conditions under service operations. The refractoriness was determined using Shuen's formula. This can be calculated using Shuen's formula [15].

$$Refractoriness\ (K) = \frac{360 + Al_2O_3 - RO}{0.228} \qquad (6)$$

Where,

K = Refractoriness
Al_2O_3 = Percentage alumina in the clay (%)
RO = Sum of other oxides in the clay material excluding SiO_2 and Al_2O_3 (%);
The values of 360 and 0.228 are constant

2.5 Cold Crushing Strength

The samples were put on the load of a compressive strength mechanical testing machine (Seldner 7940 Rieldling). A force was axially applied to the test sample at a uniform rate until the sample breaks. The force at which the specimen ruptured was noted. Each sample was recorded. This represents the load required to determine the cold crushing strength of the specimen; the surface area of the samples was also calculated and recorded [16, 17].

$$Cold\ crushing\ strength, CCS = \frac{Compressive\ force\ (N)}{Area\ (m^2)}\ cc \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 Chemical Composition

From chemical analysis result obtained (Table 1), the silica (62.74%) content of Abusoro kaolin sample is high. Therefore, Abusoro kaolin clay is regarded as siliceous in which according to Yami and Umaru [18] and Nnuka and Agbo, [19] is within the standard range (46, 62%). The alumina, Al_2O_3 (31.42%) content of the kaolin clay sample is found to agree with the standard values [20]. Also, the alumina content to the silica content could apparently be taken as ratio 1:2 of Al_2O_3 to SiO_2 which agrees with the standard and is in tandem with Sanni [21]. Hence, the selected kaolin clay sample is regarded as alumino-silicate kaolin clay [22, 23]. This has confirmed the report that kaolin and fireclay materials with less than 45% alumina are the major refractory clay deposits that are most abundant in Nigeria. Therefore, the content of alumina in Abusoro kaolinitic clay samples is in tandem with other researches [24]. The iron oxide (Fe_2O_3) content of the kaolin clay samples of Abusoro is 1.43%. It can be deduced that Abusoro has low iron oxide content, and it is within the acceptable limits. Therefore, the low iron oxide content is suitable and appropriate for the production of excellent refractory materials without any threat to good performance [25]. Moreover, the extra cost for the removal of iron oxides through beneficiation is significantly reduced [26, 27]. This is, therefore, the basis for utilizing raw samples of Abusoro kaolin clay.

3.2 XRD Patterns

The XRD analysis of the raw Abusoro kaolin clay specimen is given in Fig. 2a-b. The XRD identification revealed some number of peaks as a result of the different minerals. However, the XRD exhibits various patterns attributed to the nature of clay structure with various diffraction peaks with the first peak at around 8.89^o (2ɵ). According to Grim, [28] any peak that occurs at 10^o (2ɵ) in a clay sample regarding the first order spacing is as a result of its poor crystalline characteristics. Therefore, Abusoro clay is regarded as poor crystalline clay. However, the primary mineralogical content of the sample includes Quartz (blue), SiO_2, Kaolinite (purple), $Al_2Si_2O_5$ $(OH)_4$ and Halloysite (green), $Al_2Si_2O_5$ $(OH)_4.2H_2O$ respectively as shown in Fig. 2a-b. The quartz (SiO_2) is found to be the major mineral in the Abusoro clay which is in agreement with the result obtained in the chemical composition.

3.3 Colour

The colour of the dried kaolin clay samples at ambient temperature was noted to exhibit whitish to brownish colour. The traces of iron oxide (Fe_2O_3) impurity in this clay could be the result of the brownish appearances [29-31]. The whitish appearances of Abusoro clay can be substituted and be of better used as a source of aluminium. However, the kaolin clay samples meet the recommended range of 0.5-2.4% which is acceptable for refractory bricks making.

3.4 Bulk Density

Fig. 3 depicts the results of the bulk density. As the % wt. of grog increases (20% - 30%), the bulk density decreases initially; however, the value increases with the addition of 40% wt. grog producing a maximum value of 1.74 g/cm^3. The marginal increase could be attributed to the additional weight by the grog particle at 40%. Onuoha [32] reported that low bulk density is favoured by high porosity (higher pores) which implies that less matters are available for bearing loads. Nevertheless, all bulk density values (1.73, 1.72, 1.74g/cm^3) fall within the acceptable range making the raw Abusoro clay sample highly suitable for siliceous fireclays and/or fireclays [33, 34]. This property is most desired for clay refractory in order to provide the needed high physical strength at high service temperature and high resistance to corrosion, slag penetration and abrasion. More so, it is required in the materials handling and transportation [35, 36].

3.5 Apparent Porosity

The values of apparent porosity (41.2% - 43.2%) for the three mixes of refractory samples are above the acceptable range (10-30%) and are consistent with the work of Chester, [37] for dense refractory bricks as shown in Fig. 4. Therefore, the sample clay may not be suitable for making grog as clay additives in producing dense refractory materials. However, the increase in the porosity of the raw Abusoro clay sample material would enhance its suitability as an insulating fired bricks [37-39]. The high apparent porosity is due to the addition of non-plastic materials (grog), to the siliceous clay

Table 1. Chemical Composition (wt %) of the Kaolin clay samples

Elements	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	TiO	P_2O_5	SO_3	K	S/S	RO	Al_2O_3/ SiO_2	SiO_2/ Al_2O_3
AB	62.74	31.42	1.43	0.00	0.00	0.06	0.30	0.52	0.26	0.73	1691	3.86	5.83	0.37	1.48
SV	51.70	25.44	0.5-2.4	-	0.2-0.7	0.1-0.2	-	-	-	-	-	-	-	0.492	2.03
Refractory clay	46-62	25-39	0.4-2.7	ND	0.2-1.00	0.2-1.00	ND	ND	ND	ND	-	-	-	-	-

Source: AB: Abusoro clay; Refractory clay: (Nnuka and Agbo, 2000); Standard values (SV): Refractory bricks (Parker, 1967)

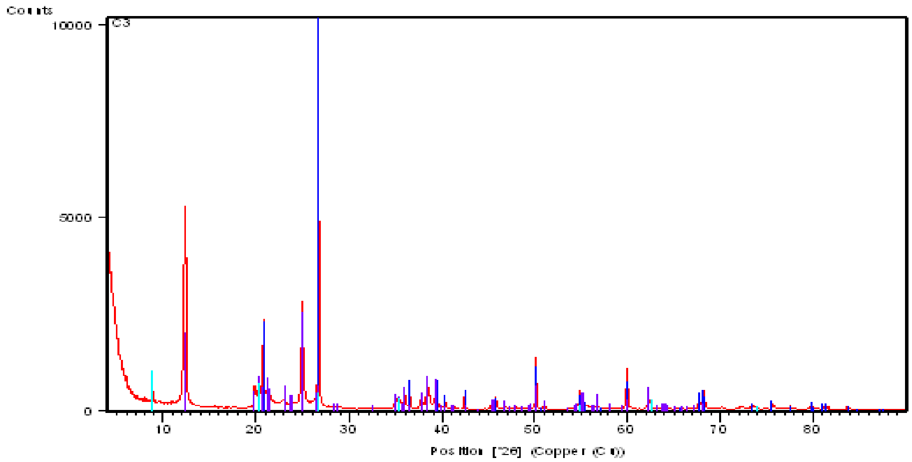

Fig. 2a. XRD pattern of raw Abusoro clay

Table 2. XRD Identified Pattern List of the Abusoro clay

Visible Ref. Code	Score	Mineral Name	Displ. [°2θ]	Scale Fac.	Chem. Formula
*01-070-3755	70	Quartz	Blue	0.994	SiO_2
*00-058-2001	39	Kaolinite	Purple	0.230	$Al_2Si_2O_5\,(OH)_4$
*00-029-1489	20	Halloysite	Green	0.189	$Al_2Si_2O_5\,(OH)_4.\,2H_2O$

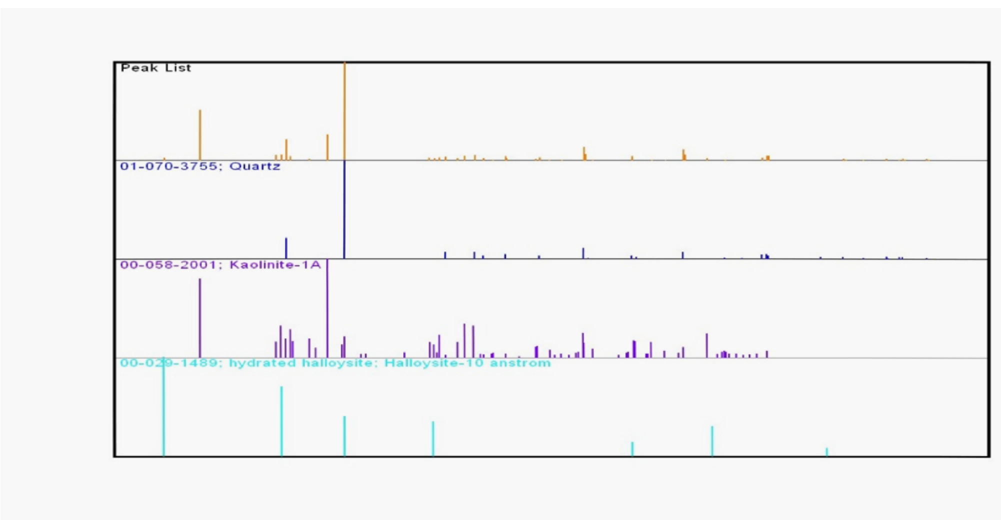

Fig. 2b. XRD Peak List of raw Abusoro clay

Table 3. Refractory properties of Abusoro Kaolin Clay

Sample Abusoro clay	%wt. Grog (%)	Linear Shrinkage (%)			Bulk Density (g/cm^3)	Apparent Porosity (%)	CCS (MPa)
		Dry	Fired	Total			
A_1	20	2.3	7.9	10.20	1.73	43.2	15.75
A_2	30	2.3	7.1	9.40	1.72	43.2	21.21
A_3	40	3.0	5.7	8.70	1.74	42.6	20.30

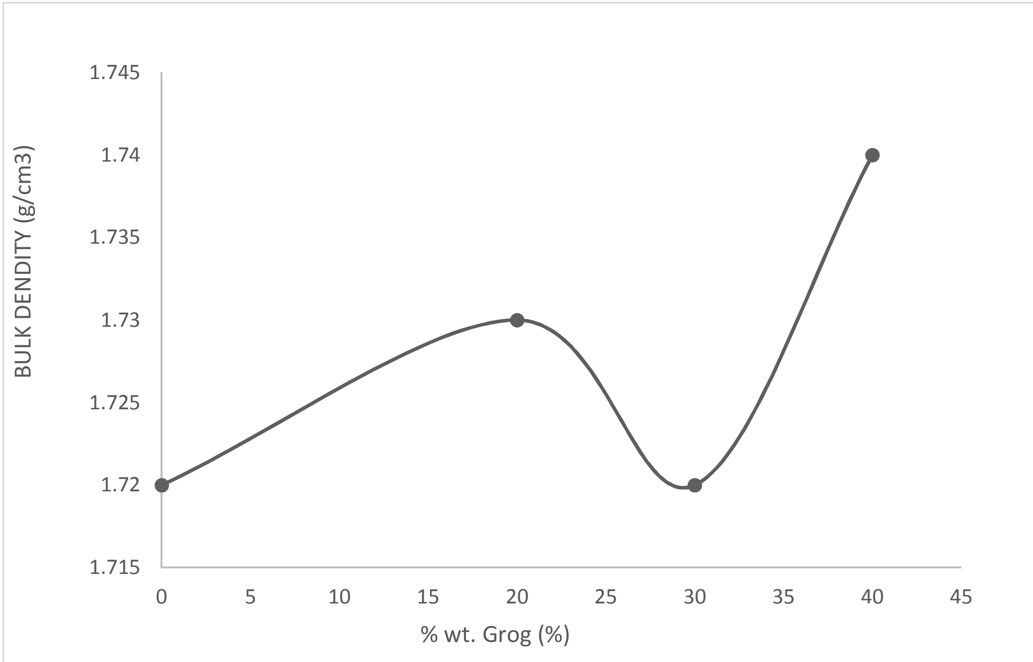

Fig. 3. Variation of Bulk density with % wt. grog on AB sample

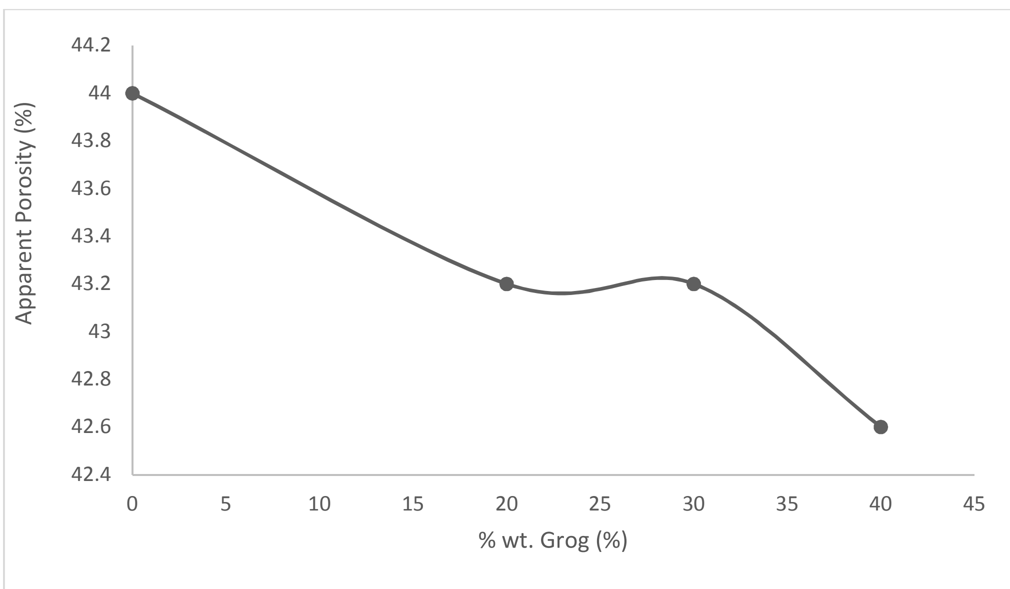

Fig. 4. Variation of apparent porosity with % wt. grog on AB sample

which originally is a factor for higher pores [32]. The addition of grog increased the total silica and alumina contents leading to reduction in the plasticity which in turn results to increase in apparent porosity. This property is necessary in insulating refractories particularly, electrical porcelain, because it increases the electrical resistivity due to the presence of pores (air) which serves as an insulator.

3.6 Linear Shrinkage

The linear shrinkage results obtained (Fig. 5) on both dry and fired Abusoro refractory bricks indicated that the values of the total linear shrinkage reduced as the % wt. of grog increases, and further increase revealed a downward trend. Generally, it is observed that the results of the variations in the linear shrinkage percentage values are within narrow range, and these may be due to the samples composition, particle size and porosity. The values of the fired linear shrinkage in comparison to the dried linear shrinkage are very low and, this is more appropriate for insulating refractories [22, 40]. The decrease in the fired linear shrinkage infers decrease in densification and hence, decrease in bulk density as shown in the results obtained (Table 3) mainly due to the non-plasticity of the grog. According to Shuaib-Babata et al., [36] an interlocking of grains in the firing of clay materials do enhance the mechanical property (strength) of the refractory. However, all the values for Abusoro clay are within the acceptable limit (8% - 13%) for use as insulating refractory materials [41].

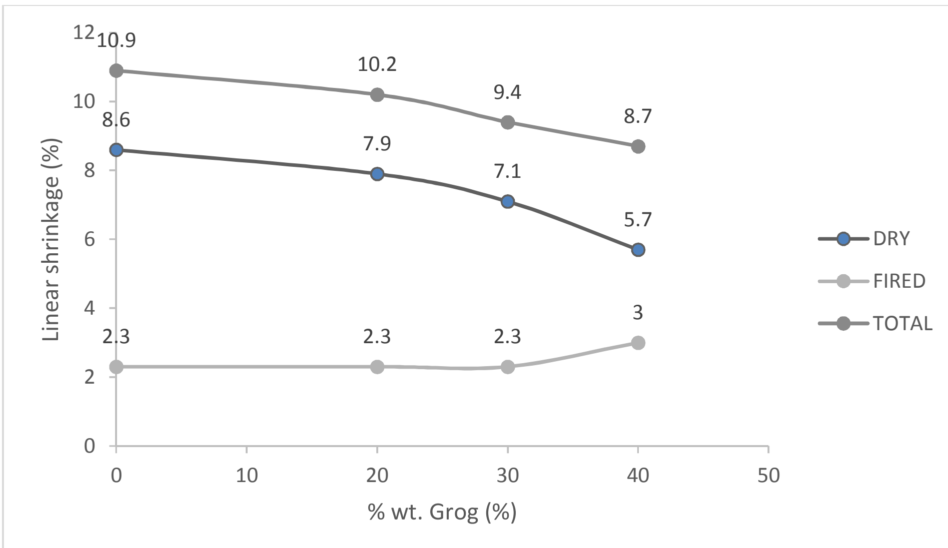

Fig. 5. Variation of linear shrinkage with % wt. grog on AB sample

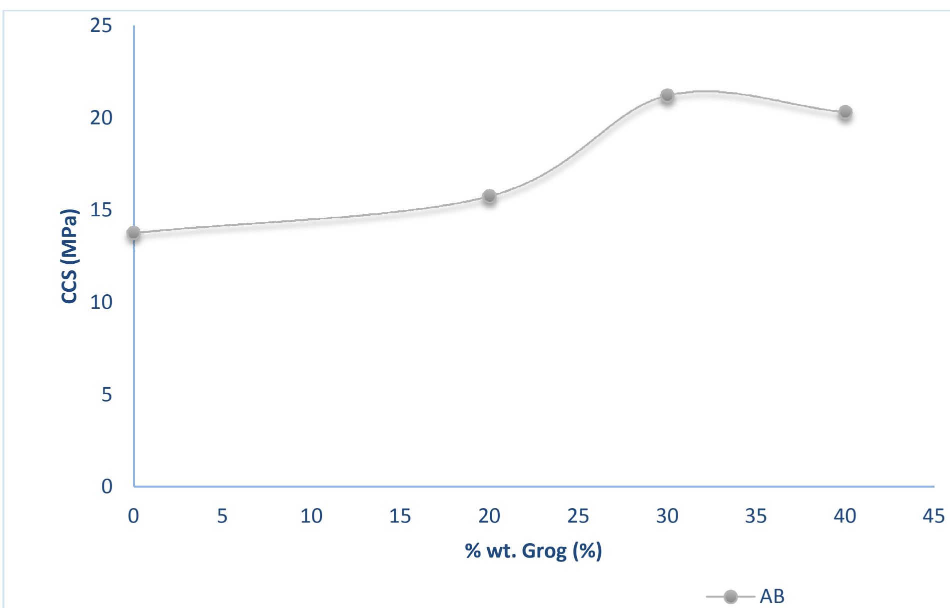

Fig. 6. Variation of cold crushing strength with % wt. grog on AB samples

Table 4. Refractoriness

Samples	Temperature (°C)
Abusoro clay (AB)	1691
*Fireclay	1500-1700
**Siliceous Fireclay	1500-1600

Sources: Misra, 1975; **Omowumi, 2001*

3.7 Cold Crushing Strengths

The cold crushing strength results obtained (Fig. 6) indicated that as the % wt. of grog increases, an initial rise in the CCS occurs, and thereafter, the value drops with further % wt. of grog. The highest cold crushing strength obtained is found to be 21.21 MPa at 30% grog. Although the values obtained for all the blends (21.21, 20.30 and 15.75 MPa) are high enough; it is an indication that the raw Abusoro clay-grog sample blend will be able to withstand some levels of loads and abrasion at ambient temperatures. It is well reported that refractory grogs are non-shrinking materials improving the stress capability of the refractory bricks [42]. The higher the efficiency of firing, the denser the brick is and the higher the cold crushing strength. The results of CCS agreed with the recommended standard values of 15 – 59 MPa (N/mm^2) [16] [43, 44] and of 9.8 – 68.8 MPa [45] for refractory fireclay bricks.

3.8 Refractoriness

Refractoriness can be defined as the ability of a material to bear high firing temperatures without weakening of both the physical and mechanical values of its properties. The refractoriness of raw Abusoro clay sample as reported in Table 4 occurred at 1691°C, a significantly high temperature. The high percentage contents of alumina (31.42%) in combining with the silica (62.74%) contribute to its high refractoriness characteristics. This is in tandem with other authors that the alumina content raises the working temperature of the refractory materials [23] [36] [46]. Moreover, they met the allowable range of 1500-1700°C for fired clay refractory materials [18] [34] [47,48]. The non-existence of manganese oxide in the raw Abusoro clay samples is also found to enhance the value of its refractoriness which is also reported by other authors [46].

4. CONCLUSION

In conclusion, this experimental study has demonstrated that raw Abusoro clay belongs to alumino-silicate family. The physico – mechanical properties of the moulded insulating fired bricks from Abusoro in Ondo State with the refractory grog compared favourably with recommended standard. It is therefore recommended that in the making of insulating refractory materials utilizing raw Abusoro clay, an average of 30 – 40% grog is selected for optimum performance.

ETHICAL APPROVAL

As per international standard or university standard guideline ethical approval has been collected and preserved by the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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