

Analysis and Geopolymerisation of Barikin Ladi and Bokkos Kaolin in Nigeria

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ABSTRACT

Conventional construction materials are recently overstretched and posing a threat that led to more emphasis to look into alternative construction materials that are environmentally friendly and affordable. This has led to the evolution of this study that aimed at analyzing different kaolin within Nigeria and assessing its potential after synthesis in an alkaline medium. Kaolin samples were sourced from three locations, namely Bokkos White (BW), Bokkos Brown (BB), and Barikin Ladi (BL) from plateau state, Nigeria; and characterized to determine their physical properties, elemental composition, and mineralogy. Geopolymer paste was produced by activating the metakaolin with an alkaline solution comprising of Sodium hydroxide (NaOH) and Sodium silicate (Na_2SiO_3) at varying alkaline ratios; 0.20, 0.25, 0.30, and 0.35 at a constant Molarity (8M) of NaOH solution. The geopolymer paste produced was prepared and cast using mould size 10cm x 10cm x 0.15cm and cured in an oven for 60°C at varying duration; 1, 2, and 3 days. Compressive strength and water absorption tests were conducted. The results indicate BW kaolin possesses the requisite alumina and silica composition for geopolymer reaction, unlike the BB kaolin while the BL kaolin showed no geopolymer potential. Also, at an optimum reaction condition of 8M and an alkaline ratio of 0.25, BW kaolin resulted in a stable metakaolin-based geopolymer. Furthermore, it was observed that extended oven drying of the samples resulted in an average percentage reduction in compressive strength by 2.84%. This study demonstrates the potential of BW kaolin as a local source of stable geopolymer for application in the construction industry.

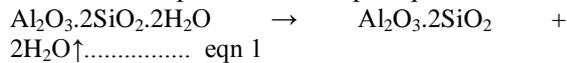
Keywords: Kaolin, Synthesis, Geopolymer, Compressive Strength, Calcination, Alkaline Ratio.

I. INTRODUCTION

The problem associated with the environment is on the increase due to various human activities which are resource exhausting, energy-intensive, and releases a large number of greenhouse gases into the atmosphere. However, many studies had been carried out on the development of new materials which offers technical benefits and can also be produced in a way as to safeguard our environment, among these materials are kaolin geopolymer which shown an interesting potential (Yunsheng et al., 2010), (Zhanga et al., 2016). According to the Nigerian National Bureau of Statistics (NBS) data, there is more than two billion metric tons of kaolin deposit scattered in different parts of the country including plateau states (<https://www.nigerianstat.gov.ng>).

According to Bloodworth kaolin is a commercial term used to describe white clay which is composed essentially of kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$]; and the kaolinization process is due to hydrothermal alteration of alumina-silicate bearing rocks which generate high heat flow granites that may provide optimum thermal condition required to drive groundwater convection cells (Bloodworth et al., 1993). Kaolin is a white, greyish-white, or slightly colored double-layered clay mineral type containing 10-95% kaolinite, with quartz, feldspar, and mica as other minerals. It is made up of tiny, thin, pseudohexagonal, flexible sheets of triclinic crystal with a diameter of 0.2–12µm. (Aroke et al., 2013). However, it is called kaolin when found in its natural form but can be metakaolin after thermal treatment. Furthermore, metakaolin is usually produced by thermal treatment, i.e., calcination of kaolin clays within a definite temperature range (Ilic et al., 2010). The heating process drives off water from the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and collapses the material structure, resulting in an amorphous aluminosilicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), metakaolinite and

the process is known as dihydroxylation process as the chemical is presented in simple equation 1.



Numerous researchers conducted work in the area of characterization, calcination, curing temperature, and improvement of kaolin as an alternative construction material. For example, in the area of processing and characterization of kaolin (Liew et al., 2012; Kumar et al., 2013; Aroke et al., 2013 & Sengupta et al., 2008) conduct research and found that kaolin contains minerals that can be processed to useful material. However, (Elimbi et al., 2011; Soleimani et al., 2012; & Ilic et al., 2010) explored the effect of calcination temperature and the implications of the transformation of kaolin to metakaolin or from crystalline to amorphous state. Temperature is very important in obtaining optimal calcination temperature of kaolin in the transformation of crystalline to amorphous which necessitates research into calcination temperature. Such studies are that of (Elimbi et al., 2011) who subjected kaolinite to calcination temperature between 450 and 800°C, Davidovits and Davidovits (1988), calcined kaolinite clay at 500, 650, 700, and 750°C respectively intending to get the most reactive metakaolin. Further studies by (Palomo et al., 1992) investigate between the 600-700°C temperature range; (Cioffi et al., 2003) worked with 500, 550, 650, and 750°C respectively; (Zhang and Sun, 2006) calcined it at 700°C; whereas (Zibouche et al., 2009) treated it at 800°C; (Chareerat et al., 2006) calcined a kaolinite clay at the temperature range of 400, 500, 600, 700 and 800°C for 2, 4 and 6hr respectively. All of these studies converged to a conclusion that the optimal calcination temperature of kaolin to metakaolin for geopolymerisation is between 600°C - 650°C.

The term geopolymerisation was first coined by Davidovits as far back as 1978, where he described the novel alternative material with a representation of a broad range of materials characterized by chain and networks of inorganic molecules, meaning the mineral polymers resulting from geochemistry or geosynthetic as geopolymer process (Davidovits, 2000). Likewise, geopolymerization was alternatively presented as a reaction that chemically integrates minerals involving silico-aluminates sources in which silica and alumina act as precursors that readily dissolve in the alkaline solution and are synthesized to the process of geopolymerization (Khale and Chaudhary, 2007). Furthermore, geopolymers are amorphous,

inorganic polymeric nano precipitates which do not contain chemically bound water other than the hydrogen-bonded entrapped water, contrary to alkali-activated cement that are hydrated and crystalline precipitates (Kriven, 2017). Some research findings have shown that geopolymerised kaolin can be affected by curing temperature in terms of material compressive strength (Rovnanik, 2010 & Hounsi et al., 2013). Also, recent experimental results presented by some researchers have agreed that silicon oxide (SiO₂), sodium oxide (Na₂O), and molar ratio plays a major role in the formation of geopolymerization of kaolin and metakaolin (Cheng et al 2015; Heah et al 2012 & Munoz et al., 2015). However, previous researchers such as (Chareerat et al., 2006) who synthesized geopolymers using a mixture of 20% metakaolinite and 80% of fly ash, (Liew et al, 2012) calcined kaolin to produce cement powder by applying geopolymerization process with alkali activator mixture of 6-10 Molarity NaOH and Na₂SiO₃ solution and (Heah et al, 2012) who prepared alkali activator of Al₂O₃/Na₂O molar ratio of 0.63-1.27, Sodium silicate and sodium hydroxide of 0.16-0.36 and SiO₂/Na₂O molar ratio of 3.19-3.67) to mixed with kaolin at a solids-to-liquid ratios range of 0.60-1.20, have all obtained geopolymers with varied characteristics.

Therefore, this study focuses on analyzing and geopolymerising kaolin with the aid of alkali-activated materials for use as an alternative construction material. Furthermore, the study tends to address the issue of environment and high cost of construction due to over-dependence on conventional construction materials.

II. MATERIALS AND METHODS

Materials

Four different Kaolin Clay samples were used for this study; Bokkos white from Kulba village, Bokkos LGA in plateau state on location (N09° 25' 44.5", E008° 55' 56.7") 1360m height above sea level, Bokkos brown also from Kulba village Bokkos LGA in plateau state on location (N008° 56' 007 E008° 56' 007") 1360m height above sea level, then from kurujenta village in Barkin Ladi LGA in plateau state on (N09° 41' 29.0", E008° 52' 34.3") 1265m height above sea level). The Alkaline activators used for the research work; Sodium Hydroxide (NaOH) and Sodium Silicate NaSiO₃ which were purchased from Bijo Surgical and Chemical Ltd, Abuja.



Figure 1: Bokkos white Kaolin

Figure 2: Bokkos brown Kaolin
 Figure 3: BarkinLadi Kaolin

Sample Preparation

The Kaolin samples were air-dried for days under normal atmospheric conditions, manually crushed, and passed through sieve size 425 um (No.40) to obtain uniform and well-graded particles.

Specific Gravity

The specific gravity of the kaolin samples was determined following BS 1377, part 2 1990 for soils. While, the materials used are a 500ml pycnometer, digital weighing balance, kaolin samples, and distilled water.

Calcination

The kaolin samples calcination were carried out at Nigerian Building and Road Research Institute (NBRI) laboratory, Abuja. Calcination was conducted with ELE Muffle Furnance 83-4170/01 model at a constant temperature of 650°C for 90 minutes.

Loss on Ignition

A crucible was placed in a furnace and heated at 650°C for at least 30 min. and allowed to cool in the desiccator to ambient temperature, weigh to the nearest 1 mg, (Ma). Weigh into the crucible 5g of the dried kaolin samples to the nearest 1 mg, (Mb), and heat in the furnace at 650°C for at least 60 min. The hot crucible containing the residue on ignition was placed in the desiccator and allowed to cool. After cooling in the desiccator to ambient temperature, weigh the crucible containing the dry residue to the nearest 1 mg (Mc).

The loss on ignition of the dry mass of a solid sample expressed in percentage is calculated as; equation (1): $W_v = \frac{(M_b - M_c)}{(M_b - M_a)} \times 100$

$W_v =$ Loss on ignition of the dry mass of solid sample (%)

X-Ray Fluorescence Procedure

The oxide composition of the raw kaolin is very important and various have shown the validity of using X-ray fluorescence (XRF) to

determine the oxide composition (Raven et al., 1995;Worasith et al., 2018).samples were determined using X-ray fluorescence (XRF) at the Nigerian Geological Survey Agency, Kaduna. Sample for X-ray fluorescence analysis was prepared by pressing powdered samples into cellulose before analyzing the samples on a PanAnalytical XRF spectrometer using calibration software prepared from standard reference materials.

X-Ray Diffraction Procedure

The XRD analysis was conducted at the Nigerian Geological Survey Agency, Kaduna. The clay sample was pressed in a stainless steel sample holder. The X-ray diffraction pattern was recorded using $CuK\alpha$ radiation (wavelength $\lambda_1=1.54056\text{\AA}$, $\lambda_2=1.54439\text{\AA}$, intensity ratio $\alpha_1/\alpha_2=0.500$) on a PW1800 diffractometer equipped with a cathode anode operating at 30kV and 55mA with fine divergence and receiving slit of 2mm irradiated

length between 0.040 and $70^\circ(2\theta)$ at a step size of 0.030°.

Mix Proportion and Curing

NaOH solution having a concentration of 6, 8, and 10 Molarity was prepared in a volumetric flask and was allowed to cool down to room temperature. Prepared NaOH solution was mixed with a standard solution of Na_2SiO_3 at $Na_2SiO_3/NaOH$ ratio ranging from 0.2 to 0.45 to obtain the alkaline activated solution. The solution was allowed for 24 hours before use. The kaolin powder and alkaline solution were mixed at a solids-to-liquid ratio of 0.60 constant to activate geopolymerization and were well stirred until a homogeneous mix is obtained. The detail of the experimental design is presented in Table 1. The fresh paste was then rapidly poured into molds and the samples were firmly packed to fill the entire mould. Lastly, the samples were oven-dried at a constant temperature of $60^\circ C$ for 1, 2, and 3 days.

Table 1: Experimental design and mix proportion

MOLARITY	STANDARD SOLUTION		NaSiO ₃ /NaOH	Qty of water to dissolve NaSiO ₃	KAOLIN (g)	ALKALINE/SOLID RATIO (0.6g)	DESIGNED ALKALINE SOLUTION	
	NaOH (g/mol) in 1LTR of water	NaSiO ₃ (g)					NaOH (g)	NaSiO ₃ (g)
6	240	48	0.20	218	1000	600	500	100
		60	0.25	273	1000	600	480	120
		72	0.30	327	1000	600	462	138
8	320	64	0.20	291	1000	600	500	100
		80	0.25	364	1000	600	480	120
		96	0.30	436	1000	600	462	138
		112	0.35	509	1000	600	444	156
		128	0.40	582	1000	600	429	171
		144	0.45	655	1000	600	414	186
10	400	120	0.30	545	1000	600	462	138
		140	0.35	636	1000	600	444	156
		160	0.40	727	1000	600	429	171
		180	0.45	818	1000	600	414	186

Compressive Strength Test

The compressive strengths of the hardened geopolymer materials were measured using the ELE machine ADR 1500/2000 Mechanical Tester as referred to (ASTM C109-05, 2008) based on the basic principle of Force/Area with 50mm

maximum platen travel. For this research work, a total of 39 hardened geopolymer samples were produced.

Water absorption

For the water absorption test, the geopolymer materials are dried in an oven for a specified time and temperature and then placed in a desiccator to cool. Immediately upon cooling the specimens are weighed. The materials are then emerged in water for 24 hours or until equilibrium. Specimens are removed, patted dry with a lint-free cloth, and weighed. The test procedure for water absorption was carried out according to ASTM D570 standard procedure.

III. RESULT AND DISCUSSION

Physical Properties of Kaolin

The loss on ignition of the raw kaolin samples as shown in table 2, are all below the maximum of 10 for class N Pozzolana as recommended by (ASTM C618, 1978). This indicates BarkinLadi kaolin has the lowest organic matter while Bokkos white kaolin has the highest organic matter. The high LOI value for Bokkos white kaolin might also be due to an increase in the volatile non-carbon component of the sediment (Meyers and Teranes, 2001). One of the most influential is the lattice water in clays (Ran et al., 2000).

Table 2: Loss on Ignition and Specific Gravity

	Bokkos white kaolin (BW)	Bokkos brown kaolin (BB)	Barkinladi kaolin (BL)	Cement
Loss On Ignition	4.33	3.23	0.49	-
Specific Gravity	2.565	2.539	2.704	3.15
% Specific gravity lower than cement	18.57	19.40	14.16	-

The specific gravity of the Kaolin samples is 2.565, 2.539, 2.704, and 2.653 for Bokkos White, Bokkos Brown, and BarkinLadi kaolin respectively. When compared with the average specific gravity of cement (3.15) it shows that kaolin is lighter with an average percentage of 18.57% BW, 19.40% BB, and 14.16% BL; this suggests the potential in the production of light Geopolymer materials.

X-ray Fluorescence Analysis (XRF)

In the XRF analysis, the results of the chemical composition of the clay fractions and their concentration were obtained with major elements present expressed in form of their oxides. The results from table 3 showed the oxide compositions of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ in Bokkos white (BW) kaolin and Bokkos brown (BB) kaolin samples exceeded the 70% summation recommended by (ASTM C311, 2007) for pozzolanic kaolin with requisite Alumino-silicate source. Conversely, the XRF result

revealed BarkinLadi (BL) has zero Al_2O_3 . Also from Table 3, BW with a higher molar ratio of 1.88 $\text{SiO}_2/\text{Al}_2\text{O}_3$ is selected among the samples that can best undergo the geopolymerization process when compared with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of BB and BL kaolin samples of 1.73 & 0.00 respectively. This was a follow to of some previous work conducted by (Barbosa et al., 2000) who calcined kaolin for geopolymer and found that $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.30, and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of 10.0 were the optimum chemical composition. (Liew et al, 2012) process and characterized calcined kaolin powder and recorded the highest compressive strength at $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.10 and formerly (Davidovits and Galilee., 1982) give a range of 3.5 to 4.5 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio as the optimum for obtaining geopolymerization. The experimental result from table 3 showed BL has zero $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio which indicates a high amount of quartz with no kaolinite and so it will not support geopolymerization.

Table 3: Chemical composition of Bokkos white, Bokkos brown, and BarkinLadi kaolin

	Bokkos white (BW)	Bokkos brown (BB)	Barkinladi (BL)
SiO_2	55.60	60.90	82.60
Al_2O_3	29.50	35.20	0.00

Fe ₂ O ₃	9.61	0.81	6.15
K ₂ O	1.48	1.02	7.03
SO ₃	0.00	0.00	0.00
CaO	0.03	0.01	0.03
TiO ₂	2.20	0.94	1.46
ZnO	0.02	0.00	0.02
SiO ₂ /Al ₂ O ₃	1.88	1.73	0.00

X-ray Diffraction Analysis (XRD)

Figure 4 represents the XRD analysis of raw BarkinLadi white kaolin (RBW). The diffractogram showed intense diffraction peaks of kaolinite at angles 11.5° and 26° 2theta, while less intense peaks of kaolinite as the principal mineral with associated minerals of quartz and muscovite occurred at 21°, 38.5°, 45.5°, 55.5° and 70.5° 2theta. Also, from fig 5, the diffractogram showed hump occurring at 20° - 30° 2theta with diffraction peaks of Phengite, Quartz, and Anatase. This is in line with the study of (Liew et al., 2007) who calcined kaolin at 800C for 2h and reported that the XRD diffractogram showed humps at 19.8°- 21.9°, 35.0°- 39.2° which are associated with kaolinite and quartz. Kaolinite was not seen after calcination as shown in fig 5, the study of (Belver et al., 2002) reported that Most of the diffraction peaks of

kaolinite disappeared and a halo at 2Theta from 15° to 30° owing to the amorphous silica appeared. He went further to explain that after calcination, kaolin was transformed into metakaolin, which shows a semi-crystalline to the amorphous pattern. This is in agreement with the study of (Zhang et al., 2007) who reported that Dehydration by thermal treatment converts kaolin to calcined kaolin (metakaolin). Therefore it was concluded that dehydration by thermal treatment has occurred indicating the formation of metakaolin as shown in figure 5. However, diffraction peaks of Quartz could still be seen after calcination which revealed the thermal stability of the mineralogical impurity. On other hand, minerals of Phengite and Anatase also occurred as impurities. Kinds of literature of (Elimbi et al., 2011), indicated that impurities are not dissolved during geopolymerization.

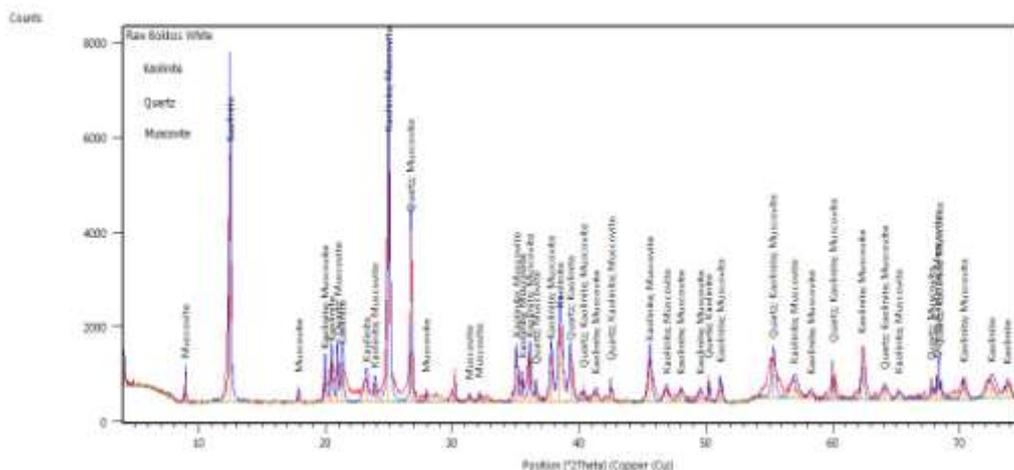


Figure 4: Raw Bokkos White Kaolin (RBW)

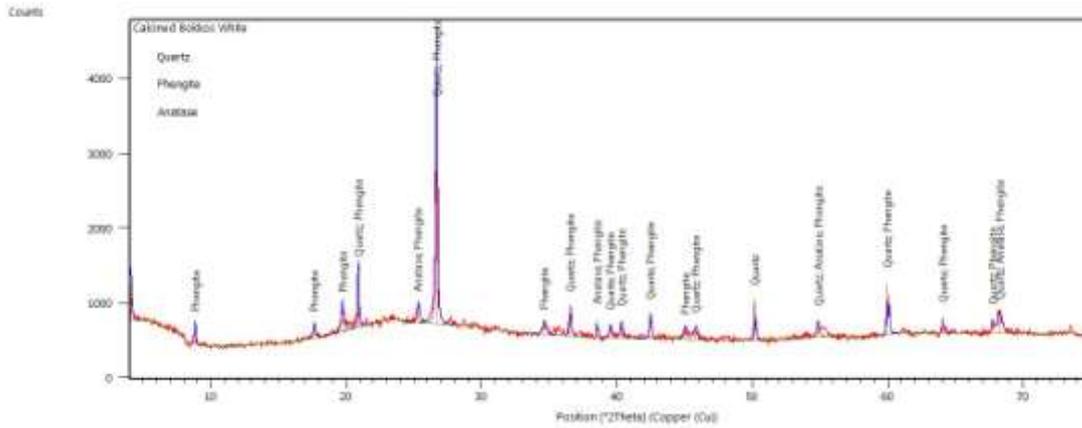


Figure.5: Calcined Bokkos White Kaolin (CBW)

Similarly, figure 6 presents the XRD of RBB kaolin. It showed the basic minerals of Quartz, Kaolinite, Muscovite, and Rutile as dominant clay minerals. The intense diffraction peaks were seen around 12.5° , 21.3° , 23.2° and 25° theta. Thermally treated samples of RBB as

shown in figure 7, the X-ray diffractogram also shows the presence of characteristics peaks of Quartz and Muscovite. Also, the diffractogram revealed a low hump between 20° - 26° theta indicating the complete amorphization of the calcined BB kaolin.

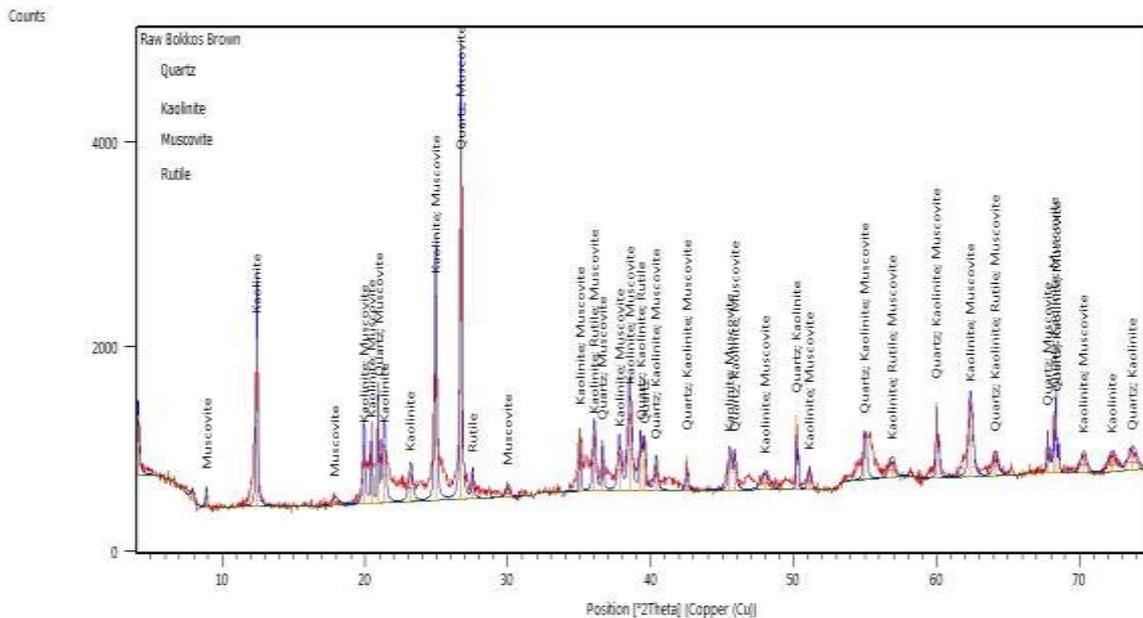


Figure 6: Raw Bokkos Brown Kaolin (RBB)

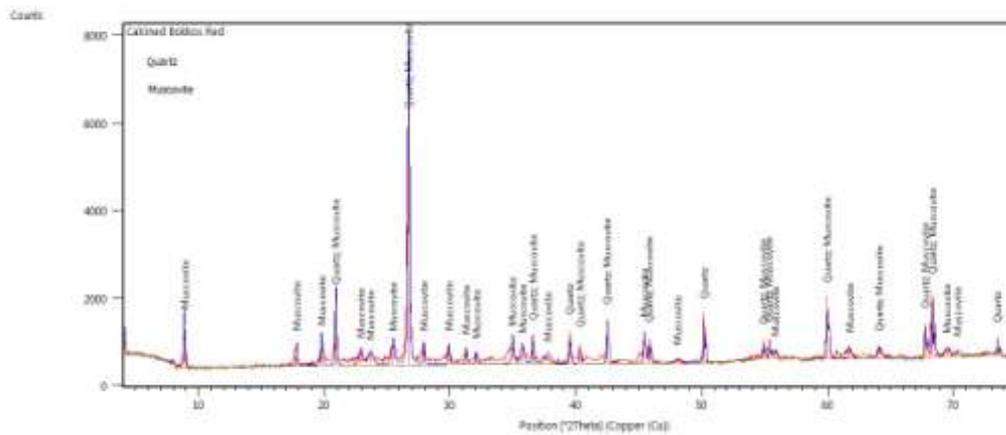


Figure 7: Calcined Bokkos Brown Kaolin (CBB)

Water Absorption

Figure 8, it showed that all the geopolymer materials recorded high water absorption which resulted in low strength. This is associated with too many voids in the samples as a result of improper compaction. This is in line with

the research of (Zuhua et al., 2009) which showed that, if excess water exists around the hydrolysis species, the polycondensation would be hindered and reagent will leach out from the surfaces of the geopolymer which may account for the low compressive strength development.

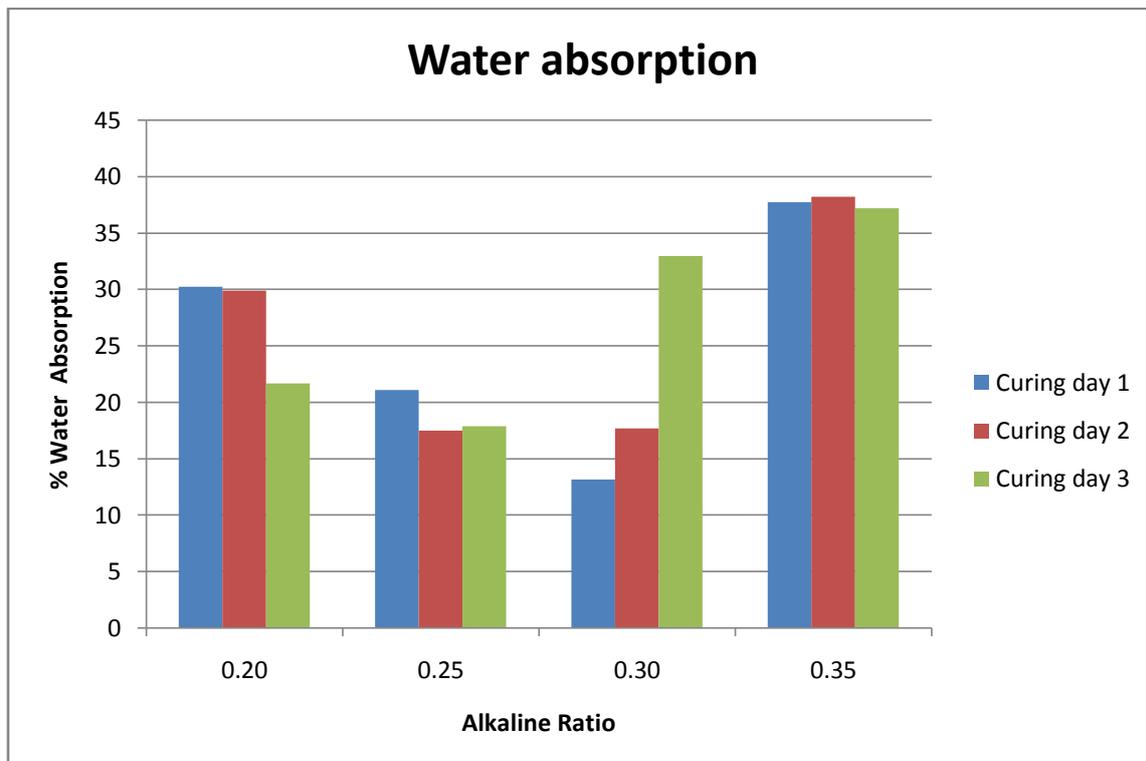


Fig. 8 Water Absorption, Alkaline Ratio & Curing day

Compressive Strength

According to the author (Liew et al., 2012) Alkaline ratio, and method of curing affects the strength of geopolymer materials. Therefore,

geopolymer materials produced with 6 & 10 molarity disintegrated during curing processes. Hence, they were not subjected to a compressive strength test. This may be associated with the low

dissolution ability of calcined kaolin at a low NaOH concentration of 6 M and thus causing insufficient Na^+ ion to allow for complete polymerization of the network. On the other hand, a higher NaOH concentration of 10M has a high dissolution ability as excess Na^+ ions left in the system weaken the structure (Rowles and Connor, 2003). Also, NaOH solution of 8 M provided optimum alkalinity for dissolution of aluminosilicates sources, where sufficient Al^{3+} and Si^{4+} ions are released from the aluminosilicates and participated in the geopolymerization process. Therefore, geopolymer materials produced with an alkaline ratio of 8M as shown in fig. 9 showed strength development with varying alkaline ratios at different curing days. The alkaline ratio from 0.20 to 0.25 and NaOH concentration of 8M showed an increase in strength of geopolymer

materials with increased alkaline ratio, and decreases with curing days, while alkaline ratio from 0.30 to 0.35 and NaOH concentration of 8M revealed a decrease in strength of geopolymer materials with increased alkaline ratio, and increases with curing days. Therefore, it was concluded that the optimum strength of 3.758N/mm^2 for geopolymer materials was achieved at curing day 1 and an alkaline ratio of 0.25. Although, the compressive strength was low when compared with the works of (Zuhua et al., 2009); (Cheng et al., 2015), and (Rovnanik, 2010) who all geopolymerized metakaolin and achieved strength above 30 MPA. The reason for the low strength might be due to the incomplete reaction of the geopolymer mixes. Also, geopolymer materials disintegrated on the third day of curing due to a large degree of drying shrinkage and cracking.

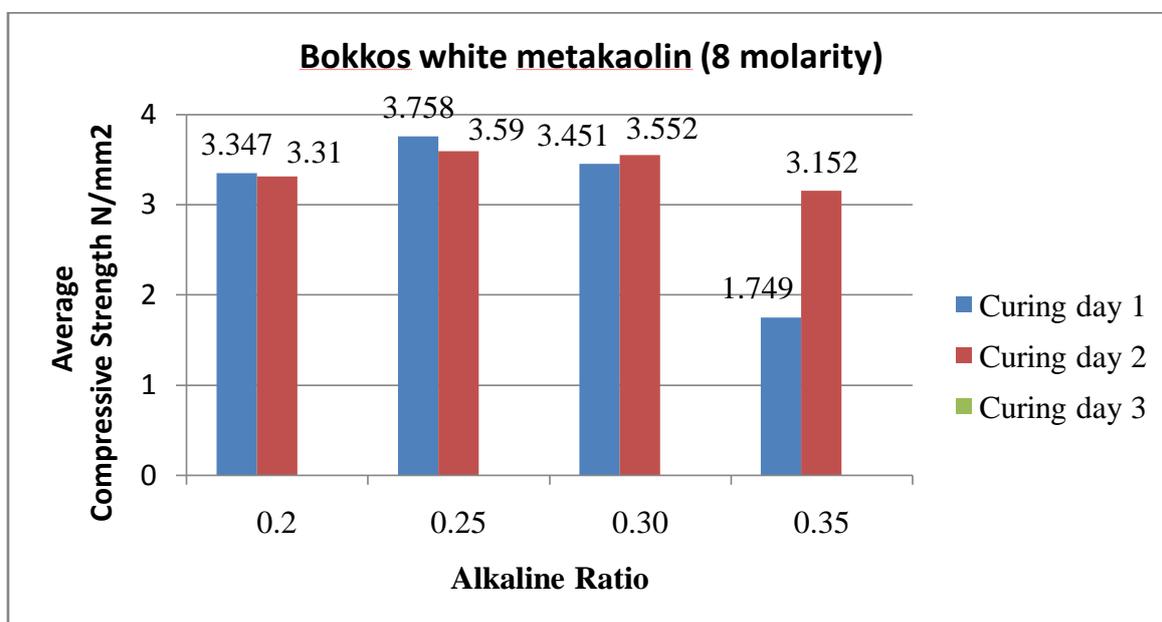


Fig. 9 Compressive Strength, Alkaline Ratio and curing day

IV. CONCLUSION

The study conducted determines certain characteristics (specific gravity, loss on ignition, XRF, XRD, compressive strength, and water absorption) carried out on kaolinite, metakaolinite, and the geopolymer materials which led to the following conclusions:

- (i) The study shows that metakaolinite is a good aluminosilicate source and can be geopolymerised using alkali activation materials.
- (ii) The result showed that the kaolin samples possess the requisite alumina and silica composition for geopolymerization.
- (iii) From the analysis made, it was found that Sodium Hydroxide (NaOH) concentration,

calcined kaolin to alkaline activator ratio, Sodium Silicate (Na_2SiO_3) to Sodium Hydroxide (NaOH) ratio, heating temperature, and time have a great effect on the mechanical properties of geopolymer material.

- (vi) At optimum reaction condition of 8M and the alkaline ratio of 0.25, Bokkos white metakaolin resulted in a stable geopolymer material with 3.758 and 3.590N/mm^2 strength.
- (v) It was also observed that the Si/Al ratio of kaolin has a significant effect on the formation of geopolymer material.
- (vi) Revealed in the strength-curing relationship that extended oven drying of the geopolymer samples to the third day lead to the disintegration

of the samples and hence geopolymer alumina-silicate inorganic polymers are best cured at ambient temperatures.

(vii) It was concluded that BW kaolin demonstrates the potential as a local source of stable geopolymer for application in the construction industry.

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