Characterisation of Some Selected Clays from Ekiti State for Refractory Application

ABSTRACT

Clays from Isan and Ire both in Ekiti state were obtained and were analyzed for chemical composition, mineralogical composition and their physical properties. The chemical composition of the clay samples as revealed by the X-ray Fluorescence Spectrometer showed that the main constituents are SiO_2 and Al_2O_3. The SiO_2 content is 53.30% and 56.90% for Isan and Ire while the Al_2O_3 content is 25.95% and 21.45% for Isan and Ire respectively. Other minor constituents present include Fe_2O_3, TiO_2, CaO, K_2O and MgO. The principal minerals found in the clay samples according to the X-ray Diffractometer results are quartz and kaoline. The linear shrinkage, permeability, apparent porosity, bulk density, thermal shock resistance, refractoriness, loss on ignition, cold crushing strength, and moisture content for Isan clay is 9.64%, 0.000862, 45%, 1.59g/cm^3, 7cycles, 1685°C, 9.29, 43.65 and 5.63% while that of Ire clay is 13.21%, 0.001171, 40%, 1.50g/cm^3, 6 cycles, 1665°C, 12.86, 47.72 and 27.23%. Further research should be advanced to improve the critical physical properties of Isan and Ire clays to ensure these raw materials are suitable for the refractory application.

Keywords: clay, chemical composition, mineralogy, refractory, silicate-aluminate, thermal shock resistance

1. INTRODUCTION

Inorganic materials known as refractory materials can endure high temperatures (often exceeding 1500°C) when they are subjected to the physical forces and chemical exposure of molten metal, slag, and gases in the furnace. For many processes in the chemical, ceramic, petroleum, petrochemical, foundry, and iron and steel industries, refractories are required. Despite the vast deposits of the raw materials needed to make refractory products such as clay, Nigeria is not self-sufficient in the production of refractory [1 – 2]. Kaolinite (Al_2O_3, $2SiO_2.2H_2O$), Chromite ($FeOCr_2O_3$), Magnesite ($MgCO_3$), and numerous forms of clays are the raw materials used to make different refractory products. The two main forms of refractories utilized in Nigerian industries are aluminium silicate and magnesite. Although, refractories are commonly used by the metallurgical industry, the chemical, glass, and petrochemical sectors also make use of them. As of the year 2000, these sectors required well over 300,000 tons of refractory materials [3]. Refractories are utilized wherever high temperatures are needed such as crucibles, thermocouple heaters, refractory cements, refractory bricks for furnace linings, and tubes for electric furnaces [4 – 5].

"Refractory materials play useful and very crucial roles in the industrial development of any nation. It was reported that virtually all the refractory requirements in the metallurgical industries in Nigeria are imported" [1]. "The Nigerian metallurgical industries are struggling today because of many factors which include the short supply of refractory materials. It was also reported that Ajaokuta Steel Complex requires about 43,503 tonnes per year of fireclay refractories for its operations; and these refractories are sourced abroad" [6]. "Despite having extensive clay mineral deposits in Nigeria, Nigeria continues to depend on the importation of refractory materials for many of its industries. Nigeria imported about 27 million metric tonnes of refractory materials in 1987" [7]. "Most metallurgical processes are heat-generating systems. Such systems require materials that can withstand not only the high temperature generated but equally must be able to withstand both physical and chemical action without deteriorating. Engineering materials that possess these attributes are refractory. The base material for refractory production is clay. Clays are naturally occurring sediments produced by chemical actions resulting from weathering of rocks" [8]. "It is an earthly fine-grained material, which develops plasticity when mixed with water; clay has silica (SiO_2), alumina (Al_2O_3) and water as primary constituents. Other constituents are iron, alkaline, and alkaline earth metals" [9].

The chemical, mineralogical and physical properties of clays vary greatly depending on the source. There is a need to assess clay samples which can be a potential raw material for refractory production to meet the increased demand by the metallurgical industries. The aim of this study is therefore to investigate the chemical composition, mineralogical characteristics and physical properties of clay samples from Isan-Ekiti and Ire-Ekiti both in Ekiti state, Nigeria.

2. EXPERIMENTAL PROCEDURES

2.1 Sample collection

The clay deposits investigated were collected from Isan-Ekiti (7° 55' 0" N, 5° 19' 0" E), and Ire-Ekiti (7° 45' 42" N, 5° 23' 41" E) both Ekiti state, Nigeria. The clay samples were collected at depths of 0.4m and 0.5m. From each site, the clay samples were obtained from two (2) points that were at least 50m apart. From each sampling point, 20 kg samples were collected and packed in newly cleaned polyethene bags which were properly sealed to avoid contamination.

2.2 Sample preparation

The clay samples were air-dried and sieved through 100 meshes. Test samples for various analyses were mixed with 8 per cent water and stirred to form a homogeneous plastic paste. 8 % water was determined as the optimum percentage necessary for optimum plasticity [8]. A plastic mass (12cm by 6cm) was moulded, dried at a temperature of 110°C and fired in a muffle furnace at intervals of 100°C for every 10 minutes until a temperature of 1110°C was attained. These prepared samples were then used for the determination of different parameters.

2.3 Chemical composition and mineralogical analysis

The ground clay samples were dried and the chemical composition in wt% of the elemental oxides was determined using Energy Dispersive X-ray Fluorescence Spectrometer (ED-XRF) model PW1660, XRA. The mineralogical characteristics of the samples were analyzed with the aid of X-ray diffractometer.

2.4 Physical properties tests

The samples were tested for apparent porosity, bulk density, thermal shock resistance, linear shrinkage on firing, cold crushing strength and refractoriness following standard procedures [10].

2.4.1 Loss on ignition

The loss on ignition (LOI) of the clay (mainly volatile matters) was determined by measuring the weight loss of a known mass of the sample after firing in the furnace at 1000°C for 1 hour and 30 minutes. Loss on ignition was calculated using the relation:

$$LOI\ (\%) = \frac{W_{i-}W_f}{W_i} \times 100 \quad (1)$$

Where w_i and w_f are initial and final weights respectively.

2.4.2 Apparent porosity

The volume of the pore space as a percentage of the sample's overall volume is known as porosity. A test specimen of 30mm x 30mm x 20mm was cut from a burnt refractory brick and it was subsequently dried in an oven at 110°C to a consistent weight (D). The dried specimen was placed loosely in distilled water and heated for two hours before being allowed to cool to room temperature and having its weight (S) recorded. The sample was taken out, and the weight (W) of the saturated or soaked object in the air was noted. The apparent porosity was computed using the formula:

$$\text{Apparent porosity} = \frac{W - D}{W - S} \times 100 \quad (2)$$

where W stands for the weight that has been saturated or soaked, D stands for dried weight, and S stands for suspended weight.

2.4.3 Bulk density

The bulk density of a refractory brick is represented by the weight per unit volume including pore space. A moulded fired brick specimen measuring 30mm by 30mm by 20mm was prepared. The brick was air-dried for 24 hours and oven dried at 110^{o}C to a constant weight (D). After which it was transferred to a beaker and boiled with distilled water for 2 hours to assist in releasing trapped air. It was then allowed to soak and the saturated weight free of excess water (W) was taken. The specimen was then suspended in water using a beaker and the suspended weight (S) was taken. The bulk density was then calculated using the relationship:

$$\text{Bulk density} = \frac{D}{W-S}\rho_w \qquad (3)$$

where, D= Dried weight, W= saturated weight, S= suspended weight, ρ_w= density of water

2.4.4 Linear shrinkage

The linear shrinkage is determined by measuring the dimensional changes between the dried and fired bricks. In this work, the distance between the two ends of the sample was measured with a vernier calliper after the drying and firing processes. The linear shrinkage was calculated thus:

$$\text{Linear shrinkage} = \frac{L_B - L_D}{L_B}\times 100 \qquad (4)$$

where, L_B = Dry dimension, L_D = fired dimension

2.4.5 Refractoriness

This is a measure of a material's degree of fusibility, and it indicates the temperature at which the material softens. This characteristic identifies a material's capacity to tolerate a deformation temperature before buckling or bending under its weight. Refractoriness is the capacity to use the material without worrying about the furnace wall being thermally deformed.

$$\text{Refractoriness} = \left(\frac{360 + \%Al2O3}{0.228}\right) - Ro \qquad (5)$$

Where R_o = Sum of all other components apart from alumina and silica in the composition.

2.4.6 Thermal shock resistance

The amount of heating and cooling (cycles) required to produce a noticeable crack on the sample is known as thermal shock resistance. The specimen was heated in a muffle furnace set to 1200°C for 10 minutes, this was followed by air cooling for another 10 minutes, and the samples were observed for any traces of crack.

2.4.7 Cold crushing strength

This is the load at which the specimen develops cracks. The test piece was obtained from the heated brick into roughly 25 mm-sized cubes. The two faces normal to the direction in which forming pressure was applied were prepared as bearing faces, and the test piece was marked to show this orientation. Between the press platens and the test piece's bearing faces, cardboard was inserted. The load was applied steadily until the test piece was unable to hold it. The area of the test piece before the application of load was computed and recorded, and the maximum recorded load was taken as the crushing load. The cold crushing strength was determined using the formula:

$$\text{Cold crushing strength} = \frac{L}{A} \quad (6)$$

where, L= Maximum load (KN); A= Cross sectional area.

2.4.8 Moisture content

An aluminium can was cleaned and weighed, and the clay sample to be tested was put into the can, weighed and recorded. The can containing the clay was then oven dried for 24 hours at a temperature of 105°C and 110°C. It was removed from the oven and reweighed to determine the weight of the dry sample. The moisture content was obtained from equation 7.

$$\text{Moisture Content} = \left(\frac{m_2 - m_3}{m_3 - m_1}\right) \times 100 \quad (7)$$

Where m_1= wt. of can (g), m_2= wt. of can + wet clay (g) and m_3= wt. of can + dry clay (g)

2.4.9 Permeability

Permeability is defined as a property of a porous substance that allows for the flow or seepage of water via its connecting void. It gauges how quickly a fluid will move through porous materials. Refractories that are exposed to gases and liquids should be impermeable to them. This will stop liquids and gases from penetrating a furnace's refractory walls and leaking out. The lower surface of the fired samples was exposed to an aperture, and the sides were sealed. A bell jar was positioned within the cylinder, which had been filled with 2000 cm^3 of water. The pressure difference between the surfaces was measured by a manometer. Permeability was calculated from the equation:

$$K=\frac{QL}{AHT} \quad (8)$$

Where Q = quantity of water flow, L = length , T = time, A = area, H= manometer head difference

3. RESULTS AND DISCUSSION

The results of the chemical composition analysis by XRF of the clay samples obtained from both Ire-Ekiti and Isan-Ekiti are shown in Table 1. The diffraction patterns of the clay samples as revealed by the XRD are shown in Figures 1 and 2. The results of the physical properties tests of the samples which include linear shrinkage, permeability, apparent porosity, bulk density, thermal shock resistance, refractoriness, loss on ignition, cold crushing strength and moisture content are shown in Table 2.

Table 1. Chemical composition of Isan and Ire clays

Constituents	Isan clay Composition %	Ire clay Composition %	*High-melting clay	*Standard clay for refractory bricks
Fe_2O_3	3.98	3.18	1-9	0.5-2.4
TiO_2	2.56	1.03		
CaO	4.31	3.12	0.5-2.6	0.1-2.0
K_2O	-3.33	-0.21		
SiO_2	53.30	56.90	53-73	51-70
Al_2O_3	25.95	21.45	16-29	25-44

MgO	0.48	0.49	0.5-2.6	0.2-1.0
LOI	9.29	12.86	4-12	8-18

*Source: [8 ,11]

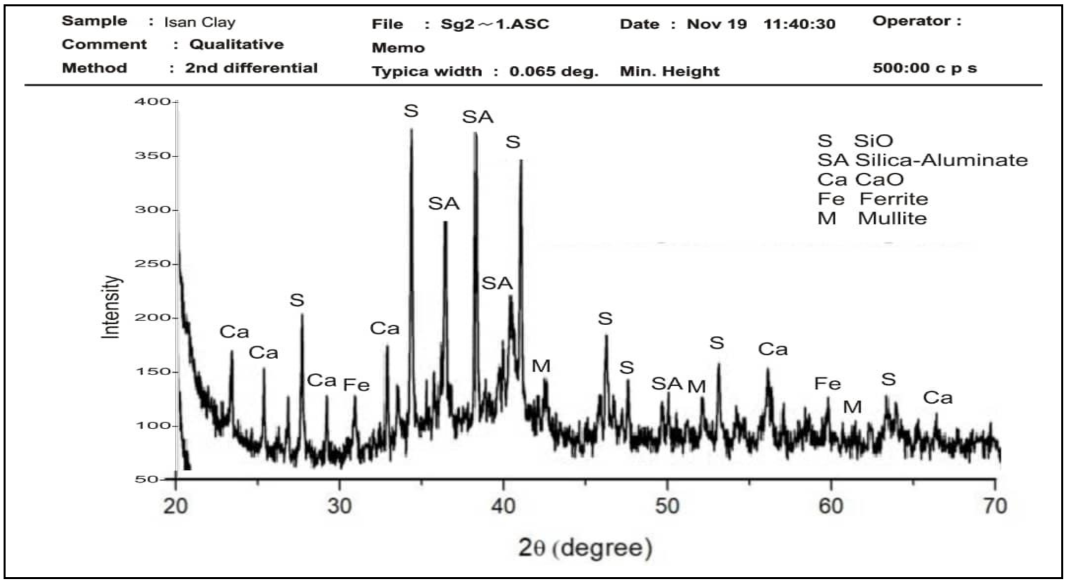

Fig. 1. XRD pattern of Isan clay revealing the mineralogical composition.

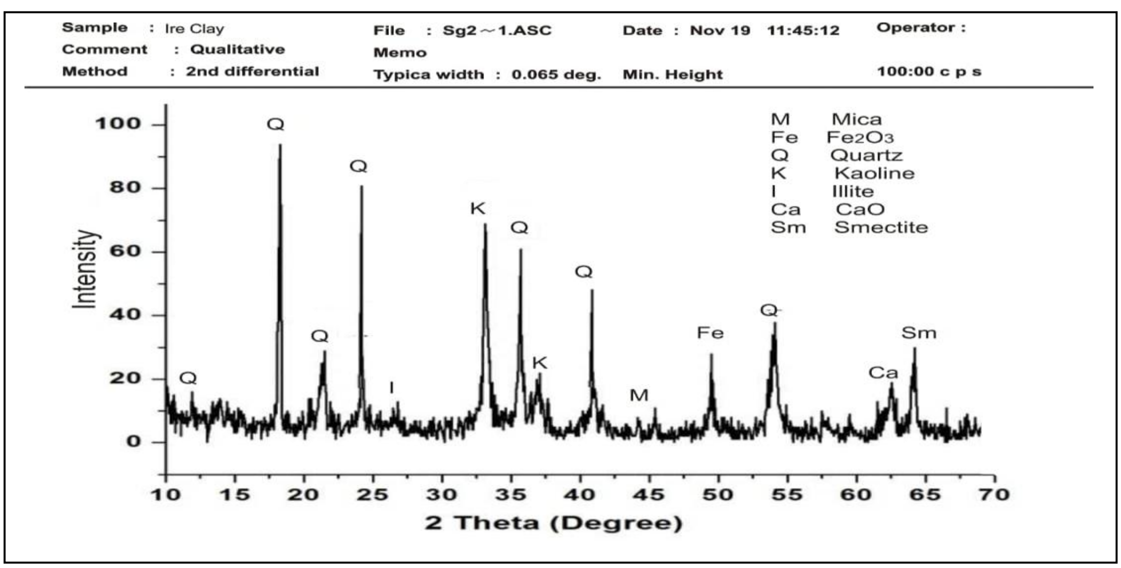

Fig. 2. XRD pattern of Ire clay revealing the mineralogical composition.

Table 2. Physical properties of Isan and Ire clays

Properties	Isan	Ire	*Standard clay for refractory bricks
Linear shrinkage (%)	9.64	13.21	2 – 10
Permeability	0.000862	0.001171	25 – 90
Apparent porosity (%)	45	40	20 – 30
Bulk density (g/cm^3)	1.59	1.50	1.71 - 2.8
Thermal shock resistance (cycles)	7	6	20 – 30
Refractoriness (^{o}C)	1684.76	1665.42	1500 - 1750
Loss on ignition (%)	9.29	12.86	9 – 14
Cold crushing strength	43.64694	47.72066	15.0 minimum
Moisture content (%)	5.63	27.23	1 – 13

*Source: [12]

According to the chemical analysis of the two clay samples, as presented in Table 1, SiO_2 and Al_2O_3 are the two major oxides present in the clay samples from Isan and Ire Ekiti. The alumina (Al_2O_3) content of Isan clay is 25.95% while that of Ire is 21.45%. They are both high-melting clays and their alumina content is within the acceptable range for both refractory clay and high-melting clay [8, 11]. Hence, they will be good raw materials for the production of refractory bricks. The silica (SiO_2) content is 53.30% and 56.90% for Isan and Ire clays respectively while other minor constituents present include Fe_2O_3, TiO_2, CaO, K_2O and MgO. Samples with high silica concentration are categorized as acidic refractory materials [13]. The mineralogical characteristics as presented in Fig. 1 and 2 revealed that the principal minerals found in the Isan and Ire clay samples are quartz and kaolin.

The linear shrinkage, permeability, apparent porosity, bulk density, thermal shock resistance, refractoriness, loss on ignition, cold crushing strength, and moisture content for Isan clay is 9.64%, 0.000862, 45%, 1.59g/cm^3, 7cycles, 1685°C, 9.29, 43.65 and 5.63% while that of Ire clay is 13.21%, 0.001171, 40%, 1.50g/cm^3, 6cycles, 1665°C, 12.86, 47.72 and 27.23%. LOI for all the clays falls within the internationally acceptable limits for refractory application [11]. The refractoriness of clays from selected sites was within the standard limits. The clay samples had refractoriness levels exceeding 1300°C. At 1000°C, the samples didn't exhibit any signs of failure. This indicates that the sample had substantial levels of sintering. As a result, the samples can be utilized to melt low and medium-temperature metals. The permeability of the clays was within the recommended range while their apparent porosity was above the standard limit. The porosity of refractory clay material is directly related to the air pockets contained in it, the higher the porosity of the clay material, the higher its insulating properties [14]. High porosity in refractory materials translates to increased air pockets and improved thermal insulation. The thermal shock resistance of these clays was below the standard range of 20 - 30 cycles. However, the bulk densities of the clays were below the standard values for refractory materials.

4. CONCLUSIONS

The chemical composition, mineralogical composition and physical properties of clay samples obtained from Isan-Ekiti and Ire-Ekiti were successfully carried out. SiO_2 and Al_2O_3 are the major constituents of Isan and Ire clays. The refractoriness and loss on ignition of clays from the selected sites were within the standard limits. However, the apparent porosity and cold crushing strength were above the standard limit. The permeability, bulk density, and thermal shock resistance of these clays were below the standard range for clay suitable for refractory bricks. Further research should the conducted to improve the critical physical properties of the Isan and Ire clays for suitability in the refractory application. Major players in the raw materials industry should pay more attention to the research and development of abundant clay reserves within the country.

COMPETING INTERESTS

Authors have declared that no competing interests exist

AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration among the authors. All authors read and approved the final manuscript.

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