

Investigating the Industrial Potentials of Some Selected Nigerian Clay Deposits

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How to cite this paper: Jongs, L.S., Jock, A.A., Ekanem, O.E. and Jauro, A. (2018) Investigating the Industrial Potentials of Some Selected Nigerian Clay Deposits. *Journal of Minerals and Materials Characterization and Engineering*, 6, 569-586. <https://doi.org/10.4236/jmmce.2018.66041>

Received: October 8, 2018

Accepted: November 12, 2018

Published: November 15, 2018

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Abstract

One of the most important useful and widely abundant industrial minerals in the world is the clay minerals. Their applications in various industries are dependent on their properties. In this study, the mineralogical and physico-chemical properties of RahinSho (RC), Major Porter (MP), Wereng camp (WC), Kwi (KC) and Naraguta (NC) clay deposits in Plateau State, Nigeria were investigated to evaluate their potentials for some industrial uses. The x-ray diffraction studies revealed the kaolins as the dominant clay minerals in all the samples. The non-clay minerals found were quartz and muscovite. The chemical analyses by x-ray fluorescence also indicated that the silica (SiO₂) values of the samples ranged from (41.20 - 62.26)% while the alumina (Al₂O₃) range was (17.25 - 37.15)%. Some considerable amounts of impurities found were Fe₂O₃ (0.43 - 27.52)%, TiO₂ (0.05 - 3.28)%, K₂O (0.13 - 3.01)%. The oxides of Na, Ca and Mg were within acceptable limits in the clays for most purposes. The loss on ignition ranged from 4.30% - 12.43%. The physical properties investigated were particle size distribution that contained heavy clay-size materials ranging from 67.88% - 91.88%, plasticity index had range of values from 15.90% - 33.68%, and drying and firing shrinkages were 1.10% - 2.22% and 1.65% - 4.49% respectively. All the samples attained a temperature of 1500°C without fusion except Naraguta clay that fused at 1300°C. At the temperature of 1200°C, RC, MP and WC clays retained their natural colours of white and near-white respectively, while KC and NC clays changed colours from orange pink and light brown to moderate pink and moderate reddish brown respectively. These results compare very well with several clays elsewhere. Based on these characteristics, the clays were observed to be potentially suitable for the production of paints, tiles, ceramics, refractories, sanitary wares and clay bricks. Minimal processing will increase the potential of RC and MP to meet up with specification for paper, fertilizer and/or pharmaceutical uses.

Keywords

Clay, Deposit, Characterization, Industries

1. Introduction

Clay deposits contain clay minerals, which are essentially hydrated aluminium silicates and are usually in association with non-clay minerals such as quartz, feldspar, mica, calcite, and so on [1]. Common clay mineral groups are the kaolins, smectites, chlorites, illites, mixed-layered and others. Clay minerals have been mined and used for pottery and bricks since the Stone Age. Today, they are amongst the most important minerals used by environmental, manufacturing and process industries [2]. The properties of the clay minerals differ greatly amongst themselves because of differences in structure and compositions, and that each group has different applications because of the differences in their physical and chemical properties [3]. The mineral content of these deposits can be identified by x-ray diffraction.

Clay is an abundant raw material. Its exceptional and some specific properties lead to various industrial applications that depend also on its dispersions and rheological properties, the presence of organic materials and impurities, type and amount of exchangeable ions and soluble salts, and textural properties [4]. Plasticity is one of the most important clay properties that are related to different parameters. The most disaggregated clay minerals with major ionic exchange capability are more plastic. Montmorillonitic minerals are most plastic, then illitites, and least kaolinitics. In each of this group exists significant variability of characteristics, crystalline structures, particle size distribution and specific surface, with a major capability to absorb water [5]. The ability of clay minerals to attract strongly water molecules to form a slurry and mud is used in the paint and pottery/ceramic industries as a carrier and shaping of ceramic products respectively [2].

The industrial utilization of a clay deposit depends on its geological, mineralogical, chemical and physical properties. The assessment of economic potentialities of a clay body must involve the evaluation of the separameters [6]. Some of the commonest and important applications of clays are in the manufacture of paper, paint, plastics, ink, roofing sheets, pottery, bricks, ceramics, floor tiles and rubber. Clays also find various applications in the manufacture of cement, fertilizers and insecticides [7]. They are used in advanced chemical processing because of their reactivity and catalytic activity [8]. Clays are also utilized in pharmaceuticals and food processing industries [9]. Some of these applications require the processing or the blending with other materials so as to improve on some desired characteristics of the finished product [10].

Numerous studies exist on clay deposits that are widely spread in Africa and especially Nigeria [11], [12]. Some clay deposits in Nigeria have been investi-

gated for various applications. The clay deposits in Cross Rivers State have been evaluated and found potentially suitable for the manufacture of bricks, refractories, tiles and pottery [13] [14] [15]. Also, tests on clay deposits in Onibode, Ijopo in Ogun State and Are-Ekiti State revealed that their properties compare favorably with imported refractories [16]. The mineralogical, physical, geochemical and economic appraisals of some clay and shale deposits in South Western and North Eastern Nigeria have been discussed [10]. Clay deposits as Giru in Kebbi State, Kankara in Katsina State and Darazo in Bauchi State have been reported to have required properties by the Raw Materials Research and Development Council [17] and National Metallurgical Development Centre, Jos [18]. In this study, clay deposits from RahinSho, Major Porter, Wereng Camp, Kwi and Naraguta in Plateau State, Central Nigeria were characterized for some physical, chemical and mineralogical compositions with the view of determining their industrial applications.

The results of this characterization shows that the samples of NC and KC cannot be used as refractory clays but suitable for the production of building bricks and sewer pipes while RC, MP and WC suggests their applications in the paper, paint, ceramic, sanitary and tile industries.

2. Materials and Methods

2.1. Sample Collection and Preparation

Clay samples were collected from five different locations in the Upper part of Plateau State, Central Nigeria. RahinSho and Major Porter deposits are located in Barkin Ladi, Kwi and Wereng Camp clay deposits are in Riyom, while Naraguta deposit is located in Jos North Local Government Area as shown in **Figure 1**. The study areas are bounded between latitudes $8^{\circ}30'E$ and $9^{\circ}00'E$ and longitudes $9^{\circ}30'N$ and $10^{\circ}00'N$.

5 kg of fresh samples in lump form were obtained randomly from ten different points within each deposit from underground local mines pit at the depth of 10 - 20 cm. The samples were air-dried for several days and crushed using a set of Denver crushers by Denver Equipment Co. England. Each crushed sample was thoroughly mixed, coned and quartered. Two opposite composite representatives were obtained and consequently milled and pulverized. These were packaged in small polyethylene bags as representatives of the samples for the required tests [19].

2.2. Methods of Analysis

2.2.1. Mineralogical and Chemical Properties of Clay Samples

X-ray diffraction

The identification of clay minerals of each clay sample was carried out using a Panalytical BV Empyrean PW 1800 X-ray diffractometer. All pulverized samples of (1.5 μm) size were oven-dried and about 0.5 g of each was mounted and analyzed using a copper (Cu) target radiation at 45 KV and 20 mA at the scan speed

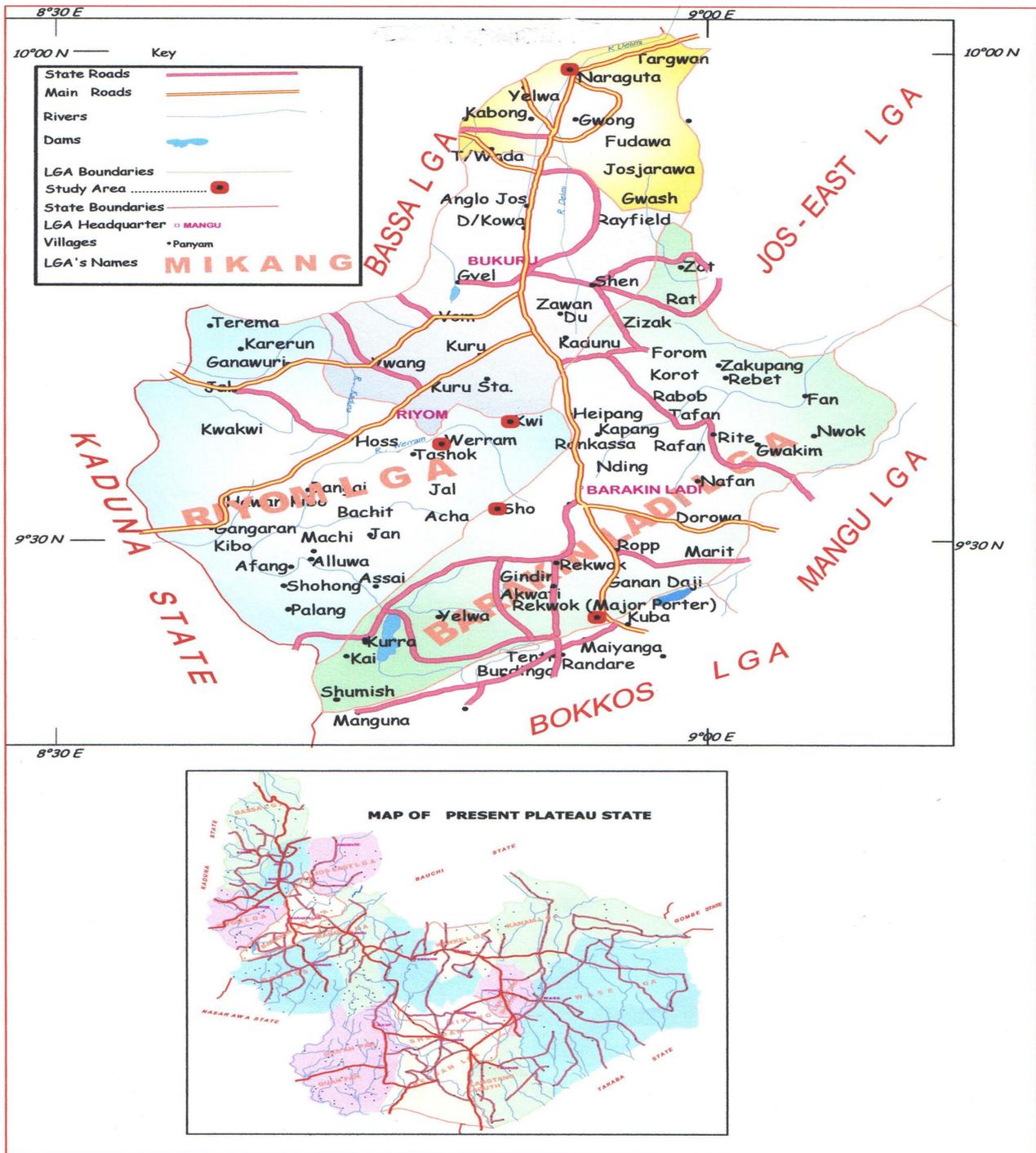


Figure 1. Map of the study sites [adapted from Ministry of Land and Survey, Plateau State].

of 2° per minute. The interpretation of the diffractograms obtained for each sample was done by comparing the peaks with those of standard minerals [20].

X-ray fluorescence

The chemical compositions of the pulverized samples were determined by Energy Dispersive X-ray Fluorescence (EDXRF) of the model PW4030 X-ray photometer that uses a rhodium anode tube. The sample film was placed firmly

in a waxed and gold plated sample holder. The Energy Dispersive patterns were obtained with the help of a computer attached to the instrument and each compound recorded in percentage [21].

Loss on ignition

Loss on ignition was determined according to the Lechler and Desiletes method, [22]. The samples were oven-dried at 110°C. Then 1g of the sample of clays was placed in preheated, cooled and pre-weighed silica crucibles and heated to 1000°C in a furnace for an hour. The crucibles and contents were removed, cooled in a desiccator to room temperature and weighed again. The loss in weight was calculated.

2.2.2. Physical and Thermal Properties of Clay Samples

Clay pH

The clays pH were determined using the Rex pH Meter (model pHS – 25) and the procedure adopted according to [23]. The clay to water ratio was 1:5 w/v and the pH meter was calibrated with buffer solutions of pH 9.2, 7.0 and 4.0. The pH of each sample was read and recorded at room temperature.

Plasticity index of clay samples

The Atterberg plasticity method prescribed by [24] was used to calculate the plasticity index of the clay samples from their respective liquid and plastic limits determined.

Particle-size analysis

The particle size test was carried out by using the standard Hydrometer method [23]. 50 g of milled oven-dry clay was weighed into a 250 cm³ beakers and mixed with 100 cm³ calgon, then allowed to soak for 30 minutes. The mixed suspension was transferred into a sedimentation cylinder and filled up to mark point with distilled water.

The hydrometer was inserted into the mixture in the cylinder and the readings were taken after interval of 40 seconds twice. After 2 hours, another hydrometer reading and temperature were recorded. After 40 seconds and 2 hours, all the sand and silt particles would have settled and only clay will remain in suspension. The percentages silt and clay were then calculated and the interpretation of result was made by using a textural triangle.

Drying and firing shrinkage of clays

The clay drying and firing shrinkages were determined from brick bars prepared using a mechanical hydraulic press (model D-7064 Paul Weber) with its accessory moulds and the method adopted was [25].

Refractoriness of clay samples

Fired clay bricks were used to estimate the refractoriness of the clay samples according to the procedure by [26]. Square shape pieces were cut with a hacksaw from the fired bricks made from different clay samples. The samples were fired in a carbolite furnace Model RHF 1600 at the rate of 5°C per second at the temperatures ranging between 1300°C and 1500°C. The piece that fuses at any of the temperature was taken to be the fusion point and thereby its refractoriness.

Colour test of clay samples

The colour of the clay samples were determined by using the American Rock-Colour Chart Test. The colours of both the raw and fired clays were ascertained by comparing with that of the chart based on the Munsell charts plot according to the method [27].

3. Results and Discussion

3.1. Mineralogical Composition of the Clays

The mineralogical composition of the clays determined using X-ray powdered diffraction is presented in **Table 1** and the diffractograms shown in **Figures 2-6**. The samples were scanned at a position of $0^\circ - 40^\circ$ of 2-theta angle using a copper element target showed several peaks with respect to the different minerals found in each sample.

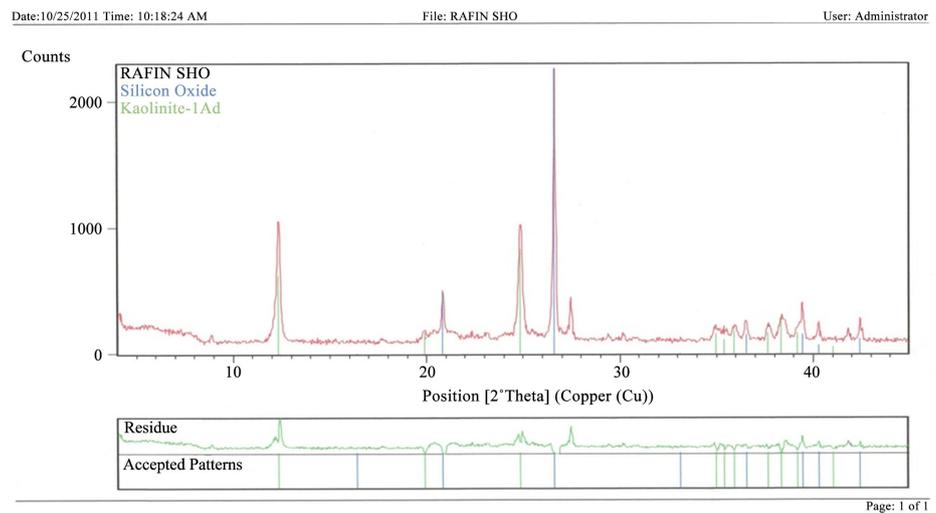


Figure 2. X-ray diffractogram of RahinSho sample.

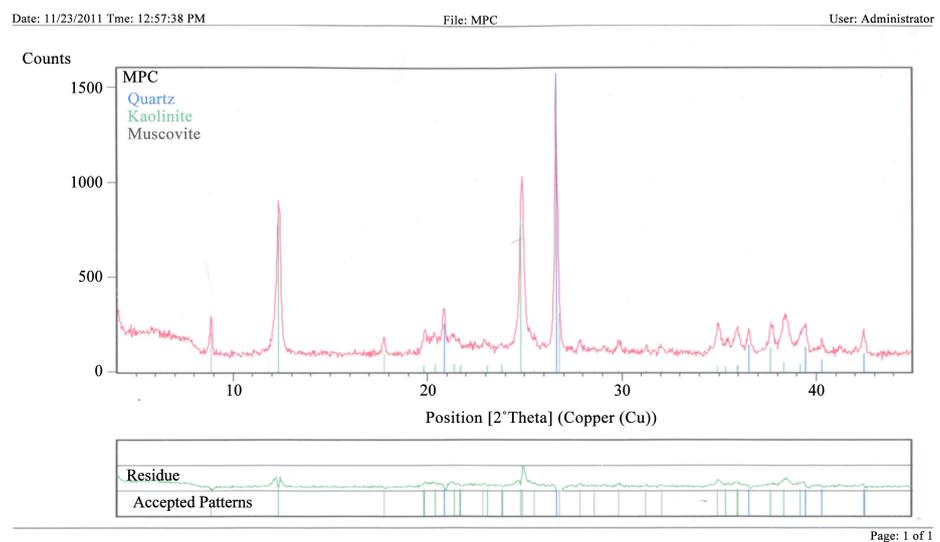


Figure 3. X-ray diffractogram of Major Porter sample.

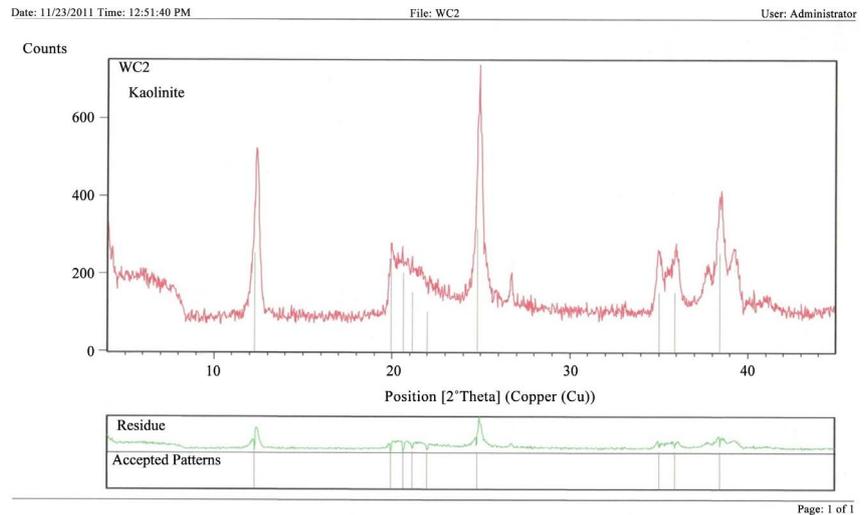


Figure 4. X-ray diffractogram of Wereng Camp sample.

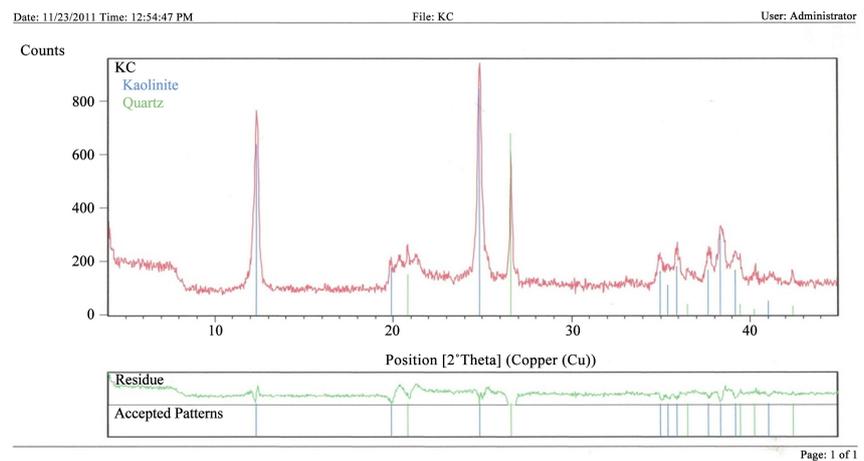


Figure 5. X-ray diffractogram of Kwi clay sample.

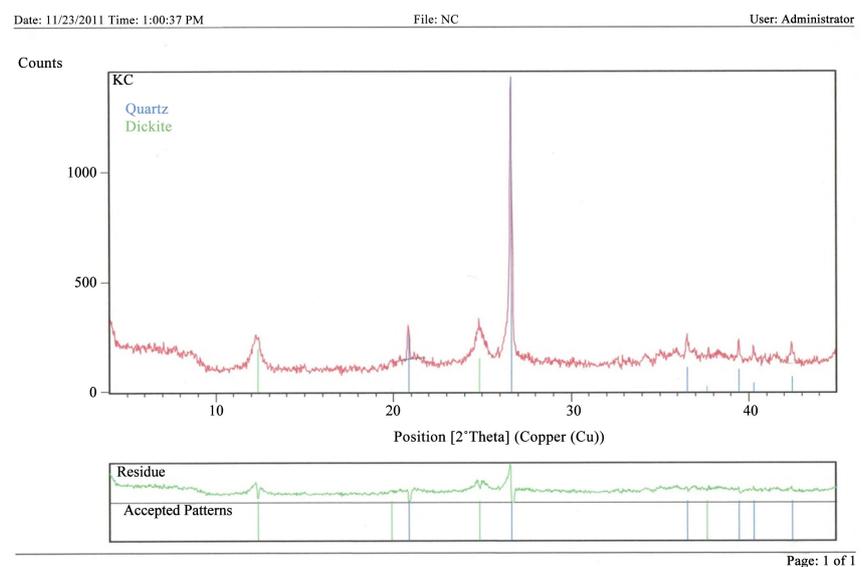


Figure 6. X-ray diffractogram of Naraguta clay sample.

Table 1. Mineralogical compositions of the clay samples and some reference clay materials.

Minerals (%)	RahinSho Clay	Major Porter Clay	Wereng Camp Clay	Kwi Clay	Nara-guta Clay	Reference clays			
						*Ibadan Clay	*Kan-kara Clay	**China Clay	^NAFCON Recommended
Kaolinite	56.24	41.40	98.11	87.99	-	91	96	85	85
Dickite	-	-	-	-	17.93	-	-	-	-
Illite	-	-	-	-	-	3	3	15	3
Quartz	39.70	30.45	-	12.01	82.07	6	2	Tr	4
Muscovite	-	28.16	-	-	-	-	-	-	-
Felspar	-	-	-	-	-	-	-	-	2
Others	4.05	-	1.89	-	-	-	-	-	8
Total	99.99	100.01	100.00	100.00	100.00	100.00	99.00	100	98

*[28]; **[29]; ^[30]; Tr = trace.

The results indicate that the samples were composed of different types of minerals. The kaolin group of clay minerals is most predominant, while the main non-clay minerals are quartz and muscovite.

Kaolinite type of mineral was found in RahinSho (RC), Major Porter (MP), Wareng Camp (WC) and Kwi Clay (KC) deposits, while the dickite type was found in Naraguta Clay (NC) deposits. The main non-clay minerals are quartz found in varying proportions in all deposits except WC sample and muscovite found only in MP sample.

Clays are particularly noted to contain many mineral types, and are very diverse in composition. Many of their properties depend on the nature and amounts of the various minerals present. The analysis of the clay samples in **Table 1** shows that the proportion of the predominant clay mineral kaolins are in the order: WC (98.11%) > KC (87.88%) > RC (56.24%) > MP (41.40%) > NC (17.93%) while quartz varies from 12.01% to 82.07%, muscovite has a value of 28.16% and other minerals range from 1.89% to 4.05%.

Quartz and muscovite are found in high proportion in these clays and this indicates that all the clay samples formed at the deposits are either of residual weathering or hydrothermal formation. Such clay minerals are formed as alteration products associated with geothermal areas and hot springs, and as aureoles around hydrothermal ore deposits. This type of kaolin clays undergo little or no transportation and usually contain a much larger proportion of primary minerals [1]. The identification of the kaolinite type of mineral in RC, MP, WC and KC samples as shown in **Figures 2-5** suggests formation from weathering process which involves physical disaggregation and chemical decomposition that change original minerals to clay minerals. Kaolinite is found in most weathering zones and soil profiles [2].

The proportion of dickite, one of the two well-formed of all kaolin mineral found in NC sample was quite low (17.93%). The occurrence of this mineral type

is not common but mainly formed as a product of acid hydrothermal fluids. It is also occasionally found in iron beds as a white powder in cavities and center of noodles [31]. This explains the reason for the very high content of iron oxide in this deposit as observed from the chemical analysis. The absence of primary minerals in WC clay also explains the reason for the corresponding high proportion of its clay minerals at 98.11%.

3.2. Chemical Analysis of the Samples

The result of the chemical analysis summarized in **Table 2** shows that all the samples contain SiO_2 and Al_2O_3 as the major components. Silica ranged from 41.20% - 62.26%, alumina (17.25% - 37.15%) and LOI (4.3% to 12.43%), while Fe_2O_3 , TiO_2 and K_2O were in moderate to major concentration levels.

The high amounts of SiO_2 , Al_2O_3 and LOI define the clay samples as hydrated alumino-silicate type of minerals [26]. This is attributed to the fact that kaolin clays are principally composed of SiO_2 , Al_2O_3 and water, which have a chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, also represented as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The average SiO_2 , Al_2O_3 and water contents in the clay samples constitute about 96.08% for (RC) clay, 95.05% for (MP) clay, 95.68% for (WC) clay, 90.03% for (KC) and 63.58% for (NC) samples.

In most samples, SiO_2 and Al_2O_3 are the distinctive major constituents. The only exception is observed with NC clay that has very high Fe_2O_3 of approximately 28% and the Al_2O_3 content (17%) is much lower than in other samples. This explains the probable reasons for the low value of the clay mineral of Naraguta clay shown in **Table 1**. However, the high amounts of the SiO_2 , Al_2O_3 and Fe_2O_3 in some of the samples suggest that the clays could be used for a variety of purposes [19]

Table 2. Chemical composition of clay samples.

Oxides (%)	RahinSho Clay (RC)	Major Porter Clay (MP)	Wereng Camp Clay (WC)	Kwi Clay (KC)	Naraguta Clay (NC)
SiO_2	62.26	55.10	50.15	46.48	41.20
Al_2O_3	29.44	34.73	37.15	31.12	17.25
Fe_2O_3	0.43	1.39	1.93	5.54	27.52
TiO_2	0.05	1.54	2.82	3.10	3.28
Na_2O	0.13	0.23	0.08	0.12	1.17
K_2O	2.19	1.97	0.13	0.33	3.10
CaO	0.46	0.43	0.06	0.23	0.33
MgO	0.33	0.15	0.07	0.14	0.57
LOI	4.30	5.22	8.38	12.43	5.13

The results of the chemical analysis show that the clay samples have SiO₂ content in the order RC (62.26%) > MP (55.10%) > WC (50.15%) > KC (46.48%) > NC (41.20%). These values except for KC and NC are slightly above the ideal SiO₂ value of pure kaolinites (46.54%) [32]. The deviation suggests the presence of free SiO₂ as crystalline quartz usually occurring in residual clays or in combination with other compounds as impurities of fluxes, feldspar or mica [33]. This could also be attributed to the high amount of quartz and muscovite found from the mineralogical compositions of RC and MP samples. Free quartz and high SiO₂ affect clays by reducing physical properties such as plasticity, crushing strength, refractoriness in many cases, and also the drying and firing shrinkages [31].

The Al₂O₃ content also follows the order: WC (37.15%) > MP (34.73%) > KC (31.12%) > RC (29.44%) > NC (17.25%). WC, MP and KC samples reflect values close to that of pure kaolinite with 39.50% which also indicates the quality of the pure clay minerals [26]. The higher the Al₂O₃ content of clay, the higher its refractoriness and a good range is between 25% - 45% [34]. This shows that all the clay samples except NC have a moderate to high grade refractory properties. The low Al₂O₃ content of NC depicts its non-refractory nature and therefore can be considered only for non-refractory and low heat uses. Free alumina compounds also affect clays by reducing their plasticity because they are non-plastic by nature.

The analysis also reveals the presence of some significant impurities such as the oxides of Fe, Ti (coloring agents) and the oxides of Na and K (fluxing agents). The amount of Fe₂O₃ in some of the samples were high and are in the order: NC (27.52%) > KC (5.54%) > WC (1.93%) > MP (1.39%) > RC (0.43%). High amount of Fe in clays effect an alteration in their color, reduce the refractoriness which act as weak fluxes and may form scum and visible spots on burnt clay bodies [35]. This explains the reason for the colouring of the natural clays of NC and KC samples, and this also implies that the samples cannot be used as refractory clays that require less than 5% Fe₂O₃ [31]. However, they can be suitable for the production of building bricks and sewer pipes [9]. RC, MP and WC samples with lower amount of iron content suggests use in the paper, paint, ceramic, sanitary and tile industries [2].

The oxide of Ti follows similar trend as Fe₂O₃ in the order NC > KC > WC > MP > RC. Minerals of titania act as feeble fluxes at temperatures of 1500°C and above [36]. Many kaolinites contain titania along with Fe rich oxides as impurities mainly those found in soils under tropical conditions. The high combined concentrations of Fe and Ti in KC and NC samples is advantageous in brick making as it gives attractive reddish brown colour appearance [6]. The percentages of Na₂O are relatively low (0.12% - 0.23 %) except in NC (1.17%) that is slightly high. The presence of significant amount of K₂O in some of the samples can be attributed to the alkali bearing minerals such as muscovite or their sulphates [37]. The effects of all the alkalis in clays are to reduce physical properties such as refractoriness, vitrification temperature, plasticity and shrinkages [38].

The impurity oxides of Ca and Mg are generally low (0.07% - 0.57%) and are also within acceptable limit for industrial uses as shown in **Table 5**.

The alumina content of RC (29.34%) is similar to Ball Clay Tennessee (29.44%) while the content of silica for RC (62.26%) is slightly higher than for Ball clay Tennessee (53.96%). The metal oxides of these clays are also similar as shown in **Table 2** and **Table 4** respectively. This implies that the clays will be used for similar areas of application. RC and Ball clay Tennessee will have a lower refractoriness compared to flint clay Negev with higher alumina (47.00%) and lower silica (36.00%) depicted in **Table 4**.

Also WC with 37.15% alumina and 50.15% silica is similar to China clay Qty having 37.65% alumina and 46.88% silica shown in **Table 2** and **Table 4** respectively. The chemical properties of these clays differ with Building Brick clay Glacial with lower alumina (17.10%) and higher silica (60.10%) shown in **Table 4**. In addition, the clays are also expected to have different application areas.

3.3. Physical and Fired Properties of Clay Samples

The results of physical and firing characteristics of the clay samples are presented in **Table 3**. The pH (5.20 - 6.40) of the samples indicates that the clays are of acidic origin, appearing as weak acids. This is in agreement that most clay suspensions lay between the pH range of 4.2 and 7.0 [31]. The particle-size analysis shows that WC has the highest (91.88%) while NC has the lowest (49.88%) clay contents. Particle size distribution in this present study is defined in terms of the inherent crystallite size of the minerals present in the clays instead of the grain size produced by a comminution process and natural clays are best defined in terms of their crystallite compositions [39]. The grain size composition of clays control ceramic strength, shrinkage, paper filling/coating and glossiness [40]. The proportions of the clay size materials are in the increasing order of: NC (49.88%) < RC (67.88%) < MP (73.88%) < KC (84.88%) < WC (91.88%). Based on the proportion of the ratio of sand: silt: clay textural triangular diagram, all the samples fall within the clay size fractions (<2 μm or 0.002 mm) with the exception of NC which falls within the clay-size fraction of silt-clay [23]. Values above 55% clay on the triangle are considered heavy clay and this further confirm that all the clay samples except NC are heavy clay deposits.

The clay content for WC and KC samples are close to, while MP, RC and NC are higher than the calculated mineralogical composition shown in **Table 1**. This suggests that the muscovite found in MP sample probably has its particle size at the size of the clays, and some of the silt size in the samples could also have their grain size the same as that of the clays thereby resulting in their increased proportion by size analysis [31]. However, silt is considered to be quartz in mineralogical terms, even though their particle sizes differ [41]. The high proportion of clay particles of the kaolins make them suitable for most industrial uses because grain size is an important specification in some industries such as paint, paper, plastics and insecticides [3].

Table 3. Physical and fired properties of the clay samples.

Sample Clays	Particle Size (%)			Plasticity (%)			Shrinkage (%)		pH	Colour		Refractoriness (°C)
	Clay	Silt	Quartz	LL	PL	P _I	Drying	Firing		Natural	Fired 1200°C	
RahinSho Clay	67.88	24.00	8.12	57.30	25.45	33.68	1.10	1.65	6.0	Whiter than N9	Whiter than N9	>1500
Major Porter Clay	73.88	18.00	8.12	45.38	29.48	15.90	1.10	2.23	6.1	White N9	White N9	>1500
Wereng Camp Clay	91.88	6.00	2.12	61.15	44.05	17.20	2.23	4.99	5.6	Near White 5YR 8/1	Near White	>1500
Kwi Clay	84.88	14.00	4.12	63.90	28.60	33.30	1.14	2.40	5.2	Moderate Orange Pink 5YR 8/4	Moderate Pink 5R 7/4	>1500
Naraguta Clay	49.88	43.00	7.12	48.03	23.50	24.53	2.22	3.30	6.4	Light brown 5YR 5/6	Moderate reddish brown 10R 4/6	Fused at 1300

LL = Liquid Limit; PL = Plasticity Limit; PI = Plastic Index.

Table 4. Chemical analysis of some reference clays.

Oxides (%)	China Clay Qty	Fire Clay Yorkshire	Building Brick Clay Glacial	Flint Clay Negev	Ball Clay Tennessee	(Belpahar Refractory Clay India	Residual Kaolin Ibadan	Kankara Clay Katsina
SiO ₂	46.88	56.60	60.10	36.00	53.96	50.00	63.20	44.09
Al ₂ O ₃	37.65	26.90	17.10	47.00	29.34	31-33	25.61	38.67
Fe ₂ O ₃	0.88	1.70	5.40	1.20	0.98	3.5	1.52	1.13
TiO ₂	0.09	1.30	1.20	3.00	-	1.38	0.22	2.21
Na ₂ O	0.21	0.22	0.70	0.30	0.12	} 1.36 - 2.0	0.24	0.36
K ₂ O	1.61	1.26	2.70	0.30	0.28		1.75	0.52
CaO	0.03	0.20	3.70	0.20	0.37		0.61	0.10
MgO	0.13	0.30	2.80	0.20	0.30	0.38	0.05	0.15
LOI	8.00	1.26	6.40	13.00	14.01	9-14	13.50	14.43

Source: [45].

Table 5. Specification of some industrial clays.

Oxide %	Plastics	Paints	Rubber Paper Textile	Ceramics	Refractory Bricks	Brick Clay	Tiles	Sanitary Wares	Table Wares
SiO ₂	45.78	45.30 - 47.90	44.90	45.90	67.50	51 - 70.00	70.00	54.00	46.0
Al ₂ O ₃	36.46	37.90 - 38.40	32.35	33.50 - 36.10	26.00	25.44	19.00	30.00	31.00
Fe ₂ O ₃	0.28	13.40 - 13.80	0.43	0.60	0.50 - 1.20	2.40	1.60	1.40	1.10
TiO ₂	-	13.80	-	0.03	-	-	1.60	1.20	0.90
Na ₂ O	0.25	0.20 - 0.35	0.14	1.60	1.50	3.50	0.5	0.50	0.40
K ₂ O	0.25	0.40 - 1.00	0.28	1.60	1.10 - 3.10	-	2.0	3.10	2.20
CaO	0.50	0.03 - 0.25	Tr	0.50	0.30	0.20	0.2	0.30	0.40
MgO	0.04	0.20 - 0.30	Tr	0.40	0.19	0.70	0.4	0.40	0.40
LOI	-	-	-	12.40	-	-	5.40	8.80	-

Source: [45].

The plasticity index of the clay samples ranged between 15.90% to 33.30% (**Table 3**) and this indicates that the clay samples are of low and medium plasticity. The order of the plasticity index are as follows: RC (33.68%) > KC (33.30%) > NC (24.53%) > WC (17.20%) > MP (15.90%). These values fall within the characteristic plasticity range for kaolinites (10% - 60%) as observed on the plasticity clay identification chart [42]. Depending on the finest size and cation exchange characteristics of the particle size, the plasticity may vary from high to low and most natural clays are complex mixtures of kaolinites with hydrous mica, primary mica, and quartz, along with traces of other minerals [43]. The presence of these in addition to the kaolinites will greatly modify the plasticity of the clays. Chemical nature of the surfaces of clay minerals and their ability to hold water films that act as lubricants, also influence plasticity [44]. This explains the the probable reasons why the plasticity index of RC and KC clays are high with values above 33%; NC clay is moderate with 24.53%, while MP and WC are slightly above 15%. The presence of appreciable amount of muscovite—an alkali-bearing mineral and quartz (**Table 1**) which are non-plastic in character, further confirm the low plastic index in MP sample. MP and WC clays are likely to exhibit low-dry strength, indicating low moisture content. The more plastic a clay, the more water it will tolerate without becoming fluid. The extent of this property depends on factors such as specific surface area, size finest, exchangeable cations, composition of the particles and the influence of organic colloids [31].

The average liquid limit ranges from 45.38% to 63.90%. The values for NC and MP are 48.03% and 45.38% respectively. This shows that the clays can be worked through limited range of water content which is a vital property in the ceramic and paper industries, where the behaviour of the clay-water mixture is important [45]. The plastic limit of clays indicates the minimum amount of water required for clays to become plastic. The highest plastic limit (44.05%) in WC sample could be attributed to the high proportion of the clay material in the deposit. Generally, these clays are fine grained; well crystallized/ordered kaolinite and so have low to moderate plasticity and is important during the blending, moulding and drying stages of the clay [31].

The results of the drying and firing shrinkages for all the samples in **Table 3** are quite low. The drying shrinkage ranged from 1.10% to 2.23% while the firing ranged from 1.65% to 4.99%. The low shrinkages as compared with China clays (10% - 13%) fired at 1280°C could be due to the high amount of quartz in the clays. The presence of free quartz in clays reduces shrinkages and the low shrinkage values could be attributed to the probable fact that the samples were not heated to the vitrification temperature of 1280°C [46]. However, the highest shrinkages observed in WC with 2.33% and 4.99% for drying and firing shrinkages respectively could be due to the high proportion of the clay material. These have more pore spaces contained in the minerals which gradually become filled with molten material, and which on cooling solidify to form glass [35]. Low shrinkages are required in ceramics and heavy clay products.

The colour determination on the natural and fired clays is important in certain industries and it is also an essential requirements. Most kaolin clay deposits like China clays occur naturally as white, while others as fired white. Deviation from that is an indication of the presence of some impurity materials such as iron, cobalt or copper compounds [2]. The colour test result reveals that RC and MP samples retained their white colours after firing as well WC. KC and NC clays show slight colour change from moderate orange to moderate pink and light brown to reddish brown respectively. This coloration is due to the presence of high Fe and Ti oxides and they give pleasant colours in the production of bricks and pottery [26]. The white and near white-burning colours of RC, MP and WC samples make them suitable for the manufacture of white wares, refractories, paper and paint [47].

The refractoriness of the samples except NC is as high as 1500°C and it's an indication of a good refractory property. Clays that could be used as fireclays must not fuse below 1500°C and must be one above 1600°C [34]. NC sample fused at 1300°C and therefore cannot be considered as fireclay. This is attributed to the low alumina content, high proportion of fluxing (Na, K, Ca and Mg) and colouring agents (Fe, Ti) as revealed by the chemical analysis in **Table 2**.

Comparison of the clays mineral compositions with some well-known clay deposits (**Table 4**) indicates that the WC clay is well over the values of some reference and commercial clays but similar to Kankara and Ibadan kaolins, while KC clay is similar to China clay and is within NAFCON recommended for kaolin clays as shown in **Table 1**. The values of RC, MP and NC are lower than the reference clays largely due to the high amount of quartz and muscovite found in these deposits. Nevertheless, these clays have indicated high potentials for various industrial applications for kaolins minerals [47].

Also, a comparison of the clay samples in terms of their chemical compositions with some selected indigenous and foreign clays (**Table 4**) shows that RC falls within fall Yorkshire fire clay, Tennessee ball clay and Ibadan residual Kaolin. It is also observed that WC Al_2O_3 content is within the same range with Qty China clay, Negev flint clay and Kankara clay, except that SiO_2 content is slightly higher. The result of KC composition falls within the Indian refractory clays but also has a slight higher content of Fe_2O_3 . The variations observed in the oxide concentrations from one sample to the other suggest the differences in the environment of the geological formation of the clays and the associated impurities at the location of the sample deposits [2].

The chemical compositions of the clay samples in **Table 2** are also compared to some industrial clays shown in **Table 5**. It is observed that RC falls closely within the values of refractory bricks and sanitary wares applications while MP clay has Al_2O_3 content similar to required values for uses in plastics and rubber, paper and textile industries. However, the deposit contains slightly higher SiO_2 . The results of WC sample closely agree with the values for applications in the plastics, paints and ceramics industries. The values of KC sample has composi-

tion similarly for use in table ware though it has slightly higher Fe_2O_3 and TiO_2 contents, while NC composition is also similar in application for tiles and brick clays making. Generally, the clay samples in the present study have favourably met the requirement for the different industrial uses as shown in **Table 5**.

4. Conclusion

The results of the mineralogical, chemical and physical properties show that all the samples are suitable for various industrial uses. The proportion of the kaolinite for Wereng camp and Kwi clays met the standard specification for kaolin by NAFCON. The chemical composition as well as the physical characteristics also revealed that these clays compare favorably with the specifications of some industrial and reference clays. Each sample deposit has industrial potentials. The naturally white colour of RahinSho and Major Porter clays make them suitable for paper, paint, rubber/plastic, white-ware (sanitary/dinner wares) and refractories productions. Also processing RahinSho and Major Porter to remove sand, Fe, Ti oxides to the desired levels and required size of the minerals could increase their application in paper, plastic/rubber; fertilizer production and even in pharmaceutical. Wereng camp clay with a near-white colour and high proportion of clay-size particles can be successfully used for paint, tiles, sanitary-ware and refractories production. Kwi clay deposit can be used for the production of low grade paint, sewage-pipes, clay bricks and pottery while Naraguta clay deposit's is suitable in the production of clay bricks and sewer pipes due to the high concentrations of Fe_2O_3 , TiO_2 , K_2O ; moderate plasticity and low shrinkages.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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