

PORCELAIN CERAMICS FROM AGRIC-WASTE RICE HUSK ASH (RHA)

^aH. U. Jamo, ^bI. A. Auwalu, ^cM. A. Y. Hotoro

Department of Physics, Kano University of Science and Technology Wudil, P.M.B. 3244 Kano.

Abstract

In this study, rice husk ash (RHA) was used as a fluxing agent, in a porcelain body, was determined. The RHA was used as a substitute for quartz at different replacement levels (0wt%-25wt%). The mixed powder was pressed into pellets and bars at pressure of 91 MPa. All the pellets were sintered at the temperatures of 1000°C, 1100°C, 1200°C and 1300°C for 2 hours soaking time, at a heating rate of 5°C per minute. The Vickers hardness, bending strength and compressive strength tests are directly related to the increase in temperature and substitution. The microstructural observations show that as the temperature increases to the grain size becomes smaller because of the quartz conversion to cristobalite due to increase in temperature and substitution of quartz by RHA. The compressive strength was the highest at a temperature of 1200°C on 20wt% substitution of RHA. The improvement in the properties could be attributed to sharp changes in the microstructural features as a result of increase in mullite and glassy phase simultaneously.

1.0 Introduction

RHA is obtained by burning the rice husk, and in particular in plants where rice milling is performed with cogeneration or similar facilities or in plants for the production of parboiled rice. In general, the RHA so obtained is dumped as a waste. Globally, approximately 600 million tonnes of rice paddy is produced each year [1]. Assuming a husk to paddy ratio of 20%, and an ash to husk ratio of 20%, the total global ash production could be as high as 21,000,000 tonnes per year. RHA is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to the burning technique. The silica in the ash undergoes structural transformations depending on the conditions (time, temperature, etc.) of combustion. At 550–800 °C amorphous ash is formed and at higher temperatures than this, crystalline ash is formed. These types of silica have different properties, the correct specifications of which are important to produce ash for the particular end use [2]. The presence of silica in RHA has been known since 1938 [3] an extensive literature search has highlighted many uses of RHA as silica replacement. Two main industrial uses have been identified: as an insulator in the steel industry and as a pozzolan in the cement industry. RHA is used by the steel industry in the production of high quality flat steel. Moreover, RHA is an excellent insulator, having low thermal conductivity, high melting point, low bulk density and high porosity[4]. It is this insulating property that makes it an excellent ‘tundish powder’ that prevents rapid cooling of the steel and ensures uniform solidification in the continuous casting process. On the other hand, substantial research has been carried out on its use in the manufacture of concrete. In particular, there are two areas for which RHA is used: in the manufacture of low cost building blocks, and in the production of high quality cement. The addition of RHA to cement has been found to enhance cement properties. In general, concrete made with Portland cement containing RHA has a higher compressive strength [5]. The use of rice husk ash in the form of silica in the ceramic field was also reported Prasad *et al.*, [6], Bondioliet *al.*, [7] and Kitouni *et al.*, [8] also investigated physico-chemical properties of RHA for its application. Prasad *et al.*, studied the effect of RHA in porcelain composition [9] and found improvements in the properties with the reduction in the maturing temperature. They found out that 10 wt% of RHA can be used to replace quartz in a porcelain composition. However, this is not enough, as RHA still remain a problem to the environment. There is still need for some alternative means to be used to in order to further reduce this menace. Hence, this study therefore, wishes to find out the mechanical properties of porcelain body by replacement of quartz by 20 wt% of RHA at different temperatures.

2.0 Experimental Procedures

The RH was thoroughly washed with distilled water in order to remove adhering soil and dust. After that it was dried in an oven at 100°C for 24 hours. Then the dried husk was subjected to the chemical treatment; 2M HCL, 5% solid at 25 °C before calcinations to increase silica content. After the leaching process, the treated husk was washed with distill water and then dried again. The treated husk was then subjected to calcinations at 700°C for six (6) hours, after which it was subjected to the XRF analysis. The machine used for the analysis was XRF Bruker S4 Pioneer which was operated at 60 KV and 50 mA.

Corresponding Author: Jamo H.U., Email: jamouhfce@gmail.com, Tel: +2348026274525

Porcelain raw materials was grounded separately in a ball mill. The powder was sieved using 50µmsieve and dried in an oven. The RHA was gradually incorporated into the body of porcelain powder (Table 1). The composition was mixed using a ball mill for 1.5 hours. The mixed powder was pressed into pellets and bars at pressure of 91 MPa. All the pellets were sintered at the temperatures of 1000°C, 1100°C, 1200°C and 1300°C for 2 hours soaking time, at a heating rate of 5°C per minute. The physical and mechanical properties of the pellets such as bending strength, Vicker’s hardness and compressive strength were determined. The chemical composition of the RHA was studied using X-Ray Fluorescence (XRF) while the crystalline structure of the pellets was identified through XRD and the microstructural features were studied by SEM.

The formula for the measurement of exterior volume, V, is as follows.

$$V = M - S \text{ (cm}^3\text{)} \tag{1}$$

Where;

V = Exterior volume (cm³)

M = Saturated mass (wet) (g)

S = Floating in water mass (g)

The bulk density, B, expresses as a g/cm³, was calculated as follows:

$$B = \frac{D}{V} \text{ (g/cm}^3\text{)} \tag{2}$$

Where;

B = Density (g/cm³)

D = Dry mass (g)

V = Exterior volume (cm³)

The Vickers hardness number, HV, is given by:

HV = Constant × (Test force / Surface of indentation)

$$HV = 0.102 \times \frac{\left(\sin \frac{136^\circ}{2}\right)}{d^2}$$

The formula for the bending strength of a beam in three-point is as follows.

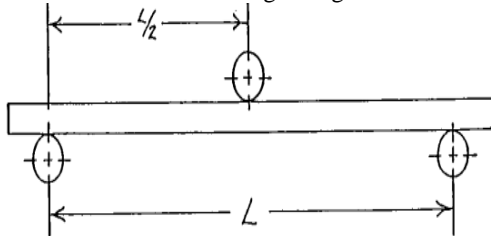


Figure. 1: The three point fixture configuration

$$S = \frac{3PL}{2bd^3} \text{ (MPa)} \tag{3}$$

Where:

P = break load, (N)

L = outer (support) span (N)

b = specimen width and (cm)

d = specimen thickness (cm)

The compressive strength can be calculated by the formula;

$$\sigma_{comp} = \frac{F_r}{A} \text{ (MPa)} \tag{4}$$

Where

σ_{comp} = resistance of compression (MPa)

F_r =load at fraction (N)

A =area of the disc surface (cm²)

Table 1: Body composition with progressive replacement of quartz by RHA in a standard whiteware composition (wt %)

Mix Number	Kaolin	Feldspar	Quartz	RHA
AP1	50	25	25	0
AP2	50	25	20	5
AP3	50	25	15	10
AP4	50	25	10	15
AP5	50	25	5	20
AP6	50	25	0	25

Results and discussion

X-Ray Fluorescence (XRF) analysis is proficient in analyzing material contents inside the raw materials, hence the amount of chemical elements can be observed. The presence of various elements within the raw materials can be seen in Table 2. This table shows the result of XRF analysis of kaolin, feldspar, quartz, RHA.

Table 2: Chemical analysis of the materials

Sample	Content (% wt)											
Oxides	SiO ₂	Al ₂ O ₃	FeO ₃	K ₂ O	P ₂ O ₅	CaO	MgO	CO ₂	SO ₃	Na ₂ O	TiO ₂	LOI
RHA	93.70	2.11	-	1.18	0.96	0.81	0.53	0.10	0.45	-	-	0.16
Kaolin	69.30	24.30	0.27	2.44	-	-	-	0.10	-	-	0.27	0.36
Feldspar	72.70	16.40	0.40	0.50	2.42	-	-	-	6.87	0.29	-	0.10
Quartz	99.40	0.22	-	-	-	-	-	0.10	-	-	-	0.28

It is evident that SiO₂ is the major composition in all the raw materials viz: kaolin, feldspar, quartz, RHA with 93.7 wt%, 69.3 wt%, 72.7 wt% and 99.4 followed by alumina with 2.1 wt%, 24.3 wt%, 16.4 wt% and 0.2 wt% respectively.

Figure 2 shows the result of bulk density of the mixed samples containing RHA. It could be seen from the figure that the bulk density has an increasing trend. The bulk density increases with increase substitution of quartz by RHA. With an approximate values of 2.28 g/cm³ the maximum bulk density was reached on 15 wt% of RHA at a temperature of 1000°C, further substitution causes the bulk density to decrease. At the temperatures of 1100°C, 1200°C and 1300°C the maximum was reached on 20 wt% of RHA with an approximate values of 2.38 g/cm³, 2.42 g/cm³ and 2.35 g/cm³ respectively. This could be as a result of increase in mullite which mainly originates from kaolin, feldspar and RHA. The incorporation of RHA in the porcelain ceramics has reduced the maturing temperature to 1200°C, as against the 1280°C reported by Martin-Marquez [9].

In terms of temperature the bulk density increases as the temperature increases between the temperatures of 1000°C to 1200°C. The increase in bulk density due to increase in temperature could be due to decrease in internal pores as the temperature increases which causes the densification to increase [10-16]. However, as the temperature increases to 1300°C the values for bulk density decreases, this could be as a result of bloating.

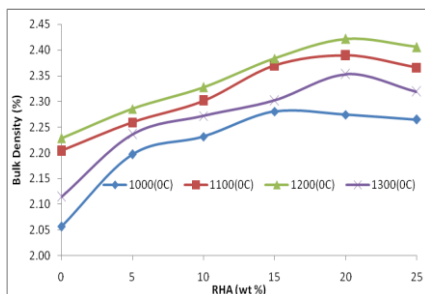


Figure 2: Effect of temperature on bulk density of samples with different percentage of RHA

The result of Vicker's hardness of the samples is shown in Figure 3. In conformity with the bulk density result presented in Figure 1 the Vicker's hardness increases with increase substitution of quartz by RHA. However, the sample containing 20 wt% of RHA showed highest hardness with 1052 HV at the temperature of 1200 °C. The increase in Vickers hardness could be attributed to internal stresses that arises, first because of the difference in thermal linear expansion coefficients of quartz and the glassy phase and secondly because of polymorphic transformation in SiO₂ from RHA. The stresses can be reduced substantially by decreasing disparity of the initial and residual quartz [17]. This is in conformity with the XRD presented in Figure 5 both quantitative and qualitative (Table 3) analysis. The SEM (Figure 6) observation are supportive of the Vicker's hardness result. A similar conclusion had been also reached by Pérez [18], that the hardness in particular and mechanical strength in general of porcelain is influenced mainly by stresses set up in the glassy phase. SiO₂ from RHA makes up part of the crystalline phases of porcelain that develop the needed hardness to the porcelain. A considerable part of SiO₂ and Al₂O₃ passes into molten feldspar, which increases the hardness of the sample.

With the complete replacement of quartz by RHA, the hardness of the sintered porcelain decreases. The decrease in the hardness in the samples containing more than 20 wt% of RHA lies in the increase in the excess glassy content. It is evident that although hardness of the samples containing more than 20 wt% decreased marginally, higher amount of RHA are responsible for the formation of additional liquid phase and enhancement of the densification process. Hence, the substitution of quartz by RHA in the porcelain ceramic did not only lead to the reduction in maturing temperature compared to the standard porcelain but also increased marginally the hardness of the porcelain ceramics at the respective temperatures, except for the body with 25 wt%.

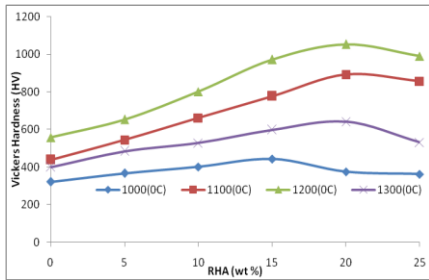


Figure 3: Effect of temperature on Vickers hardness of body mixes with different percentage of RHA

The bending strength of the samples is plotted as a function of temperature (Figure 4). It's values increases with increase in temperature and replacement. The maximum bending strength was achieved with an approximate values of 19 MPa on 15 wt% of RHA, 30 MPa, 34 MPa and 26 MPa on 20 wt% RHA. The RHA particles have significant effects on bending strength of porcelain bodies. The dissolution of SiO₂ from RHA improves the inter planar spacing within the porcelain body and glassy matrix. With incorporation of RHA, the maturing temperature decreased by 80°C in a sample containing 10 wt%, 15 wt% and 20 wt% respectively. The hardness of sample containing 20 wt% has 17% increase over the standard porcelain ceramic. Substitution above 20 wt% of RHA causes the bending strength to decrease because of excess glassy formation.

In terms of temperature the bending strength increases from 1000 °C to 1200 °C and decreases after reaching maximum at a temperature of 1300°C. The quartz grains in different sizes have significant effects on flexural strength of porcelain bodies. It is proposed by Stathis [19], that bending strength of the porcelains increases with an increase in inter planar spacing of quartz crystals, and consequently, the glassy matrix surrounding the quartz grains.

Jamo [20] explained that there is a fluxing stress which acts as pre-stress, improving the bending strength. The major crystalline phase is quartz, the trace crystalline phase is mullite. This phenomenon indicated that part of the SiO₂ from RHA combined with Al₂O₃ to give mullite, part of the SiO₂ from RHA melted in the glass phase whose content increased with increasing temperature, and the rest of the SiO₂ remained in the body. As the samples were heated above the temperature of 1200°C the mullite needles coarsen, leading to a smaller number of larger needles the larger do not inter lock as efficiently as the smaller ones, resulting in decrease in bending strength. This is in line with the SEM analysis presented in Figure 6.

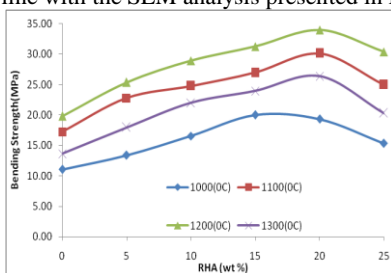


Figure 4: Effect of temperature on bending strength of body mixes with different percentage of RHA

The result of compressive strength is presented in Figure 5. The compressive strength increases with the increase in temperature and increase in replacement of quartz by RHA. The maximum values of compressive strength was achieved with values of 31 MPa for 1000 °C on 15 wt% of RHA, while 39 MPa, 44 MPa and 34 MPa for the temperatures of 1100 °C, 1200 °C and 1300°C on 20 wt% of RHA respectively. The felt like interlocking of fine mullites needles are responsible for the porcelain strength and is improved by SiO₂ and Al₂O₃ from RHA, the matrix reinforcement hypothesised that induced thermal compressive stresses due to thermal expansion mismatch lead to strength improvement, and the dispersion-strengthening hypothesis posit that the dispersed particles limit the of Griffith flaws, leading to increased compressive strength[16]. Decrease in the values of compressive strength was recorded when the substitution was increased from 20 wt% to 25 wt% due to excess glassy formation.

Similarly, the compressive strength increases as the temperature increases from 1000 °C to 1200 °C. The values of compressive strength decreases at a temperature of 1300°C. An increase in sintering temperature promotes the compressive strength. In addition, the existence of oxides, such as Al₂O₃, SiO₂ and K₂O, in the RHA were beneficial to the formation of mullite and low melting liquid. With the increase of sintering temperature, the low-viscosity liquid flowed and filled the pores and consequently helped the compressive strength. This result is similar to a study conducted by Bragança *et al.* [21].

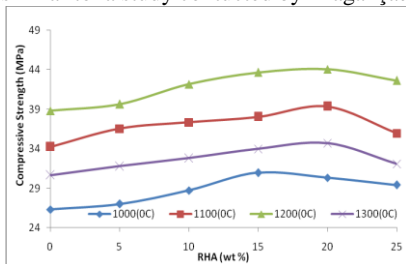


Figure 5: Effect of temperature on compressive strength of body mixes with different percentage of RHA

Two factors could influence the samples' compressive strength in this experiment: densification process and mullite crystals. From 1000°C to 1200°C, the compressive strength increased because the effect of densification is dominant and no obvious mullite crystals were observed in SEM micrographs (Figure 6). This improvement of compressive strength is ascribed not only to the enhanced densification, but also to the formation of mullite crystals. It could also be explained by the formation of network structure consisting of many interlocked felt-like mullite crystals, which were embedded in glassy phase in high-iron and medium iron samples.

Between the temperatures of 1000°C and 1200°C the mullite needles interlock effectively, and the dispersed particles limit the Griffith flaws leading to strength improvement. But sintering above the temperature of 1200°C over firing takes place Griffith flaws were developed, dispersed particles could no longer limit the flaws, mullite needles coarsen in larger needles and consequently, the compressive strength decreases. It could be concluded that 20 wt% substitution of RHA is the best composition, hence the XRD and the microstructure analysis were observed on the best composition.

Figure 6 shows the XRD qualitative analysis for mixed samples containing 20 wt% of RHA sintered at different temperatures. Three major phases identified are quartz (ICDD 046-1045), mullite (ICDD 074-4143) and cristobalite (ICDD 039-1425). The peaks intensity for mullite and cristobalite increases between the temperature of 1000 °C and 1200 °C and decreases at a temperature of 1300 °C. The increase in mullite is a result of reaction between Al₂O₃ and SiO₂. While the increase in cristobalite peaks is as a result of quartz dissolution. In line with the XRD qualitative analysis the quantitative analysis (Table 4.2), shows that the quartz decreases while mullite increases and cristobalite increases, as the temperature increases from 1000 °C to 1200 °C. At a temperature of 1300 °C a reverse trend was noticed. All the values of three minerals decreases.

Figure 6 shows the SEM analysis of the polished samples containing 20 wt% of RHA sintered at different temperatures. They were pressed at the mould pressure of 91MP, and the soaking time was 2 hours.

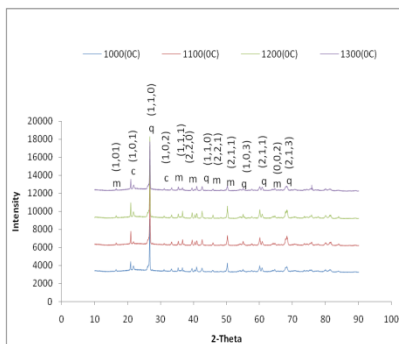


Figure 6: The XRD curves of the mixed samples containing 20 wt% of RHA sintered at different temperatures

Table 3: XRD quantitative analysis of the body mixed samples containing 20 wt% RHA sintered at different temperatures

Temperature (°C)	Quartz (%)	Mullite (%)	Cristobalite (%)	Glassy Phase (%)
1000	64.1	15.2	6.9	9.8
1100	61.6	18.0	10.3	10.1
1200	53.0	28.7	15.8	3.5
1300	52.3	20.7	13.1	13.9

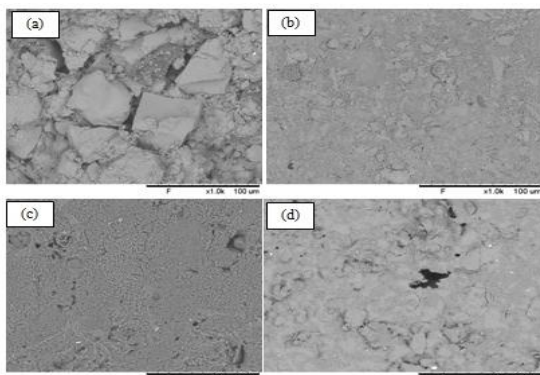


Figure 7: The SEM of the mixed samples containing 20 wt% of RHA sintered at different temperatures of (a) 1000 °C (b) 1100 °C (c) 1200 °C (d) 1300 °C. All micrograph were taken with 1000X magnification

It can be seen from Figure (7a) that the grains are big due to undissolved minerals at the temperature of 1000 °C, but as the temperature increases to 1100 °C the grains becomes smaller (Figure 7b). Least porosity can be seen from Figure 7c. More mullite and cristobalite are also formed as the temperature increases, the grain size become smaller, densification took place because of

glassy phase that are formed as a result of increase in temperature and substitution of quartz by RHA. As the temperature reaches 1300 °C (Figure 7d) pores re-emerged, this could be as result of bloating(i.e., pore volume expansion), which arises from higher pressures (at high temperatures) of gases such as nitrogen, carbonmonoxide and carbondioxide entrapped within closed pores.

Conclusion

The microstructures of porcelain ceramics is dependent on the temperature and wt% RHA substitution. Mechanical properties of porcelain is greatly improved by these microstructures. Increase in sintering temperature leads to in increase in compressive, bulk density and decrease in porosity. Introduction of RHA into the pocelain body causes densification to increase, bulk densityto increase. The maximum values of compressive strength, bending strength Vicker's hardness and bulk density were achieved at a temperature of 1200°C on 20wt% substitution of quartz by RHA. The increase in the mechanical properties and the substantial decrease in porosity of the mixes containing RHA, are attributed to the glassy formation and densification of the individual grains during the vitrification process.

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