

Refractory Characteristics of some Nigeria Kaolin Deposits

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Abstract: Refractories for industrial furnace operations in ferrous and non-ferrous industries in developing world are imported. There is growing efforts geared towards import substitution as kaolin deposits are abundant. This paper characterizes an industrial refractory material (kaolin) from two locations in Nigeria and evaluates its firing behavior when rice husk ash (RHA as C) is used as the binder. The physical properties such as water absorption, linear shrinkage and flexural strength of samples fired from 900^oC to 1200^oC were evaluated. Physical properties measured indicated that 80vol % kaolin A (SiO₂-44.98%, Al₂O₃-39.72%, TiO₂-0.65% and Fe₂O₃-0.28%) mixed with 20vol % RHA binder produced bulk density of 2.20g/cm³, apparent porosity (20.5%), permeability number (62), linear shrinkage (4%), thermal shock resistance (30cycles), cold crushing strength (15000 KN/m²) and refractoriness > 1500^oC. These properties were superior to those obtained from kaolin B (SiO₂-44.48%, Al₂O₃-38.69%, TiO₂-1.06%, and Fe₂O₃-1.30%) and from the various mixes. The presence of TiO₂ in kaolin promotes the formation of solid solution of aluminum oxide and titanium dioxide (Al₂O₃.TiO₂) known as aluminum titanate. This solid solution will cause among others low modulus of elasticity and very low coefficient of thermal expansion, leading to excellent thermal shock resistance. Thus these kaolin deposits are potential material for the production of refractory linings for heat treatment and melting furnaces in ferrous and non-ferrous industries.

Keywords: *Rice husk ash; Refractory properties; Kaolin.*

1 INTRODUCTION

The technical requirements of refractory materials are associated with their dimensional parameters (e.g. linear shrinkage and bulk density), mechanical strength, water absorption, chemical stability and wear resistance. The presence of porosity, defects and second phases in a fired refractory affect the physical properties of the materials [1-4]. Desired refractory properties are developed through processing and consolidated during firing as a consequent of physical and chemical reactions which occurs [5-11]. Kaolinitic clay acquire refractory characteristics during firing [12 -14] as a result of the high amount of alumina and low percentage of alkaline oxides impurities, which cause sintering consolidation through liquid phase formation. In principle, through the knowledge of the microstructural aspect and characteristics of the refractory body, and changes in process conditions could improve the properties to the point of reaching furnace lining specifications.

RHA rich in SiO₂ (>85%) and containing very little amount of Al₂O₃ has been found useful to increase the compressive strength of geopolymer mortar having low Al₂O₃ content at room temperature [15]. In recent years,

RHA was used in partial replacement for Portland amount in concrete.

RHA is unusually high in ash compared to other biomass fuels, close to 20% with the ash composed of 92-95 % silica, highly porous and lightweight, and possessing a very high external surface area. Its absorbent and insulating properties are useful to many industrial applications. In Nigeria refractory for industrial furnace operations in ferrous and non-ferrous industries world are imported. There is growing efforts geared towards import substitution as kaolin deposits are abundant in the country. This study is therefore aimed at characterizing selected kaolin deposits in Nigeria to ascertain its suitability for use as furnace lining.

2 APPROACH AND METHODS

The materials used are kaolin samples from two different locations and RHA (as binder). Kaolin samples were obtained from two locations in southwest Nigeria, i.e. sample A from Abeokuta and Sample B from Iwo deposits (both are towns in southwest Nigeria) and mixture of samples A and B. These samples were mixed

with Rice husk ash (RHA) as binder in volume proportion between 0-20 vol %. The chemical compositions of these materials are shown in Table 1. Table 2 shows the

refractory properties of the kaolin samples. Samples A and B were mixed together in various proportions and the binder added (see Table 3).

Table 1: Chemical composition of Kaolin A and B and Rice Husk Ash (RHA).

constituent	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI
% A	44.98	39.72	0.65	0.28	0.08	0.09	0.37	0.05	13.74
% of B	44.48	38.69	1.06	1.30	0.18	0.08	0.02	0.09	13.70
% of RHA	93.15	0.21	0	0.21	0.41	0.45	3.21	0	2.36

Table 2: Refractory Properties of Kaolin A and Kaolin B

Sample	Bulk Density g/cm ³	Apparent Porosity	Permeability	Linear Shrinkage (LS) %	Thermal shock Resistance cycles	Cold crushing strength (CCS) KN/m ²	Refractoriness °C
A	2.25	22.28	62	4	30	15,500	>1500
B	1.97	19.95	78	4	30	11,700	>1500

Table 3: Refractory Properties of cast samples of Kaolin A and Kaolin B with RHA

Sample of kaolin %		RHA % C	L S %	CCS KN/m ²	Refractoriness °C
A	B				
100		0	4	15500	>1500
95		5	4	12400	>1500
90		10	4	11750	>1500
85		15	4	8000	>1500
80		20	4	15000	>1500
	100	0	4	11700	>1500
	95	5	6	11000	>1500
	90	10	4	10200	>1500
	85	15	6	10000	>1500
	80	20	4	8200	>1500
80	20	0	4	10000	>1500
77.5	17.5	5	4	9100	>1500
75	15	10	4	9000	>1500
72.5	12.5	15	4	8100	>1500
70	10	20	4	8000	>1500
60	40	0	4	11000	>1500
57.5	37.5	5	4	10600	>1500
55	35	10	4	10000	>1500
52.5	32.5	15	4	9400	>1500
50	30	20	4	9200	>1500
40	60	0	4	11400	>1500
37.5	57.5	5	4	10600	>1500
35	55	10	4	10000	>1500
32.5	52.5	15	4	9400	>1500
30	50	20	4	10300	>1500
20	80	0	4	11000	>1500
17.5	77.5	5	4	10000	>1500
15	75	10	4	9500	>1500
12.5	72.5	15	4	9000	>1500

10	70	20	4	8000	>1500
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2.1 Bulk Density

The as-mined kaolin ores were crushed in a jaw-air crusher and ground to fine grains of 100 meshes. The different samples were blended with the RHA, water added at a measure of 10 cl/200g powdered material and molded. The test samples were then prepared into test laboratory sizes of rods 5.08cm length and 5.08cm diameter. The prepared test samples were first air-dried and then oven dried at 110⁰C for 24 hours before firing at 1100⁰C for another 24 hours and subsequently placed in a desiccator. The test samples were weighed to an accuracy of 0.001g (dried weight), after which the samples were individually transferred to a beaker and heated for 30 minutes to assist in releasing the trapped air. The samples were cooled and soaked weight (W_s) taken. The samples were then suspended in water and the suspended weight (S_s) taken. The bulk density was calculated from using Equation 1.

$$B_o(\text{g/cm}^3) = D\rho_w / (W_s - S_s) \quad (1)$$

D = dried weight in g, W_s= soaked weight in g, S_s = suspended weight in g, ρ_w= density of water (1g/cm³)
 The test was repeated for the various Kaolin/additive mix and the average of the evaluated values recorded.

2.2 Apparent Porosity

The test pieces are made in a mould of internal diameter of 1.52cm and height 2.7cm and pressed at a pressure of 7 metric ton in a hydraulic press. The test samples produced were dried and fired at 1100⁰C.

The hot test piece boiling water method was used for apparent porosity response of the test samples. The sample was weighed dry, soaked in boiling water and the saturated sample is immersed in cold water before weighing. Thereafter, the porosity is determined (see Equation 2).

$$AP \% = (w_b - w_a) \times 100 / (w_c - w_b) \quad (2)$$

w_a = weight of dry test piece, w_b = weight of the test piece soaked with water and suspended in water, w_c = weight of the test piece soaked with water and suspended in air.

2.3 Permeability to Air

Test samples were air dried for 24 hrs and then dried at 110⁰C for 12 hrs in an oven. The permeability-testing machine consisted of a cylindrical arrangement in which a bell jar was put in place to displace certain volume of air,

which was equal to the volume of water placed in the cylinder. A manometer was connected to measure the pressure during the displacement of air. The samples were completely sealed on the sides and the lower surface was exposed to an orifice. The cylinder was filled with 200cm³ of water and the bell jar was put in place. The orifice was opened and time taken for 2000cm³ of water to displace equal volume of air through the samples was taken.

The pressure difference between the surfaces was measured by the manometer and the test piece permeability determined using equation 3.

$$P_A = VA/APT \quad (3)$$

P_A = Permeability to air, cm³/min, V = Volume of air displaced, cm³, H= Height of specimen, cm, A = Cross – sectional area of specimen, cm², T=time taken, min, P = Pressure of air, cm of H₂O.

2.4 Thermal shock resistance

The test samples were inserted into a furnace kept at 1100⁰C and maintained for 10 minutes. The samples were removed one after the other and then cooled for 10 minutes. The specimens were returned to the furnace for a further 10 minutes. The process continued until the pieces were readily pulled apart in the hands. The number of cycles withstand before fracture were recorded for each test specimen.

2.5 Linear Shrinkage

Test pieces were made into standard slabs and marked along a line in order to maintain the same position after heat treatment. The pieces were air-dried for 24 hours and oven dried at 110⁰C for another 24 hours, fired at 1100 °C for 6 hours and cooled to room temperature (32 °C). Dried (D) and fired lengths (F) of test pieces are measured using a pair of vernier caliper and the linear shrinkage determined using Equation 4.

$$\text{Linear shrinkage} = 100X (D-F) / D \quad (4)$$

2.6 Compressive Strength

The samples were placed one after the other on a compressive strength tester and load was applied axially by turning the hand wheel of a tensometer at a uniform rate till failure occurred. The tensometer readings were recorded and compressive strength (cold crushing strength - CCS). CCS = Maximum load to failure/Cross - Sectional areas (KN/m²)

2.7 Refractoriness

The Orton standard cone method (ASTM Manual 1957) was deployed. Test cones were made from each of the Kaolin/additive mix. Each of these test cones was mounted on a refractory plaque along with a standard cone of known refractoriness. The cone was then inserted into the furnace and temperature rose to 1000⁰C. The temperature was raised at the rate of 25⁰C per hour till the maximum temperature of 1700⁰C was attained. The standard orton cone and the test pieces were arranged, observed for sign of crack and the number of the best matching standard orton cone was quoted as the pyrometric cone equivalent temperature of the material. The results from the tests are presented in Figures 1a-4e.

3 RESULTS AND DISCUSSION

3.1 Bulk density

The bulk density (2.2g/cm³) of sample A decreases as the amount of RHA in it decreases from 20-12 vol % and reaching a minimum of 1.25g/cm³. For sample B, this increases until a maximum value of 2.2g/cm³ is attained at 7 vol % RHA addition. Further reduction in percent RHA from 12 vol % causes increase in the bulk density of sample A to a maximum value of 2.25g/cm³ at 0% while this decreases the bulk density of sample B to a minimum of 1.25g/cm³ (see Figure 1a). It was apparent that higher volume fraction of RHA in sample B (>10 vol %) will increase its density and reduce that of the sample A. When samples A and B are mixed with RHA, the bulk density increases with decrease in binder fraction and attaining a maximum of about 2.0g/cm³ (see figs 1b-1c). Thus the density of sample A can be reduced by adding 5-15 vol % binder, while this will increase density of B.

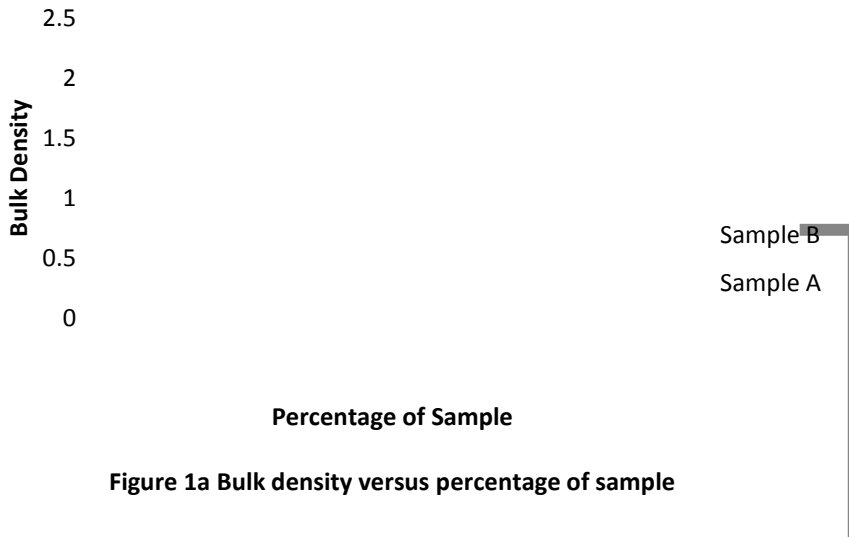


Figure 1a Bulk density versus percentage of sample

Sample A+B and C

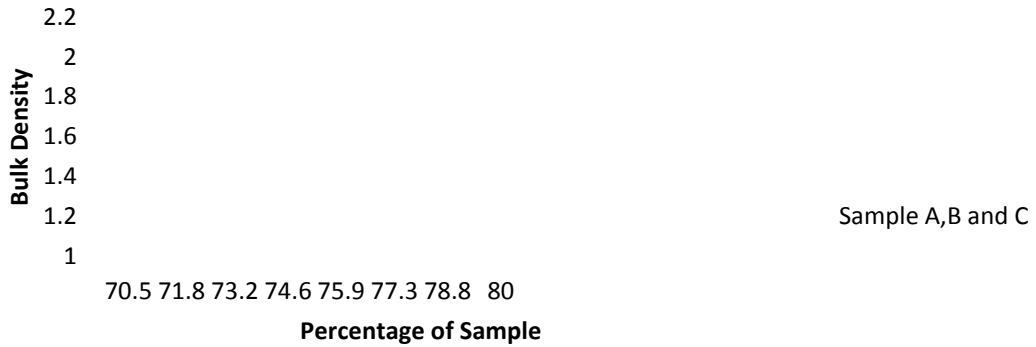


Figure 1b Bulk density versus percentage of sample

Sample A+ B and C

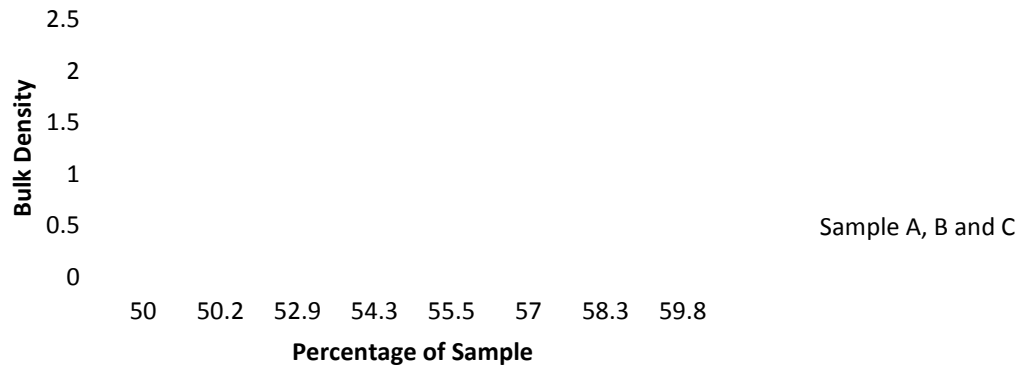


Figure 1c Bulk Denity versus Percentage of Sample

Sample A+ B and C

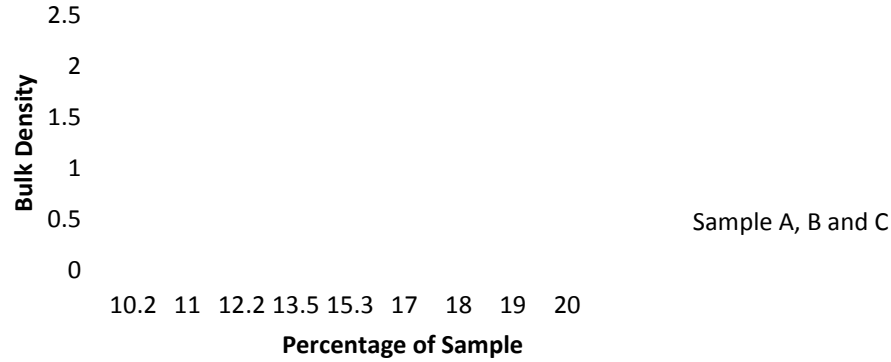


Figure 1e Bulk Density versus Percentage of Sample

3.2. Apparent Porosity (AP)

Within the range of binder considered, AP of sample A increases with decrease in RHA content from 20-15% and maximum of (23.5%) attained. However, the AP of B decreases and reached a minimum of 26.5%. Decreasing binder content from 15%, AP of A decreases slowly to a

minimum of 22.5%, while that of B increases sinusoidally. Between 18-20 vol % of binder, the AP of A can be reduced significantly, and that of B between 12-18% (see Figure 2a). The AP of mixture of A and B with RHA increase with the amount of RHA and sample B in the mix. The mix porosity is comparable to that of simple A, when A is about 35 vol % (see Figures 2b-2e).

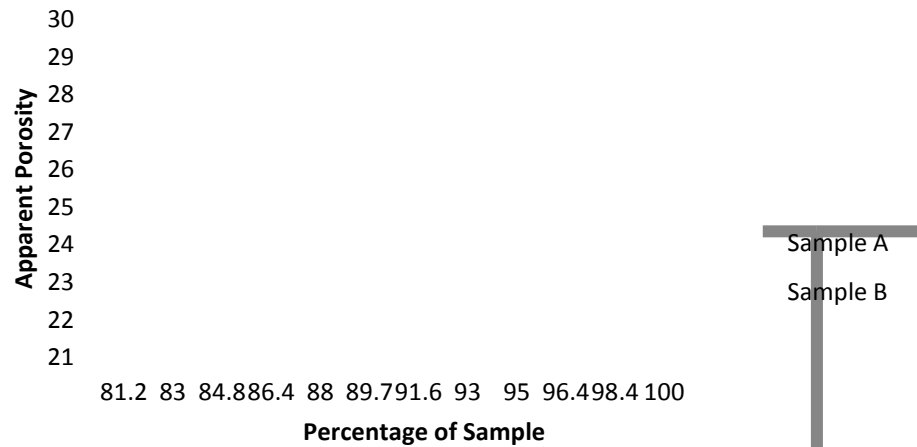


Figure 2a Apparent porosity versus percentage of sample

Sample A+ B and C

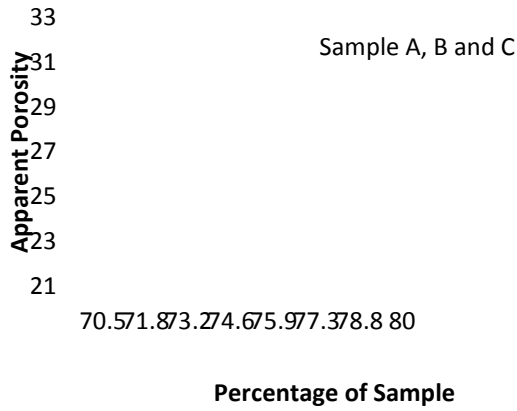


Figure 2b Apparent porosity versus percentage of sample

Sample A+B and C

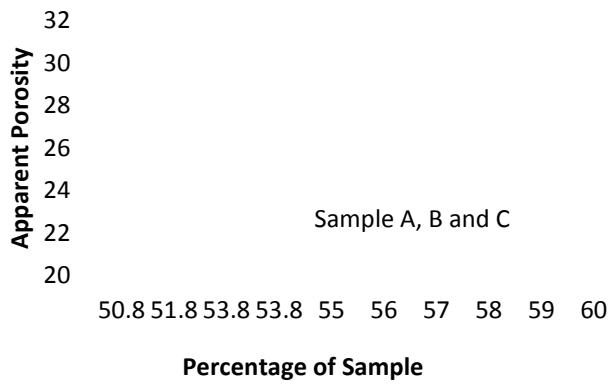


Figure 2c Apparent Porosity versus Percentage of Sample

Sample A+B and C

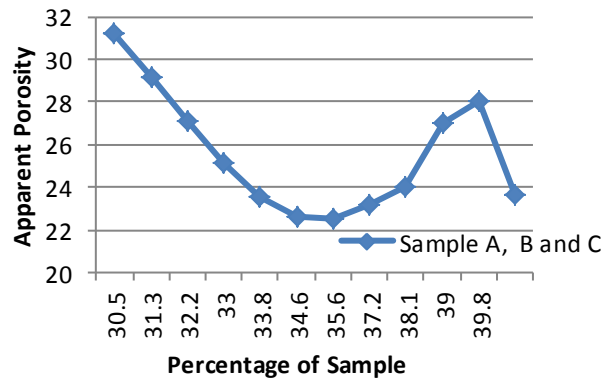


Figure 2d Bulk density versus percentage of sample

Sample A, B and C

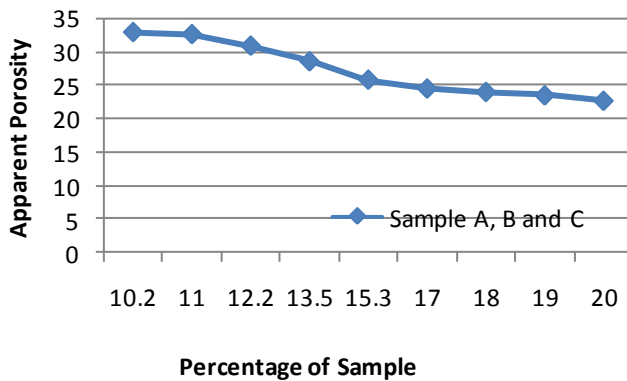
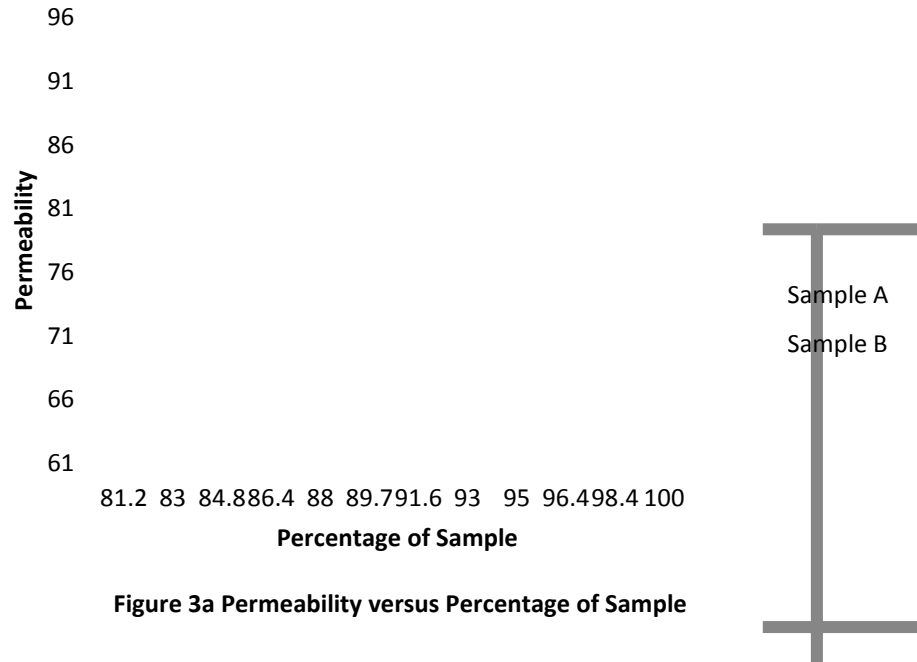


Figure 2e Apparent Porosity versus Percentage of Sample

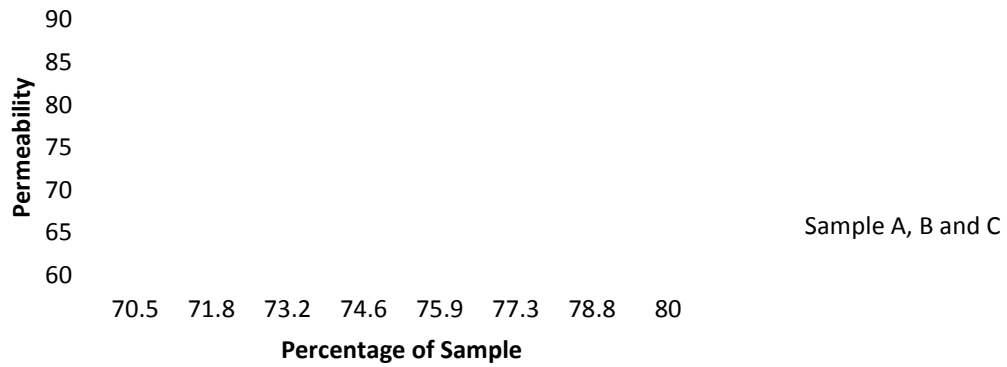
3.3. Permeability

The permeability of A decreases as RHA content decreases from 15% with minimum of 62.5%. Sample B permeability decreases as binder content goes down from 20 to 5% and it is minimum at 70%. It is in this range that permeability of B can be improved. For A the

permeability cannot be improved upon by RHA addition (see Figure 3a). Permeability of B can be improved by blending with 75 vol % or 13-15 vol % of sample A (see Figures 3b and 3c). In Figures 3c and 3d, the addition of A to B does not significantly improve the permeability of B even in the presence of the binder.



Sample A+B and C



Sample A+B and C

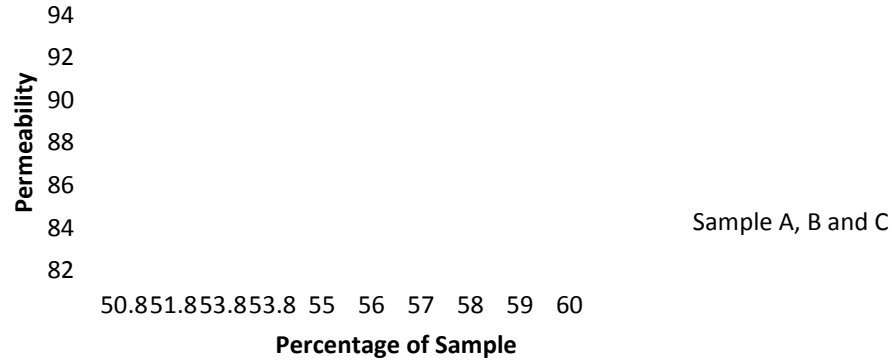


Figure 3c Permeability versus Percentage of Sample

Sample A+B and C

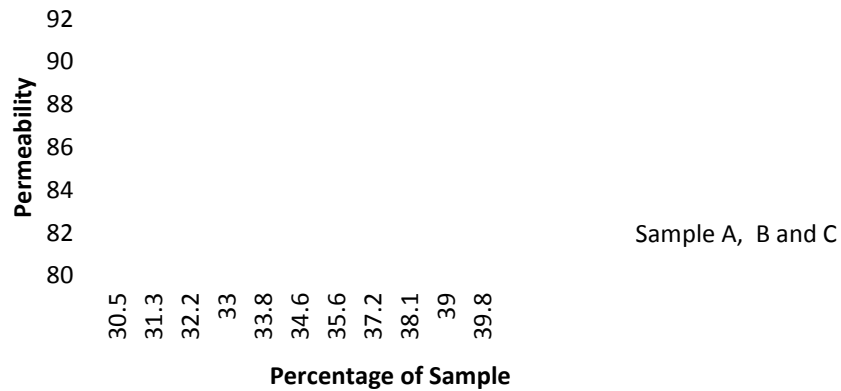


Figure 3d Permeability versus percentage of sample

Sample A+B and C

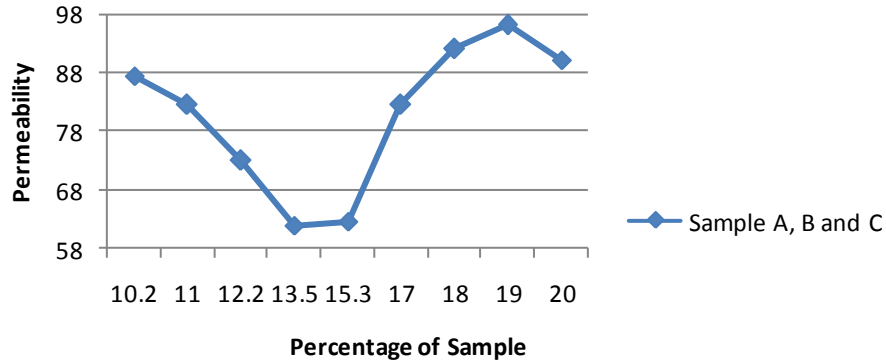


Figure 3e Permeability versus Percentage of Sample

3.4 Thermal Shock resistance

The thermal shock resistance of samples A and B individually improves with increase in binder addition to 15vol %. However, the thermal resistance of A is higher

(32) than that of B (18) (see Figure 4a). The thermal resistance of B can be enhanced through blending with 12-20 vol % A or 50-55 vol % A and adding RHA between 5-15 vol percent (see Figures 4b-4e).

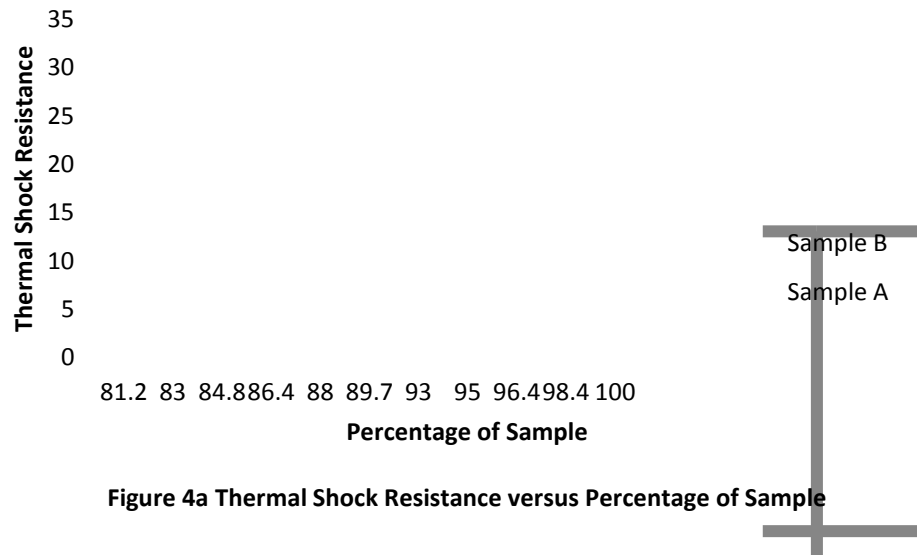


Figure 4a Thermal Shock Resistance versus Percentage of Sample

Sample A+B and C

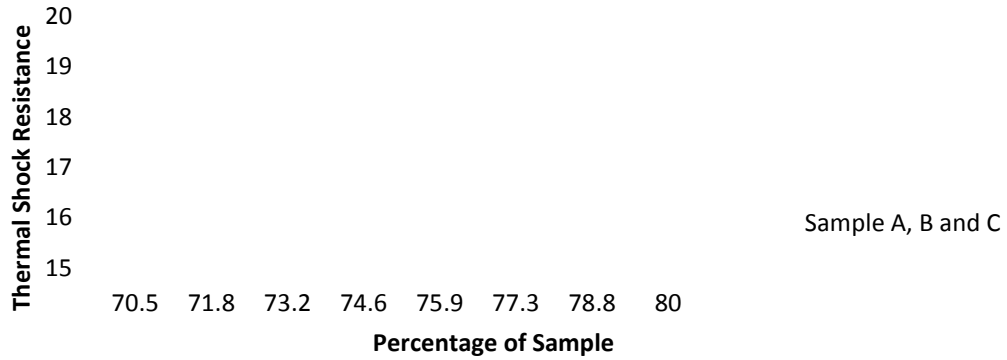


Figure 4b Thermal Shock Resistance versus Percentage of Sample

Sample A+B and C

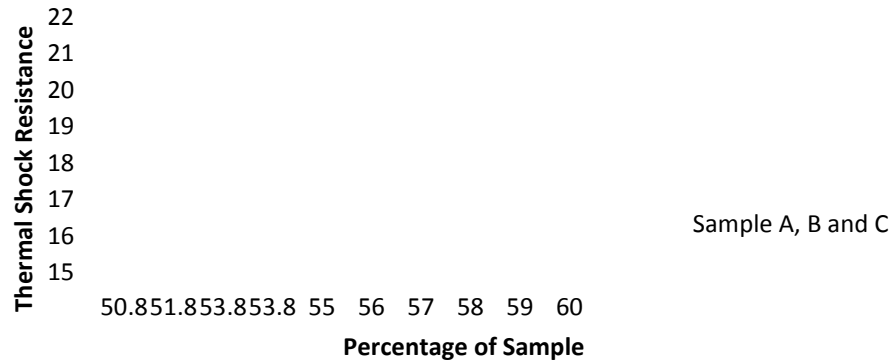


Figure 4c Thermal Shock Resistance versus Percentage of Sample

Sample A+B and C

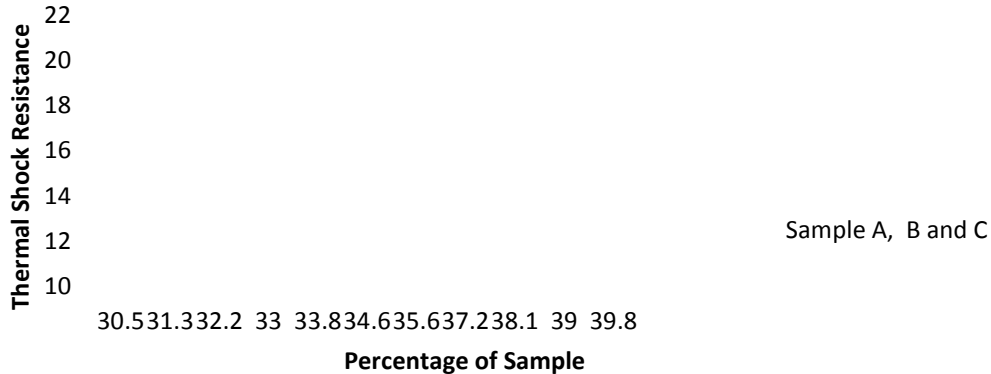


Figure 4d Thermal Shock Resistance versus Percentage of Sample

Sample A+B and C

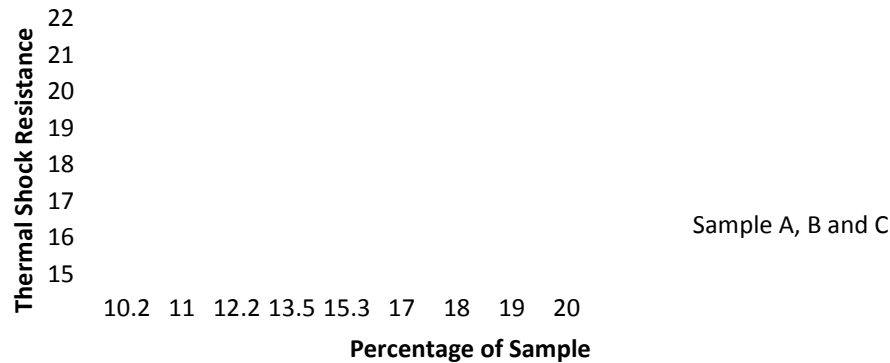


Figure 4e Thermal Shock Resistance versus Percentage of Sample

3.5 Linear shrinkage, cold crushing strength, refractoriness

The linear shrinkage of sample A is not affected by the addition of RHA and sample B. However, for sample B RHA addition of 5 and 15 vol % causes an increase in linear shrinkage from 4-6% (see Table 3). The cold crushing strength of the sample A with 20 vol % RHA addition is superior to that of other mixes (15000KN/m²). The strength of sample B decreases with the addition of RHA. Blending samples A and B and adding the binder does not improve the strength (see Table 3). Despite the nonlinear refractory properties of the kaolin samples with the binder the refractoriness of the mixes are higher than 1500°C (see Table 3).

3.6 Summary

Sample A has superior refractory properties over that of sample B with or without RHA, in terms of bulk density, thermal shock resistance and cold crushing strength. Sample B, is however superior to A in apparent porosity, permeability and linear shrinkage (see Tables 1 and 2). It should be noted that the refractoriness of both samples is above 1500°C.

The addition of sample A with the RHA has been seen to improve linear shrinkage, apparently porosity and thermal shock resistance of B. Although, cold crushing strength is slightly affected but comparing results with standard insulating fire refractory given by Vaghan F (1958), Kaolin A with 20 vol % RHA are of similar properties.

The presence of TiO₂ in kaolin A and B will promote the formation of solid solution of aluminum oxide and titanium dioxide (Al₂O₃.TiO₂) known as aluminum titanate. This solid solution will cause among others low modulus of elasticity and very low coefficients of thermal expansion, leading to excellent thermal shock resistance (see Table 2). These properties result from a high residual porosity and from micro-cracks resulting from highly anisotropic thermal expansion in the individual aluminum titanate. The high TiO₂ content of kaolin B is thus responsible for its inferior properties in terms of low thermal shock resistance, high permeability and high porosity to that of kaolin A.

The relatively lower amount of Fe₂O₃ in kaolin A is an indication that this kaolin is more adequate to the fabrication of ceramic products with color (see Table1). The amount of TiO₂ in kaolin B is higher than that of kaolin A. This may cause a yellowish color that is not satisfactory for white wares. Thus kaolin A can be used to process white wares. The presence of 0.37 % K₂O in kaolin A and when blended with RHA having 3.21% K₂O will form a liquid phase that contributes to densification at high temperatures.

4 CONCLUSIONS

1. The SiO₂ and alkali oxide content of the kaolin is significantly increased by RHA. This increase in the content of acid/basic components of the kaolin are responsible for the impressive properties of kaolin A over that of B.
2. The oxides SiO₂ and TiO₂ have over bearing effect on refractoriness of A and B. Low content of these oxides in A is responsible for the superior refractoriness of A over B.

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