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Comparative analysis of physical and chemical characteristics of selected clays deposits found in Kebbi State, Nigeria

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The intent of this paper was to explore the physical and chemical characteristics of clays in Kebbi State, Nigeria, and the clays were compared with standard clay which is considered with highest quality standard in casting. Clay's deposits from Dukku River along River Rima, Jega River which is the tail end of River Niger and Yauri were investigated for their potentials as raw materials used for casting and ceramic industries. Samples were collected from three local governments' areas at the bank of the rivers. Chemical analyses of individual clay were determined by employing four different techniques as follows; Complexiometric Titration, Atomic Absorption Spectrophotometer (AAS), X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF). The data collected from the analyses revealed that the structures of clay minerals were mainly kaolinite, Smectite (bentonite), and illite, and non-clay minerals for the three places were mainly quartz, feldspars and gibbsite. The results obtained revealed high silicate clays and moderate alumina content with trace elements of oxides (Fe_2O_3, CaO, K_2O, TiO_2, MgO, MnO and Na_2O) also present within acceptable limits. Physical tests results at 900 and 1300°C were used to determine firing shrinkage, colour, and modulus of rupture, bulk modulus, apparent density, crack formation, apparent porosity, water absorption and bulk densities. The modulus of rupture, bulk densities, and fired linear shrinkage of all the samples increase with increasing firing temperature. The findings of this work revealed that the clay minerals from Dukku and Yauri had the necessary properties for the foundry work and refractory applications, but clays from Jega, can be exploited for commercial purposes after beneficiation by reducing the level of iron, quartz and other impurities.

Key words: Clay minerals, chemical analysis, firing characteristics, oxides.

INTRODUCTION

A number of researches have been carried out so far on clays from various States across Nigeria in order to identify compositional variation using different analytical methods. According to Bergaya (2000), "clay" has

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ambivalent definitions. On one it is used to define any soil particle smaller than 2 µm, but on the other hand it includes a large group of microcrystalline secondary minerals based on hydrous aluminium or magnesium silicates that have sheet-like structures. Clay is the common name for a number of fine-grained, earthy materials that becomes plastic when wet. Chemically, clays are hydrous aluminium silicates usually containing minor amount of impurities such as potassium, calcium, iron, magnesium, sodium, and titanium (Patterson and Murray, 2004). They are plastic due to their water content become hard, brittle and non-plastic upon drying or firing (AboutClay.com, 2006). Clays have become important and abundant raw materials in modern technology and have wide range of applications in agriculture, ceramics, foundry, plastics, rubber, paint, pharmaceutical, oil and gas, insecticides, textile, and adhesives industries (Omowumi, 2000). They are a powerful and abundant material in nature, presenting several properties which may justify their use in many industries. For each application, the chemical and physical characteristics as well as the properties of the clays must be carefully designed to obtain the desired results (Silva–Valenzuela et al., 2013). These include clay mineral composition, presence of organic materials, type and amount of exchangeable ions and soluble salts and texture. Klinefelter and Hamlin (1957) explained that clays are composed of certain groups of hydrous aluminium, magnesium, and iron silicates that may contain sodium, calcium, potassium and other ions. These silicates collectively make up the clay minerals and the major clay groups are kaolins, chlorites, hormites, smectites, and illites. The clay minerals are identified using many techniques which include x-ray diffraction, electron microscopy, infrared spectrometry, and differential thermal analysis (Beutelspacher and Van der Marel, 1968; Newnan, 2000; Murray et al., 1997; Hubbard et al., 2003), respectively.

There are three main groups of clay minerals, each with its own particular properties. They are: Kaolinite; Illite; and Montmorillonite (Ivana et al., 2014). Globally, clay has a wide spread occurrence. Clay deposits as one of the major Nigerian natural resources, cover an estimated reserve of billions of tons, and are found in many states of the country (Khan, 2005). While the geology of many places where clay deposits occur has received little attention, efforts have been made to assess these deposits in order to determine their usability. Omowumi (2000) and Abolarin et al. (2004) have shown that some Nigerian clays are good for based on their natural water content, the natural swelling and the cold crushing strength. Omowumi (2000) and Abolarin et al. (2004) have found clays in Obe, Okija, Ubiaja, Iyuku Erusu, Ire, Gombe and Damaturu useful for furnace construction as a result of their thermal shock resistance, crushing strength, bulk density and refractoriness values. Kankara clay was found to be suitable for use in preparation of synthetic foundry sand (Onyeji, 2010; Bergaya, 2000).

There are large deposits of clay in Dukku, Yauri and Jega in Kebbi State and that the communities use the clay only for making pots and bricks for mud houses. Despite the huge occurrence of clays in these places, the chemical and physical characteristics of the deposits are unknown. Therefore, the intent of this study was to analyze the chemical and physical characteristics of clays deposits in order to determine their suitability for industrial applications. These characteristics will be compared with the imported clay. Figure 1a and b reveals soils appearance for Dukku (grayish white) and Yauri (black/brownish) indicating that both lie on a swampy ground.

EXPERIMENTAL PROCEDURE

Materials preparation

Three different clay minerals were collected from Dukku, Jega, and Yauri Rivers banks, Kebbi State, Nigeria and were compared with ball and China clays recommended values in order to determine their suitability for foundry applications. Stratified random samplings were used within 250 m^2 area; fifteen locations each were located and samples were collected at a depth of a meter each for these areas understudy. Samples from each location were mixed together and crushed using hammer mill and 50 kg each were obtained. To ensure homogeneity, each of the samples was prepared using Moore and Reynolds (1997) procedure. Basic characteristics of clays under studied are given in Table 1 in comparison with standard.

The clay samples from the three locations were physically processed and analyzed, using X-ray Fluorescence, X-ray Diffraction and spectrophotometer methods. The clay samples from the fields of the three locations were washed and sieved with sieves of various mesh sizes. The fine powders clay were dissolved in perchloric acid and filtered. The filter papers were washed several times with distilled water and the residues on the filter papers were found to be mainly quartz for both samples with varying concentrations. The filtrates were used for both qualitative and quantitative analysis. Atomic absorption spectrometric analysis and x-ray fluorescence analysis were carried out.

The porosity and density of the samples were determined using simple weighing method. The apparent porosity, apparent density and bulk density were calculated using the following formula.

Apparent porosity (%) = 100 $[m_2 - m_3]/m_1 - m_2$ (1)

Apparent density = $m_1/m_2 - m_3$ (2)

where m_1 = dry weight, m_2 = saturated weight (in water) and m_3 is the suspended weight (in air).

Clay purifications

Individual clay from these areas was mixed with enough water to produce a fluid slip about the consistency of a thick cream by mixing with a laddle or stick. The slips were screened by pouring through a 30-mesh screen and then through a 60-mesh screen to remove the granular impurities. The slips were allowed to settle for three days and water decanted revealing a plastic mass of clays

(a)   (b)

Figure 1. a) Dukku Site and b) Yauri Site.

Table 1. Basic characteristics of the clays understudy in comparison with standard.

Characteristics/ Parameter Name	Standard/Recommended Values	Dukku Clay	Jega Clay	Yauri Clay
Status of raw material	After grinding	After grinding	After grinding	After grinding
AFS GFN	50-60	45.4	40.43	54.0
Clay content	32.6	34.0	22.90	35.4
Green compressive strength, kN/m^2	50-70	60.30	53.2	54.2
Dry compressive strength, kN/m^2	200-550	442.0	325.6	450.3
Colour	Pearl-white	Light brown	Light brown	Dark brown
Moisture (%)	8.01	6. 90	6.60	7.65
Ignition loss (%)	10.42	9.20	9.15	9.50
Colour after ignition	Yellow honey	Yellowish	Yellowish brown	Dark bloody-orange

AFS: American Foundrymens Society; GFN: Grain Fineness Number.

from the three locations. The clays mass were transferred individually to a stout canvas bag which was hanged to remove water until the slips gradually become harder. The individual clays were removed from the bag and dried in an oven at 100°C overnight until they were bone dried. This was ground and screened to fineness using a 60-mesh screen (Gupta, 2008; Hubbard et al., 2003). Representative samples were obtained by quartering method (Beutelspacher and Van der Marel, 1968) for further experimental work.

Sample dissolution for analysis

0.5 g of the representative samples from Dukku, Jega and Yauri each were weighed and put into 3 beakers individually. Thereafter, about 10 ml each of concentrated perchloric acid ($HClO_4$) was added and each beaker was heated until white dense fumes of perchloric were observed. The beakers were kept in such condition for 5 - 10 min. Samples were cooled and about 100 ml each of boiling water was added. The contents of the beakers were stirred and filtered through filter papers into 250-ml graduated flasks. The residues on the filter papers were washed with hot water several times to get rid of all perchloric acid. The residues on the filter

papers were silica (SiO_2) and the filtrates were used in both the qualitative and quantitative determination of the clays contents.

Particle size analysis

Particle size analyses were undertaken using the Boyoucos method (Hubbard et al., 2003). 50 g of fine earth was first treated with physical and chemical dispersants and then separated into sand (particle sizes between 0.05 and 2 mm), silt (particle sizes between 0,002 mm and 0.05 mm) and clay contents (particle sizes <0.002 mm) by the means of a series of hygrometer readings in a settling soil solution over time.

Samples were first left 18 h with approximately 200 ml of water plus 20 ml of a chemical dispersant solution after which they agitated in a milkshake maker (provided by Agric laboratory) for 15 min at 5000 rpm. The resultant solution of soil, water and dispersant was then passed through a 212 μm sieve which retained sand fraction. The remaining solution containing clay, silt and dispersant was then added to a 1-L measuring cylinder, made up to 1000 ml total volume and agitated vigorously with a rod for 1 min, subsequently being left to rest and settle for 22 h over which a series of readings were undertaken.

Table 2. Physical properties of clays.

Property	Location														
	Dukku Clay					Jega Clay					Yauri Clay				
	Temperature (°C)					Temperature (°C)					Temperature (°C)				
	900	1000	1100	1200	1300	900	1000	1100	1200	1300	900	1000	1100	1200	1300
Wet-dry shrinkage (%)	3.7	3.8	3.8	4.0	4.2	3.7	3.8	3.9	4.0	4.2	3.7	3.8	3.8	4.0	4.2
Dry-fried shrinkage (%)	1.14	1.46	2.39	2.23	3.31	1.13	1.40	2.39	2.23	3.3	3.13	1.45	2.39	2.25	3.30
Total shrinkage (%)	4.8	5.2	6.1	6.9	7.5	4.8	5.2	6.2	6.2	7.5	4.8	5.2	6.1	6.2	7.5
Water absorption (%)	20.6	17.7	15.6	12.9	11.0	20.7	16.7	14.6	11.2	10.1	21.4	16.9	14.0	11.2	9.8
Bulk density (g/cm^3)	1.7	1.7	1.73	1.78	1.83	1.6	1.62	1.68	1.75	1.82	1.72	1.73	1.79	1.82	1.85
Apparent density (%)	2.5	2.4	2.4	2.3	2.1	2.5	2.4	2.3	2.2	2.0	2.5	2.4	2.4	2.3	2.2
Apparent porosity (%)	29.1	28.1	26.9	22.5	20.1	29.4	28.2	26.4	22.3	21.0	29.9	27.4	25.2	22.5	20.2
Modulus of rupture	21.4	23.5	26.1	28.2	31.5	22.9	24.8	29.2	31.5	34.2	23.5	28.8	31.5	33.2	35.9
Cold crushing strength (kg/cm^2)	210.2	222.5	244.7	277	328	211	225	250	285	330	220	260	280	310	350
Firing colour	White brown	White brown	White brown	Yellow brown	Dark brown	pink	Light brown	Light brown	Brown	Dark brown	Brown	Brown	Brown	Yellow brown	Dark brawn
Crack formation	No crack	No crack	No crack	No crack	Slight crack	No crack	No crack	No crack	No crack	Very small crack	No crack	No crack	No crack	No crack	Slight crack

The particle size analyses of the three samples were conducted and method used for the clay determination was pipette method, without the addition of chemical dispersant.

Grain size and its distribution

Many properties of moulding sand and clay like permeability, adhesiveness, surface fineness, strength etc, depend upon the grain size and distribution of clay particles. Grain size is determined by shaking a known amount of clean, dry clay downward through a set of 11 standard sieves for 15 min (Abubakar, et al., 2014). The amount of clay remaining on each sieve is weighed, and the weights are used to compute and American Foundry Society (A.F.S.) grain fineness index (GFI) (Hubbard et al., 2003).

Grain shape

Grain shapes in foundry casting represents a compromise between permeability, bonding ability, and smoothness of the finished surface of the cast part. Generally, ideal

foundry sand and clay is sub angular in shape and allows individual grain the ability to interlock sufficiently well to form good mould and still providing necessary pore spaces for gases to escape without breaking the bould during casting process (Khan, 2005).

Instruments used and procedures

The following instruments were used for this work. Atomic Absorption Spectrophotometer, UNICAM 969, X-Ray Diffraction (XRD), Rich-Siefert model 3000 TT- X-ray powder diffractometer, Energy Dispersive X-Ray Fluorescence, model Pal analytic PW4030, and Compleximetric filtration. The procedures used by Abubakar et al. (2014), El- Geundi et al. (2014) and Njoka et al. (2015) were used in the present study, and Atterberg limits were determined as described by Melo et al. (2001).

Physical tests

The following physical tests were carried out using one

standard method (Gupta, 2008) and were as follows: The color, test for plasticity, test for water of plasticity, apparent porosity, apparent density, green strength, permeability number, moisture content, thermal shock resistance, sintering point, refractoriness, test for drying shrinkage, test for firing shrinkage and test for water absorption of the three types of clay were conducted and results were shown in Tables 2 and 3.

Colour

The colours of dried clay samples at room temperature were determined using a colour chart. Clays sample from Dukku and Jega possess a light yellow appearance possibly due to presence of trace of iron oxides which could have introduced reddish or brownish colour. The clay samples from Yauri appeared to have possessed a reddish and brownish colour which indicates the presences of large amount of iron oxides hematite (Fe_2O_3) as shown from the results of chemical analysis of clays samples. This is in agreement with the results obtained by Omowumi (2000), Abolarin et al. (2004), Klinefelter and Hamlin (1957) and Onyeji (2010).

Table 3. Other physical properties of clays under consideration.

Property	Location value		
	Dukku	*Jega*	*Yauri*
Modulus of plasticity	4.23	3.91	4.52
Moisture content	4.71	4.54	4.90
Green strength (KN/m^2)	28.2	27.16	29.5
Sintering point (°C)	> 1400	> 1400	> 1400
Permeability number	53.18	52.16	53.45
Refractoriness (°C)	1650	1650	1700

Swelling capacity

The swelling performance of crude clays was evaluated based on Foster method (1956). 0.5 g of each samples have been slowly added to 100 ml graduated cylinders containing 50 ml each of deionized water, 10% solutions of sodium lauryl-ether sulphate (SLES) and cethy trimethyammonium chloride (CTAC), and allowed to stand overnight.

Loss on ignition

The Loss on ignition (LOI) of the 3 samples was determined as follows: The weight of empty porcelain crucibles were determined and recorded W_1. 2 g each of the dried pulverized clays were added and the weight of the crucible + clays was determined as W_2. The samples were then ignited in the laboratory kiln at 1300°C. After cooling the samples, the weights of the crucibles + samples after ignition were determined as W_3. The loss on ignition was then calculated using this formula.

$$LOI = 100(W_2 - W_3) / (W_2 - W_1) \qquad (3)$$

Green compressive strength

A portion of the rammed specimens were maintained in the green condition by taken them out of the moulding box, and without delay putting them immediately on the universal testing machine. Compressive loads were then applied until the specimens failed, and the force required to cause the compression failure were determined and recorded.

AFS clay content

AFS clay content includes all particles finer than 20 μ in size, whether they are clay particles, silt or organic matter (Ivana et al., 2014). The total clay content in sand is determined by washing 50 g sample of moulding sand using 475 cm^3 of water and 25 cm^3 of standard sodium hydroxide (NaOH) in a jar. Several agitation and washing is required to fully remove the clay. The remaining sand was then dried and weighed to determine the amount of clay removed from the original samples collected from the three places.

Moisture content

Specimens weighing 50 g were carefully prepared and put inside an oven which was maintained at a temperature of 110°C for 2 h to allow for the escape of moisture. After which, they were taken out of the oven and reweighed. The percentage of moisture was calculated from the difference in the weights of the original moist and consequently dried clay samples using the expression:

$$Moisture\ content = w_1 - w_2/w_1 \qquad (4)$$

Where, w_1 = weight of the moist clay specimen; w_2 = weight of the dried clay specimen.

Permeability

Air of volume 200 cm^3 held in the bell jar was forced to pass through test specimens of dimensions 50.8 mm diameter and 50.8 mm long at a pressure of 980 Pa (10 g/cm^3) indicated by the manometer reading, and the time required for the air to pass through the specimen was determined. The permeability number calculated using the formula:

$$P_A = V \times H/A \times P \times t \qquad (5)$$

where, V = Volume of air = 200 cm^3
H = Height of the clay specimen = 50.8 mm = 5.08 cm
P = Air pressure = 10 g/cm^2
A = Cross sectional area of clay specimen = $\pi/4 \times (5.08)^2$
t = Time in minutes for complete air to pass through.

RESULTS AND DISCUSSION

Physical properties

The results of the physical and mechanical properties of the three types of clay deposits determined are presented in Tables 2 and 3.

Shrinkage

This is an indicator of the firing efficiency of the clay samples. Omowumi (2000), in his work quoted a recommended range of 4-10% for fire clay and Abolarin et al. (2004) pointed that lower value were more desirable as this means the clay is less susceptible to volume change. Both clays understudy falls within the two recommendations. Hubbard et al. (2003) also recommended linear shrinkage range of 7-10% for refractory clays; therefore, the three clays can be classified, based on this range as refractory clays.

Quantitative analysis of samples from the three locations

Physical properties

In Tables 2 and 3, the physical and mechanical properties of the clays are shown. As observed, the total shrinkage, bulk density, modulus of rupture, and cold crushing strength of the three samples increases with increasing firing temperature, while water absorption, apparent density and apparent porosity decreases with increasing firing temperature as observed in Figure 2. It was observed that clay from Jega has the lowest moisture content of 4.54 followed by Dukku clay with 4.71, while Yauri clay has the highest content (4.90) which are all within the acceptable standard (Omowumi, 2000). The apparent porosity of 29.1% for Dukku, 29.4% for Jega, and 29.9% are all within the standard for the production of fire clay and siliceous fireclay with 20 - 30% and 23.7% respectively (Omowumi, 2000). The linear shrinkage of all the three samples after dying and firing fall within the acceptable value of 4 to 10% for fireclay. High shrinkage values may result in warping and cracking of the clays and this may cause loss of heat in the finished products. The cold crushing strength obtained for the three clays are 210 kg/cm^2, for Dukku, 211 kg/cm^2 for Jega and 220 kg/cm^2 for Yauri which are all below the specification for the manufacture of fireclay.

As observed in Figure 2a, water absorption is a function of temperature. For all the three clays, the water absorption decreased when the firing temperature increased. It is well known that water absorption is closely related to densification, and the amount of quartz influences the quantity of the amorphous phase after sintering (Gupta, 2008).

The hydration process gives rise to clay samples that easily swells, and can have significant effect on the suitability of the clay in its application in many fields. The physical test shows that Dukku, Yauri and Jega clay samples showed higher degree of plasticity. This shows that these clays will be suitable for refractory firebrick production and for the production of ceramic wares after proper processing and purification (Gupta, 2008; Klinefelter and Hamlin, 1957). The minor oxides components (impurities) which occur in variable quantities are important as their presence imparts some properties to clay. The brown and red colour from Dukku, Jega and Yauri samples were associated with the presence of hematite (Fe_2O_3). The values of Fe_2O_3 obtained were high especially Yauri clay.

Chemical composition

In Tables 4, 5, 6 and 8, the elemental chemical compositions of the clays are shown. The major constituents of samples are silica and alumina. The silica contents in the clays are all greater than 50%, while alumina contents are less than 40% and iron III oxide for Dukku and Jega clays are less than 5%, but Yauri clay contains this oxide as much as 11%. Other substances such as oxides of titanium, magnesium, manganese, calcium and potassium are in small proportions. The results shows that the clay samples from both areas belong to the family of aluminosilicate and semi-acid refractory since the alumina values falls within the classification (Abolarin et al., 2004).

The results of the full assays based on the major and minor compounds and their average concentrations were as follows: Major compounds for the three areas, using AAS and XRF are: SiO_2 (52.45 - 55.85), Al_2O_3 (30.58 - 37.32) and minor compounds: MgO (2.41 - 1.10), Fe_2O_3 (11.00 - 2.30), CaO (1.0 - 3.50), K_2O (0.2 - 0.55), TiO_2 (0.02 - 0.25), and Na_2O (0.04 - 0.50). The results of this study show that Dukku clays are the type of clay in which silica is in the range of 55.4 to 55.59% and alumina is in range of 35.5 to 35.6%. The clay of Jega shows that silica is in the range of 52.58 to 55.85% while alumina is the range of 35.12 to 37.32% and that of Yauri indicates that the silica in the clay is in the range of 52.45 to 53.70%, while the alumina content is the range of 30.58 to 32.50%. The major contaminant of these clays is iron, which is expressed as iron (III) oxide, which occurs in the range of 4.5 to 4.0% for Dukku, while Jega has 2.3 to 4.5%, but Yauri has the highest iron (III) oxide in the range of 10.5 to 11%. Such level of iron oxide usually imparts reddish colour to clay when fired, so making it attractive as a ceramic raw material (Omowumi, 2000). Lime CaO, TiO_2, and K_2O occurred in all the places. The general evaluation of the results presented in Tables 4, 5, 6, and 8 showed that both samples were kaolinite clays. Theoretically, the ratio of Al_2O_3: SiO_2 for kaolinite clay mineral is 1:2, while smectite clay mineral is 1:1. However, in this work, samples from Dukku, Jega, and Yauri at the depth of 1 m had a higher amount of SiO_2 than the theoretical value. This excess could be attributing to the presence of quartz in the samples as reported by Ivana et al. (2014) and the mineralogical values obtained (Table 8). The presence of CaO is due to the presence of $CaCO_3$ which is always present in association with any clay deposit. The presence of lime can be problematic, and this is because calcium carbonate is converted to calcium oxide by heat and this oxide become hydrates. As observed in Tables 4, 5 and 6, the average silica and aluminium percentages of Dukku, Jega, and Yauri meet the standard for refractory bricks as observed in Table 7. The alumina content in clay has direct relationship to its refractoriness such that the higher the alumina in clay the higher the refractoriness (Gupta, 2008; Smith and Brown, 1999; Hubbard et al., 2003). The loss of ignition of the three clays are all within the acceptable value of 8-18% for ceramic and refractory brick production as reported by Gupta (2008).
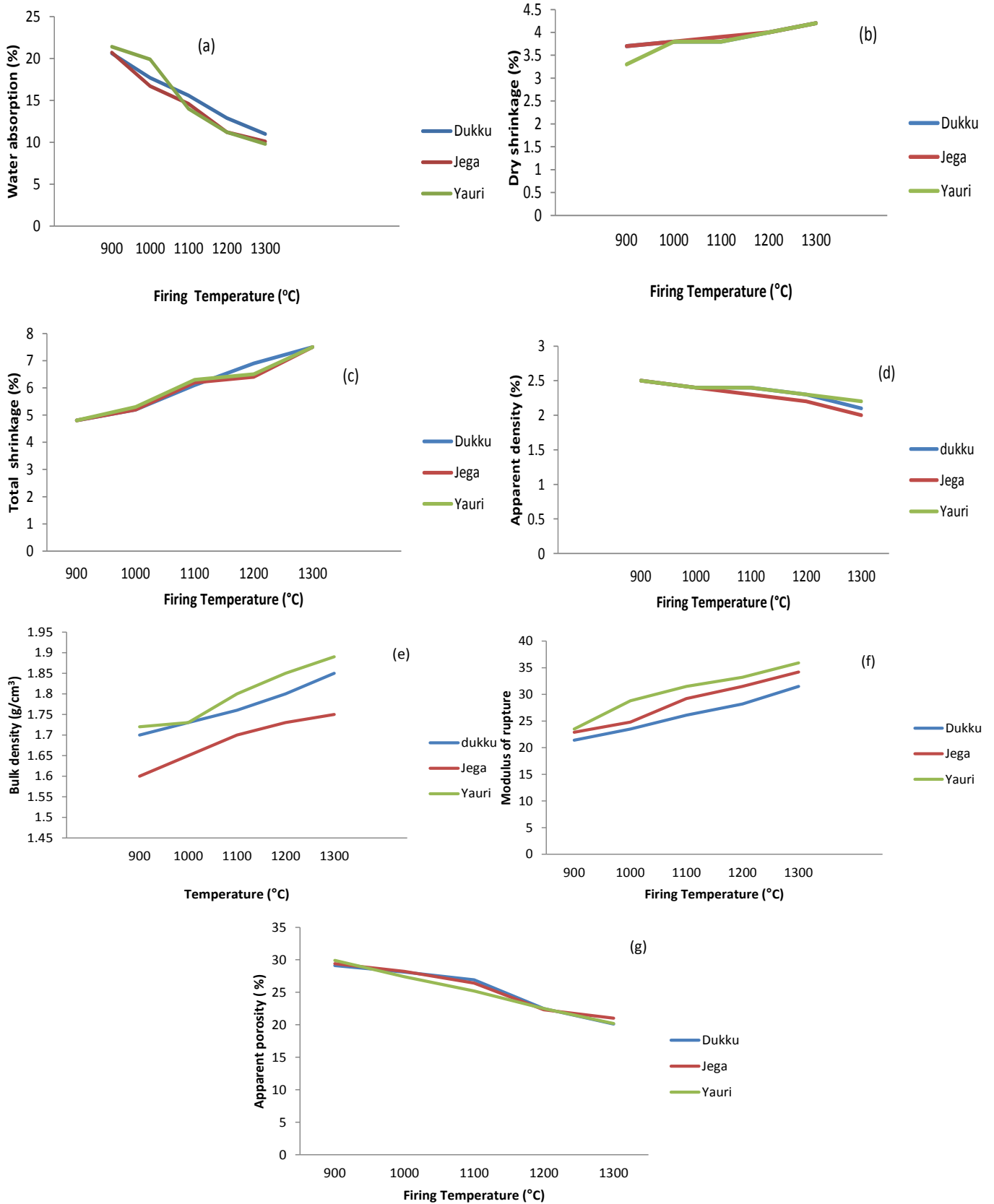
Figure 2. Physical properties of samples from different firing temperatures (a) water absorption, b) dry shrinkage, c) total shrinkage, d) apparent density, e) total density, f) modulus of rupture, g) apparent porosity from Table 2).

Table 4. The Comparison of the chemical analysis of local clay using complexiometric titration.

Location	Constituent								
	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO
Dukku Clay	+	+	+	+	+	+	+	+	
Jega Clay	+	+	+	+	+	+	+	+	
Yauri Clay	+	+	+	+	+	+	+	+	

Table 5. Comparison of the chemical composition of local and imported clay using AAS (%).

Composition (%)	Local clay under studies			Standard composition	
	Dukku Clay	Jega Clay	Yauri Clay	China Clay	Ball Clay
SiO_2	55.40	52.58	52.45	50.18	44.63
Al_2O_3	35.60	37.32	30.58	33.34	36.31
Fe_2O_3	4.00	4.50	10.50	1.88	0.96
MgO	2.20	2.30	2.41		
CaO	2.20	2.90	2.59		
Na_2O	0.04	0.12	0.10		
TiO_2	0.05	0.10	0.25	0.01	3.57
K_2O	0.33	0.55	0.45		
Others	0.18	0.39	0.67	14.59	13.91
LOI	9.20	9.15	9.50		

Table 6. Comparison of the chemical composition of local and imported clays using XRF (%).

Composition (%)	Locally available clay under studies			Standard composition	
	Dukku clay	Jega clay	Yauri clay	China clay	Ball clay
SiO_2	55.59	55.85	53.70	50.18	44.63
Al_2O_3	35.50	35.12	32.50	33.34	36.93
Fe_2O_3	4.50	2.30	11.15	1.88	0.96
MgO	1.90	1.60	1.00		
CaO	2.10	3.50	1.00		
TiO_2	0.02	0.02	0.03	0.01	3.97
K_2O	0.48	0.20	0.50		
Others	0.41	0.43	0.15	14. 59	13.91
LOI	8.25	8.18	8. 70		

Table 7. Chemical composition of refractory clays by international standard (Gupta, 2008).

Constituent	Fired clay (%)	Refractory bricks (%)
SiO_2	55-75	51-70
Al_2O_3	25-45	25-40
Fe_2O_3	0.5-2.0	0.5-2.4
K_2O	<2.0	
MgO	<2.0	
L10	12-15	

The results of mineralogical analysis of the clays samples in the present investigation are presented in Table 8, showing that the clays samples from three areas (Dukku, Jega, and Yauri) are predominantly kaolinite and

Table 8. Average mineralogical composition (%) of the clay samples using XRD.

Mineral	Dukku clay	Jega clay	Yauri clay
Kaolinite	43	38	48
Smectite	25	20	22
Illite	7	9	6
Quartz	23	30	28
Gibbsite	1	2	1
Others	1	1	1

Smectitic, with some quantities of quartz, illite and gibbsite. Smectite alone constitutes between 38 to 48%, kaolinite values are between 20 to 25%, illite varies from 6 to 9%, while quartz is between 23 and 30% and gibbsite ranged from 1 to 2% and others are between 0 to 1%. The clay samples are all of sedimentary origin and seem to have gone through different levels of transformation before deposition, which does affect their physical properties like plasticity and shrinkage.

Particle size

The particle size distribution of clay samples favour plasticity and mouldability and this makes the Dukku and Yauri clays suitable for casting. The results of grain size analyses are presented in Table 9. The amount of fines in the samples from the three areas varies from 68.5 to 90.4 for Dukku, the percentage of clay particle size is 40.0 and 58%, while that of Jega varies from 58.4 to 75.2; the percentage of clay particle size is 35.0 and 48% and that of Yauri varies from 68.9 to 92.0 while the percentage of clay particle size is 45.0 and 65%. These values are relatively high and good for their plasticity and mouldability (Allen, 1986), using the USDA textural triangle for textural classification; the deposits for the three areas were found to be essentially clay as shown in Figure 3.

Most of the particles passed through 149 µm, whereas only approximately 85% of particle sizes are smaller than 45 µm. It shows that the corresponding clays, silt and sand fractions are indicated according to the International Society of Soil Science (Baccour et al., 2009). The clays and silt fraction (approximately 40%) was associated with clay minerals that were responsible for the plasticity.

Conclusion

Clays from three locations in Kebbi State, Nigeria, have been characterized by chemical, physical and mineralogical composition along with particles size distribution using XRF, XRD, AAS, laser particle size JL-1155 for particles size distribution and complexiometric titration techniques. From the results obtained, the following conclusions have been drawn:

(1) The chemical compositions shows SiO_2 and Al_2O_3 having dominance in all the samples; SiO_2 (52.45 - 55.85), Al_2O_3 (30.58 - 37.32) and minor compounds: MgO (2.41 - 1.10), Fe_2O_3 (11.00 - 2.30), CaO (1.0 - 3.50), K_2O (0.2 - 0.55), TiO_2 (0.02 - 0.25), and Na_2O (0.04 - 0.50) are within acceptable limits (Dietert, 1966). The chemical compositions determined when compared with standard recommended properties of clays showed that only Dukku and Yauri deposits characterized possessed the right properties for refractory and fireclay brick production. However, the presence of high Fe_2O_3 content reduces quality of products. This does not however make others totally unsuitable for other applications, but it implies that its reusability has to be closely monitored to ensure timely reconditioning to guard against the production of defective products.
(2) The concentrations of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, TiO_2, and K_2O are different in these Local Government areas, reflecting differences in the composition of the fluid from which they are formed.
(3) The results of the physical analysis depict the Dukku and Yauri clays have properties within the acceptable range according to international standard for fireclay, and refractory production (Tables 7 and 8).
(4) Finally, on the basis of the overall properties of the three areas under studies, they have been rated in the following order of preferences; Yauri deposit, Dukku deposit, and Jega deposit respectively.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

Table 9. Some physical properties of the clays.

Location	Average % of particles				Atterberg Limits			Average % Moisture Content at (115°)	% Clay Content	pH	% Lost on Ignition
	Gravel (>2 mm)	Sand (0.063-2 mm)	Silt (0.002-0.063 mm)	Clay (< 0.002 mm)	Liquid limit (%)	Plastic limit (%)	Plasticity Index (%)				
Dukku	1.5	21.5	35.2	41.8	79.85	28.70	51.20	3.90	67.35	6.80	9.20
Jega	3.5	10.5	28.5	40.5	82.0	22.50	34.5	2.95	63.35	6.02	9.15
Yauri	1.0	27.75	31.25	56.50	58.50	26.80	58.50	4.35	78.35	6.51	9.5
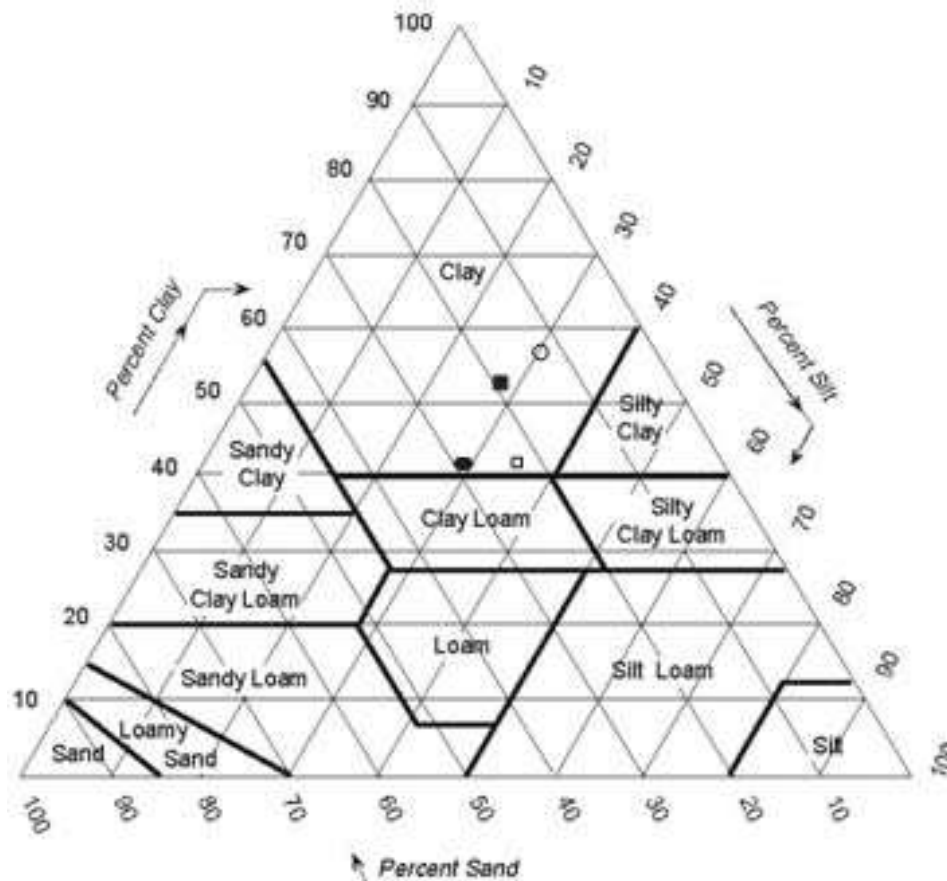
Figure 3. USDA triangular diagram for the textural classification of samples (Allen, 1986).

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