

Refractory Properties of Alumina/Silica Blend

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Abstract: In this paper, refractory properties of a blend of alumina/silica fired at 800, 900 and 1,000 °C for varying times of 30 minutes, 1, 3, and 5 hours are validated against those of standard indigenous kaolinitic clay. Characterisations of the indigenous clay and blend using X-ray fluorescence complemented with X-ray diffraction (XRD) in relation to literature revealed that the indigenous clay is essentially siliceous alumina-silicate containing about 51% silica and 40% alumina with high content of alkali oxide but low ferrous oxide content. XRD analysis of the synthetic alumina/silica blend showed that the firing temperature and time only had significant effect on the phase transformation at temperature of 1,000 °C and time of 5 hours. At this condition, marginal presence of tridymite was identified in the alumina/silica blend. Further refractory tests of shrinkage, bulk density, water absorption rate, apparent porosity, cold compression strength reinforced with scanning electron micrography present pronounced colour variation in the indigenous kaolinitic clay across the firing conditions which is absent in the alumina/silica blend. The synthetic alumina/silica blend exhibits refractory properties that approximate those of standard alumina-silicate for refractory purposes. Linear shrinkage in the refractory blend is within permissible limit of 0-4%, bulk density 1.55-1.89 g/cm³, water absorption is 21.7-30.4 % while compressive strength is in the range 1,125-2,017 KN/M². The apparent porosity at 45% is however outside the standard for fireclay refractory. These results suggest that a blend of alumina/silica can be explored for refractory purpose.

Keywords: Firing conditions, morphology natural clay, refractory properties, silica-alumina blend

1. Introduction

Traditional refractories for the lining of metallurgical furnaces, and other related process reactors are usually sourced from inorganic non-metallic oxides or metallic oxides such as SiO₂, Cr₂O₃ or clay based materials (Esezobor et al., 2014; Sugita, 2008) which is a composite of these nonmetallic and metallic oxides (Al₂O₃, SiO₂, MgO) (Dmitrij, 2011; Gupta, 2008). These materials must necessarily possess high melting temperature greater than 1500⁰C coupled with excellent resistance to molten metal, ferruginous slag and flue gases (Titiladunayo and Fapetu, 2011, Gosin and Karaklit, 2010). In addition, they must be able to bear the burden of the furnace without failure.

Clays of the kaolinitic group have been found to possess these attributes and as such, represent the natural source of raw-materials for the production of refractories of all forms, shapes and application. The specific kaolinitic group known as fireclay which is basically aluminosilicate (Al₂O₃.2SiO₂.xH₂O) has had the widest exploration for refractory purpose owing to its ease of fabrication, excellent resistance to chemical attack; and

being relatively inexpensive compared to other clays. Thus, the fireclay group finds application as insulation behind hot-face materials, furnace linings, and specialty applications such as laboratory crucibles and setters (Andrews et al., 2013). This group however varies in the distribution of the major constituting oxides depending on the history of the geological process that had occurred in a particular deposit site. Therefore, composition of alumina and silica in fireclay alumina-silicates range between 25-45% and 50-80%, respectively (Sadik et al., 2014). Invariably clay deposits having alumina and silica content within this range may be considered adequate for the production of refractory bricks or insulators.

However, it has been reported that the alumina and silica contents are not the only parameter that determines the adequacy or otherwise of a particular clay type for refractory purposes. Some other constituents such as the distribution of combustible materials, alkali metal oxides and ferrous oxide equally influence the qualification of clay for refractory purpose. For instance, Hassan (2005) and Jock et al. (2013) reported that impurity oxides such as TiO₂, Fe₂O₃, CaO, MgO and alkali oxides act as

fluxing agents at high temperatures decreasing the eutectic temperature of aluminosilicate refractories. Tripathi et al. (2012) equally stated that these oxide combine with mullite to reduce the refractoriness of alumina. They also facilitate the development of liquid phase in the clays at high temperature (Amkpa et al., 2017). So, there is a close window on the distribution of these oxides in fireclay. Thus, the quality of any fireclay refractory is primarily dependent on the distribution of these impurity oxides in the clay and this eventually determines the environment and conditions of application.

Though, Nigeria is credited with extensive clay endowments which could be explored for refractory purposes. Preliminary findings on the mineral/chemical constituents indicate that the deposits are mainly of the kaolinitic group but with wide variations in the distribution of impurity oxides (Musa et al., 2012; Akinwale, 2008; Borode et al., 2000; Hassan and Adewara, 1993). Detailed investigations demonstrate that these deposits have alumina/silica distribution in the range Al_2O_3 (28-45%)/ SiO_2 (65-85%) (Sadik et al., 2014). Such distributions of alumina/silica content falls within the specification for refractory brick as provided in American Society for Testing and Materials (ASTM) standard (ASTM F1312-90, 2013). However, Hemrick et al. (2005) shows that the refractory properties obtained from these clays are broadly inadequate to permit their wholesome deployment as containment/insulation linings for high temperature and corrosive environments. This shortcoming has been related to the wide distributions of the impurity oxides in these clays. Hence, several investigators (Apeh et al., 2014; Esezobor et al., 2014; Tripathi et al., 2012; Amuda et al., 2005; Lawal et al., 2005) have either blended clays from different deposits, or introduced some organic material to improve refractory and insulating properties. In some instances, ceramic metallic oxides were equally blended with clays to improve either thermal shock resistance or linear shrinkage (Apeh et al., 2010; Apeh et al., 2011; Apeh et al., 2013).

Amuda et al. (2005) blended Onibode and Ijoko clays both from Ogun State, South West, Nigeria to improve the refractory properties of individual clays. While, some improvements in refractory properties were reported, the issue of the distribution of impurity oxides such as iron oxide and alkali oxides was not addressed. Lawal et al. (2005) improved insulating properties of clays by blending with cowdung generating about 40% increase in porosity resulting in corresponding improvement in insulation. Hassan and Aigbodion (2014) blended Kankara clay from Katsina State in Nigeria with coal ash in amount between 5 and 25% to enhance linear shrinkage, cold crushing strength and thermal shock resistance of the clay. And few years ago, Apeh (2014) enhanced refractory properties of some local clays by blending with alumina. These works reported improvement in refractory properties of the

relevant clays but the presence and distribution of the alkali metal oxides and other combustible materials were not investigated; whereas literature has shown that these oxide do have deleterious effect on refractory property (Omotoyinbo, 2008).

Therefore, it appears that if a blend of pure quartz and alumina is explored, it may be possible to generate synthetic aluminosilicate refractory clay devoid of the deleterious impurity oxides with properties comparable to those of standard refractory clay. More so, Sadik et al. (2014) highlighted some reported works on the blending of quartz and alumina to generate aluminosilicate refractory with zero presence of impurity oxides and combined moisture. But such strategy has not been adopted and reported widely; and thus, little or no information is available on the derivable refractory property from such novel blend. This has prevented wide scale commercial production of such synthetic aluminosilicate clay. Therefore, in the present work, the refractory properties of synthetic aluminosilicate generated by blending virgin silica sand with processed alumina are presented. This is essentially an exploratory investigation that seeks to provide the foundation for further extensive study in this area.

2. Materials and Methods

2.1 Materials and Preliminary Treatment

Virgin clay was mined from Lagos Mainland, South West, Nigeria on a global position system (GPS) Latitude N $6^\circ 30.502'$ and Longitude E $3^\circ 23.055'$ at a depth of 1 m below the surface. Silica sand was obtained from Badagry Beach, Badagry, South West, Nigeria on a GPS Latitude N $6^\circ 25'$ and Longitude E $2^\circ 53'$ at the Seashore while processed alumina was provided by an aluminum primary smelter plant. The virgin mined clay formed via surface weathering (erosion) may contain some other impurity elements which may influence its refractory properties. Viscous sodium silicate was used as a binder. A stainless steel cylindrical mould with detachable base was fabricated. Figure 1 shows the processed clay, silica sand, alumina and the fabricated stainless steel cylindrical mould.

The as-mined clay was crushed using a jaw crusher, vigorously agitated in 20 liter water and soaked for seven days; after which the clarified water was sieved off. The water soaking was necessary to remove both live and dead organic matters (lighter materials and as such floated on the surface of the water) which could have affected the physico-chemical characteristics of the clay. The clay sediment was then sun-dried for about fourteen days producing a caked lump of clay. Maximum drying was obtained at fourteen days because below this duration, the water absorbed into the clay during soaking was not completely dried-off. This is so because Clay is ordinarily characterized by slow drying behaviour (Bennour et al., 2015). The sun-dried clay was re-crushed, pulverized and sieved through an 80 μm

aperture sieve to obtain fine clay. The silica sand and alumina were similarly treated to remove contaminants. However, in the case of alumina, a further controlled heating (pyrolysis) to drive off combined water was conducted.

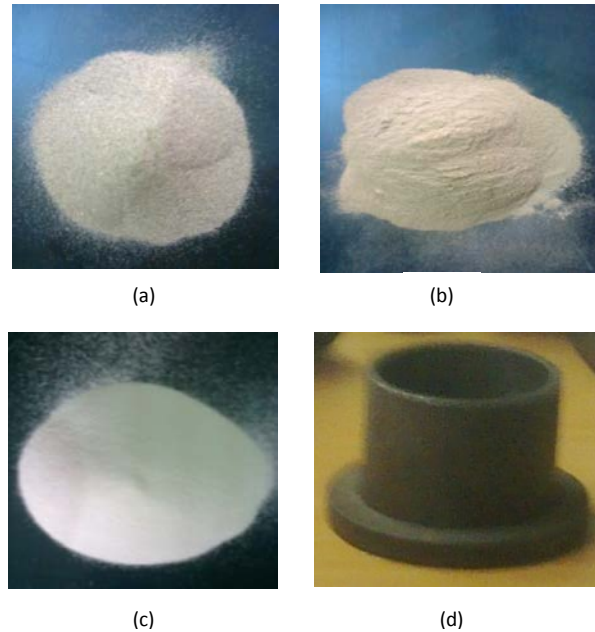


Figure 1: Pre-treated materials and fabricated mould: (a) clay sample, (b) silica sand, (c) alumina and (d) stainless steel mould with detachable base

2.2 Experimental Procedure

The mineral-chemical constituent of the clay sample was determined using energy dispersive X-Ray fluorescence spectrometer (EDXRF) Model 9900 Intel high power series. A specific amount of the pulverised clay sample carefully aggregated with sodium silicate binder was pressed in a laboratory hydraulic press to form pellet. This was then loaded into the spectrometer's sample chamber and excited at a voltage of 25KV with a system current of 1 mA for a period of 45 seconds. The analysis was done using the system software after preliminary calibration. The process was repeated thrice and the average values calculated. The values from the EDXRF were validated with those from secondary spectroscopy of atomic absorption spectrometry. The difference in values ranges between 1 and 4% particularly for the trace elements.

XRD was conducted on the samples to identify the mineral oxides present in the various samples. The XRD characterisation was conducted using the XRD configuration of the Reflection Transmission Spinner with a Goniometer setting position of PW 3050/60 on a 2θ axis with minimum step size of 0.0040 and generator settings at 30 mA, 40 KV using a PANalytical's X'pert

Pro Multi-purpose Diffractometer System. The diffraction spectra were compared with the International Centre for Diffraction Data (ICDD)'s crystallographic database. This was equally repeated for the fired samples.

Trial runs conducted to determine the amount of water necessary for plasticity established optimal plasticity at about 10% of clay sample. Hassan and Aigbodion (2014) equally reported plasticity in clay at 10% water content. Therefore, 20g of the various samples were weighed and 2g of water was added and mixed properly to obtain plastic and mouldable clay. Twelve (12) rammed test samples were prepared with a cylindrical mould of 3.8 cm diameter and 1.3 cm length size, air dried and then further dried via oven drying for 24 hours and then weighed before firing. Four (4) of these test pieces were each fired to 800°C, 900°C and 1,000°C and soaked at these temperatures for 0.5, 1, 3 and 5 hours in a carbolite furnace preparatory to the various tests of apparent porosity, bulk density, linear shrinkage and compressive strength. These tests were equally repeated for the alumina/silica blend. The alumina/silica blend was fixed at ratio 52/40 alumina/silica in reference to the distribution of alumina and silica in the clay sample. Sodium silicate solution at 8% was used as binder.

Apparent porosity and bulk density of the samples were determined by drying freshly compacted samples in the oven at 110°C for 24 hours to obtain specific constant weight (W_a). Thereafter, each of the samples fired at the various temperatures and times was soaked in water for seven hours and the wet weight of the samples taken as W_w . The specimens were later individually suspended in a beaker of water with the aid of a thread and the suspended weight of the specimen was taken as W_s . The apparent porosity (AP) was calculated using Equation (1) (Amuda et al., 2005) while the bulk density (BD) was determined using Equation (2) where ρ_w is the density of water (Ichetaonye, 2014).

$$AP = \frac{W_w - W_a}{W_w - W_s} \quad (1)$$

$$BD = \left(\frac{W_a}{W_w - W_s} \right) \times \rho_w \text{ (g/cm}^3\text{)} \quad (2)$$

Linear shrinkage in percent was determined by adding both the dry shrinkage and the fired shrinkage of the fired samples. The length dimension of freshly compacted samples were measured as L_g and after drying in the oven at 110°C for 24 hours as L_d . The dry shrinkage (DS) was then calculated using Equation (3); while the fired length of the samples after firing at specific temperature was measured as L_f . The fired shrinkage (FS) was then calculated with Equation (4).

$$\%DS = \left(\frac{L_g - L_d}{L_g} \right) \times 100\% \quad (3)$$

$$\%FS = \left(\frac{L_d - L_f}{L_g} \right) \times 100\% \quad (4)$$

The water absorption rate in the samples was determined by soaking a known weight (W_d) of fired dry sample in 200 ml boiling water for about seven hours followed by cooling down to room temperature whilst still in the water. Excess water was removed from the sample using damped cloth prior to weighing. The wet weight (W_w) was then measured and water absorption rate (WR) was calculated using Equation (5).

$$\%WR = \left(\frac{W_w - W_d}{W_d} \right) \times 100\% \quad (5)$$

Loss on Ignition (LOI) in the various samples were determined by firing the clay and the alumina/silica blend to specified temperatures; and calculating the percent weight loss by finding the difference between the weight before (M_1) and after (M_2) firing. LOI was calculated using Equation (6).

$$\%LOI = \left(\frac{W_1 - W_2}{W_1} \right) \times 100\% \quad (6)$$

The cold crushing strength (CCS) in the fired samples was determined by placing the samples in a compressive testing machine and applying a load axially at a uniform rate until fracture occurred using a well calibrated scale. The load at fracture (KN) on a cross sectional area (m^2) was noted and the CCS was calculated using Equation (7).

$$CCS = \left(\frac{FractureLoad}{CrossSectionalArea} \right) \left(\frac{KN}{m^2} \right) \quad (7)$$

Morphology of the fired samples was examined in an ASPEX 3020 Scanning Electron Microscope using secondary electron imaging (SEI) mode at an accelerating voltage of 15 KV.

3. Results and Discussion

3.1 Compositional Analysis of Samples

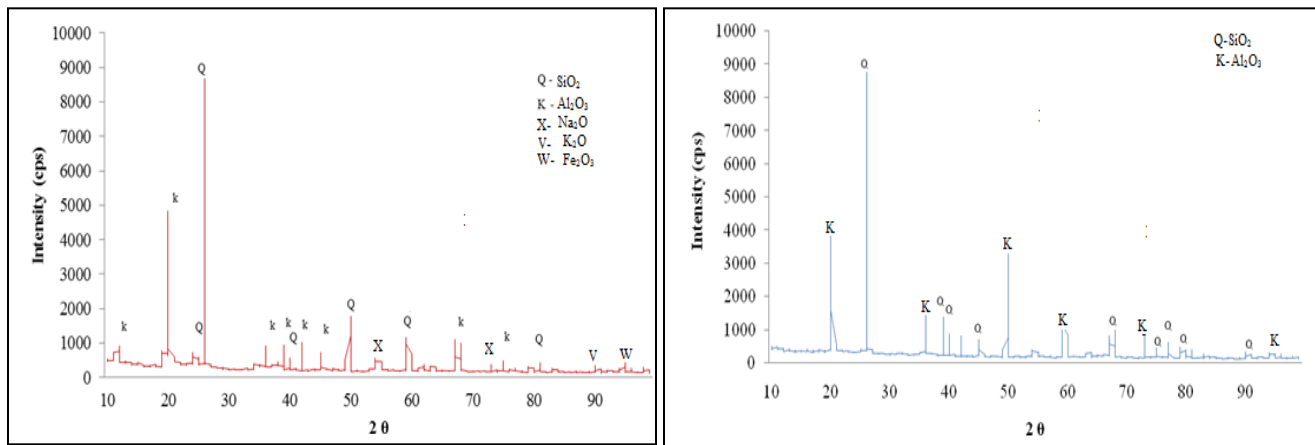
The composition analysis of the natural clay as determined by EDXRF is given in Table 1. It indicates that the natural clay is basically aluminosilicate containing about 51 % SiO_2 and 40 % Al_2O_3 and also having an iron content of 1.03 wt. %. LOI is quite negligible. This suggests that the aluminosilicate is of the hydrated type. The impurity oxides of CaO, TiO_2 , MgO, Na_2O and K_2O at a combined composition of about 8 % is quite high and outside the allowable limit of 5% reported in literature (Jock et al., 2013). For instance, alkali metal oxides (Na_2O , CaO, and K_2O) act as fluxing agents and reduce the fusion temperature of refractory clays (Omotoyinbo and Oluwole, 2008). This negatively affects the thermal shock resistance and linear shrinkage of refractory brick. In comparison with standard classification established for refractory, the clay could be classified as siliceous acidic fireclay and of the kaolinitic group. The pre-treated alumina and silica sand samples are considered pure having principal mineral content of more than 99 % of the individual compounds with trace presence of impurity oxides. Most significant is the very low percentages of alkali metal oxides in both the alumina and silica sand samples unlike the natural clay samples. The very low presence of these impurities in the alumina and silica sand samples is expected to result in improved refractory properties in alumina/silica blend compared to the natural clay sample. The XRD spectra in Figure 2 in relation to the ICDD diffraction files confirms the presence of principal mineral in the natural clay (2a) and only alumina and silica in the blend (2b).

3.2 Colour Variation in Clay Samples at Different Firing Temperatures

Figures 3-6 of natural clay revealed that at firing temperatures of 800 °C, 900 °C and 1,000 °C, there was a pronounced change in colour of clay sample from creamy white in the unfired state (see Figure 3) to brown (see Figure 4) and white brown (Figures 5, 6) as the firing time increases. This colour change was as a result of the presence of iron III oxide in the natural clay together with other impurity elements such as K_2O , Na_2O , CaO and high LOI which often adversely affects refractory properties. Onche et al. (2006) reported similar colour variation in kaolinitic clay fired to 1,200 °C.

Table 1. Spectrometric analysis of work samples

Mineral Compound	Chemical Composition (wt. %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	K_2O	LOI
Clay Sample	51.31	39.51	1.03	0.14	0.01	0.06	6.02	1.33	0.06
Alumina	-	99.30	0.05	0.22	-	0.25	0.09	-	0.09
Silica Sand	99.20	-	-	0.60	-	0.13	0.07	-	-



(a) (b)
Figure 2: XRD spectra of: (a) natural clay sample and (b) silica/alumina synthetic blend



Figure 3: Unfired natural clay samples (Control)

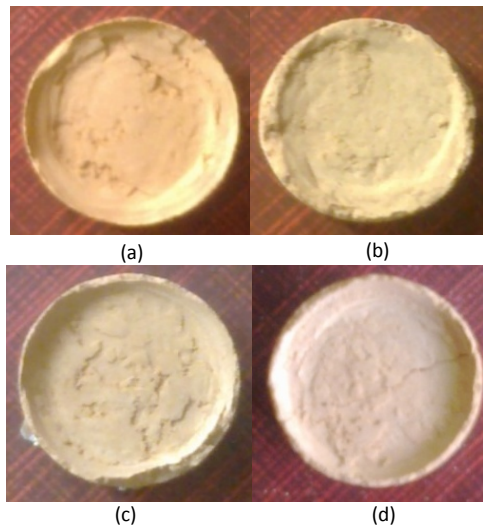


Figure 5: Natural clay samples fired at 900^o C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

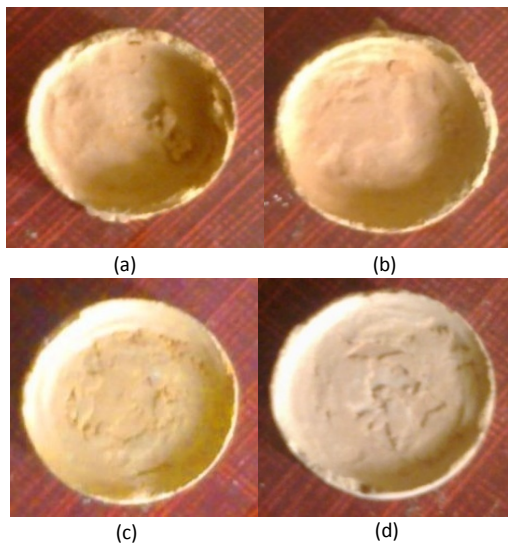


Figure 4: Natural clay samples fired at 800^o C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

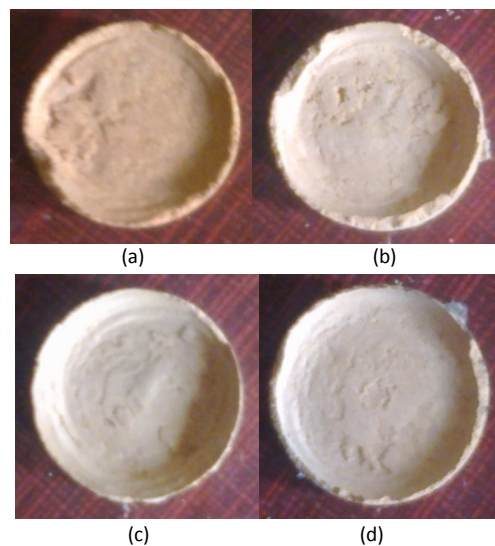


Figure 6: Natural clay samples fired at 1,000^o C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

Whereas Figures 7-10 of synthetic clay pellets revealed that at firing temperatures of 800 °C, 900 °C and 1,000 °C, there was a slight change in colour of the clay sample from dull silver to bright silver. The absence of pronounced colour variation in the blend during firing was attributed to the absence of iron III oxide as well as other impurity elements in the blend.



Figure 7: Unfired synthetic clay sample (control)

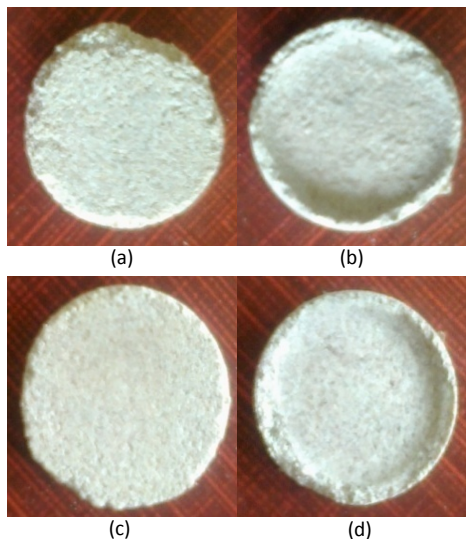


Figure 8: Synthetic clay samples fired at 800 °C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

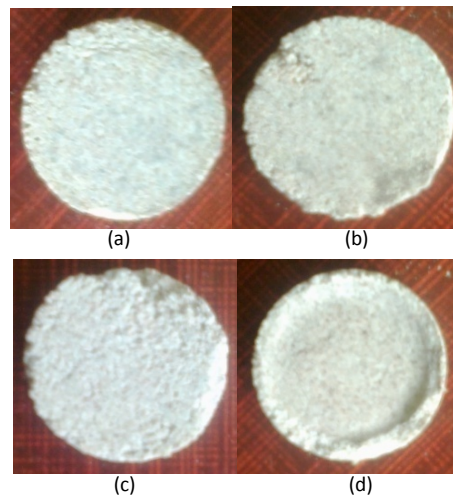


Figure 9: Synthetic clay samples fired at 900 °C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

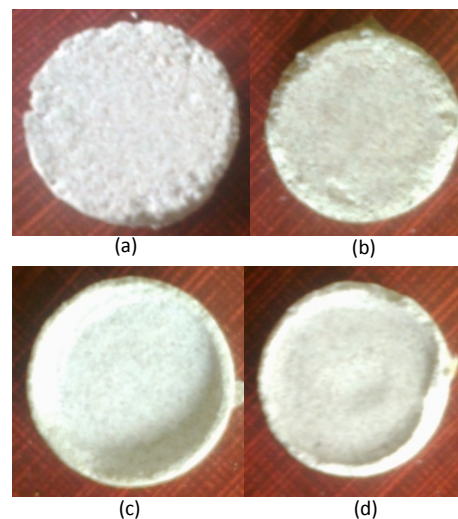


Figure 10: Synthetic clay samples fired at 1,000 °C at different time intervals: (a) 0.5, (b) 1, (c) 3 and (d) 5 hr

One significant observation was that there was no cracking in both the natural clay and the synthetic across all firing temperatures and times. Table 2 provides a summary of the characteristics of the pellets under all firing temperatures and times.

Table 2: Physical characteristics of the sample pellets at different firing conditions

Material	Time (Hr.)	Firing Temperature (°C)					
		800		900		1,000	
		Colour	Crack	Colour	Crack	Colour	Crack
Natural Clay	0.5	Deep brown	-	Brown	-	Brown	-
	1	Reddish brown	-	Light brown	-	Yellowish brown	-
	3	Yellowish brown	-	Creamy brown	-	Light brown	-
	5	Greyish brown	-	Creamy brown	-	Creamy brown	-
Al ₂ O ₃ /SiO ₂ Blend	0.5	Dull silver	-	Bright silver	-	Bright silver	-
	1	Dull silver	-	Bright silver	-	Bright silver	-
	3	Dull silver	-	Bright silver	-	Bright silver	-
	5	Dull silver	-	Bright silver	-	Bright silver	-

3.3 Weight Variation of Natural and Synthetic Clay

The weight variation expressed in terms of percent weight loss in the pellets at different firing conditions is presented in Figure 11. The figure shows that the weight loss in the natural clay pellets is more affected by both the firing time and firing temperature. The percent weight loss increases with increasing firing time more than with firing temperatures. But, in the synthetic clay pellets, it is affected significantly by both the firing temperature and time. In the synthetic clay, the loss increases with both firing time and temperature. The percent weight loss in the natural clay ranges between 8.21 and 41.07% whilst in the synthetic clay, it is between 9.75 and 17.8% across the firing conditions. The increase in weight loss with firing time is attributed to the increase in the release of chemically bonded water and other organic combustible constituents of the natural clay. Lawal et al. (2008) reported similar increase in percent weight loss with increasing firing temperature. In the case of the synthetic clay however, the sodium silicate slurry used as binder in forming the alumina and silica blend dissociates into free water and sodium silica gel at the firing temperatures; and this increases as the firing time increases. They subsequently escaped from the matrix of the synthetic clay in increasing percent with increasing firing temperature and time.

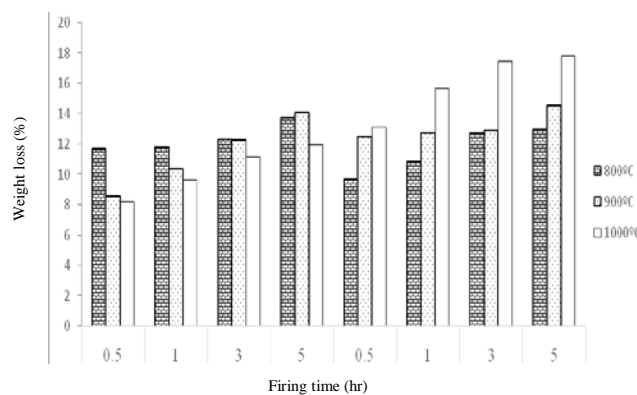


Figure 11: Percent weight loss in fired natural and synthetic clay at different firing conditions

3.4 Linear Shrinkage of Natural Clay and Synthetic Clay

The total linear shrinkage in both the natural and synthetic clays shown in Figure 12 indicates that, for the natural clay, the total shrinkage increases with increase in both firing temperature and time. The same trend is obtained in the synthetic clay but only at firing temperature of 900°C and 1,000°C at firing time of 3 and 5 hrs. The linear shrinkage in the natural clay ranges between 4 and 9.4 whilst in the synthetic clay, it is in the range 0 and 4. Gupta (2008) reported that the acceptable range for linear shrinkage in refractory is 7-9%. The range of linear shrinkage achieved in the current

investigation is generally within the established range. It is interesting to note that the synthetic clay provides linear shrinkage in the very low range (0-4%). This is probably due to low strain of expansion and contraction on account of the absence of impurity constituents in the synthetic clay unlike in the natural clay.

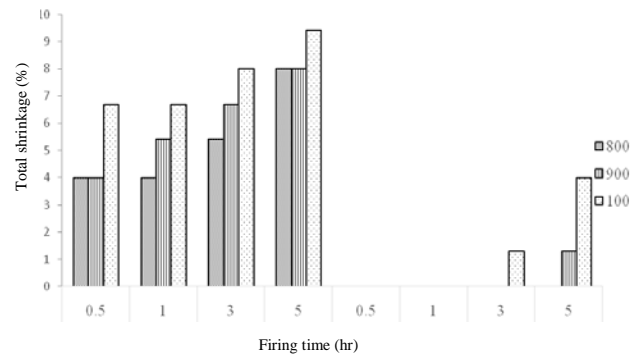


Figure 12: Total shrinkage of natural and synthetic clay at different firing conditions

3.5 Apparent Porosity of Natural Clay and Synthetic Clay

Figure 13 shows the variation in apparent porosity with firing temperatures and times. In the natural clay, porosity decreases with increasing firing temperature and time. The maximum apparent porosity in the natural clay is about 35% at firing temperature of 800°C and firing time of 0.5 hr and the least porosity is 22.7% at 1,000°C for a firing time of 5 hrs. This trend in the natural clay is expected because increasing firing temperature permits the closing up of the voids created by escaping volatile and combustible matter which eventually restricts the escape of the gaseous substance. In the synthetic clay, however, the apparent porosity increases with increasing firing temperature and time unlike in the natural clay. The increase in apparent porosity with increasing firing conditions in the synthetic clay is most likely due to the greater spores and cleave created by the breakdown of the sodium silicate binder in spite of the firing conditions closing up the spores.

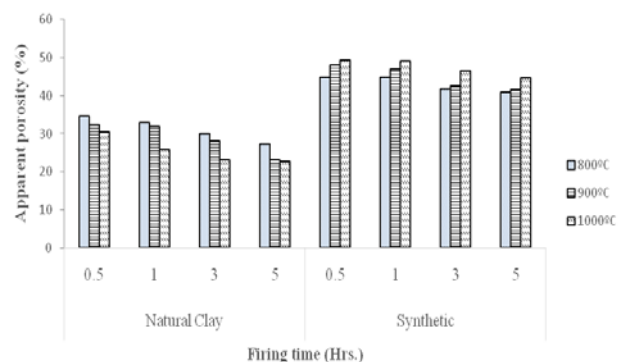


Figure 13: Apparent porosity of natural and synthetic clay at different firing conditions

Literature indicates that apparent porosity should not be greater than 24% in fireclay refractory and for refractory insulator, it should be greater than 60% (Gupta, 2008). The present investigation in relation to standards indicates that the apparent porosity in the synthetic clay at about 45% is outside the window permitted for fireclay refractory and below that for refractory insulator. This suggests that the apparent porosity obtained in the present investigation is not acceptable; and there may be the need to explore another binder other than sodium silicate. The trend in apparent porosity is similar to the trend obtained with water absorption rate in the pellet samples as shown in Figure 14.

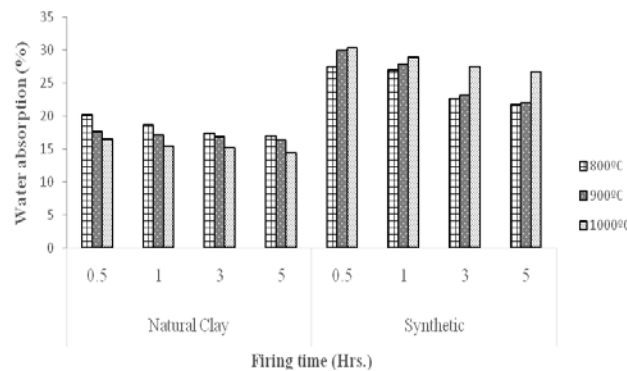


Figure 14: Water absorption of natural and synthetic clay at different firing conditions

The mechanism prevailing in apparent porosity also dominates during water absorption rate. The water rate can be taken as a measure of resistance of refractory to liquid penetration. A very high water absorption rate indicates a very poor resistance to liquid penetration.

3.6 Bulk Density of Natural and Synthetic Clay

Figure 15 shows the variation of bulk density with firing conditions for both the natural and synthetic clays. The bulk density increases with increasing firing conditions for both natural and synthetic clays. But, the influence of the firing conditions is more pronounced in the natural clay than in the synthetic clay. The bulk density in the natural clay ranges between 1.72 and 2.15 g/cm³; and in the synthetic clay, it is between 1.55 and 1.89 g/cm³. The bulk density measures the change in weight of clay with respect to the total volume of material at a given condition of temperature and firing time; where the total volume is the sum of both closed and open pores. Thus, increasing the firing time temperature and time permits greater release of chemically combined volatile matter leading to the closure of internal pores. This closing up of internal pores reduces the effective volume resulting in increased bulk density for a given weight of pellet. It is however significant to note that the range of bulk density obtained in the present investigation for both

natural and synthetic clays falls within the maximum standard limit of 1.98 g/cm³ for fireclay refractory.

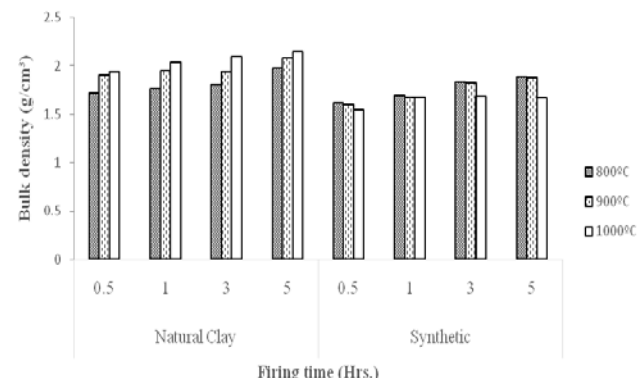


Figure 15: Bulk density of natural and synthetic clay at different firing conditions g/cm³

3.7 Cold Crushing Strength of Natural and Synthetic Clay

The cold crushing strength of both the natural and synthetic clays at different firing conditions is shown in Figure 16. The figure shows that the cold crushing strength increases with increasing firing conditions for both the natural and synthetic clays. The increase in strength with firing conditions in the pellets could be attributed to increasing solid state fusion within the individual grains in the pellets at higher firing temperatures and time. However, the increase in strength with increasing firing conditions is greater in the natural clay than in the synthetic clay. This may be attributed to the breakdown of the sodium silicate binder in the synthetic clay which weakens the cohesive bond between individual grains in the pellet.

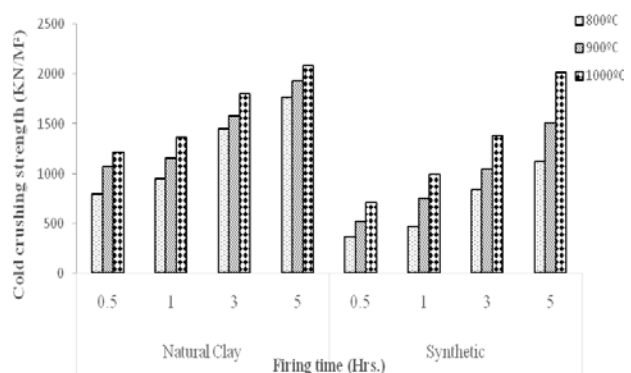
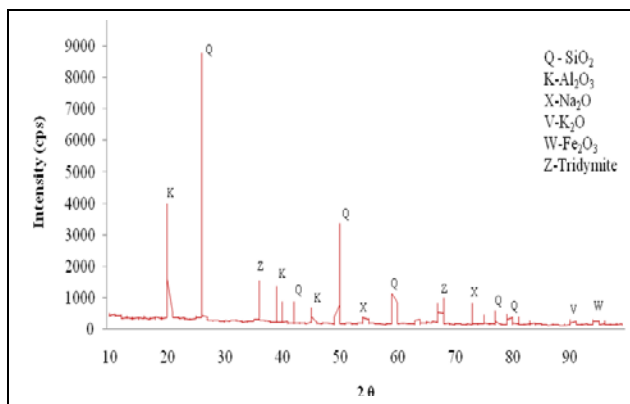


Figure 16: Cold crushing strength of natural and synthetic clay at different firing conditions

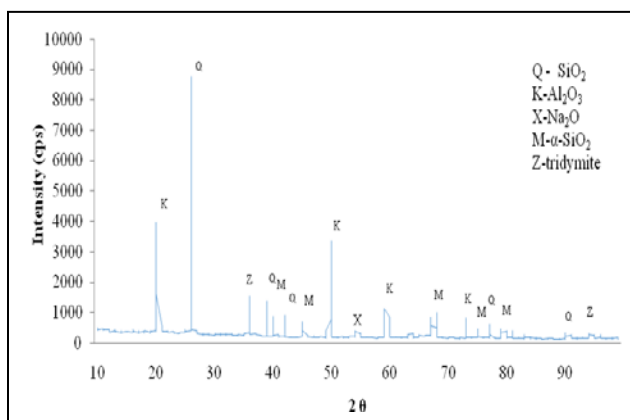
3.8 XRD Diffraction Spectra of fired Natural and Synthetic Clay

Figure 17 shows the XRD spectra for both the natural (17a) and synthetic clay (17b) fired at 1,000°C for 5 hrs.

The spectra is not significantly different from those of the control sample shown in Figure 2 except for shift in the diffraction angle (26°) to higher angle (29°) which may suggest the existence of volumetric stain in the sample. The analysis of the figure in relation to ICDD database indicates that there is no polymorphic transformation in the natural clay samples; because the maximum firing temperature ($1,000^\circ\text{C}$) is below the transformation temperature ($1,250^\circ\text{C}$) for polymorphic transformation in aluminosilicate fireclay. Therefore, the behaviour of the natural clay sample is influenced by physical process rather than chemical polymorphic transformation. In the synthetic clay, however, the silica quartz transformed to tridymite at temperature above 870°C with volumetric expansion. The expansion generates increased pores in the sample; and this might have contributed to the increased porosity obtained in the synthetic samples in Figure 13.



(a)



(b)

Figure 17: XRD spectra for: (a) natural and (b) synthetic clay fired at $1,000^\circ\text{C}$ for 5 hrs

3.9 Morphological Characteristics of Natural and Synthetic Clays

The morphological texture of the pellets presented in Figure 18 shows dispersive chaff-like texture indicating that the grains are poorly aggregated in the natural clay while in the synthetic clay the texture illustrates the

existence of aggregated partitioning of the individual grains. This may be due to improper mixing in the unfired state. The figure further revealed that the natural clay fired at $1,000^\circ\text{C}$ for 5 hrs present increased closed network of structures. This is attributed to the closing up of internal pores in the clay at this firing condition; and this is apparently responsible for the decrease in porosity and increase in both bulk density and cold crushing strength in the natural clay as firing conditions increases (see Figures 13, 15 and 16). In the synthetic clay, however, there is increased disaggregation in the texture at the firing condition due to the breakdown of the sodium silicate binder; and this accounts for the trend observed in the apparent porosity and bulk density, respectively. It is to be noted that similar trend is observed at other firing conditions.

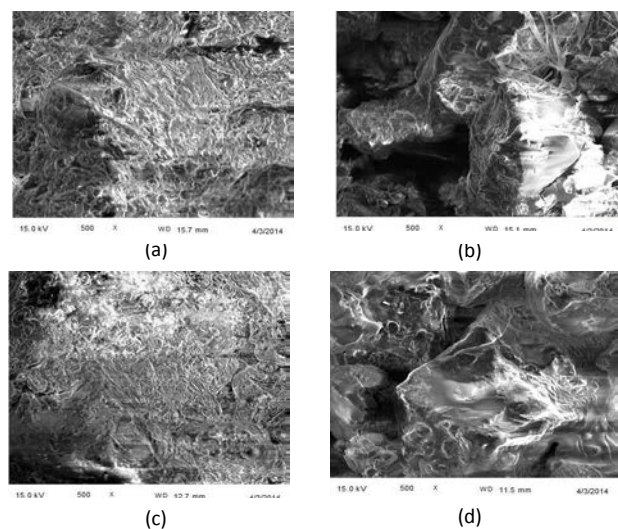


Figure 18: Morphological texture of the clay samples: (a) natural clay before firing, (b) synthetic clay before firing, (c) natural clay after firing at $1,000^\circ\text{C}$ for 5 hrs, and (d) synthetic clay after firing at $1,000^\circ\text{C}$ for 5 hrs

4. Conclusion

Refractory properties of a blend of alumina/silica fired at 800 , 900 and $1,000^\circ\text{C}$ for varying times of 0.5 , 1 , 3 and 5 hours have been validated against those of standard indigenous kaolinitic clay; and the following conclusions emerged from the investigation:

1. EDXRF combined with XRD identifies the main constituent of the natural clay as Al_2O_3 (40%) and SiO_2 (51%) with impurity oxides at about 8%.
2. The alumina/silica blend exhibits no colour variation across all firing conditions due to the absence of impurity oxides such as Fe_2O_3 , CaO , TiO_2 , MgO , Na_2O and K_2O unlike in the natural clays which shows significant colour variation at the firing conditions.
3. The firing temperature and time have no significant effect on the refractory characteristics of the

synthetic alumina/silica blend except at temperature of 1,000°C and time of 5 hrs with the marginal formation of tridymite.

4. There is increase in weight loss with firing time in both the natural and synthetic clays. But the weight loss in the natural clay is attributed to the increase in the release of chemically bonded water and other organic combustible constituents of the natural clay. Whereas, in the synthetic clay, the sodium silicate slurry used as binder in mixing the alumina and silica dissociates into free water and sodium silica gel at the firing temperatures; and subsequently escapes from the matrix of the synthetic clay.
5. The range of linear shrinkage achieved in the current investigation is generally within the established range. It is interesting to note that the synthetic clay provides linear shrinkage in the very low range (0-4%). This is probably due to low strain of expansion and contraction on account of the absence of impurity constituents in the synthetic clay unlike in the natural clay.
6. The apparent porosity in the synthetic clay is outside the window permitted for fireclay refractory and below that for refractory insulator. This suggests that the apparent porosity obtained in the present investigation is not acceptable; and there may be the need to explore another binder other than sodium silicate. Similar trend is obtained in the water absorption rate.
7. The range of bulk density obtained in the present investigation for both natural and synthetic clays falls within the maximum standard limit of 1.98 g/cm³ for fireclay refractory.
8. The cold crushing strength increases with increasing firing conditions for both the natural and synthetic clays but the increase is more pronounced in the natural clay than in the synthetic clay. This may be attributed to the breakdown of the sodium silicate binder in the synthetic clay which weakens the cohesive bond between individual grains in the pellet.
9. The alumina/silica blend characterisation suggests that the blend has refractories properties within the standard for fireclay refractory but the apparent porosity is outside the acceptable range provided in standards..

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