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The Effects of Kaolin and Bauxite Clay Mix Ratios on Physical and Thermal Properties of Refractory Bricks

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***Abstracts* - Refractory bricks (refractories) are used in the construction of furnaces internal linings that hold, melt and transfer raw materials being processed. Kenya imports refractories mainly for its cement, metal smelting and sugar processing industries. Alumina, silica and iron oxides in kaolin, bauxite and ball clays made them suitable as composite refractory clays. The physical and thermal properties of the developed composite bricks were determined at different mix ratios and their results compared with American Society of Testing Materials standards. Kaolin and bauxite clays were mixed at different ratios with 10% binder (ball clay). Developed bricks were moulded to volumes of 343 cm^3, subjected to a pressure of 4.1N/m^2 and dried at 110℃. The bricks were fired in the furnace at a rate of 7°C/min up to 200°C for 6 hours, 650°C for 3 hours, 950°C for 4 hours and 1250°C for 8 hours and left to cool to room temperature. Then, they were subjected to physical and thermal tests and data obtained analysed using Statistical Analysis of Systems software at 5% level of significance. Cold crushing strength, thermal shock resistance and bulk density were directly proportional to the increase in kaolin ratio, but inversely proportional to bauxite. Decrease in linear shrinkage and apparent porosity was directly proportional to bauxite ratio, but inversely proportional to increase in kaolin. As kaolin ratio increased from 2:7 to 7:2, apparent porosity decreased from 38% to 29% and bulk density increased from 1.45kg/cm^3 to 1.61kg/cm^3, cold crushing strength increased from 22 to 3.3KN/m^2, linear shrinkage decreased from 8.89% to 3.69%, and thermal shock resistance increased from 14 to 27 cycles, respectively. This study adds knowledge to existing literature on refractories based on unexploited local clays.**

Key words: Composite, Refreactory bricks, Physical and Thermal properties

INTRODUCTION

1. Background

Refractory bricks (refractories) are the main components in metallurgical and cement processing industries in the construction of furnaces and kiln internal linings [14] Kiln internal linings are used as vessels for holding, melting and transferring raw materials under process. The major consumers of refractory products are cement, sugar, incineration, metal processing industries, chemical, glass, boilers and petrochemical industries.

The demand for refractory products is bound to increase tremendously owing to the increased growth of Kenya's manufacturing sector [21]. East African Portland Cement alone consumes approximately 1200 tons of refractory bricks annually for production of clinker [17].

In the year 2012, Kenya imported refractory bricks worth 3 billion Kenyan shillings mostly from India and China for its cement, metal smelting and sugar processing industries. But, according to [13], Kenya has a potential of cutting down imports of refractory bricks by 20% and increase exports by 15 % in a span of 10 years by utilising the abundant deposits of clay raw materials for local production.

Individual raw materials rarely meet the desirable refractory properties and a range of raw materials are therefore utilized to achieve the desirable chemical, physical and thermal properties of refractory bricks [11]. The principal raw materials used in the production of refractory bricks are Alumino-silicate based clays. The major types of refractories in Kenya are kaolin, bauxite and ball clays which are listed among the primary raw materials for refractory brick production. According to [16], Kenya is endowed with vast deposits of kaolin, bauxite and ball clays at Nakuru, Kericho and Nyeri that can be exploited for production of refractory bricks. Unfortunately, there has not been economical utilization of these clays locally. Hence, production of refractory bricks in Kenya will add value to local clays and help in achieving the Vision 2030 [17].

2. Materials and Methods

2.1 Source of clays

The raw materials used in this study were kaolin, bauxite and ball clays due to their availability and good properties such as high alumina and silica content. Kaolin, bauxite, Kisii soapstone and Salama clays were collected from Naivasha (Eburru Complex), Kericho (Kipchimchim), Kisii (Tabaka) and Machakos, while the ball clay was sourced from Nyeri (Mukurweini).

2.2 Characterization of clays

Chemical properties were analysed at the Ministry of Environment and Minerals Resources, Department of Mines and Geology. These clays were dried, crushed, sieved and mixed in different ratios before being compressed, bonded and fired. Then, their physical and thermal properties such as bulk density, porosity, water absorption, cold crushing strength and linear fire shrinkage were analysed at Kenya Industrial Research and Development Institute (KIRDI). Results obtained from the above mentioned analysis were compared with the ASTM values and conclusion drawn based on their findings.

2.3 Physical and thermal properties of composite refractory bricks

The mix ratios of Kaolin (Ka), Bauxite (Ba) and Ball (Bc) clays were prepared as shown in Table 1. The physical and thermal properties of the developed bricks that were investigated included porosity, bulk density, cold crushing strength, thermal shock resistance and linear shrinkage.

Table 1: Mix ratios for different clay materials

Treatment	(Ka :Ba :Bc) Ratios	Replication
1	9:0	5
2	0:9	5
3	2:7	5
4	1:2	5
5	1:1	5
6	2:1:	5
7	7:2:	5

Where; Ka is Kaolin, Ba is Bauxite and Bc is Ball clay.

2.4 Development of composite refractory brick samples

Kaolin, bauxite, Salama clay, Kisii soapstone and ball clays were dried and thoroughly mixed to obtain a homogeneous sample and 8% of water was added to improve plasticity. The samples were stored in stop pad container for 24hrs to allow moisture distribution and weathering, which improve plasticity in the clays. The samples were put in a cubical mould box of 343cm^3 and pressed using hydraulic jack to a pressure of 4.1N/m^2. The bricks were then withdrawn from the mould and weighed before leaving them in open air for 24hrs to dry naturally, and then place them in an oven for 24 hrs at a temperature of 110°C to expel any moisture as recommended by [1].

The dried brick was fired in an automatic digital electric furnace at a heating rate of 7°C/min up to 200°C for 6 hours, 650°C for 3 hours, 950°C for 4 hours and 1250°C for 8 hours, as indicated in Figure 1 according to [5]. After firing, the bricks they were cooled in the furnace at a rate of 1°C/min as recommended by [4] and [10].

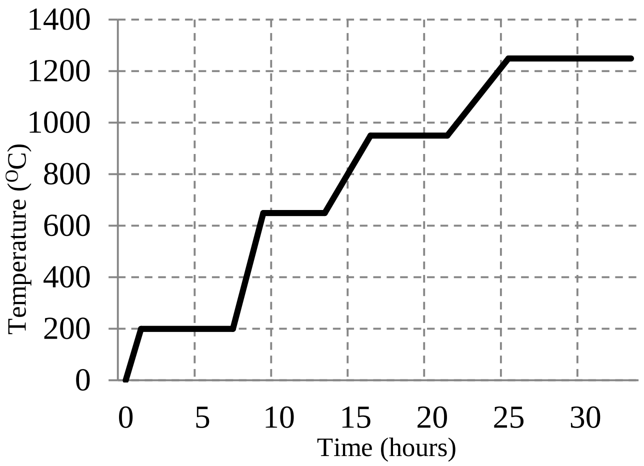

Figure 1: Heating Regime [5].

2.4.1 Apparent porosity

Apparent Porosity (AP) of the developed bricks from each mix ratio was determined in accordance with ASTM C 20 standard. The cuboids' samples of side 70mm were initially dried in an oven at 110°C for 24 hours to obtain a constant weight which was recorded as D using digital weighing scale. The dry sample was suspended in distilled water and boiled for two hours. It was then reserved and suspended to cool at room temperature and its weight recorded as S. Afterwards, it was removed from distilled water and the surface wiped off. The sample was then weighed and recorded as W. Eventually; apparent porosity was calculated using equation 1.

$$AP = \frac{S-D}{S-W} \times 100\% ---------1$$

Where; AP is Apparent Porosity, D is dry weight, S is Suspended weight in distilled water and W is Weight in air.

2.4.2 Bulk density

The procedures used for the determination of apparent porosity were applied in the determination of bulk density in accordance with ASTM C20 since bulk density is a function of the method of manufacture. Bulk densities of the bricks were determined using equation 2.

$$BD = \frac{D}{S-W} \times 100\% \text{---------------------------}2$$

Where: BD is Bulk density, D is dry weight, S is Suspended weight in distilled water and W is Weight in air.

2.4.3 Cold crushing strength

Cold Crushing Strength (CCS) is the amount of load that the refractory material could withstand after it has been fired to a temperature of 1250°C. The cold crushing strength of a refractory sample was determined according to [7]. The samples were fired in a furnace at 1250°C for a period of six hours before cooling to room temperature. Each sample was placed on a compressive tester and loaded axially at a uniform rate until failure occurred, then readings taken. Eventually, CCS was obtained using eq. 3 as recommended by [12] from the maximum load (known as the crushing load).

$$CCS = \frac{Maximum\ load\,(KN)}{Cross\ sectional\ area\ (m^2)} \text{-----------------}3$$

Where; CCS is cold crushing strength of the sample.

2.4.4 Linear shrinkage

The samples of the refractory materials were molded into cubicles with sides of 70 mm and hydraulically compacted at 4.1N/m^2. A green brick (unprocessed brick) length was measured on each sample and recorded as L_1. The samples were dried in an oven at 110^{0}C for 24hrs, and then placed inside a furnace preset at 1250^{0}C before cooling to room temperature at a rate of 1^{0}C/min. Then, linear shrinkage of the samples was determined in accordance with [8] using equation 4.

$$\%\ LS = \frac{L_1 - L_2}{L_1} \times 100\% \text{------------}4$$

Where: LS is linear shrinkage, L_1 is green brick length and L_2 is fired length.

2.4.5 Thermal shock resistance

Thermal shock resistance was determined by heating the sample in a furnace to a preset temperature of 1100°C for 30 minutes. Afterwards, the sample was removed from the furnace and cooled for 10 minutes in accordance with [9] standard. The sample was recharged for another 10 minutes at 1100^{0}C and then cooled again for 10 minutes. This cycle of heating and cooling was repeated until the brick fractured. The number of complete cycles before occurrence of failure on each sample was taken as the measure of the thermal shock resistance according to [4]

3. Results and Discussion

3.1 Physical properties of refractory bricks

Figure 2 presents unfired (physical appearance of green-composite brick) bricks made of individual clay materials. After firing, observations were made to determine clays that met minimum requirements for the purposes of narrowing down to an appropriate composite refractory material. The physical colour of unfired individual kaolin, bauxite, soapstone, salama and ball clays were ivory white, brown, ivory white, sienna brown and dim grey, respectively.

(Where: BC is Ball clay, NC is Kaolin, BX is Bauxite, SC is Salama clay and KSI is Kisii soft stone).
Figure 2: Various colours of unfired/ green bricks.

After the sintering process at 1250^{0}C, the colour of bricks turned white, reddish, snow white, wine red and tan for kaolin, salama, soapstone, bauxite and ball clays, respectively as seen in Figure 3. The red colour indicates the presence of Fe_2O_3 content.

Figure 3: Fired bricks of individual clays.

The physical appearance of these bricks after firing revealed that soapstone (snow-white) at a sintering temperature of 1250^{0}C - started forming glass due to high levels of potassium (5.6%). Salama and ball clays experienced several cracks at lower temperatures due to the presence of iron oxide and reaction of water of crystallization. Also, bauxite bricks chipped off more than those made from kaolin which demonstrated low plasticity and incomplete sintering process. Hence, observations made on the fired bricks made of individual clays materials, led to the conclusion that mixed ratios of kaolin, bauxite and ball clays would be suitable for manufacturing composite refractory bricks. Results obtained agree with [20] who reported that aluminum oxide (Al_2O_3) of 26.29 – 30.68% and silica (SiO_2) 45.22 – 48.66% is suitable as refractory materials.

To ascertain the best binder ratio, mix ratios of kaolin and bauxite were subjected to varying ratios of ball clay at 5%, 10%, 15% and 20%, respectively as shown in Figure 4 and judged on consistency, holding, colour and zero cracks. Eventually, ball clay of 10% binder was found ideal for the mix ratios.

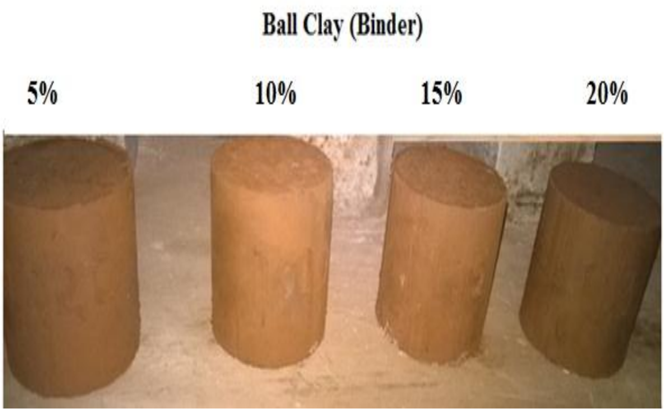

Figure 4: Binder ratios.

Refractory bricks of different mixed ratios were prepared using the procedures mentioned for the individual materials. Different bricks from the 5 mix ratios shown in Figure 5 were replicated five (5) times and fired to a maximum temperature of 1250^{O}C.

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Figure 5: Fired bricks samples at different mix ratios.

The results of apparent porosity, bulk density, cold crushing strength, linear shrinkage and thermal shock resistant for each mix ratio are shown in Tables 2 and Figures 6 through 10.

Table 1: Physical and thermal properties of kaolin and bauxite clays.

Ba:Ka Ratios	AP(%)	BD (g/cm^3)	CCS (MN/m^2)	LFS (%)	TSR (CYC)
Bauxite	43^a	1.56^c	17^f	9.7^a	8^f
2:7	38^b	1.56^c	22^e	8.89^b	14^e
1:2	36^c	1.54^c	24^d	7.23^c	15^e
1:1	35^c	1.60^c	27^c	6.43^d	20^c
2:1	33^d	2.03^a	30^b	4.44^e	22^b
7:2	29^e	2.23^b	33^a	3.69^e	27^a
Kaolin	27^f	1.60^c	27^c	2.81^f	18^d
(ASTM)	20-30	1.71-2.10	15	4-10	20-30
LSD	1.716	0.102	1.0634	0.2353	1.2484

NB: Mean values followed by the same letter superscript (a, b, c, d, e or f) are not significantly different at α= 0.05 and Least Significant Difference (LSD).

3.1.1 Apparent porosity

Apparent porosity is a key property on brick insulation and heat conservation in a furnace or kiln. Low apparent porosity indicates better insulation and heat retention of refractory bricks. From the results presented in Table 2 and Figure 6, it is evident that apparent porosity depends on the characteristics of the original material. The apparent porosity of the pure kaolin and bauxite clay alone were 27% and 43%, respectively.

The apparent porosity for bauxite was higher than for kaolin which could be attributed to the air pockets contained in it. Hence, the lower the porosity of the refractory brick, the better the insulation of the material. Results obtained in Table 2 show that if kaolin and bauxite are mixed in ratios of 1:2 and 1:1, they would exhibit similar but inferior apparent porosity at LSD of 1.716.

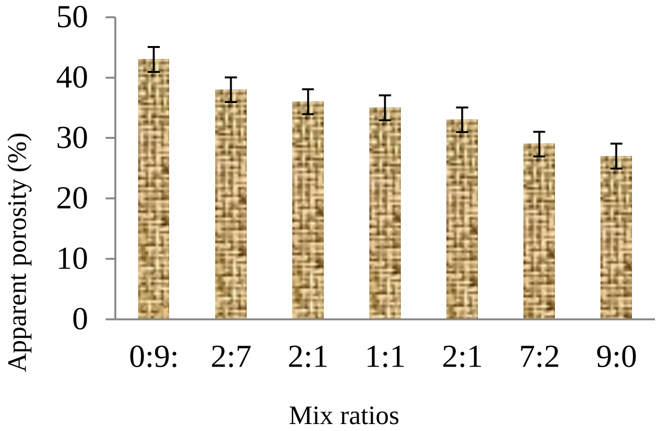

Figure 6: Effect of mix ratios on apparent porosity.

The apparent porosity values of 27% and 29% for kaolin and 7:2 mix ratio, respectively agrees with the values specified by [6] of 20 – 30%. Mix ratios 2:7, 2:1 and bauxite had the highest porosity of 38%, 36% and 43%, respectively which were far much above the standard. Error bars on mix ratios 2:7, 1:2, 1:1and 2:1 overlap which shows that they are not significantly different at α= 0.05 and LSD of 1.716. This implies that these ratios are not appropriate for refractory bricks since the apparent porosity is higher than the ASTM values. This finding implies that when kaolin was mixed with bauxite at a ratio of 7:2, apparent porosity improved from 43% to 29% which qualifies it as refractory brick material.

It was also realized that as the quantity of kaolin was increased in the mix the apparent porosity decreased from 38% to 29%, and the vice versa as amount bauxite increased in the reverse order.

3.1.2 Bulk density of composite bricks

High bulk density is commonly desired for clay refractories because high fired-density usually confers high physical strength at high service temperatures and high resistance to service corrosion, slag penetration, abrasion and loading especially during transportation. The effects of mix ratios on bulk density are presented in Table 2 and Figure 7. The bulk densities for kaolin and bauxite clays were $1.61g/cm^3$ and $1.45g/cm^3$, respectively. It was evident; from these results that bulk density was dependent upon the characteristics of the original material and increased proportionally with increase in kaolin but vice versa with decrease in bauxite content. As the quantity of kaolin in the ratio was increased from 20% to 70%, bulk density increased from $1.54g/cm^3$ to $2.23g/cm^3$. This could be attributed to the porosity of bauxite clay which is higher than that of kaolin. This suggests that kaolin has higher specific gravity compared to bauxite which depends on the type of raw materials as [15] observed.

Results obtained in Table 2 show that bulk densities obtained with ratios of 2:7, 1:2, 1:1, kaolin and bauxite were not different at α= 0.05 and *LSD* of 0.102 but were lower than the ASTM values of 1.71 – $2.10g/cm^3$. Mix ratios of 2:1 and 7:2 had recommendable values since they met the minimum requirements for refractory bricks.

The value of bulk density equal to 2.03g/cm^3 lies within the findings of [22] and [2], who reported values of 2.02-2.11 g/cm^3 and 1.94-2.04 g/cm^3, respectively. Mix ratios 9:0 to 1:1 had values ranging from 1.61g/cm^3 to 1.45g/cm^3, which disagree with ASTM values of 1.71 to 2.10g/cm^3.

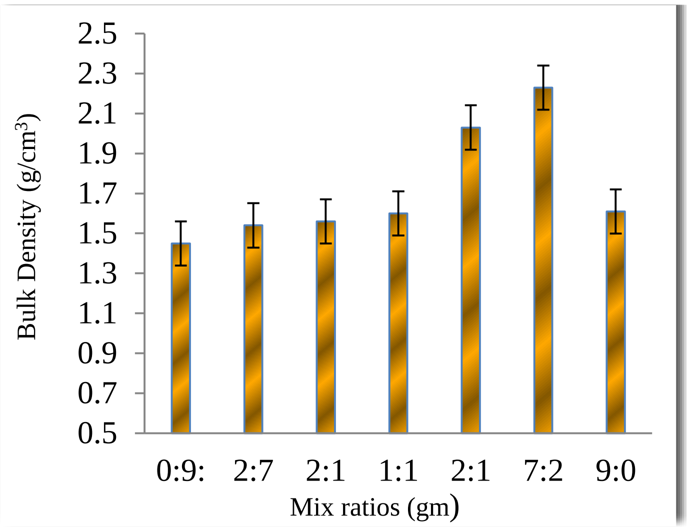

Figure 7: Effect of mix ratios on bulk density.

3.1.3 Cold crushing strength

Cold crushing strength indicates the ability of refractory bricks to withstand handling, transportation and installation at low temperatures. Table 2 presents mean values of cold crushing strength for various ratios of kaolin to bauxite bounded by ball clay while Figure 8 is used to compare cold crushing strengths using error bars at 5% level of significance with LSD of 1.0634. The values obtained accounted for good bonding and vitrification during firing.

Kaolin and bauxite presented cold strengths of 27MN/m^2 and 17MN/m^2, respectively. This showed that kaolin has more cold crushing strength than bauxite as an individual raw refractory material. Cold crushing strength for 2:7 ratio was 22MN/m^2 which increased to 33MN/m^2 as kaolin increased to 7:2. As Kaolin increased, the cold crushing strength increased too. This showed that cold crushing strength of the produced refractory brick depended upon the original material where Kaolin had better chemical properties - silica content of 46 and 55% which was responsible for high strengths.

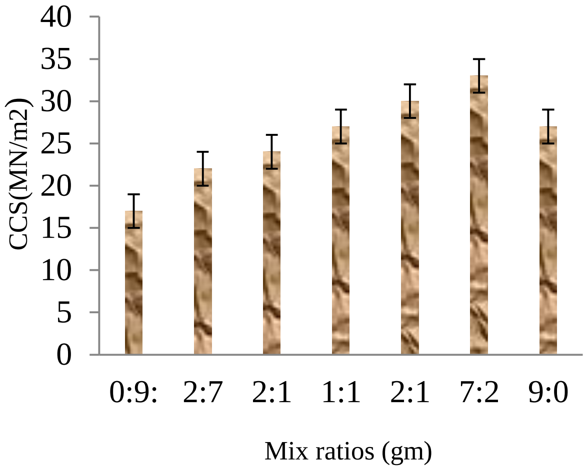

Figure 8: Effect of mix ratios on cold crushing strength.

The ratios of 9:0 and 1:1depict similar cold crushing strength property with 27MN/m^2 since their error bars are overlapping, while other ratios portray different values at α= 0.05and Least Significant Difference of 1.0634. The values of cold crushing strength obtained in this study were ranging between 17MN/ m^2 and 33 MN/m^2. These were higher than the [7] value of 15MN/m^2 due to high silica content of 46% to 55% as supported by [20] who stated that presence of high silica content and alkali in clay are responsible for high compressive strengths. This showed that the bricks had been properly fired which enabled them to withstand loading and could easily be transported without damage as stated by [3] Mix ratio 2:1 and 7:2 agrees with values reported by [4] of between 29.42MN/m^2 to 55.9MN/m^2 .

3.2 Thermal properties

3.2.1 Linear shrinkage

Linear shrinkage is an important parameter in the standardization of refractory bricks. It is an indicator of the efficiency of a firing regime and indicates the size of a mould. The results on this parameter are presented in Table 2 and Figure 9.

It was observed from Table 2 that linear shrinkage was inversely proportional to increase in kaolin and directly proportional to decrease in bauxite. At a mix ratio of 0:9, linear shrinkage was 12.62 % which reduced to 2.81% with increasing kaolin. This could be attributed to the particles sizes distribution in kaolin. Kaolin and bauxite mix ratios of 2:7, 1:2, 1:1, 2:1, 7:2 and 9:0 produced linear shrinkage values ranging from 8.89 to 2.81% which fell within the recommended limit of 4-10%. It was also observed that all ratios produced different linear shrinkage values at α= 0.05 *and LSD of* 0.2353 as shown by the un-overlapping error bars in Figure 9.

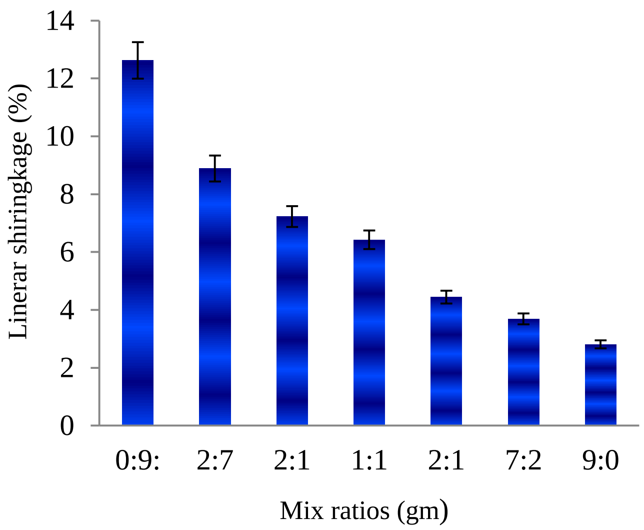

Figure 9: Effect of mix ratios on linear shrinkage.

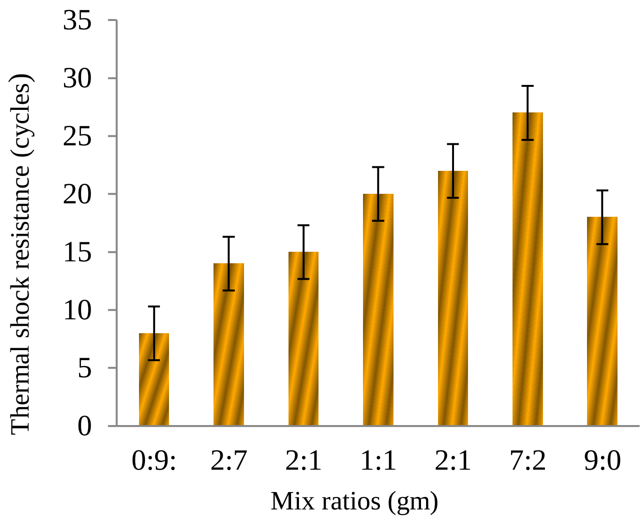

Figure 10: Effect of mix ratios on thermal shock resistance.

Lower linear shrinkage values are more desirable and values below 4% would be acceptable as [2] pointed out. The values of linear shrinkage using 7:2 and 9:0 ratios were 3.69 and 2.81 which compares with values obtained by [4] who reported linear shrinkage from 3 % to 3.6%. Hence, these two mix ratios were appropriate for manufacturing of composite refractory brick. This means that the produced brick would be less susceptible to volume change.

3.2.2 Thermal shock resistant

Thermal shock resistance is the ability of a refractory brick to withstand sudden temperature changes without fracture. This was determined by the number of thermal cycles (heating and cooling) the refractory bricks underwent. The results of the means on this parameter are presented in Table 2 and Figure 10.

The results obtained show that thermal shock resistance increased with increase in the amount of kaolin content. Without kaolin (0:9) thermal shock resistance was 8 cycles and as kaolin content increased to 7:2, it increased to a maximum of 27 cycles. Kaolin and bauxite at ratios 1:1, 2:1 and 7:2 showed recommendable results of 20, 22, and 27 cycles, respectively. Thermal shock resistances for ratios 2:7 and 1:2 were not significantly different at $\alpha = 0.05$ and LSD of 1.2484. These thermal shock resistances fell below the minimum [9] value of 20 cycles.

The thermal shock resistances for mix ratios of 1:1, 2:1, 7:2and 9:0 agrees with [15] and [19] who reported thermal shock resistance values ranging from 17 to 28 cycles and [9] values of 20 – 30 cycles. The numbers of cycles are used to measure the longevity of refractory bricks which in turn would result to cost savings due to minimal replacement. The results obtained of 27 cycles for 7:2 mix ratios are recommendable for refractory brick production.

The refractory brick made with mix ratio 7:2 has the highest value of bulk density, cold crushing strength, linear firing shrinkage, thermal shock resistance and lowest value of apparent porosity and linear fired shrinkage. This implies that good refractory brick were produced with this ratio.

A. Conclusions

Apparent porosity decreased with increase in kaolin, but increased with increase in bauxite. Mixing kaolin, bauxite and ball clays at a ratio of 7:2 produced the best apparent porosity of 29% which was within the ASTM C20 values. Bulk density was directly proportional to increase in kaolin but inversely proportional to bauxite. The mix ratio of 7:2 yielded the highest value of 2.23 kg/cm^3. Cold crushing strength increased with increase in kaolin, but decreased with increase in bauxite. Mixing kaolin, bauxite and ball clay in the ratio of 7:2 produced a cold crushing strength of 33 MN/m^2. Linear shrinkage decreased with increase in kaolin, but increased with increase in bauxite. All the mix ratios of kaolin and bauxite clays produced linear shrinkage values within the ASTM C133 range of 4-10% though 7:2 yielded the lowest value. Thermal shock resistance was directly proportional to increase in kaolin, but inversely proportional to increase in bauxite. Mix ratios of 1:1, 6:3 and 7:2 yielded thermal shock resistances above the minimum ASTM value of 15 cycles.

B. Recommendations

Besides encouraging investors to utilize local clays to manufacture refractory bricks and in so doing create employment, reduce importation and improve the balance of trade, further research can be conducted in the following areas:

1. Physical and thermal properties of the composite refractory brick at a temperature of 1600^oc.
2. Thermal conductivity tests for insulating refractories where the thermal gradients from the hot face to the cold face dictate the use of a refractory material for the specific uses.
3. Physical and thermal properties of composite brick from other local clay materials.

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