



## ASSESSMENT OF SOME NIGERIAN CLAYS FOR INDUSTRIAL APPLICATIONS

O.M. Chima<sup>1\*</sup>, C. Onuoha<sup>2</sup>, T. O. Nwokeocha<sup>3</sup> and M. A. Allen<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Michael Okpara University of Agriculture Umudike., Nigeria.

<sup>2</sup>Department of Metallurgical and Materials Engineering, Federal University of Technology Owerri, Nigeria.

<sup>3</sup>Department of Industrial Production Engineering, Nnamdi Azikiwe University Awka, Anambra State, Nigeria.

<sup>\*</sup>chimamelford@gmail.com

### ABSTRACT

Two Nigerian clays were characterized for various industrial applications. Clay samples from Ameke-Item in Uzoakoli and Akara-Isu in Abia North deposits, both in Abia State, Nigeria were used for the study. The clay samples were analyzed using x-ray diffractometer and x-ray fluorescence to determine their mineralogical and chemical oxide compositions respectively. They were further processed and subjected to physico-mechanical property tests using ASTM standards. The results obtained show that the minerals in Ameke-Item clay are mainly kaoline and quartz while those found in Akara-Isu are kaoline, quartz and pyrite. The percentage composition of the dominant oxides such alumina, silica and iron oxide for Ameke-Item clay were 28, 51, and 8% respectively while Akara-Isu clay has composition of 30, 50, and 3.8% for the respective oxides. The physico-mechanical tests show that the range of values of (1610-1570<sup>o</sup>C, 30-29 cycles, 54-45N/mm<sup>2</sup>, 1.88-1.78g/cm<sup>3</sup>, 30-22.5%, 6.7-12.66% and 8.5-4.0%) were obtained for refractoriness, thermal shock resistance, modulus of rupture, bulk density, apparent porosity, water absorption and linear shrinkage respectively in the clays. It was found that these properties met industrial standard accepted for the development of industrial products such as glass, electrical porcelain insulator, ceramic wares, floor and wall tiles, building brick and electronic product. Hence, it could be concluded that these clay deposits are suitable for production of such industrial products.

**Key words:** Clay, kaoline, quartz, alumina, silica, products.

### 1.0 INTRODUCTION

Clay is a very fine-grained unconsolidated rock matter which is plastic when wet but becomes hard and stony when heated. It has its origin in natural processes mostly complex weathering, as it is a transported and deposited by sedimentation within geological period [1]. Clay is composed of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and water (H<sub>2</sub>O) plus appreciable concentration of oxides of iron, alkali and alkaline earth and contains groups of crystalline substances known as clay minerals such as quartz, feldspar and mica [2]. Hence, clays are regarded as industrial minerals composed mainly of hydrous-aluminosilicates with other minerals such as hematite, calcite, and rutile in trace quantity [3].

Clay minerals have fine grained and flaked shape with particle sizes ranging from a few microns to few hundred microns. [25]. It consists of two basic structures; tetrahedral and octahedral structures. The tetrahedral structure is made up of silicon ions bonded to oxygen atoms on the four sides. The octahedral structure has aluminium and magnesium ions bonded with oxygen and hydroxyl ions. These sheet-like structures are connected to each other in certain ways to form clay minerals. It is the changes in the structures of these structural sheets that give rise to the formation of different clay minerals [4]. Clay mineral is grouped into classes namely; kaolinite, illite and smectite (montmorillonite). Kaolinite consists of

silica and alumina plates which are strongly connected. This accounts for its stability. Illite has layers made from two silica plates and one alumina plate with potassium ions between each layer. This enhances the structure of illite better than smectite. Smectite has layers made from two silica plates and one alumina plate which have a very weak bond between the layers. This allows the passage of large quantities of water into the structure which gives rise to the swelling of such clays [5].

Clays are among the oldest industrial raw materials. They are available in different parts of the world. Their properties make them useful in many industrial applications such as cement industry, ceramics industry, foundry industry, civil and electrical engineering, cosmetics, oil, and polymers [6]. It is useful in pharmaceutical applications for production of drugs. This application is traceable to its surface area, particle size and structure [7]. It also serves as a good raw material for production of ceramic wares, floor and wall tiles, paper, paint and as catalyst in oil refinery [8,9]. Its uses extend to development of refractory products used in lining metallurgical furnaces and cement kiln [10]. Clay minerals such as sepiolite are useful for production of biomedical materials which are implants that are capable of substituting the body components [7]. Smectites is a type of clay used for production of fertilizer. This is an alternative technology to the application of soluble and synthesized plant nutrients which may avoid some challenges associated with the use of soluble fertilizer [7]. High quality clays have been used to develop insulating materials such as porcelain used in electrical power transmissions [11]. In many parts of the world, clay has been used to produce building bricks which are useful for construction purposes [4].

Industrial application of clay material is determined by its properties and performance. The properties of clay

depend on its structure, mineralogical and oxide composition and the processing methods. Scientific and technological advancements keep opening up discoveries for new areas of application as years roll [4].

However, evaluation of the properties of clays for the development of these industrial products is a difficult task for most local industrialists. Most of them do not have access to the equipment used to carry out these studies. Beside this, previous characterization studies done on clay properties were limited to one or few applications [12, 13, 14, 14, 15]. Hence, there is need to study the properties of some local clays for wider applications and also to give the industrialists access to the information. This will guide them on how to exploit useful clay raw materials to develop relevant industrial products.

Therefore, this study seeks to use standard experimental methods to determine the properties of these local clays and establish their usefulness for industrial applications. Knowledge obtained from this study can assist for best exploitation of clay, help in development of new quality product, promote local content development and will definitely open up new discoveries for further application of this raw material.

## **2.0 MATERIALS AND METHODS**

### **2.1 Materials**

The materials used in this study were two clay samples obtained from deposits in Ameke-Item in Uzoakoli and Akara-Isu in Abia North, both in Abia State, in Eastern part of Nigeria. The equipment and machines used in the work include computerized empyrean X-ray diffractometer, X-ray fluorescence spectrometer (Magi X Pro XRF Spectrometer), electric furnace, (Thermodyne 46200), ceramic kiln (model 88FC2468), electrical transverse strength

machine (model 235), digital weighing machine and ASTM sieves.

## 2.2 METHODS

### 2.2.1 X-ray Diffraction (XRD)

#### Analysis

The samples were prepared for x-ray analysis with backload preparation method as recommended by [13]. The samples of the clays were separately crushed and ground to fine particles. They were further analyzed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and receiving slits with Fe filtered Co-K $\alpha$  radiation. The mineral peak phases were identified using X'Pert Highscore plus software. The receiving slit was placed at 0.040 $^{\circ}$ . The counting area was from 5 to 70 $^{\circ}$  on a 2 $\theta$  scale. The result is graphically shown in Figures 1A and 1B.

### 2.2.2 X-ray Fluorescence (XRF) Spectroscopy Analysis

The chemical oxide composition was determined using x-ray fluorescence with an ARL 9800 XP spectrometer. The method adopted is as recommended in the literature [13]. The results of the chemical oxide composition are presented in Table 1

### 2.2.3 Raw material preparation, processing and moulding of test samples

The raw dry clay samples were crushed in a mortar to fine grain sizes. The samples were soaked in a plastic container of water and allowed for three days [13]. The clay was dispersed and dissolved in excess water. The soluble oxides capable of retarding mullite formation and affecting the high temperature characteristics were decanted out with the excess water to produce clay slurry.

The dissolved clay was sieved using two sieves of 0.425 mm and 0.18mm sizes. The filtrate was allowed to settle for three days after which excess water was

decanted off. The clay slip obtained was sun-dried for 2 days. The processed clay was ground and further sieved to produce finer clay particles of 100 $\mu$ m which was later mixed with 35% water to produce plastic clay material used to mould specimen samples of different sizes which were suitable for the respective tests. The samples were dried at 110 $^{\circ}$ C and thereafter fired at 1200 $^{\circ}$ C before testing for the refractory properties.

### 2.2.4 Determination of the refractory properties of the materials

#### 2.2.4.1 Refractoriness

The refractoriness or softening point was determined using pyrometric cone equivalence (PCE) method in accordance with ASTM C24-79. The refractoriness of the test samples was rated based on their softening temperature and is expressed as their pyrometric cone equivalent which is expressed as the number that represents the softening temperature of sample. The test pieces and the standard cones were mounted in the electric furnace and were heated. The temperature was raised at the rate of 5 $^{\circ}$ C per minute during which softening of Orton cone occurred along with the specimen test cone and until the tips of the test cones had bent over the level with the base. The test sample cones were then compared with the standard cones and were said to have the pyrometric cone equivalent (PCE) of the standard cone that it resembled most in bending behaviour. The refractoriness of each test cone was considered as the number of the standard pyrometric cone that has bent over to a similar extent as the test cone. The temperature corresponding to the cone number was read off from the ASTM Orton series.

### 2.2.4.2 Thermal Shock (Spalling) Resistance

The thermal shock resistance was determined by prism spalling test method according to ASTM C-484 standard with help of an electrical furnace. The thermal shock resistance property was measured as the number of thermal cycles (heating, cooling and testing for failure) withstood before crack or failure occurred. The test pieces of dried refractory bricks were placed in the cold furnace and heated at the rate of 5<sup>0</sup>C/minute until the furnace temperature got to 1200<sup>0</sup>C. The samples were then removed and cooled in air for 10 minutes and then observed for cracks. In the absence of cracks or fractures, the cycle of heating, cooling and observing for cracks was repeated until cracks were observed. The number of complete cycles that produced visible cracks in each specimen was noted. This constituted the thermal shock (spalling) resistance.

### 2.2.4.3 Modulus of Rupture

The electrical transversal strength machine was used to determine this property when a breaking load, (P) of 4.42KN was applied to fracture the sample whose dimensions were 8cm length, 4cm width and 1,5cm height. The other parameters used to calculate the modulus of rupture were the distance between supports of the transversal machine (L), the height (H) and the width (B) of the broken pieces. Thus, the modulus of rupture was then calculated as:

$$\text{Modulus of rupture } \text{N/mm}^2 = \frac{3PL}{2BH^2} \quad (1)$$

### 2.2.4.4 Bulk Density, Apparent Porosity and Water Absorption

ASTM C 20-80a, standard test method for testing for bulk density, apparent porosity and water absorption was used to for this test. The long rectangular shaped test sample measuring 9.5cm length, 2cm width and 5cm height was used to determine these three properties. The

weight in air of the fired specimens were measured using digital weighing balance and recorded as (W<sub>1</sub>) They were later transferred into a vessel of boiling water for 30 minutes after which the boiling was discontinued and the specimens were allowed to cool to room temperature in the vessel of water. The specimens were suspended in a beaker of water and reweighed to get the suspended weight (W<sub>2</sub>). They were later removed from the water and gently cleaned before weighing them again for the third time to get the soaked weight (W<sub>3</sub>). The values of bulk density, apparent porosity and water absorption were calculated using the respective formula:

$$\text{Bulk density (g/cm}^3\text{)} = \frac{W_1}{W_3 - W_2} \quad (2)$$

$$\text{Apparent porosity (\%)} = \frac{W_3 - W_1}{W_3 - W_2} \times 100 \quad (3)$$

$$\text{Water absorption (\%)} = \frac{W_3 - W_1}{W_3} \times 100 \quad (4)$$

### 2.2.4.5 Linear Shrinkage

This test was done to determine dimensional stability of the sample after a given period of time and temperature change and the testing method was in line with ASTM C-326 standard for testing linear shrinkage of refractory material. The lengths of the samples were measured when they were dried and when they were fired as L<sub>1</sub> and L<sub>2</sub> respectively. The linear shrinkage was calculated as:

$$\text{Linear shrinkage (\%)} = \frac{L_1 - L_2}{L_1} \times 100 \quad (5)$$

## 3.0 RESULTS AND DISCUSSION

### 3.1 Results

The results of the mineralogical and chemical oxide analysis of the clays are shown in Figures 1-2 and Table 1 respectively. The refractory properties of the two clays are presented in Table 2.

### 3.1.1 Mineralogical phase analysis for the Clay samples

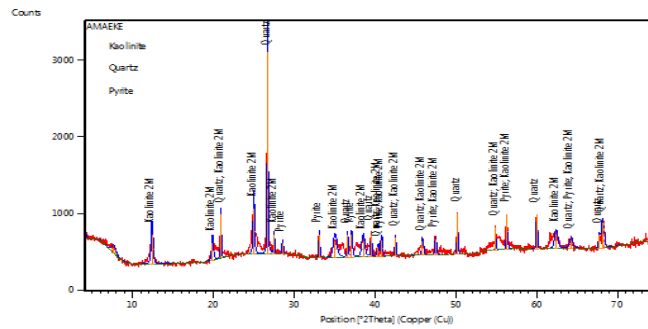


Figure 1A: X-Ray Diffraction Pattern for Ameke-Item Clay Sample

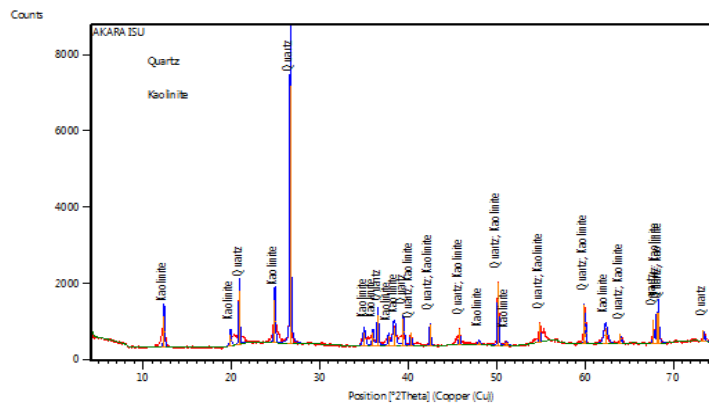


Figure 1B: X-Ray Diffraction Pattern for Akara-Isu Clay Sample

### 3.1.2 The Chemical Oxide Analysis of the Clay Samples

Table 1: Oxide composition of the clay samples.

Oxide	Percentage Composition of Oxide																	
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SiO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CuO	ZnO	Ga <sub>2</sub> O <sub>3</sub>	MoO <sub>3</sub>	Ag <sub>2</sub> O	Re <sub>2</sub> O <sub>7</sub>	Bi <sub>2</sub> O <sub>3</sub>	PbO
Ameke-Item Clay	28	51	6.8	1.53	-	1.43	0.07	0.02	0.05	8.15	0.01	0.01	0.01	0.4	0.78	0.06	1.2	0.62
Akara-Isu Clay	30	58.1	3.5	0.67	0.13	1.76	0.08	0.02	0.02	3.98	0.01	0.01	-	-	0.65	0.05	0.5	-

### 3.1.3 Refractory Properties of the Clay Materials

Table 2: The Refractory Properties of the Clay Materials

Refractory Properties	Ameke-Item Clay	Akara-Isu Clay
Refractoriness( <sup>0</sup> C)	1610	1570
Thermal shock resistance (cycle)	30	29
Modulus of rupture(N/mm <sup>2</sup> )	45	54
Bulk density (g/cm <sup>3</sup> )	1.78	1.88
Apparent porosity (%)	30	22.5
Water absorption (%)	12.66	6.70
Linear shrinkage (%)	4.0	8.4

## 3.2 Discussion

### 3.2.1 Mineralogical phase analysis

The result of the mineralogical phase analysis confirmed the presence of kaoline and quartz in Ameke-Item clay while kaoline, quartz and pyrite were found in Akara-Isu clay. These mineralogical constituents of the clays determine its application. It has been reported that kaoline is a clay mineral which is made up of a layered silicate mineral with one tetrahedral sheet of silica ( $\text{SiO}_4$ ) linked through oxygen atom to one octahedral sheet aluminium [15]. Its ability to disperse in water makes it an ideal pigment [16]. It is usually soft and white with fine particle size and a low shrink-swell capacity and cation exchange capacity [17]. These properties make it useful in many applications such as paper industry. It serves as a paper coating which improves its appearance by contributing to brightness, smoothness, gloss and printability. It is also used as filler in paper industry to reduce cost. Other industrial applications include production of paint, cable insulation and fertilizer [16]. It has also been reported that kaoline is a type of clay mineral widely used in the manufacture of catalyst because of its refractory characteristics at high temperature. This confirms the clay's suitability for use as catalyst substrate in the catalytic cracking of petroleum as reported by Murray, (2007) [18]. Its application extends in the synthesis of zeolite which is used as catalyst in the petroleum and petrochemical industries [19].

The presence of quartz in the two clay samples as revealed by the x-ray diffraction result is an indication of their potential for the development of a lot of industrial products. Quartz is a hard crystalline mineral composed of silicon and oxygen atoms which are linked in a continuous frame work of silicon-oxygen tetrahedral ( $\text{SiO}_4$ ) [20]. They are used in

glass industries for production of glass container, glass plate and fiber glass [21]. Quartz is chemically inert when in contact with most substances. It also has electrical and heat resistance properties which make it valuable in the production of electronic products [21]. Hence, it is a component raw material for the production of electrical porcelain insulator used in electrical power transmission.

Quartz has been reported to have the ability for its crystal to vibrate at a precise frequency. This makes it useful as crystal oscillators. These frequencies are exact which indicate that quartz crystals can be used to make extremely accurate time keeping instrument and equipment that can transmit radio and television signals with precise and stable frequencies. Literatures have also shown that quartz sands are used in petroleum industry to force down oil and gas into wells under very high pressure. This fractures reservoir rocks and keeps it open after the release of the pressure which facilitate the flow of natural gas into the well bore [21].

### 3.2.2 Chemical Oxide Composition Analysis

The percentage oxide constituents of the clays are shown in Table 1. It indicates that Ameke-Item contains  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_3$  at the respective compositions of 28%, 51%, 8.15% and 6.8%. Other oxides were found in trace quantities. The result also shows that the sample of Akara-Isu clay contained  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_3$  as the dominant oxides having the percentage composition of 30%, 58.1%, 3.98% and 3.5% respectively. These dominant oxides have much influence on the behaviour of the clay materials. According to the results obtained, it was found that both clays have high alumina silica ratios ( $\text{Al}_2\text{O}_3/\text{SiO}_2$ ). This has been reported as an indication of industrial potential for the development of high refractoriness under load. The presence of alumina is responsible for initial formation of a liquid phase which

produces a suitable bond for refractory material [22].

The iron oxide content in the two clays is high and such percentage composition of the oxide usually imparts a reddish colour to the clay when fired [1]. This is evident in the reddish colour of the fired samples. The reddish coloration enhances its esthetic value and qualifies it for ceramic and structural application.

The alumina content of both clay falls within the range of refractories [1]. Its content in the clay is a strong indicator of refractoriness. This dictates the temperature at which the sample begins to deform under its own weight and hence, makes it suitable for production of refractory bricks utilized for lining the furnaces.

### **3.2.3 Refractory Properties of the Clay Samples**

#### **3.2.3.1 Refractoriness**

From the results obtained in physico-mechanical property tests, it was observed that the refractoriness of 1610<sup>0</sup>C and 1570<sup>0</sup>C were obtained in Ameke-Item and Akara-Isu clay respectively. These values are within the acceptable range of 1500 – 1700<sup>0</sup>C required for refractoriness of a refractory product as reported by [23, 24]. High refractoriness in clay material is traceable to the percentage constituent of alumina. The presence of alumina is responsible for mullite formation which has direct effect on the refractoriness.

#### **3.2.3.2 Thermal Shock Resistance**

Thermal shock resistance test shows that Ameke-Item clay and Akara-Isu clay has 30 and 29 cycles. This refers to the resistance performance of the clay materials to sudden change of environmental temperature condition which can cause crack, failure or damage of the product during service. The values of thermal shock resistance yielded by the two clays were found within the specified standard of 25 – 30 cycles for refractory

material [25,26]. The excellent thermal shock resistance observed in the material is traced to thermal expansion, thermal conductivity, structure, and grain composition [27]. Porosity in clay structure is inversely related to its thermal conduction capacity [28]. Therefore, the high value of apparent porosity in the clay sample was assumed to have enhanced its insulating characteristics which improved the thermal shock resistance property. This quality indicates that these clay materials would be suitable for production of furnace lining used for high temperature engineering processes.

#### **3.2.3.3 Bulk Density, Apparent Porosity and Water Absorption**

It has been reported that these three properties are interrelated [26]. The values of apparent porosity in Ameke-Item clay and Akara-Isu clay are 30 and 22.5% respectively. These values indicate good insulating behaviour required in bricks used for insulating purpose. The values correlate with bulk density values of 1.78 and 1.88g/cm<sup>3</sup> and water absorption values of 12.66 and 6.77% of the respective clays. It follows that high apparent porosity yields low bulk density with more rate of water absorption. These properties depend on clay mineralogy, oxide composition and processing method. These properties were appropriate when compared with accepted standard for refractory bricks production. [10, 23]

#### **3.2.3.4 Linear Shrinkage**

Linear shrinkage values of 4.0 and 8.40% were obtained in Ameke-Item and Akara-Isu clays respectively. These values are within the range of value of 4 -10% recommended [29]. This indicates good stability of the material.

#### **3.2.3.5 Modulus of Rupture**

The values of modulus of rupture for Ameke-Item and Akara-Isu clays are 45 and 54N/mm<sup>2</sup> respectively. This indicates a

good transverse strength in the clay materials. It was noted that the values obtained for this test in the two clays show that the modulus of rupture is inversely related to the apparent porosity. This was confirmed by the high apparent porosity and low modulus of rupture value for Ameke-Isu clay. This correlates with the fact that in clay-based systems, strength decreases with increase in porosity [28].

#### 4.0 CONCLUSIONS

From the results obtained in this study, the following conclusions were drawn:

1. The two clay samples are composed of kaoline and quartz minerals as the major minerals. This qualifies them as potential raw materials for many industrial applications such as paper making, glass making, fertilizer production, catalyst for petroleum production, porcelain insulator, etc.
2. The clay materials possess excellent refractory properties suitable for foundry application.
3. The high quantity of iron oxide in the two clays which added reddish coloration to the clay bricks makes them useful in structural application as well as in production of ceramic wares.
4. It is needful to exploit these local raw materials for the development of industrial products in the country.

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