Characterization of Ezzodo clay deposit for its industrial potentials

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Abstract

This study evaluates the characterization of Ezzodo clay obtained from Enugu state, Nigeria for its industrial applicability. The chemical analysis of the clay showed silica (61.83%) and alumina (16.43%) as the major constituents while other metal oxides such as Fe_2O_3 (6.48%), CaO (1.85%), K_2O (2.26%) and Na_2O (1.31%) are present in appreciable amounts. The physical analysis showed a variation in the linear shrinkage (1.31 to 5.72%), total shrinkage (5.06 to 9.46%), apparent porosity (35.78 to 27.62%), apparent density (2.55 to 2.43 g/cm^3), bulk density (1.67 to 1.73 g/cm^3), water absorption (21.85 to 16.86%) and modulus of rupture (19.32 to 32.36kgF/cm^2) with increase in firing temperature from 900 to 1200^{0}C. The clay showed moderate plasticity with a modulus of plasticity of 1.35 and had a refractoriness of up to 1200^{0}C. The result of this study showed that Ezzodo clay has good industrial potentials and can be utilized in the manufacture of ceramics, high melting clays, refractory, bricks, tiles and colour vase but requires additives to help obtain the desired properties. It can therefore be utilized to help reduce the bulk of clay minerals imported from foreign nation into Nigeria.

Keywords: Ezzodo clay, physicochemical characterization, ceramics, Industrial potentials.

1.0 Introduction

Clay can simply be referred to a product formed from the disintegration or chemical weathering of feldspathic rock and is a viable mineral that exhibits high economic significance and usefulness [1]. It is an unconsolidated rock matter, with very fine grain which is plastic when wet and undergoes certain transformation to become hard when heated.

The ceramic industries are the major users of clay. These industries consume about 70% of all clays marketed in crude or beneficiated form and those marketed only as finished products [2]. Clay is mainly composed of silica, alumina and water plus appreciable concentration of oxides of iron, alkali and alkaline earth, and contains groups of crystalline substances known as clay minerals such as quartz and feldspar [2]. The presence of the minor oxide impurities occurring in variable amounts in clays tends to impart some properties to the clay which are of technical value. Characterization of the clay available in any region helps in its applicable and general usage either in ceramic, drilling mud, refractories, plastics, paints, textiles and adhesives, paper foundry, pharmaceuticals, rubbers [3].

Many researchers have over the years carried out studies on the characterization and properties of clays found in different parts of Nigeria in order to provide useful information on their applicability [4-8]. Consequently, such clays as mayo-belwa, nsu, ukpor, afuze, usen, uzalla clay, kankara, adiabo and dabagi have been characterized and found useful applications for industrial purposes and ceramics [2, 9, 10]. However, the local demands for ceramic products are very high considering the population yet most of the products are imported. Presently, Nigeria spends about five billion naira annually in the importation of ceramic products. Nigeria imports more than 50 containers of ceramics products daily into the country [2]. This is not encouraging, despite the availability of both raw materials and human capacity for research and production of ceramics products of international standard and quality. Another major problem is the fact that most of the imported ceramic wares are made with colours and glazes that are not consumable and very dangerous to the human body [11]. Presently, there is a growing demand for ceramics wares such as dinner, sanitary and pottery wares, floor and wall tiles, ceiling fittings, spark plugs, beryllium oxide ceramics, chemical and refractory porcelains, electrical porcelain insulators, combustion chambers for engines and furnaces and decorative wares [4].

Therefore, in response to the challenges posed by high demand for clay base materials in Nigeria, the industrial potential of most clay deposits in Nigeria needs to be investigated.

In south eastern Nigeria there is an abundance of clay deposits which have not been characterized and may be useful in the manufacture of ceramics and most industrial products. Essodo clay is one of such which is present in abundant amounts in Igbo-Eze north local government area of Enugu state Nigeria. Despite the high concentration of the clay, there is scarcity of information on its properties or characterization for its industrial applications. This study therefore investigates the characterization and potentials of Ezzodo clay for its industrial uses to help reduce the high rate of importation of clay products in Nigeria. The chemical and physical properties of Ezzodo clay was determined and related to the application in the manufacture of useful industrial products.

2.0 Materials and Methods

2.1 Sample collection and pretreatment

Ezzodo clay sample was obtained by random sampling at different points in Ezzodo, Igbo-Eze north local government area of Enugu state, Nigeria. The samples were taken at a depth of 1.55 m and mixed properly to obtain a homogenous mixture. The cone and quartered method was employed to obtain a representative sample as described [10]. Thereafter, the collected clay was dispersed in excess water in a pre-treated plastic container and stirred vigorously to ensure proper dissolution. The dissolved clay was then filtered through a 0.425 mm mesh sieve to get rid of unwanted particles and plant materials. The filtrate was allowed to settle, after which excess water was decanted off. The clay was then sundried and oven dried at 100 ^{0}C for 3 hr, pulverized and passes through a mesh sieve of size 0.18 mm. 1.6 kg of the clay was weighed and mixed with appropriate amount of water to make it plastic for the molding process.

2.2 Molding of the Test Pieces

The clay was then molded into three types of shapes using metallic moulds and the application of lubricants to the surface of the moulds to prevent the test pieces from sticking to the surface. The first shape is cylindrical with a width of 3.5 cm and height 3 cm, the second is a rectangular piece with length 8 cm, width 4 cm and height 1.5 cm, while the third has a long rectangular shape with length 9.5 cm, width 2 cm and height 1.5 cm.

2.3 Making Moisture Determination

This was determined by weighing the cylindrical test pieces immediately after molding and recorded as the wet weight, *Wo*. The test pieces air-dried for 24 hr and then dried in an oven at 105 ^{0}C until a constant weight was recorded. After drying the test pieces were weighed and the dried weight recorded as *Wi*. The making moisture was then calculated.

$$\text{Making Moisture (\%)} = 100[Wo-Wi]/Wo$$

2.4 Determination of modulus of Plasticity

The relative plasticity was determined using the cylindrical test pieces. The original height, *Ho* of the test pieces were obtained by the use of the venier caliper by taking the average of three sides. Afterwards, a manual plastometer machine was used to deform the test pieces. The deformation height, *Hi* was recorded taking the average of three sides. The relative plasticity was then calculated [12]:

$$\text{Relative Plasticity} = Ho/Hi$$

2.5 Determination of Modulus of Rupture

Five long rectangular test pieces were made and air dried for 7 days after which they were oven dried at 105 ^{0}C until a constant weight was obtained. Four of the pieces were fired to their respective temperatures of 900, 1000, 1100 and 1200 ^{0}C in a laboratory kiln (Fulham Pottery). The electrical transversal strength machine was used to determine the breaking load, P (Kg). A vernier caliper was used to determine the distance between support L (cm) of the transversal machine. The height, H (cm) and the width, B (cm) of the broken pieces were determined and the average value obtained from the two broken parts was recorded. The modulus of rupture was then calculated [9]:

$$\text{Modulus of Rupture } (KgF/cm^2) = 3PL/2BH^2$$

2.6 Shrinkage Determination

Immediately after molding of the rectangular test pieces, a vernier caliper was used to insert a 5 cm mark on each of them, this was recorded as the original length *Lo* (cm). The test pieces were then air dried for 7days and then dried in an oven at 105 ^{0}C until a constant weight was obtained. The shrinkage from the 5 cm mark was then determined and recorded as the dried length, *Ld* (cm). Afterwards, four of the dried samples were fired to their respective temperatures of 900, 1000, 1100 and 1200^{0}C each temperature corresponding to a particular test piece. The shrinkage of the test pieces from the 5 cm mark were then determined and recorded as the fired length, *Lf* (cm). The shrinkage was then calculated [2]:

Dry Shrinkage (%) = 100[Lo - Ld]/Lo

Linear Shrinkage (%) = 100[Ld - Lf]/ Ld

Total Shrinkage (%) = 100[Lo – Lf]/ Lo

2.7 Determination of Water Absorption

The fired test pieces obtained after firing were then weighed and the weight recorded as dry weight, *M1* (g). Thereafter, the test pieces were soaked in water for one hour, then removed, cleaned and weighed immediately and recorded as soaked weight, *M2* (g). The water of adsorption was then calculated:

Water Absorption (%) = 100 [M2 – M1]/ M1

2.8 Porosity and Density Determination

After the procedure described for water absorption was completed. The suspended weight of the test pieces were then determined by the use of a lever balance and recorded as *M3* (g). The apparent porosity, apparent density and bulk density were then calculated:

Apparent Porosity (%) = 100 [M2- M1]/ [M2 – M3]

Apparent Density (g/cm^3) = M1/[M1 – M3]

Bulk Density (g/cm^3) = M1/[M2 – M3]

2.9 Loss on Ignition

The weight of an empty porcelain crucible was determined and recorded as W1 (g), 2.0 g of the dried pulverized clay was added and the weight of the crucible + clay was determined, W2 (g). The sample was then ignited in the laboratory kiln at 1200 ^{0}C. After the cooling of the sample the weight of the crucible + sample after ignition was determined, W3 (g). The loss on Ignition was then calculated:

Loss on Ignition = 100[W2 – W3]/ [W2 – W1]

2.10 Chemical Analysis

0.2 g of the clay was weighed into a beaker and 10 mL of aqua regia (HCl + HNO_3 in the ratio 3:1 respectively) was added and digested in a hot plate in a fume cupboard. 10 mL of Hydrofluoric acid was also added to aid the digestion process. After digestion 30 mL of de-ionized water was added and the mixture filtered through a filter paper into a 250 mL volumetric flask and made up to the meniscus mark with de-ionized water. The sample was then analyzed for the elemental composition by the use of the Atomic Absorption spectrophotometer (AAS) (Buck scientific model 210 VGP). The concentration of metal oxide in the clay was expressed in mg/L. The percentage composition of the elements in the clay was calculated from the equation:

% Composition = 100CV/M

Where C (mg/L) is the elemental composition obtained from the AAS, V (L) is the volume of the volumetric flask in which the digested solution was diluted and M (mg) is the mass of sample digested.

3.0 Results and Discussion

The result for the chemical analysis of Ezzodo clay is shown in Table 1. It is observed that silica (SiO_2) and alumina (Al_2O_3) form the major composition of the clay while other metal oxides are present in smaller amounts. The silica content of Ezzodo clay was found to be high and this satisfies the requirement for the manufacture of ceramics (>60.5%), refractory bricks (>51.7%) and high melting clays (53-73%) [13]. However, the silica level was found to be lower than that required for glass (80-90%) but higher than that for paper (45.0-45.8%) and paint (45.3-47.9%) [14]. The alumina composition of Ezzodo clay however fell short of the requirement for the manufacture of ceramics (>26.5%), Refractory bricks (25-44%), paper (33.5-36.1%), paint (37.9-38.4%) but met the standard required for high melting clays (16-29%) and glass (12-17%) [13, 14]. The percentage composition of alumina in clay is a strong indicator for its refractoriness and the higher the amount of alumina the more refractory the clay [10]. The low percentage of alumina indicates that Ezzodo clay is likely to have low or moderate refractory properties. The Fe_2O_3 content of Ezzodo clay was quite high and above the standard required for ceramics (0.5-1.2%), refractory bricks (0.5-2.4%), glass (2-3%) and paper (0.3-0.6%) but below that required for paper production (13.4-13.7%) [10]. However, the clay can stilled be used in the manufacture of high melting clays which requires only 1-9% of Fe_2O_3 as reported by Grimshow [14]. Furthermore, such high levels of iron oxide usually give a reddish colour to the clay body when fired making it suitable for some ceramic products such as flower vase which requires such colouration [10]. The presence of Fe_2O_3 was responsible for the reddish-brown colouration obtained after firing as shown in Table 1. The coloration makes the clay unsuitable for white ware products [1]. However, the iron content in the clay may be desirable, acting as fluxes in infusible products and highly refractory materials [9]. This is because the high iron content in the clay greatly affects the high temperature characteristics of the clay [10].

Table 1: Physicochemical properties of Ezzodo clay

Parameters	**Value**
Al_2O_3 (%)	16.43
SiO_2 (%)	61.83
Fe_2O_3 (%)	6.48
CaO (%)	1.85
K_2O (%)	2.26
Na_2O (%)	1.31
MgO (%)	0.63
MnO (%)	0.14
LOI (%)	8.79
Colour before firing	Grayish brown
Colour after firing	Reddish brown
Refractoriness (^OC)	1200
Modulus of Plasticity	1.35
Making moisture (%)	22.61
wet-dry shrinkage (%)	3.7

The presence of alkali oxides (CaO, K_2O and Na_2O) in reasonable amounts in Ezzodo clay as shown in Table 1 indicates the good fluxing ability during firing at low temperatures to form glasses of complex composition towards giving a vitreous structure to the ceramic product [11]. The presence of these oxides in clay acts as mild fluxes, they combine with the oxides of silica and alumina on firing to for eutectics and so reduce the vitrificaion temperature and refractoriness of the clay [15]. This again suggests that Ezzodo clay is likely to have low or moderate refractory properties as stated earlier. As observed in Table 1, the Loss on Ignition (LOI) of Ezzodo clay is 8.79% which accounts for the water vapour from dehydroxylation reactions in the clay minerals, carbonate decomposition into CO_2 and oxides as well as burning out of organic matter or other impurities present in the clay [11]. The LOI of Ezzodo clay was within the standard for the manufacture of ceramics (>8.18%), refractory bricks (8-18%) and high melting clays (5-14%) [14]. A low LOI is sometimes desired in the manufacture of low porous ceramic products, as a higher LOI usually implies higher porosity in the manufactured products due to the removal of LOI components during firing. As shown in Table 1, Ezzodo clay had moderate refractory properties and did not show any sign of failure at 1200 ^{0}C. However, at higher temperatures of 1300 ^{0}C signs of failure were observed. The implication is that, although the sintering level was high, it is not enough to fall within the internationally accepted range of 1580-1750 ^{0}C for refractory materials

[2], this result is corroborated by the low alumina and the presence of alkali metal oxide fluxes in Ezzodo clay which reduces its refractoriness. Similar refractoriness was reported by Abuh et al [2] in the characterization of adiabo clay for its industrial potentials.

Some of the physical properties of Ezzodo clay determined after firing at temperatures of 900 to 1200 ^{0}C are shown in Figs 1-7. The shrinkage of a clay body after firing is a very important factor to be considered. This is because high shrinkage values may result in warping and cracking of the clay and this may result in loss of heat and create an undesired finished product. The result for the linear shrinkage of Ezzodo clay after firing at different temperatures is shown in Fig 1. It is observed that an increase in the linear shrinkage of the clay from 1.31 to 5.72% with increase in the firing temperature from 900 to 1200 ^{0}C was recorded. This decrease may be attributed to the removal of certain components in the clay body with increase in temperature resulting in the sintering and subsequently vitrification of the clay body. This implies that as the temperature is increased the body tends to compress and may result in decrease in porosity. The linear shrinkage of Ezzodo clay at firing temperatures of 1100 ^{0}C (4.57%) and 1200 ^{0}C (5.72%) was within the range of 4-10% required for fireclays [10]. However, the values are lower than the standard of 7-10% for aluminosilicates and kaolinites [16]. This might indicate that Ezzodo clay is not from a kaolinite origin as deduced from the low percentage of alumina present. The low shrinkage values suggest a high content of non-fluxing impurities [2]. Also, Fig.2 showed an increase in the total shrinkage of Ezzodo clay from 5.06 to 9.46% with increase in the firing temperature. However the total shrinkage and the wet-dry shrinkage (Table 1) are of little importance since their values change with the making moisture during firing [2]. As seen in Table 1, the making moisture of 22.61% was obtained for Ezzodo clay which is quite high and accounts for the wet-dry and total-shrinkage recorded due to removal of such water during drying.

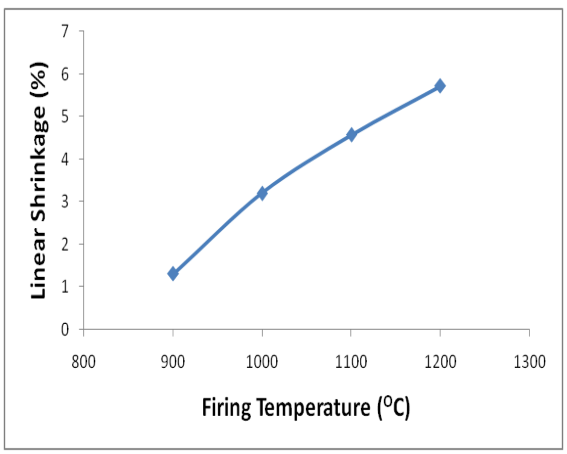

Fig.1: Effect of firing temperature on the linear shrinkage of Ezzodo clay

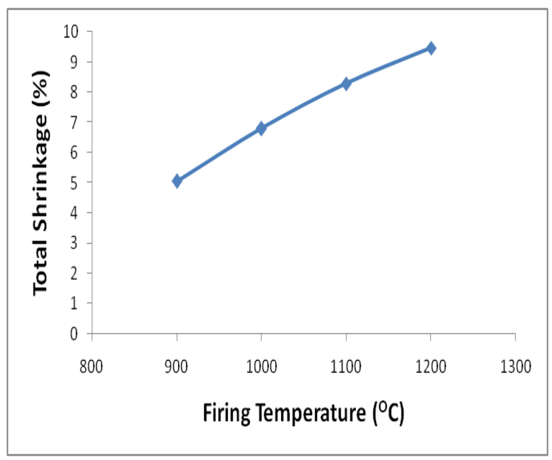

Fig.2: Effect of firing temperature on the total shrinkage of Ezzodo clay

The apparent porosity of Ezzodo clay with firing temperature is shown in Fig. 3. A decrease in the porosity from 35.78 to 27.62% with increase in firing temperature was observed. This decrease is due to the increase in shrinkage with increasing temperature as stated earlier, which resulted in the coming together and closure of the pores of the clay body. The values of the apparent porosity was within the range of 20-80% required for the manufacture of fire bricks [17] but higher than the standard range of 20-30% and (>23.7%) for production of fireclay and siliceous fireclays respectively [3]. However, the apparent porosity of 27.62% obtained at 1200 ^{0}C for Ezzodo clay was within the range. The clay could still be utilized in the production of insulating materials by the addition of some carbonaceous materials to help improve its porosity and insulating properties. Also, the slightly high porosity of the clay can be reduced drastically by the addition of glaze in the final product when a porous surface is not required in the manufacture.

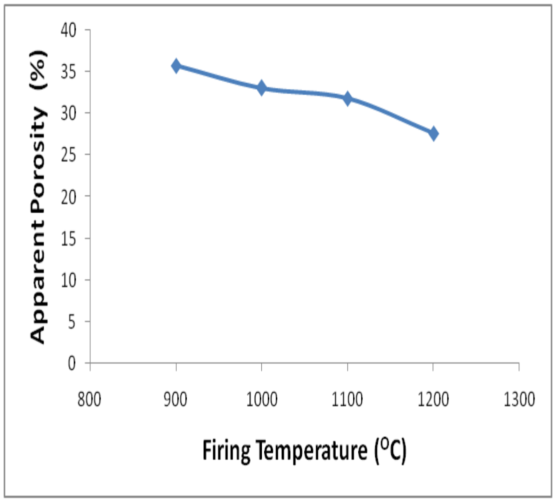

Fig.3: Effect of firing temperature on the apparent porosity of Ezzodo clay

The bulk density of Ezzodo clay showed an increase from 1.67 to 1.73 g/cm^3 with increase in firing temperature (Fig. 4). This implies that the clay becomes more compact and dense as the shrinkage increases and thus is expected to have a progressive increase in strength of the clay body. A reverse trend was obtained in Fig.5 for the apparent density in which a decrease from 2.55 to 2.43 g/cm^3 was observed with increase in firing temperature. This is expected as the apparent density always shows an opposite trend to the bulk density of fired clay bodies. The apparent density is seldom discussed in most publications from literature in details as the bulk density, as the later is related to the weight of the body to an extent. The bulk density of Ezzodo clay obtained at 1100 ^{0}C and 1200 ^{0}C of 1.70 g/cm^3 and 1.73 g/cm^3 respectively was within the internationally accepted standard of 1.7-2.1 g/cm^3 required for building and fireclays [18]. The same also applies to the apparent density which was within the standard range of 2.3-3.5 g/cm^3 as reported by Ryan [19].

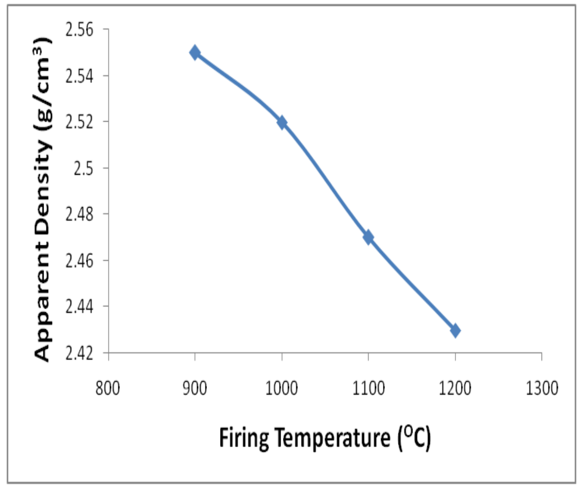

Fig.5: Effect of firing temperature on the apparent density of Ezzodo clay

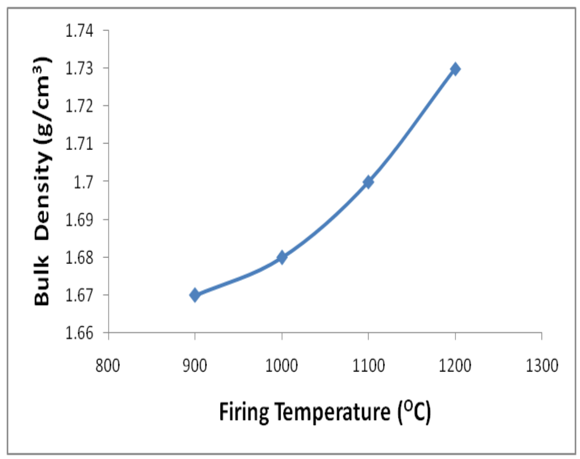

Fig.4: Effect of firing temperature on the bulk density of Ezzodo clay

The result of the water absorption of Ezzodo clay at different firing temperatures is shown in Fig.6. From the result, a decrease in the water absorption with increase in firing temperature of the clay was recorded. In fact, with increase in the firing temperature of the clay from 900 to 1200 ^{0}C the water absorption showed a decrease from 21.85 to 16.86%. This decrease is attributed to an increase in shrinkage and decrease in porosity of the clay body with increase in firing temperature. The presence or addition of glaze to the clay body also helps reduce the water absorption when required due to the reduction in porosity as stated earlier.

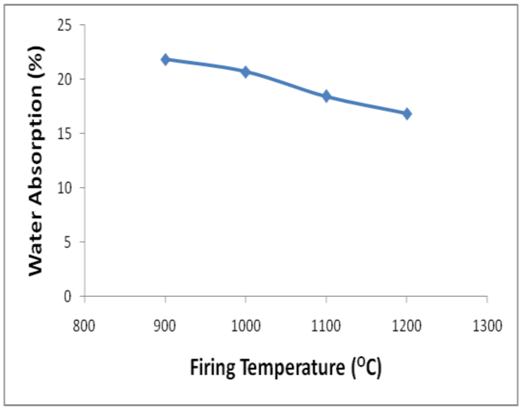

Fig.6: Effect of firing temperature on the water absorption of Ezzodo clay

Fig.7 showed an increase in the strength or modulus of rupture (MOR) of Ezzodo clay with increase in firing temperature. An increase in the MOR from 19.32 to 32.36 kgF/cm^2 with increase in the firing temperature from 900 to 1200 ^{0}C was recorded. This increase is due to the fact that the clay body becomes more compact and rigid as temperature increases as the body shrinks together. The increase can also be attributed to bond formation in the glassy phase of the body [9]. The alkali metal oxide fluxes in the clay body combine to form some considerably low temperature melting compounds, which increases the strength of the body on cooling. The MOR obtained at all temperatures was within the wide range of 1.4 to 105 kgF/cm^2 generally required for the manufacture of a wide variety of product [9]. Also, the breaking load of Ezzodo clay obtained at temperatures of 1200 ^{0}C was greater than 12kg which indicated a high shear strength of the clay body [2].

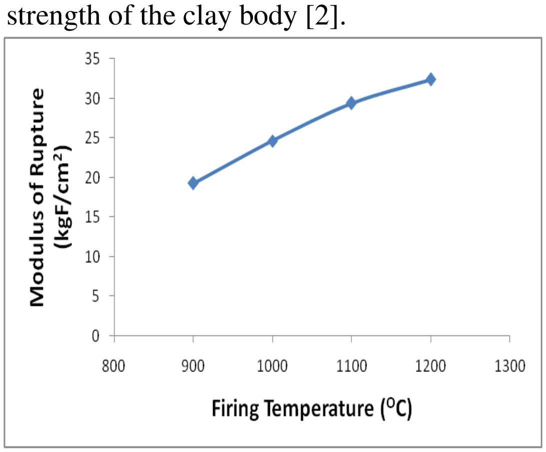

Fig.7: Effect of firing temperature on the total shrinkage of Ezzodo clay

The modulus of plasticity of Ezzodo clay as shown in Table 1was found to be 1.35, this is higher than that of 1.33 reported for adiabo clay which was said to have moderate plasticity [2]. The higher values reported for Ezzodo clay indicated better or higher plasticity which is desirable as the clay will tend to have good workability and can easily be moulded into shape. The plasticity recorded makes the clay suitable for many industrial products but the high Fe_2O_3 content and other oxide impurities limits its use in white wares and refractory. However, the clay can be utilized as an additive to improve the plasticity of short clays. The moderate plasticity of Ezzodo clay may be due to the low alumina content and the high silica content recorded. Similar results have been reported by other researchers [2, 9, 20].

4.0 Conclusion

The results of this study showed that Ezzodo clay has moderate refractory properties and can be used as part of the body formulation for high temperature refractory products. The high strength and moderate plasticity indicates its usefulness as an additive for short clays. The clay was found to be suitable for the manufacture of ceramics, high melting clays, refractory bricks, tiles, colored vaze and even porcelain but not solely. In the sense that other materials need to be added to achieve the desired properties or that Ezzodo clay can be used itself as an additive to other clays in the manufacture of a wide variety of products.

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