

Assessment of clay mineral deposits from Nkemkol in Ogoja local government area of cross river state for application as raw materials in ceramic industries

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Abstract

This research evaluated the potential of clay deposits from Nkemkol, Ogoja in Cross River State, Nigeria as local raw materials for industrial use. Four samples were gathered from various sites in the area. The clays were analyzed using X-ray fluorescence, X-ray and physical property tests to determine their geochemical composition, mineral content, and key characteristics. The analysis revealed high levels of silica (56.41%) and alumina (32.82%), which are typical of aluminosilicate clays. Iron oxide content was moderately high at 3.34% Fe₂O₃. The predominant clay minerals identified were kaolinite (18.9-37.0%) and illite (0.5-4.15%), along with non-clay minerals such as quartz, feldspars, and metal oxides. The clays exhibited significant plasticity (average plasticity index of 26.61%), facilitating easy molding and shaping. The average porosity was 21.33%, suitable for refractory applications. Firing shrinkage ranged from 6.5% to 19.2%, with density measurements between 1.54 and 1.76 g/cm³, both within acceptable limits. Post-firing strength met the minimum standard of 15 N/mm², with an estimated refractoriness of 1680.22°C. Overall, the Nkemkol clays possess favorable chemical, mineralogical, and physical properties for use in refractories and structural ceramics, pending some processing modifications. Utilizing these local deposits could enhance import substitution, foster rural industrialization, and support sustainable development in Nigeria. Further pilot testing is recommended to refine formulations and processes for specific ceramic products, along with a comprehensive national survey of clay deposits. The clays are deemed suitable for applications such as refractory bricks, ceramic tableware, architectural ceramics, wall tiles, and pottery items.

Keywords: Clay mineral deposits; Ceramic industries; Cross River State; Geochemical composition; Aluminosilicate clays

1. Introduction

Ceramics have played a vital role in human civilization for centuries, serving various purposes ranging from functional to decorative applications. Barsoum (2003) opined that the ceramic industry, which encompasses the production of a wide range of products such as bricks, tiles, pottery, sanitary ware, and advanced technical ceramics, is a significant contributor to the global economy. The success of this industry heavily depends on the availability and quality of clay resources, as clay is the primary raw material used in ceramic manufacturing. According to Guggenheim and Martin (1995), clay is a naturally occurring material composed primarily of hydrous aluminum silicates, along with other minerals and impurities. More specifically, it is mostly made up of hydrous aluminosilicate minerals that are organized in tightly packed layers or sheets using well-defined octahedral and tetrahedral geometry. According to Kerr (1952), if clay is composed of single units of alumina octahedral and silica tetrahedral, it is categorized structurally as (1:1); if clay is composed of two silica tetrahedral units, with an octahedral alumina unit sandwiched between the silica sheets, it is classified architecturally as (2:1). The unique properties of clay, including its plasticity, workability, and firing behavior,

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make it an indispensable material in ceramic production. El Quahabi *et al.* (2014) studied the ceramic industry's potential for using clay raw materials from the northern Moroccan regions of Tetouan and Meknes. The authors noted that the Tetouan clays have medium to low SSA (specific surface area) and CEC (cation exchange capacity), according to the data, the clayey samples, SiO₂ (35–54.3% wt), Al₂O₃ (20.6–43.9 % wt), and Fe₂O₃ (9.7–22.4% wt) were the principal oxides. Whereas CaO was exclusively found in some Tetouan clay, it ranges from 8.0 to 12.0% weight percent in Meknes clays. The authors also noted that the majority of Tetouan clays showed a notable densification of ceramic at fire temperatures exceeding 1000 °C, whereas Meknes clays shown this phenomenon starting at 800 °C. Consequently, the authors concluded that Tetouan and Meknes clays' chemical, textural, and ceramic qualities suggest that they are suitable for the creation of structural ceramics.

Research on the characteristics of Cotrombian clay and its potential as an adsorbent was conducted by Macias-Quiroga *et al.* (2018). The authors pointed out that according to the chemical analysis, the main oxides are SiO₂ (55.81% wt), Al₂O₃ (16.25 wt%), and Fe₂O₃ (7.51 wt%) and that the bulk clay's specific surface area, as determined by nitrogen adsorption, is 45.1 m²/g. They added that the potential of homogenized clay and organoclay for the removal of heavy metals in aqueous solutions was demonstrated by their achievement of Cr (III) and Cr (IV) removals greater than 85.05 ± 2.04% (pH between 3 and 4) and 82.93 ± 1.03 % (pH between 3 and 5), respectively.

Aghayer and Kucukuysal (2018) investigated Usak clay's ceramic qualities in relation to Ukrainian clay. The results demonstrated that the samples differed, with quartz dominating USC (unifies soil classification) and kaolinite dominating UKC (unmodified kaolinite clay). Given that USC melts around 1300°C, it is unlikely that it can be categorised as refractory. This feature does, however, point to a potential financial benefit for USC in terms of creating technological traits at reduced temperatures.

Akowanou *et al.* (2017) conducted a study to characterize clays from the "Se" region in the Southern part of Benin, which are utilized in the production of ceramic water filters. Three clay samples were obtained from a quarry in "Se", situated in the southwestern region of the Benin Republic. The samples underwent granulometric evaluation, X-ray Powder Diffraction (XRD), loss on ignition (LOI), cation exchange capacity (CEC), and measurement of Atterberg's limits for characterization. The clays' major elemental compositions were established. The chemical and mineralogical investigation reveals that all of the samples consist of different proportions of quartz and kaolinite, with muscovite and vermiculite being present as well. Additionally, they suggest that the clay components are composed of silico-aluminous clays. The CEC and N₂ adsorption results indicate a low CEC and specific surface area, which is consistent with the existence of quartz and kaolinite quartz. The examined samples demonstrated that the clays possess a high degree of plasticity, with an organic matter concentration varying from 7.8% to 9.8% (as determined by loss on ignition). The TGA (thermogravimetric analysis) research indicated that the optimal sintering temperatures range from 700°C and higher. The authors noted that based on their mineral composition and physical properties, the clays are excellent as raw material for ceramic industries, notably for ceramic water filters. Abuh *et al.* (2018) explored the ceramics application of Mgbom clay: characterisation and micro-structural research. The physical, chemical and spectral characterization of the clay was carried out. It was revealed that band corresponding with quartz, carbonates and kaolinite were observed. The x-ray examination revealed the existence of quartz (SiO₂). Kaolinite (Al₂Si₂O₅ with hematite (Fe₂O₃). The physical characterization also indicated values of modulus of plasticity (1.23) and water of plasticity (46%) which characterises the clay as strong, plastic and expansive. From the chemical composition produced for SiO₂ is deemed acceptable for paper, paint, mid-temperature refractory, glazes and clay wares ceramics but low values of Al₂O₃ and high values of Fe₂O₃.

Ombaka (2016) determined the characteristics and categorization of clay-based substances for prospective applications in Rugi Ward, Kenya. The chemical and physical characteristics of the clayey minerals govern their employment in the process industries and beneficiation necessary before usage. The study aimed at establishing the potentiality of clayey minerals from the study area, and the possibilities of exploring and utilising them in order to accelerate industrial development and improve economic self-reliance of Kenya as a nation. It was shown that the clay samples composed of albite (5 - 16.7 %), kaolinite (11.4 - 36.2 %), microcline (15.2 - 35.3 %), quartz (24.3 - 68.1 %), hornblend (7.6% in samples from Nyamwa alone) and other mineral impurities in tiny amount. The data shows that clayey minerals from the research area can be utilised for commercial manufacturing of ceramic products following beneficiation using low cost and environmentally friendly processes in order to reduce the amounts of iron, quartz, and other impurities to acceptable levels.

Ituma *et al.* (2018) explored the application of Nkpuma-Akpatakpa clay in ceramics; characterization and micro structural research. Chemical, mechanical and spectral analysis of the clay was carried out to acquire additional information from this clay found in commercial quantity at Ebonyi State Nigeria. The examined samples were constituted of quartz, qandilite, aragonite, muscorite and aratase. Porosity for the clay was too much for refractory,

thermal insulation and other high porosity desirable ceramics applications. Chemical evaluation demonstrated the presence of fluxing oxides at elevated levels which are responsible for the poor refractoriness and limits the application of the low or mid-temperature ceramics products.

Characterising the Dabagi clay deposit for its potential in ceramics was studied by Abubakar *et al.* (2014). In addition to conducting physical property tests for bulk, density, permeability, linear distortion, thermal shock resistance, and cold crushing strength refractoriness, X-ray fluorescence spectrometry was used for the chemical analysis. The findings of chemical examination indicated that the clay was constituted of silica (SiO_2), 64.50 %; alumina (Al_2O_3) 16.30 %; iron oxide (Fe_2O_3), 14.20%; calcium oxide (CaO), 0.2%; potassium oxide (K_2O), 0.74 %; titanium oxide (TiO_2), 1.71 % and other oxides in traces. While the physical investigation showed that the clay has an apparent porosity of 28.46 %, bulk density of 1.81 g/cm³, linear shrinkage of 6.8% thermal shock resistance of seven cycles, loss on ignition test 4.46 %, cold crushing strength of 14138 nm² and estimated refractoriness of 1,349 °C.

Research on analysis of Mbaukwu clay from Awka, South Anambra State, Nigeria, for Industrial Purposes was conducted by Chikwelu *et al.* (2018). The sample was examined for making plasticity, shrinkage, moisture, apparent thickness, volumetric density, loss on igniting, modulus of rupture, and water absorption applying established procedures. The findings of the chemical investigation revealed that: SiO_2 : 42.97%, Al_2O_3 : 23.34%, Fe_2O_3 : 4.95%, Na_2O : 2.04%, K_2O : 3.67%, MgO : 2.93%, CaO : 3.48%, MnO : 0.97%. Physical study indicated a mean modulus of plasticity to be 3.43 kg/cm³, mean making moisture (26.24%), total shrinkage range from 13.5- 15.4%, apparent porosity from 33.65-28.95%, bulk density of 1.66-1.71 g/cm³ throughout a temperature range of 900-1200 °C and LOI of 14.55%. The clay is fairly pure due to its alumina/silica ratio ($\text{Al}_2\text{O}_3:\text{SiO}_2$) of 0.54 comparative to 0.84 for pure kaolinite. The study also suggested that Mbaukwu clay could be suitable for manufacture of some ceramic industrial items like tiles, table ware and other ceramics wares production. Research on fabrication of electrical porcelain insulator using ceramic raw materials of Oromia region, Ethiopia was carried out by Merga *et al.* (2019). The raw materials mineralogy, chemical composition, and thermal characteristics determined by utilising x-ray diffractometer (XRD), atomic absorption spectrometer (AAS) and thermogravimetry (TGA), respectively. Based on the raw material's chemical composition, five distinct porcelain insulator test bodies were created at firing temperature of 1000 °C, 1100 °C, 1200 C and 1300 °C. Water absorbance, apparent porosity, bulk density, dielectric strength and microstructure of burnt porcelain insulators were examined as a function of firing temperature. The XRD and AAS results revealed that in Bombowha clay, kaolinite mineral was discovered to be a main mineral constituent with appreciable silica (46.84 wt%) and alumina (36.74 wt%) content with moderate plasticity (PI 1/4 19-21%). The porcelain insulator body that was tested had better characteristics than the others. It was composed of 45% kaolin, 45% feldspar, and 10% quartz. It had a water absorbance of 0.010%, porosity of 0.088%, density of 2.466 g/cm³, dielectric strength of 8 Kv/mm, and a firing temperature of 1300 °C. Additionally, it had enough glassy phase to contain the quartz and mullite phases. Therefore, the experimental result verified that standard porcelain insulator can be produced from locally accessible ceramic raw materials (clay and quartz) in Ethiopia at optimal condition.

2. Materials and Methods

The fieldwork and sampling activities involved the use of several materials such as a Brunton map, sample bags, hammer, spade, topographic maps, GPS device, clinometer, measuring tape, hammer, spade and digital camera. The sample preparation process involved the utilization of sealing bags, grinding equipment, sieve and a jaw crusher. The laboratory was equipped with an X-Ray Fluorescence Spectrometer (XRF), pressing equipment, sample mill, oven for chemical and mineralogical characterization. The necessary materials for the physical testing were grooving tools, plasticity cans, an electronic balance, a kiln, hydraulic press and a furnace. The area was dug using a digger while a soil auger was used to collect the soil from the desired depth and stored in an air tight container. A little portion of the soil was immersed in a beaker containing distilled water where the pH and conductivity were measured and recorded. The temperature of the soil was also determined insitu by creating a contact between the thermometer and the soil.

The research area consists of clay deposits found in sand mining pits located in the Nkemkol location, Ogoja local government area of Cross River State, Nigeria. A total of four samples (A, B, C and D) were chosen within the latitude range of Latitude: 6° 39' 30.24" N and the longitude range of 8° 47' 57.23" E. Figure 3.1 displays the spatial arrangement of sampling locations within the area of Nkemkol.

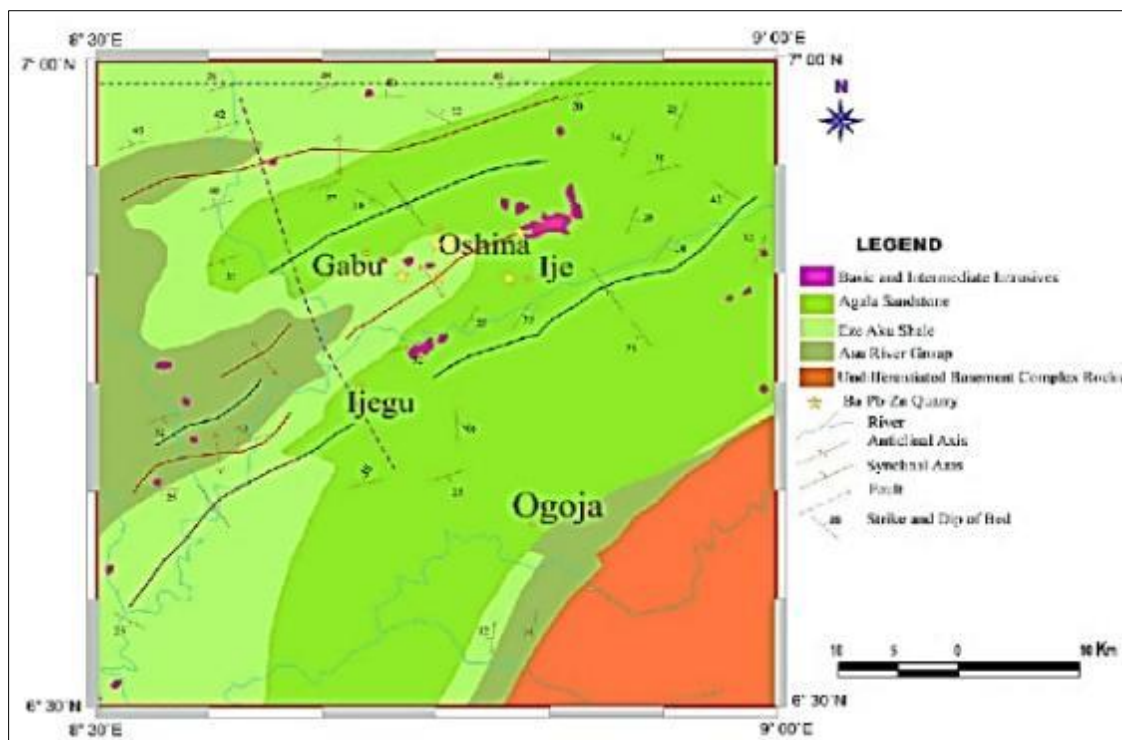


Figure 1 Geological map of Ogoja

2.1. Field Sampling

To extract the fine-grained, smooth clay sediments, excavation tools such as picks and hammers were utilized. The extraction process focused on sediment layers located between 3 to 5 meters deep within designated mining pits. Access to these clay deposits as shown in figure 3.2 was contingent upon the successful removal of the overburden layer. This overburden, characterized by its reddish-brown hue, consisted of a composite of lateritic soil, consolidated sandstone, and/or loose sand. The process involved systematically removing this overburden to expose the underlying clay unit. The clay layer, once uncovered, appeared as substantial bedrock formations with a range of colors including white, light grey, and brown. Within this clay matrix, occasional inclusions of friable sandstone were also observed. These sandstone fragments exhibited a crumbly texture, differentiating them from the more solid and consistent clay bedrock. The removal of the overburden layer was a critical step in the mining operation, as it allowed for the efficient extraction of the clay sediments. The reddish-brown overburden not only consisted of various soil types but also included different sedimentary rock formations, each requiring distinct handling techniques to avoid contamination of the clay. As the overburden was stripped away, careful attention was given to minimize disturbance to the underlying clay unit. This ensured that the quality of the clay remained intact for its intended use. Overall, the extraction process was methodically executed to maximize accessibility to the clay sediments while effectively managing the removal of the overburden. The use of picks and hammers facilitated the precise extraction of the clay, while the careful handling of the overburden helped in revealing the clay unit in its natural state, albeit with the occasional presence of friable sandstone elements.

2.2. Sample Preparation

After being allowed to air dry for two weeks, the clay samples were mechanically crushed with a jaw crusher until they were reduced in grain size to less than 150 microns. A portion of the powdered fraction, around 40 grammes, were brought to the lab for mineralogical and chemical analysis and kept in sealed bags. For physical testing, the bulk sample that remained was kept. To prevent cross-contamination, the crusher was completely cleaned before each new sample.

2.3. Chemical Analysis

The major oxide composition of the clay fraction was systematically analyzed using X-Ray Fluorescence (XRF) Spectrometry. To prepare the samples for accurate analysis, the clay was first milled to achieve a fine particle size of less than 150 microns. Each sample, consisting of approximately 30 to 40 grams of powdered clay, was carefully placed into sample cups. The XRF spectrometer was operated within a voltage range of 35 to 40 kV, which is crucial for optimizing the detection of various elements. During the analytical process, diffraction spectra were recorded, capturing the unique fluorescence emitted by the different elements present in the clay. These spectral data were then compared

against a comprehensive database to match the peaks observed. This comparison allowed for the precise determination of the weight percentages of the major oxides in the clay sample, providing detailed insight into its chemical composition.

2.4. Physical Test

A comprehensive series of tests was conducted to assess the practical performance characteristics and industrial applicability of the Ogoja clay deposits. These evaluations aimed to determine the clay's suitability for various applications and were carried out following established standards. The tests included assessments of the liquid limit, plastic limit, and plasticity index, all performed in accordance with ASTM D4318. These parameters are critical for understanding the workability and behavior of the clay under different moisture conditions. Additionally, the firing shrinkage of molded clay bars was measured following the procedure outlined in ASTM C326. This test provides insights into how the clay contracts upon heating, which is essential for predicting dimensional stability during industrial processing. The evaluation also encompassed the physical properties of the clay, such as apparent porosity, water absorption, bulk density, and apparent specific gravity. These properties were assessed according to ASTM C20 standards, providing a comprehensive understanding of the clay's density and porosity characteristics, which are crucial for its performance in manufacturing applications. To further evaluate the material's structural integrity, the compressive strength of cubic clay specimens was determined. This measure is vital for understanding the clay's load-bearing capacity and its potential use in construction and manufacturing applications. Additionally, the refractoriness of the clay was predicted based on its chemical oxide content. Refractoriness is a critical attribute for materials used in high-temperature applications, as it determines the clay's ability to withstand thermal stress without deforming or melting. Together, these tests provide a detailed assessment of the Ogoja clay deposits, offering valuable insights into their practical performance and potential industrial applications.

3. Results

The results obtained in this study are presented in figures 2 to 10. and in tables 1 and 2.

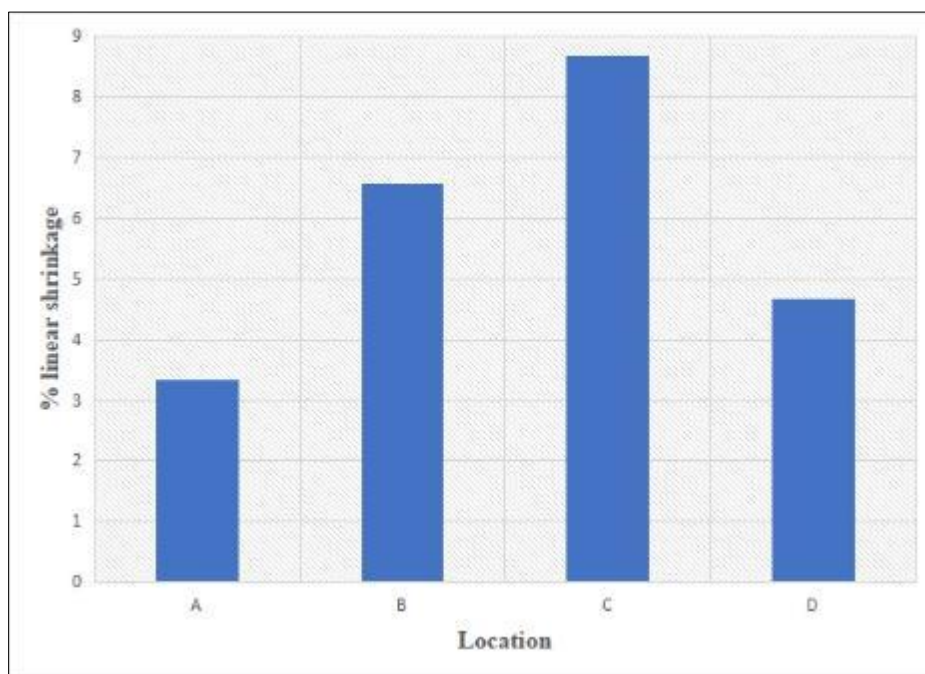


Figure 2 Linear shrinkage

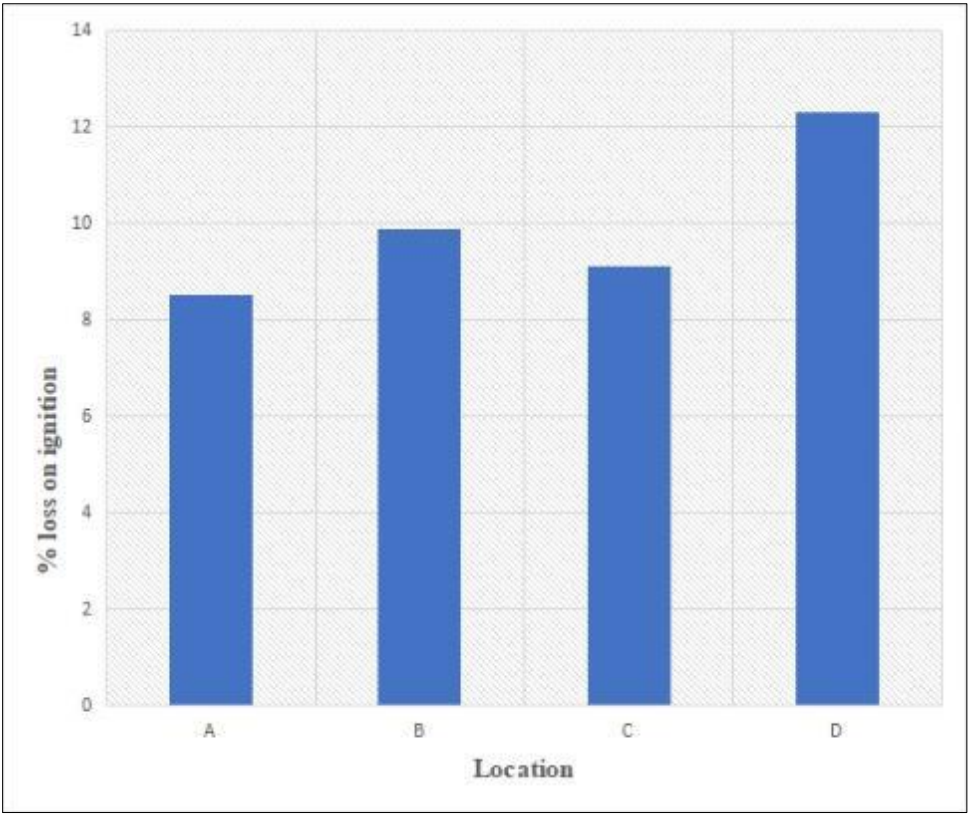


Figure 3 Loss on ignition

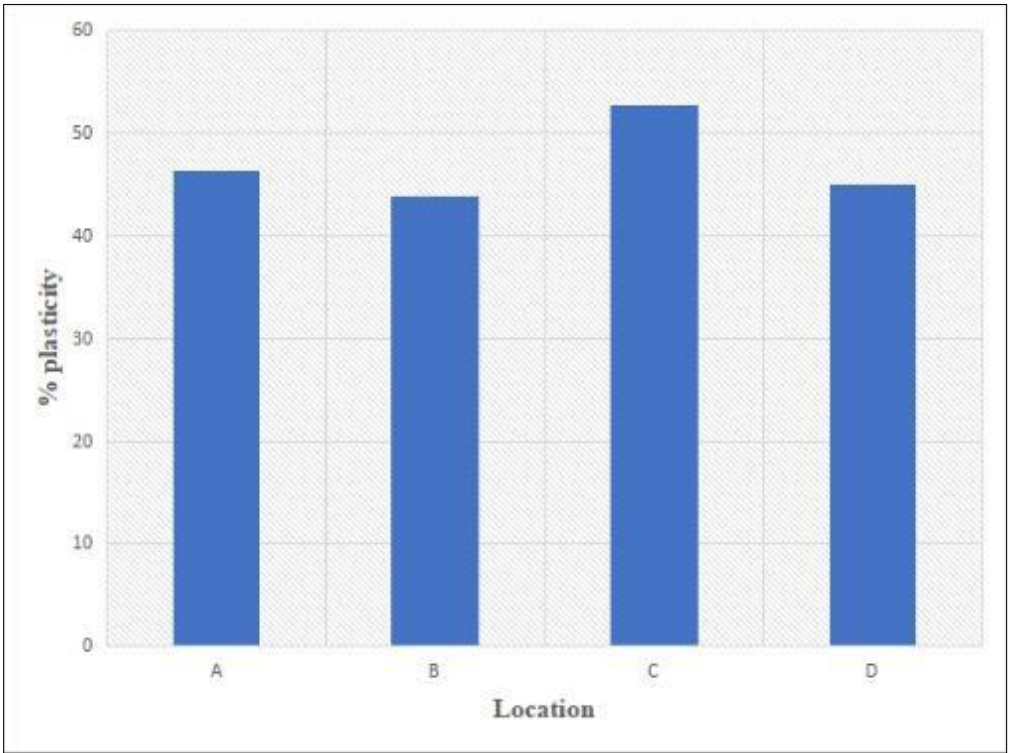


Figure 4 Plasticity

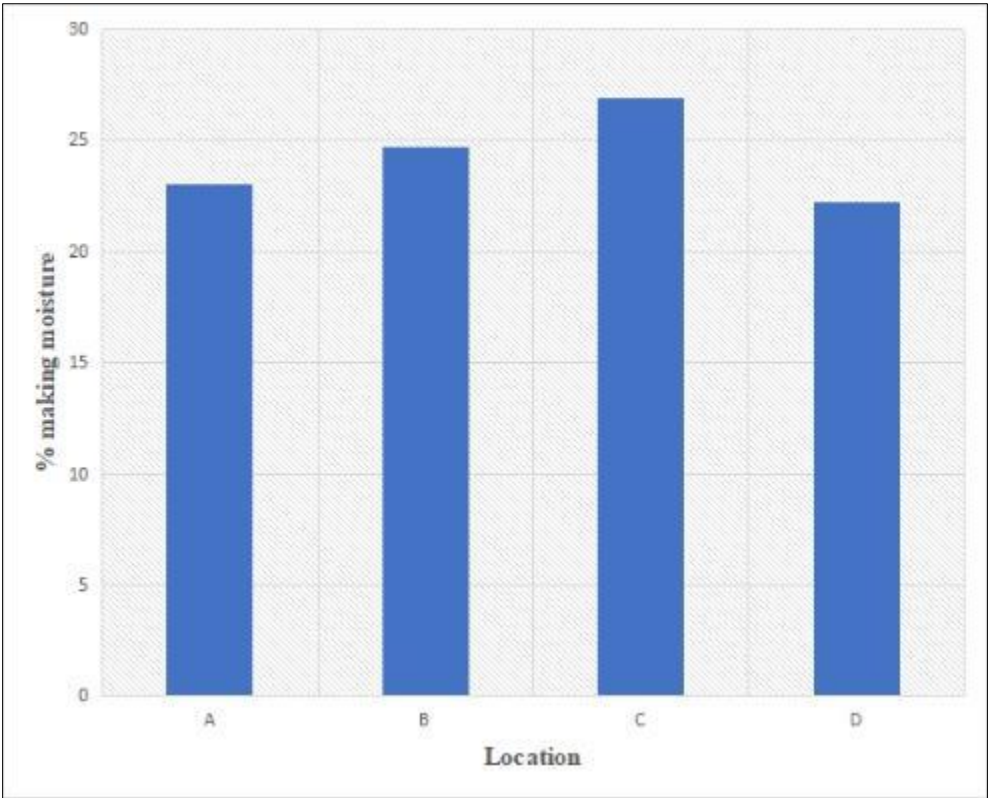


Figure 5 Making moisture

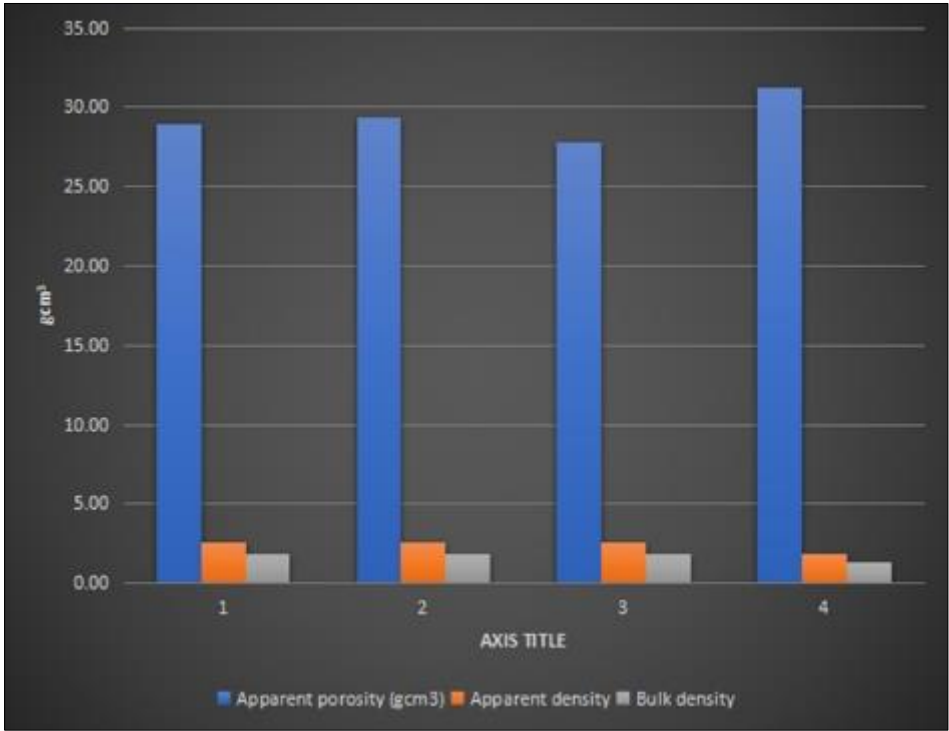


Figure 6 Chart of the apparent porosity, apparent density and bulk density

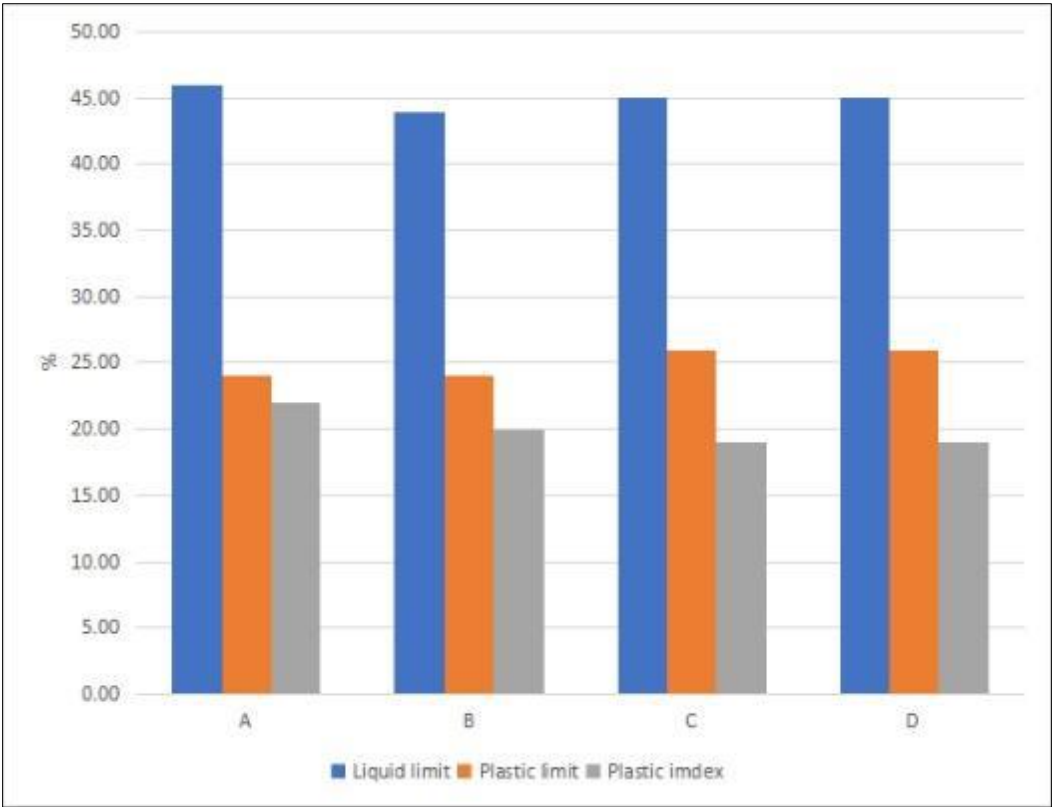


Figure 7 Liquid limit, plastic limit and plastic index

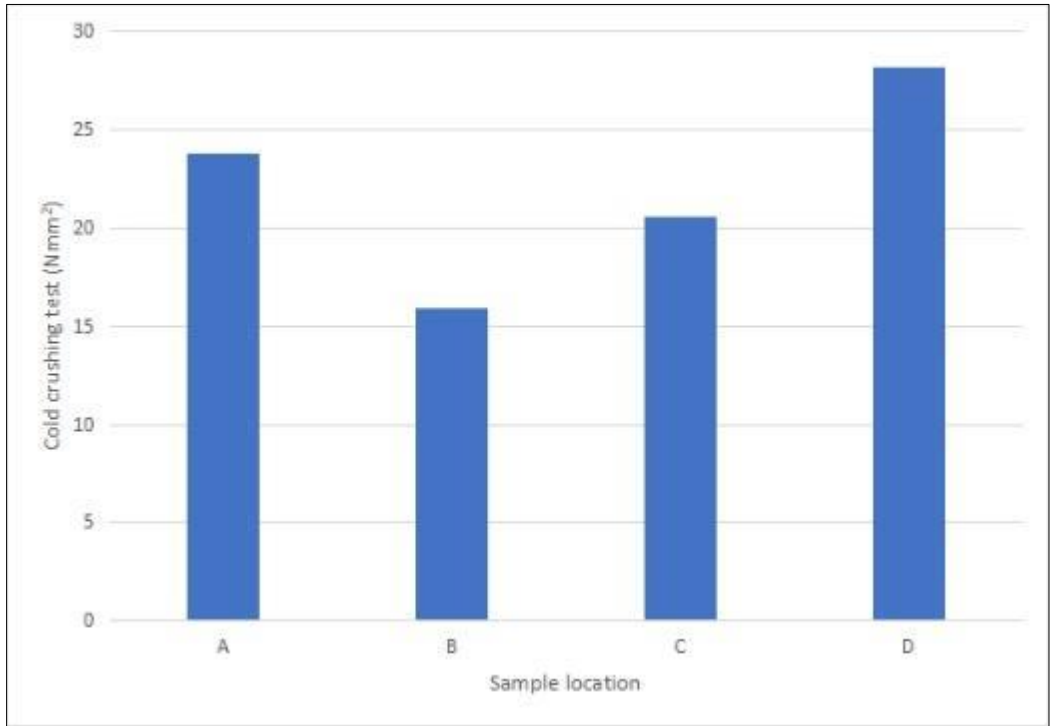


Figure 8 Cold crushing test

Table 1 Cold crushing test

Sample	Cold crushing test (Nmm ²)
A	23.8
B	15.9
C	20.6
D	28.15

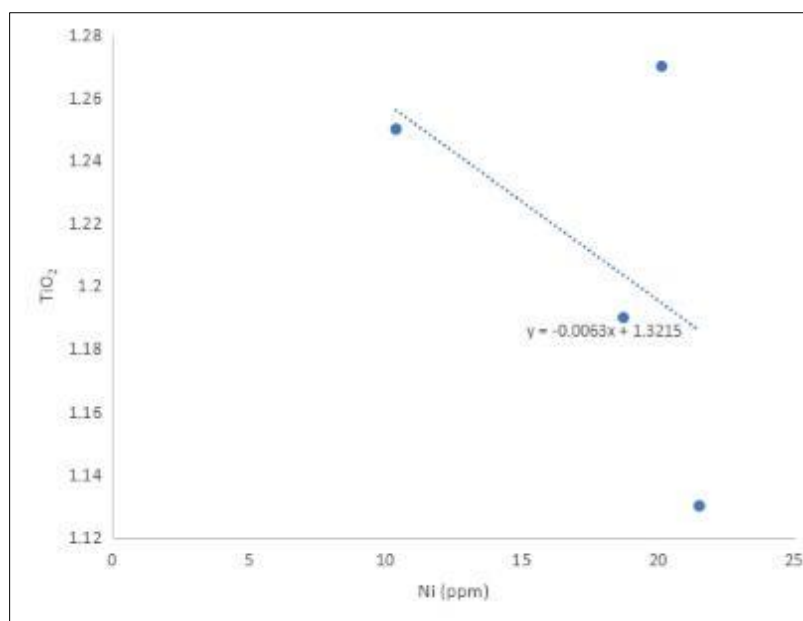
Table 2 Major oxide composition of the studied clay compared to industrial specifications

Studied sample							Industrial Specifications		
Elemental Oxides	A	B	C	D	Mean	Range	Crn %	Rf %	Bld %
SiO ₂	56.39	56.46	56.76	54.38	55.88	54.38-56.70	45.30-47.90	67.5	51.00-70.00
Al ₂ O ₃	29.6	29.02	30.1	29.25	29.38	29.02-31.23	37.90-38.40	26.5	25.00-44.00
Fe ₂ O ₃	4.66	4.75	4.88	4.95	4.63	4.06-4.98	13.40-13.80	0.50-1.20	0.2-0.7
TiO ₂	1.13	1.25	1.19	1.27	1.23	1.13-1.34	-	-	-
CaO	1.66	1.75	1.81	1.69	1.7	1.61-1.81	0.03-0.25	0.18-0.30	0.1-0.2
P ₂ O ₅	-	0.04	0.04	0.05	0.04	0.04-0.05	-	-	-
K ₂ O	0.89	0.98	0.76	0.88	0.88	0.76-1.01	0.10-0.40	1.10-3.10	-
MnO	0.07	0.08	0.08	0.06	0.07	0.06-0.08	-	-	-
MgO	4.69	4.99	4.99	4.84	4.81	4.29-4.99	0.20-0.30	0.10-0.19	0.2-0.7
Na ₂ O	0.87	0.9	0.72	0.82	0.84	0.72-0.90	0.20-0.35	0.20-1.50	0.8-3.5
LOI	0.04	0.02	0.02	0.03	0.03	0.02-0.05			
Sum	100.03	100.24	101.35	98.22					
SiO ₂ /Al ₂ O ₃	6.565	6.6955	6.7657	6.8091					
Al ₂ O ₃ /SiO ₂	0.5249	0.5139	0.5303	0.5378					
SiO ₂ /Al ₂ O ₃	1.9051	1.9455	1.8857	1.8591					
Na ₂ O/K ₂ O	0.9775	0.9183	0.9473	0.9318					
Al ₂ O ₃ /Fe ₂ O ₃	34.26	33.71	34.98	34.2					
CIA	89.6426	88.882	90.1467	89.6139					
CIW	921.257	91.8354	92.2463	92.0969					

*CIA – Chemical Index of Alteration; *CIW – Chemical Index of Weathering

Table 3 Trace element composition of the studied clay samples

Element (ppm)	A	B	C	D	Total	Mean
Al	0.060	0.656	0.067	0.067	0.849	0.212
Si	0.172	0.168	0.177	0.187	0.702	0.176
P	390	850	780	600	2620.000	655.000
K	4570	4900	5120	5350	19940.000	4985.000
Ca	0.012	0.010	0.012	0.013	0.047	0.012
Ti	0.015	0.012	0.014	0.015	0.056	0.014
V	330	280	190	200	1000.000	250.000
Cr	431	113	130	173	847.000	211.750
Mn	2220	527	1180	3440	7367.000	1841.750
Fe	0.092	0.083	0.086	0.090	0.351	0.088
Co	230	0	0	219	449.000	112.250
Ni	407	169	217	62	855.000	213.750
Cu	65	34	49	110	258.000	64.500
Zn	101	119	117	24	361.000	90.250
Rb	15	29	24	190	258.000	64.500
Sr	75	227	200	29	531.000	132.750
Y	22	43	27	206	298.000	74.500
Zr	305	177	172	23	677.000	169.250
Nb	33	17	23	27	100.000	25.000

**Figure 9** TiO₂ versus Ni (ppm)

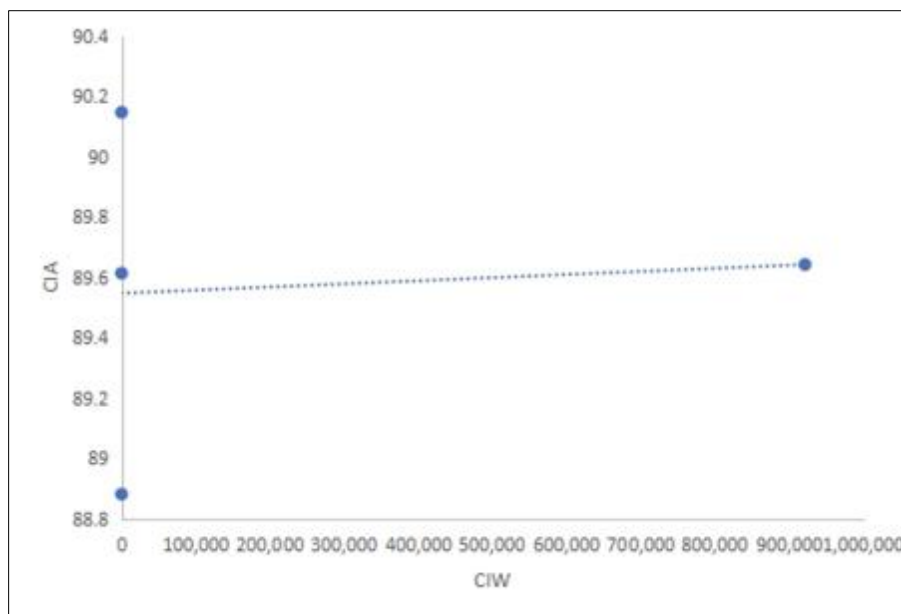


Figure 10 Bivariate plot CIA VS CIW indicating weathering conditions of samples under study

4. Discussion

The physical properties of the Nkemkol clays provide insight into their plasticity, working behavior, and fired characteristics. The Atterberg limits, which measure the plastic and liquid limits, showed high plasticity for the Nkemkol clays based on the Casagrande plasticity chart classification. The plasticity index ranged from 19.00 to 22.00% while the liquid limit was 45.00% on average. High plasticity arises due to the fine particle size, platelet shape, and high surface area of the clay minerals (Andrade, Al-Qureshi and Hotza, 2011). Clays with high plasticity exhibit good moldability and forming behavior, making them adequate for manufacturing bricks, tiles, ceramics, etc. which require shaping. However, high plasticity also causes increased shrinkage during drying and firing as seen in figures 4.1 and 4.3.

The Nkemkol clays as shown in figure 4.5 showed favourable porosity characteristics, which allow the escape of decomposed gases during firing thereby enabling vitrification and densification. Apparent porosity ranged from 12.96% to 28.33%, averaging 21.33%, which agrees with the standard range of 15-30% for refractory clays as reported by Al-Amaireh (2009). Higher porosity benefits insulation refractories by providing low thermal conductivity (Chesters, 1973 as cited in Abubakar, A. N., Abubakar, M. B., and Bawa, 2014).

The linear shrinkage, measuring the dimensional changes on drying and firing, lengths ranged from 5.28 to 7.28%, averaging 6.145%. This is close to the ideal 7-10% shrinkage for refractory fireclay bricks as stated by Yakubu and Ibrahim (2014 as cited by Sarruf *et al.*, 2024). Slight additions of non-plastic grog material may help tailor the shrinkage. The bulk density obtained from this work as shown in figure 4.5 varied from 1.28 to 1.84 g/cm³ averaging 1.70 g/cm³, which is at the lower end of typical values of 1.7 - 2.1 g/cm³ for dense fireclay refractories as reported by Yami, Hassan and Umaru (2007).

The cold crushing strength in figure 4.7, which indicates the load bearing capability after firing, ranged from 15.90 to 28.15 N/mm² averaging 22.11 N/mm². This meets the minimum requirement of 15 N/mm² specified for fireclay bricks (American Society for Testing and Materials, 1982 as cited in Eze and Iyeke, 2011). Good strength develops from densification and liquid phase sintering during firing. Based on the chemical composition using Shuen's formula, the predicted refractoriness was 1600°C which agrees with the standard range of 1500–1700°C for refractory fireclays. In all, the physical properties highlight the high plasticity of the Nkemkol clays coupled with adequate porosity, shrinkage, strength, and refractoriness for utilization in ceramics and refractories as can be seen in figure 4.6.

The structural strength of Nkemkol clay samples fired to 1100°C was evaluated via cold crushing tests. Strength values between 15.90-28.15 N/mm² were recorded, with an average of 22.11 N/mm² (Table 4.1, figure 4.7). These strength levels exceed the minimum industry standards of 15 N/mm² specified for fireclay bricks (15). Thus, the Nkemkol clays demonstrate adequate strength upon firing to be capable of serving as construction material.

The results of Major oxides analyzed are as presented in wt. percentage in Table 4.2. The major oxides present in the studied samples reveal SiO_2 (55.88), Al_2O_3 (29.98), Fe_2O_3 (4.63) and MgO (4.81). Others include; K_2O (0.88), CaO (1.70), Na_2O (0.84), MnO (0.07), TiO_2 (1.23), and P_2O_5 (0.04) respectively. The studied soil samples are characterized by high amounts of silica ranging from 54.38 to 56.76%, with considerable amount of sesquioxide Al_2O_3 (29.02- 31.23%) and Fe_2O_3 (4.06 - 4.98%) respectively. Appreciable number of bases present includes (K_2O and CaO) of 0.76 - 1.01% and 1.61 - 1.81% respectively.

Evaluation of the industrial utilization of the clays is based on their geochemical characteristics and comparison with chemical specification of some industrial clay .in terms of industrial applications (Table 4.2). These chemical compositions are within the limit of industrial specification for ceramic (Odewale, 2004), refractory bricks and building bricks (Enu and Adegoke, 1988). shows that they are fit for the manufacturing of refractory bricks and ceramics because of the sufficient amount of silica, alumina and magnesia present in the clay. In this regard, the alumina content of the clays corresponds to the refractory industrial specification and ceramics (Uddin, 2007). Also, the amounts of the alkalis K_2O , Na_2O as well as CaO , MgO for all the four clays falls above the requirements for the production of rubber and paper.

The clay deposits studied also contains considerable amounts of silt-size particles (18%-70%) which makes them unsuitable in their raw state for use as fillers and coating materials in the paint industries (Nton and Elueze, 2005). Table 4.3 present the results of chemical analysis showing the different trace element contained in the clay samples and are expressed in part per million (ppm). These include Cu, in the range of (34-110), Cr (113- 431), Ni (62-407), Zn (24-101), Co (0-230) etc. The concentration of colourants such as Co, Ni, and Cu are low which implies that they will not impact any colouration on the finished product. Others include Y (22-206) and Zr (23-305), Nb (17- 33) as shown in Table 4.3.

Furthermore, the use of the clay samples studied in the ceramic industries for the manufacturing of ceramic ware, ceramic glaze, would depend on the degree of beneficiation achievable to turn them into good quality fire clays (RMRDC, 2003 as cited in Odoma *et al.*, 2015). The clay samples studied is unsuitable for glazed products on account of its high amount of Fe_2O_3 and MgO and the presence of accessory minerals such as pyrite, apatite, siderite and magnesite (Apugo-Nwosu *et al.* 2011).

Also, from the result of the chemical analysis, it was observed that all the clay samples contain more than 50% SiO_2 as supported by Jubril and Amajor (1991) findings. This therefore makes clays from these areas suitable for heavy ceramic product. These impurities would cause undesirable colourations to the intended use, but can be removed through different beneficiation processes such as air flotation/magnetic separation/dry process, wet beneficiation and micronizing.

The ultimate goal of any geological investigation on clay deposits is to be able to recommend it for industrial use and this depends on the physical and chemical characteristics of the clay. The present results of the chemical properties of these clays reveal that the clay are kaolinitic (Onyeobi *et al.*, 2013).

These types of clays can be used for ceramic product such as floor tiles, wash hand basins, jugs, plate, tea cups kettle and water closets etc. The presences of iron oxides, titanium dioxide and chromium in all the clay samples studied make them suitable for paint production. This is because they act as pigment and creates different colour e.g. iron oxides can be used for yellow, red, brown or orange paints, titanium oxide is used for white paint while chromium for green paint. Bivariate plots of TiO_2 wt. per cent versus Ni (ppm) was adopted (Figure 4.8). This was to assess the basic and acidic trends of the clay sediment (Kefas, Onoja and Musa 2007). It was observed that the bulk of the samples fall within the acidic zone otherwise called felsic source field.

In Figure 4.9 below, the Chemical index of weathering (CIW) of Harnois (1988 as cited in Chikwelu *et al.* 2018), is an indicator to measure the degree of source weathering. About 100% of the samples have values greater than 80. All these signify variation in weathering.it was observed that the clay samples are extreme weathering (Bergaya *et al.*, 2006). In Nigeria kaolin are being imported to meet our industrial needs. The results of this investigation suggest that even the natural occurring raw kaolinitic clay of the investigated deposit are usable in their raw state in some of our local industrial sector. The extreme weathering conditions also suggest that these clays might have good plasticity and firing properties, which are crucial for ceramic manufacturing. However, the high iron content (Fe_2O_3) noted in Table 4.2 might limit their use in applications requiring pure white products. This is consistent with the findings of Apugo-Nwosu *et al.* (2011), who noted that high iron content in Nigerian clays can affect their suitability for glazed products. The geochemical characteristics revealed by these figures, combined with the major oxide and trace element compositions, indicate that the Ogoja clays have potential applications in the ceramic industry, particularly for products where high

refractoriness and plasticity are required. However, some beneficiation may be necessary to reduce iron content for certain high-grade applications.

5. Conclusion

The findings from this study demonstrate the suitability of Nkemkol clay deposits in Ogoja, Cross River State for applications in the ceramics and refractories industry, with potential utilization in refractory bricks, ceramic tableware, architectural ceramics, wall tiles, pottery items etc. The chemical composition showed predominantly aluminosilicate nature with high SiO_2 , Al_2O_3 and moderately high Fe_2O_3 . Clay minerals kaolinite and illite occur along with non-clay minerals including quartz, feldspars, mica and metal oxides. The clays exhibit high plasticity coupled with appropriate fired porosity, strength, and refractoriness. While the properties are mostly favorable, minor mineral processing and blending steps can help mitigate issues like high iron content, shrinkage, and cracking during firing. The local availability of the Nkemkol clays can promote indigenous ceramics manufacturing, substitute imports and fueling small-scale enterprises.

Recommendation

Establishing local processing facilities can significantly reduce reliance on imported materials. The Federal Government as well as relevant stakeholders can massively invest in infrastructure that supports the processing of locally sourced clay, which can enhance the quality and availability of raw materials for ceramic manufacturers, thereby fostering a self-sufficient industry. Implementing training programs for local artisans and entrepreneurs in clay extraction, processing, and ceramic production techniques is vital. This will not only improve skill levels within the community but also encourage innovation in product development, leading to higher-quality ceramics that can compete in both local and international markets. Government support through policies that promote the use of local materials in the ceramic industry is crucial. This could include financial incentives for businesses that utilize locally sourced clay or tax breaks for companies investing in sustainable practices related to clay extraction and processing. The high Fe_2O_3 content can lead to undesirably dark colors in ceramics. Hence mineral processing is required to lower the iron levels. Blending with non-plastic diluents such as feldspar and grog may help control the high shrinkage observed. Cracking and warping could also occur during drying and firing due to quartz inversion combined with elevated shrinkage. Introducing appropriate grog additions can minimize these defects by managing shrinkage rates. Further research can build on these foundational results. Pilot-scale testing should establish optimal formulations and process parameters for targeted applications through empirical adjustments. Additionally, comprehensive nationwide deposit prospecting is recommended to quantify total reserves and spatial distribution thereby facilitating organized exploitation.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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