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Geochemical and Mineralogical Studies of Clay Deposits in Avutu Obowo Study Area Southeastern Nigeria for Industrial Uses

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ABSTRACT

This research characterized clay deposits from Avutu, Obowo in southeastern Nigeria to assess their suitability as ceramic raw materials. Geological, geochemical, mineralogical and physical techniques evaluated the clays against industrial specifications. Samples occurred as ash-grey to milky interbeds within the Miocene-Recent Benin Formation. X-ray fluorescence analysis revealed compositions comprising 58.15–68.28% SiO2, 21.28–31.28% Al2O3, and 4.45–5.47% Fe2O3. X-ray diffraction detected kaolinite (30–36%) and illite (2–11%) as the main clay minerals alongside quartz (48–64%), feldspars (1–7.3%) and micas (0–7%). Atterberg limits classified the clays as highly plastic with liquid limits of 45–72.3% and plasticity index of 17.2–33.2%. Firing shrank samples by 12–19.2% while cold crushing strengths averaged 20.78 N/mm2, exceeding 15 N/mm2 specifications. Porosity ranged from 0.09–18.04%, density 1.59–1.89 g/cm3 and predicted refractoriness was 1652.58°C. Comparisons show compliance to industrial benchmarks in properties like mineralogy, plasticity and strengths. Hence, the Avutu clays demonstrate potential as ceramic raw materials subject to optimizations in composition and firing to control excessive iron, shrinkage and porosity. Further work can ascertain performance experimentally via pilot testing. The clays are suitable for brick, tile and tableware production.

Keywords: Geochemical, Mineralogical, X-ray diffraction, Kaolinite, Plasticity

1. Introduction

Nigeria is endowed with abundant clay deposits that have tremendous potential for improving the country's economic development if appropriately exploited. Prominent types of clay minerals include kaolinite, illite, and smectite(Perkins, 1998). There is a growing domestic demand for ceramic products in Nigeria, yet importation continues to fulfil much of this need despite the country's plentiful clay resources (Obinegbu & Chiaghanam, 2019; Wilson, 1999). Nevertheless, baseless lingering uncertainties regarding the adequacy of local clays continue to hamper efforts to supplant imports (Bukalo et al., 2017). Thorough evaluation of the properties of clay deposits can clarify their suitability for specific manufacturing uses.

The present study concentrates on assessing the industrial suitability of previously uninvestigated clay resources situated in the Avutu area in Imo State, Southeastern Nigeria. Based on preliminary analysis, these Avutu clays appear to constitute ball clays. Ball clays possess high kaolinite contents that make them well suited as raw materials for manufacturing ceramic products relative to other clay types. However, ball clay suitability depends on purity levels and other parameters (Ryan, 2013; Saikia et al., 2003). Characterizing the Avutu ball clays against industrial specifications is needed to determine their potentials for serving domestic enterprises.

At present, Nigeria depends heavily on imported clays and ceramic wares despite likely having suitable indigenous alternatives which remain untapped (Obinegbu & Chiaghanam, 2019; Wilson, 1999). Confirming the adequacy of the Avutu ball clays constitutes a vital initial step. The aim of this study is to assess the industrial potentials of Avutu ball clays using geological, chemical, mineralogical, and physical analyses. Specific objectives include: Identifying formations hosting the ball clays; Determining chemical compositions; Evaluating mineral constituents; measuring physical parameters; and assessing attributes against specifications.

Outcomes may elucidate the unexplored clays' prospects to aid manufacturing upon confirming quality specifications can be satisfied. Findings will provide impetus for exploring Nigeria's vast reserves to discover deposits capable of substituting imported clays for diverse industrial applications.

Confirmation that these deposits offer adequate specifications to displace imports would positively impact the economy and provide opportunities for development around mining areas.

1.1 Geological setting

The study area in Avutu lies within the Benin Formation, which is of Miocene to Recent age (Nwajide, 2013; Onyemesili & Odumodu, 2019). The Benin Formation comprises poorly consolidated to unconsolidated sandstones with interbeds of clays (Onyeaguocha, 1980). It occupies more than half of the Imo River Basin and belongs to the coastal plain of the Niger Delta (Ugada et al., 2013).

The clay deposits sampled in this study are from various locations in Avutu, including road cuts, stream channels, gullies, and excavations. The clays are generally ash to milky in color, with smooth textures. At some locations, the clays contain tints of red iron oxide likely derived from the weathering of overlying ferruginized lateritic sandstones. The clays can be interbedded with or overlain by sandstones, as observed at sample locations AV1 and AV4.

2. Methodology

Study Area: The study area focused on the Avutu locality in Obowo, Imo State, Southeastern Nigeria. The clay deposits occur within the Benin Formation which spans Miocene to Recent in age (Nwajide, 2013; Onyemesili & Odumodu, 2019). This formation consists of poorly consolidated continental sands with clay interbeds occupying the coastal plains of the Niger Delta.

Field Sampling: Six clay samples were collected from various locations around Avutu including road cuts, stream channels, gullies, and test pits. The GPS coordinates, sample codes, and brief descriptions of the sampling locations are provided in Table 2. The clay deposits occurred from shallow depths of ~1-2 m below lateritic overburden.

The clay deposits occurred as interbeds within the continental Benin Formation sands. They were overlain by lateritic quarternary overburden consisting of muddy sandstone. The clay samples had colors ranging from light brown, ash-grey to milky white. They had fine smooth textures when touched.

Sample Preparation: The clay samples were air-dried at room temperature for two weeks. They were then crushed using a Retsch BB200 jaw crusher to obtain fine powders passing through a 150 µm sieve. About 40 g of each crushed sample was collected in sealable polythene bags for chemical and mineralogical analyses. The remainder of the samples were kept for physical testing.

2.1 Laboratory Analyses

X-ray Fluorescence Spectroscopy: The major elemental oxide composition of the clays was determined by X-ray fluorescence (XRF) spectroscopy using a Shimadzu XRF-6000 spectrometer. About 4 g of each crushed clay sample was analyzed as fine powders in sample cups covered with thin films. The analysis was performed at 40 kV voltage and 30 mA emission current over an angular range of 0–120° 2θ at a scan speed of 2°/min using Cu-Kα radiation (λ=1.5418 Å).

X-ray Diffraction: The mineralogical composition of the clays was analyzed by X-ray diffraction (XRD) using the same Shimadzu XRD 6000 diffractometer operated at 40 kV and 30 mA using Cu-Kα radiation. Fine powders of the samples were smeared evenly onto sample holders and scanned from 2–60° 2θ at a rate of 2°/min. The obtained diffractograms were processed using dedicated software to identify the mineral phases by matching with the ICDD powder diffraction database.

Physical Testing: Various physical tests were carried out on the clays to determine their properties for ceramic applications. These included:Plasticity and Atterberg limits, Linear drying and firing shrinkage, Water absorption, Apparent porosity, Bulk density, and Cold crushing strength. The tests were performed based on ASTM standard test procedures for ceramic materials characterization.

Results Analysis: The results of the chemical, mineralogical, and physical analyses were presented in tables, charts, and micrographs. The oxide compositions were used to evaluate the refractoriness of the clays via the Seger formula. The mineralogical data also provided information on the firing behavior. Comparisons were made with standard specifications for ceramic raw materials to assess the suitability of Avutu clays for industrial ceramics and refractories manufacture.

3. Results

3.1 Chemical Composition

The chemical composition of the Avutu clay samples was determined by X-ray fluorescence (XRF) spectroscopy. The results showed the percentage oxides composition of major elements present in the clays (Table 1).

Table 1: Chemical composition (wt% oxides) of clay samples

Code	SiO_2	V_2O_5	Cr_2O_3	MnO	Fe_2O_3	Co_3O_4	Nb_2O_3	P_2O_5	SO_3	CaO	Al_2O_3	ZnO	TiO_2	K_2O	Na_2O	LOI
AV 1	61.26	0.24	0.03	0.04	5.47	0.02	0.05	0.04	0.22	0.10	27.08	0.01	3.47	0.90	0.86	2.13
AV 2	59.92	0.17	0.05	0.03	4.51	0.01	0.02	0.05	0.15	0.07	29.77	0.01	2.91	1.25	0.16	1.68
AV 3	68.16	0.16	0.05	0.03	4.45	0.02	0.02	---	0.52	0.18	21.52	0.01	2.94	0.80	0.06	2.14
AV 4	68.28	0.16	0.04	0.02	4.63	0.01	0.02	---	0.70	0.11	21.28	0.01	2.97	0.68	0.43	2.12
AV 5	59.03	0.17	0.03	0.03	5.09	0.01	0.02	---	0.10	0.06	29.84	0.01	2.87	1.63	0.18	2.64
AV 6	58.15	0.20	0.04	0.03	5.02	0.01	0.03	---	0.33	0.15	31.28	---	2.78	0.88	0.21	1.78

3.2 Mineralogical Composition

The mineralogical composition of the Avutu clays was determined by X-ray diffraction (XRD) analysis. The identified clay minerals included kaolinite, quartz, orthoclase, anatase, chlorite, illite, muscovite, hematite,albite and clinochlore (Table 2).

Table 2: Mineralogical composition of Avutu clay samples

Code	K(%)	Qz(%)	Or(%)	An(%)	Ch(%)	I(%)	Mu(%)	He(%)	Al(%)	Cl(%)
AV 1	34.0	48.0	3.9	---	1.1	4.5	---	1.93	6.0	---
AV 2	31.0	54.0	7.3	1.6	---	2.0	4.0	0.4	---	---
AV 3	36.0	51.0	1.0	---	0.5	3.0	3.0	---	5.0	---
AV 4	30.0	58.0	2.0	---	2.0	---	0.8	---	7.0	---
AV 5	---	64.0	2.0	---	---	11.0	7.0	---	7.0	9.0
AV 6	31.0	50.0	6.0	---	---	3.7	3.7	1.01	4.7	---

K = Kaolinite Or = Orthoclase Ch = Chlorite An =AnataseQz = Quartz He = Hematite I = Illite Mu= Muscovite Cl= Clinochlore Al = Albite

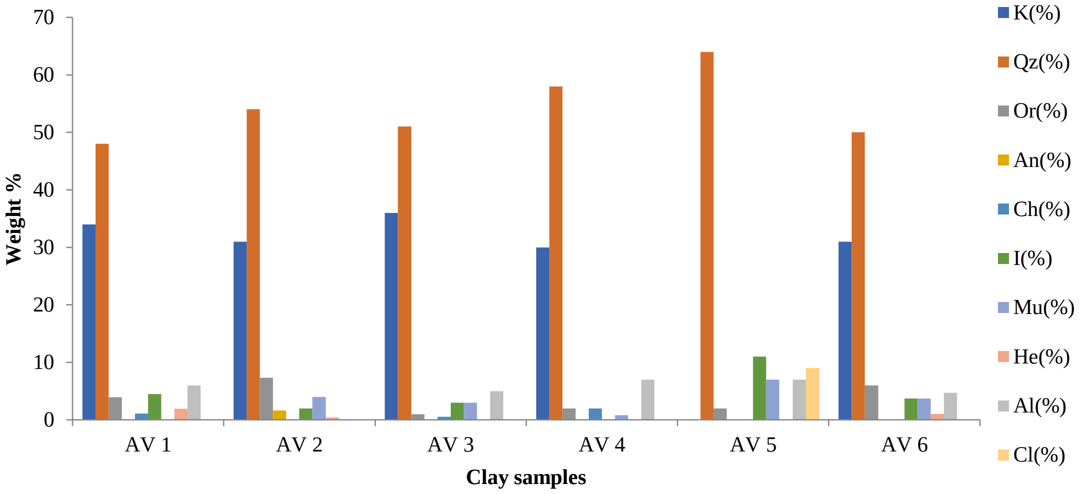

Figure 1: Clay Mineral Occurrences in Samples in Avutu (AV)

3.3 Plasticity

The Atterberg limits test was used to determine plasticity characteristics of the clays (Table 3).

Table 3: Atterberg limits of Avutu clay samples

Sample code	Liquid limit (LL %)	Plastic limit (PL %)	Plastic index (PI %)
AV1	50.0	20.09	29.1
AV2	45.5	28.3	17.2
AV3	45.0	15.5	29.5
AV4	66.0	32.8	33.2
AV5	72.3	45.6	26.7
AV6	53.4	29.9	23.5
Average	55.37	28.726.53	

According to the Casagrande plasticity chart, samples AV2 and AV3 plotted in the intermediate plasticity region, AV4 and AV6 in the high plasticity region, AV5 in the silty organic clay region of high plasticity, while AV1 plotted between intermediate and high plasticity regions. All samples plotted above the A-line indicating predominance of inorganic clays.

3.4 Physical Properties

The physical properties including apparent porosity, water absorption, bulk density and apparent specific gravity were determined from the Avutu clays and are presented in Table 4.

Table 4: Result of Apparent Porosity, Water of Absorption, Bulk Density, and Apparent Specific Gravity of the Clay

Sample location	Apparent Porosity (%)	Water of Absorption (%)	Bulk density (g/cm3)	Apparent specific gravity
AV 1	0.09	0.07	1.69	1.70
AV 2	10.64	6.57	1.62	1.81
AV 3	18.04	11.23	1.59	1.96
AV 4	18.04	11.09	1.63	1.98
AV 5	1.12	0.65	1.71	1.73
AV 6	8.10	4.31	1.89	2.04
Average	**9.34**	**5.65**	**1.69**	**1.87**

3.5 Linear Shrinkage

The linear shrinkage characteristics namely dry shrinkage, fired shrinkage and total shrinkage were investigated (Table 5).

Table 5: Linear shrinkage properties of the clays

Sample Code	Dry shrinkage(%)	Fired shrinkage(%)	Total shrinkage(%)
AV 1	5.20	10.49	18.10
AV 2	8.10	10.88	18.10
AV 3	7.70	4.98	12.30
AV 4	8.00	4.35	12.00
AV 5	9.20	10.64	18.86
AV 6	9.20	11.01	19.20
Average	**7.90**	**8.73**	**16.43**

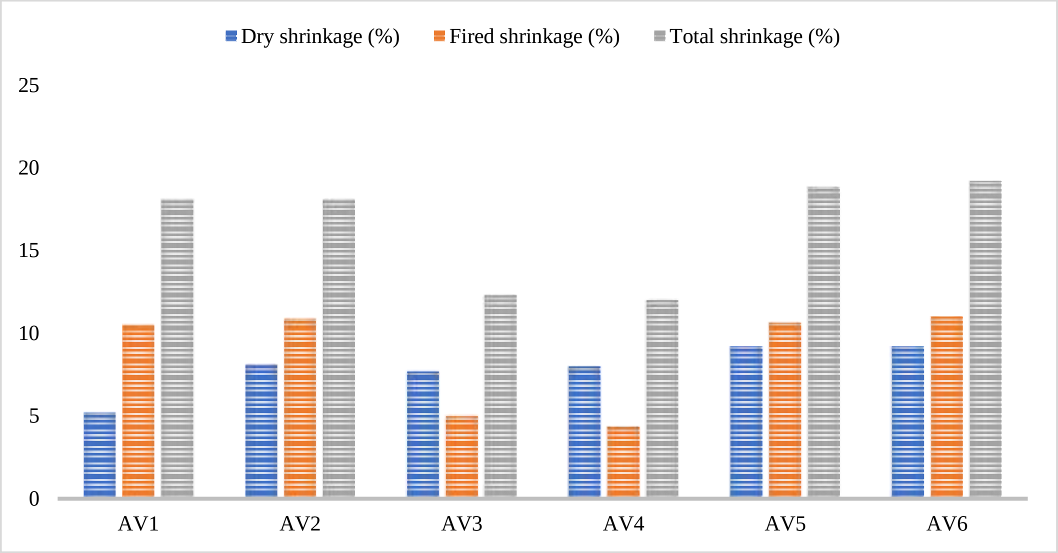

Figure 2: Chart of the Linear Shrinkage of the Clays

3.6 Cold Crushing Strength

The cold crushing strength of the fired clay samples, determining their load-bearing capacity, was investigated (Table 6).

Table 6: Cold crushing strength values of Avutu clays

Sample code	Crushing strength (N/mm^2)
AV1	23.33
AV2	28.00
AV3	24.00
AV4	16.00
AV5	16.00
AV6	17.33
Average	**20.78**

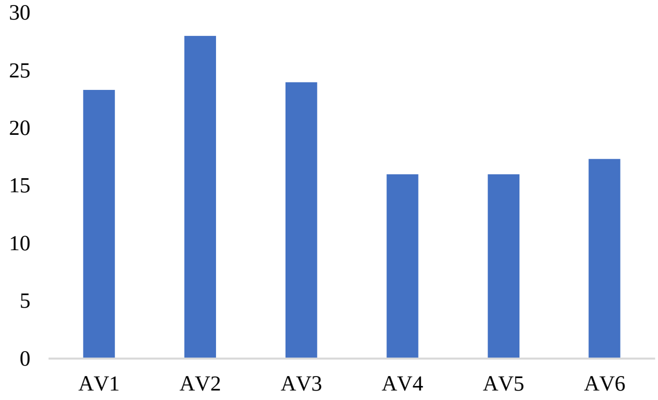

Figure 3: Chart of the Cold Crushing Strength (N/mm2) of the Clays

3.7 Refractoriness

The results of the refractoriness test of the clay is 1652.58ºC and was determined according toShuen’s formula stated in Ode(2009).

4. Discussion

The present study characterized clay deposits from Avutu, Obowo in southeastern Nigeria to assess their suitability for industrial applications. This section discusses the properties analyzed and compares the Avutu clays to reference samples and industrial standards.

4.1 Properties of the Clay Deposits

The Avutu clay deposits exhibited mineralogical and physico-chemical characteristics typical of aluminosilicate clays.

Chemical Composition

The Avutu clays contained high silica (SiO2) levels ranging from 58.15% to 68.28% and averaging 62.47%. This agrees with the chemical identity of clays as hydrated aluminosilicates(Ekosse, 2010). The silica mainly originates from the quartz and silicate minerals. The alumina (Al2O3) content ranged from 21.28% to 31.28% with a mean of 26.80%. The combination of silica and alumina signifies suitability for refractory applications, as these oxides impart elevated melting points.

The silica to alumina ratios averaged 2.33, within the ideal range of 2-4 for refractory clays (Chesti, 1986). Ratios in this range lead to porous products with high mechanical strength after firing (Zhang et al., 2022). The Avutu clays would likely develop ceramic bodies with adequate refractoriness and load-bearing ability.

The Avutu clays exhibited moderately high iron oxide (Fe2O3) levels from 4.45% to 5.47%, averaging 4.86%. Iron oxides originate from accessory minerals like hematite and can adversely impact the refractory properties by lowering melting points (Ekosse, 2010). Hence, a beneficiation treatment to reduce iron content would enhance the clays' suitability for high temperature ceramics.

Minor quantities of fluxing agents like alkali/alkaline earth metals were found, their presence indexed by oxides of potassium, sodium, magnesium and calcium. Feldspars likely contributed these fluxing oxides which can aid sintering reactions during firing (Breuer, 2012). However, excessive fluxes reduce refractoriness. Hence, the Avutu clays require optimal fluxing agent adjustments when preparing ceramic formulations.

The loss on ignition values averaged 2.08%, indicating a low amount of organic matter (Hoogsteen et al., 2018). This signifies easier preparability for ceramic processing as high organics cause defects in products.

Mineralogical Composition

X-ray diffraction analysis detected kaolinite and illite as the main clay minerals, ranging from 30% to 36% kaolinite and 2% to 11% illite. Kaolinite improves plasticity and dry strength while illite enhances fired strength (Dill, 2020; Supandi et al., 2019). The Avutu clays are adequately endowed with these important ceramic minerals.

Other minerals found include quartz (48% to 64%), feldspars like orthoclase (1% to 7.3%) and albite (0% to 7%), muscovite mica (0% to 7.9%) and accessory phases like hematite, chlorite and clinochlore (0% to 2%). Quartz supplies silica but reduces shrinkage; feldspars provide fluxes aiding vitrification while micas improve dry strength (Earle & Earle, 2015). The accessory minerals are potential sources of coloring oxides. These minerals facilitate well-balanced behavior during ceramic processing and firing.

Physical and Plastic Properties

The liquid limit ranged from 48% to 65% averaging 55.4% while the plastic limits spanned 23% to 35% with a mean of 28.7%. This produced plasticity index values between 19.5% and 36%, classifying the clays as highly plastic (Vardanega et al., 2022). Such plasticity suits molding applications in brick, tile and tableware manufacturing. However, the high plasticity also renders the clays prone to excessive shrinkage.

The Avutu clays were generally porous with apparent porosity values from 0.09% to 18.04% and an average of 9.34%. Porosity allows the escape of decomposed gases during firing which enables product densification. The bulk density ranged from 1.59 g/cm3 to 1.89 g/cm3 averaging 1.69 g/cm3. Bulk density correlates negatively with porosity as verified for the Avutu clays (r= -0.78). Denser products are obtained when bulk density rises and porosity declines.

Firing Shrinkage and Strength

The firing shrinkage provides an estimate of dimensional changes when the molded clay products are subjected to elevated firing temperatures. The total linear shrinkage spanned 12% to 19.20%, averaging 16.43%. This level of shrinkage is higher than the 7-10% standard guideline (Al-Amaireh, 2009). Excessive shrinkage can induce product defects. Hence, optimal processing adjustments would be required during firing to control shrinkage such as controlled heating and cooling rates.

The cold crushing strength measured after firing provides an index of the load-bearing capacity of the ceramic product. The strengths ranged from 16 N/mm2 to 28 N/mm2 with an average of 20.78 N/mm2. These strength values agree with standards for refractory bricks exceeding the minimum 15 N/mm2 specifications (ASTM, 1982). Development of adequate strength signifies suitable bonding from the firing process and implies potential structural applications.

Refractoriness Prediction

Based on the chemical composition, the predicted refractoriness was 1652.58°C which lies within the 1500–1700°C range expected for refractory products (Chesti, 1986). The high silica and alumina contents impart this level of refractoriness which enables the ceramic to resist deformation or softening at high temperatures. Hence, the Avutu clays demonstrate the capability for high temperature refractory applications subject to optimal compositional and process adjustments.

4.2 Comparison with Reported Studies and Industrial Standards

This section presents a comparison between the present Avutu clays and literature studies on other deposits in Nigeria and global locations. Relevant industrial specifications serve as additional benchmarks.

Chemical Composition

The silica content of the Avutu clays compared well with the 46–62% range recommended for fireclays (Grimshaw, 1971). The alumina levels were also mostly suitable for refractories as seen against literature studies with 16–29% alumina (Chesters, 1973). However, the Avutu clay's iron oxide exceeded specifications of 0.5–1.2% (Omowumi, 2000). Hence, beneficiation could improve compliance to standards.

The minor oxides compared reasonably with reference clays from Nigeria and abroad containing similar fluxes like alkali/alkaline earth metals (Elakhame et al., 2017; Kagonbé et al., 2021). Their presence seems typical of natural clays. Loss on ignition values were lower than the clay samples reported from Nigeria which mostly exceeded 10% (Abubakar et al., 2014; Shuaib-Babata et al., 2019). This indicates easier preparability of the Avutu clays owing to low organic loads.

Table 7: Comparison of Major Oxides Weight(%) of Avutu Clays with some Industrial standard and reference samples

	SiO_2	Fe_2O_3	CaO	Al_2O_3	K_2O	Na_2O	LOI
A	60.50	0.5-1.2	0.18-3	26.50	-	-	8.18
B	51.70	0.5-2.4	0.1-20	25-44	-	-	8-18
C	53-70	1-9	0.5-2.6	16-29	-	-	5-14
D	80-95	2-3	4-5	12-17	-	-	-
E	45-48.5	0.3-0.6	0.03-0.60	33.5-36.1	-	-	-
F	45.3-47.9	13.4-13.7	0.03-0.60	37.9-38.4	-	-	-
G	46-62	0.4-2.7	0.2-1	25-39	0.3-3	0.3-3	8-18
H	55-75	0.5-2.0	-	25-45	<2.0	-	12-15
Musa et al. (2012)	51.71	0.00	0.00	30.24	-	-	3.07
Nnaneme et al. (2020)	61.46	0.64	0.00	21.10	-	-	12.74
Abubakar et al. (2014)	64.50	14.26	0.26	16.30	0.74	-	4.46
Shuaib-Babata et al. (2019)	48.26	2.31	0.31	34.30	0.31	0.41	11.67
Yami, Hassan, and Umaru(2007)	67.90	2.60	-	12.88	0.06	1.97	11.67
Elakhame et al. (2017)	53.93	3.21	0.35	24.61	1.91	0.28	6.60
Kagonbé et al. (2021)	50.3	8.65	2.33	20.28	2.08	1.41	12.78
AV 1	61.26	5.47	0.1	27.08	0.9	0.86	2.13
AV 2	59.92	4.51	0.07	29.77	1.25	0.16	1.68
AV 3	68.16	4.45	0.18	21.52	0.8	0.06	2.14
AV 4	68.28	4.63	0.11	21.28	0.68	0.43	2.12
AV 5	59.03	5.09	0.06	29.84	1.63	0.18	2.64
AV 6	58.15	5.02	0.15	31.28	0.88	0.21	1.78
Average AV	62.47	4.86	0.11	26.80	1.02	0.32	2.08

A – F: Standard clay stats for industrial applications in Ceramics, Refractory brick, High Melting clay, Glass, Paper, Paint respectively in Chesters(1973) and Grimshaw(1971) as reported in Abubakar*et al.* (2014);

G – Fireclay standards (Nnuka and Agbo(2000) in Shuaib-Babata*et al.*(2019)) H – Fireclay international standards (Grimshaw(1971) in Yami*et al.* (2007))

Physical Properties

The Avutu clays exhibited density and porosity attributes aligned to specifications for fireclay and refractory bricks (Al-Amaireh, 2009; ASTM, 1982). The bulk density met the 1.7–2.1 g/cm^3 standard while porosity averages were below the 20–30% guideline for refractories. Hence, the physical characteristics seem mostly adequate. However, the total shrinkage exceeded limits. Proper processing controls during firing could rectify this issue.

The cold crushing strengths surpassed stipulated minima for fireclay bricks, averaging 20.78 N/mm^2 against the 15 N/mm^2 specification (ASTM, 1982). This demonstrates the capability to produce load-bearing ceramic products of sound mechanical quality. However, the low porosity values signify potential limitations for insulating applications. Hence, optimization of composition and firing to increase porosity could widen applicability.

Table 8: Comparison of the Average Physical Properties of Reference Samples and industry standards with those fromAvutu(AV)

Sample Location	Apparent porosity (%)	Water of absorption (%)	Bulk density (g/cm3)	Apparent specific gravity	Crushing strength (N/mm^2)	Total shrinkage (%)	Refractoriness (°C)
A	15.0 – 25.0		1.9 – 2.3	-	15 (min)	7 – 10	1500 – 1700
B	23.7	-	2	-	15	4-10	1500-1600
C	10-30	-	2.3	-	15	-	1430-1717
D	10-30	-	2-3	-	15	-	1430-1717
E	20-30	-	1.71-2.1	-	-	7-10	1500-1700
Musa *et al*. (2012)	-	-	2.19	-	13.45	9.41	1710
Abubakar *et al*. (2014)	28.46	-	1.81	-	14.14	6.8	1349
Shuaib-Babata*et al*. (2019)	27.31	-	2.21	-	358.27	8.2	>1300
Yami*et al.*(2007)	27.15	-	1.91	-	59.99	1.87	1300
Yami and Umaru(2007)^A	19.5	-	2.11	-	15.4	1.11	1370
Yami and Umaru(2007)^B	22.26	-	2.06	-	27	1	1400
Kagonbé*et al.*(2021)	-	-	1.84	-	-	1.32	-
AV 1	0.09	0.07	1.69	1.70	23.33	18.10	
AV 2	10.64	6.57	1.62	1.81	28.00	18.10	
AV 3	18.04	11.23	1.59	1.96	24.00	12.30	
AV 4	18.04	11.09	1.63	1.98	16.00	12.00	
AV 5	1.12	0.65	1.71	1.73	16.00	18.86	
AV 6	8.10	4.31	1.89	2.04	17.33	19.20	
Average AV	9.34	5.65	1.69	1.87	20.78	16.43	1652.58

A – Fireclay (ASTM, 1982) B – D: standards for Silceous fire clay, ceramics, and Refractory brick respectively (Omowumi(2000) in Abubakar et al. (2014)) E – Refractory standards (Gilchrist (1977) in Yami*et al.* (2007))

Refractoriness

The predicted refractoriness agreed with standards for fireclay which range between 1500–1700°C (Gilchrist, 1977). This theoretical estimate concurred with the trends in chemical composition and corroborates the thermal stability required for high temperature ceramics. Minor compositional adjustments to regulate fluxes and increase alumina levels could further enhance refractory properties.

Mineralogical Composition

The kaolinite content surpassed levels present in reference ball clays and global deposits which mainly fell below 45% (Bristow, 1989; Galos, 2011). Illite quantities agreed reasonably with comparative literature studies. The accessory minerals also seemed consistent with other natural clays. Hence, the Avutu deposits contain adequate proportions of essential ceramic minerals.

Table 9: Comparison of Mineralogical Composition of the Studied Clays for Avutu with reference samples and Values from other Locations and Studies

Code	K(%)	Qz(%)	Or(%)	An(%)	Ch(%)	I(%)	Mu(%)	He(%)	Al(%)	Cl(%)
AV 1	34.0	48.0	3.9	---	1.1	4.5	---	1.93	6.0	---
AV 2	31.0	54.0	7.3	1.6	---	2.0	4.0	0.4	---	---
AV 3	36.0	51.0	1.0	---	0.5	3.0	3.0	---	5.0	---
AV 4	30.0	58.0	2.0	---	2.0	---	0.8	---	7.0	---
AV 5	---	64.0	2.0	---	---	11.0	7.0	---	7.0	9.0
AV 6	31.0	50.0	6.0	---	---	3.7	3.7	1.01	4.7	---
Eastern Germany - G1	32	-	-	-	-	5		-	-	-
Western Czech - C1	45	-	-	-	-	20		-	-	-
Brazil clay – A1	57.9	35.9	-	-	-	-	-	-	-	-
Davidson	40	10	-	2	5	-	-	-	-	-
Buchanan	14	12	-	1	7		-	-	-	-
BH1	16		-	-	0	17	-	-	-	-
BH7	23		-	-	2	8	-	-	-	-
Ceramic china clay*	88	1	-	-	-	-	-	-	-	-
Ball clay group 1*	70	8	-	-	-	-	-	-	-	-
Ball clay group 4*	34	41	-	-	-	-	-	-	-	-
Filter grade C*	90	1	-	-	-	-	-	-	-	-
Paper coating SPS*	93	-	-	-	-	-	-	-	-	-
("Ball Clay," 2023)	25-80	10-25	-	-	-	-	-	-	-	-
Ball clay (Galos, 2011)	25-80	10-30	-	-	-	-	-	-	-	-

* Industrial standard: Bristow(1989) and Watts Blake Bearneplc company product specification, reported in Manning(1995)

K = Kaolinite, Qz = Quartz, Or = Orthoclase, Ch = Chlorite, I = *Illite*, HE = Hematite Al = Albite

G1, C1 – Clay samples investigated in Galos(2011)

Brazil clay samples, A1 (De-Andrade et al., 2010)

Mineral clay fractions of clays Alabama (Davidson) and Pennsylvania, USA (Buchanan) (Dixon & Jackson, 1960)

BH1, BH7 - Mineralogical composition of clay fractions from Nile Delta samples (Weir et al., 1975)

5. Conclusion

This study characterized ball clay deposits from Avutu, Obowo in southeastern Nigeria to evaluate their suitability as raw materials for diverse ceramic applications including refractories, tiles, tableware, and bricks. The analyses encompassed geological, geochemical, mineralogical, and physical techniques to benchmark the deposit attributes against industrial specifications.

Key outcomes indicate that the Avutu ball clays demonstrate largely adequate properties to serve ceramic manufacturing needs locally and nationally upon implementation of requisite beneficiation treatments and compositional adjustments. Characteristics like silica and alumina concentrations averaging 62.47% and 26.80% respectively signify suitability for refractory applications, as corroborated by the predicted refractoriness of 1652.58°C exceeding

1500°C specifications (Chesti, 1986; Gilchrist, 1977). The clays also contain sufficient proportions of essential ceramic minerals including 36% kaolinite, 11% illite, 7% muscovite, and 64% quartz.

Additionally, plasticity index values ranging between 17.2-33.2% facilitate moldability for structural clay wares while moderate porosity enables decompression of gases during firing to densify products. The cold crushing strengths averaging 20.78 N/mm2 indicate capability for load-bearing ceramics upon firing above 1000°C. While properties like silica-alumina ratios, fluxing agent levels, mineral composition, plasticity, porosity and strengths compared reasonably to industrial benchmarks, certain limitations need redressing including high Fe2O3 levels averaging 4.86%, excessive shrinkage up to 19.2% during firing and lower than stipulated porosity values below 10% in some samples.

Hence, key recommendations include: Beneficiation via magnetic separation to reduce iron oxides below 1.2% specifications (Ekosse, 2010). Adjusting clay:flux ratios by adding alumina-rich clays to regulate melting and enhance refractory properties (Zhang et al., 2022). Controlled heating/cooling plus adding grog/sand to improve porosity above 20% for insulation (Al-Amaireh, 2009; ASTM, 1982). Managing firing to limit total shrinkage between 7-10% (Omowumi, 2000). Pilot testing by experimentally firing and measuring technical properties. Techno-economic analysis of mining, processing and logistics costs to determine commercial viability.

In summary, this maiden study showed the industrial capability of the Avutu ball clays to potentially substitute imported clays for manufacturing ceramic products locally and nationally. The compositional and property attributes largely met quality benchmarks in standards and comparative literature upon implementing the foregoing recommendations. Further exploratory work can expand the prospects to additional sectors like paint, paper, polymer and pharmaceutics industries. Characterizing more clay reserves across Nigeria also promises to catalyze rural industrialization and import substitution to benefit the broader economy.

Conflict Of Interest

The author Thaddeus C. Azubuike declares no conflicts of interest.

References

Abubakar, I., Yauri, U. a. B., Faruq, U. Z., Noma, S. S., & Sharif, N. (2014). Characterization of Dabagi clay deposit for its creamics potential. African Journal of Environmental Science and Technology, 8(8), Article 8. https://doi.org/10.4314/ajest.v8i8

Al-Amaireh, M. (2009). Production of FireClay Refractory Bricks from Local Materials. 26.

ASTM. (1982). Annual book of ASTM standards, 1982. American Society for Testing and Materials.

Ball clay. (2023). In Wikipedia. https://en.wikipedia.org/w/index.php?title=Ball_clay&oldid=1165243803

Breuer, S. (2012, July 1). The chemistry of pottery. RSC Education. https://edu.rsc.org/feature/the-chemistry-of-pottery/2020245.article

Bristow, C. M. (1989). World kaolins: Genesis, Exploitation and Applications. In G. Clarke, Industrial Clays (pp. 8–17).

Bukalo, N. N., Ekosse, G.-I. E., Odiyo, J. O., & Ogola, J. S. (2017). Geochemistry of Selected Kaolins from Cameroon and Nigeria. Open Geosciences, 9(1). https://doi.org/10.1515/geo-2017-0045

Chesters, J. H. (1973). Refractories: Production and properties. The Iron and Steel Institute.

Chesti, A. R. (1986). Refractories manufacture, properties and applications. Prentice Hall of India.

De-Andrade, F. A., Al-Qureshi, H. A., & Hotza, D. (2010). Measuring and Modeling the Plasticity of Clays. Materials Research, 13(3), 395–399. https://doi.org/10.1590/S1516-14392010000300019

Dill, H. G. (2020). A geological and mineralogical review of clay mineral deposits and phyllosilicate ore guides in Central Europe – A function of geodynamics and climate change. Ore Geology Reviews, 119, 103304. https://doi.org/10.1016/j.oregeorev.2019.103304

Dixon, J. B., & Jackson, M. L. (1960). Mineralogical Analysis of Soil Clays Involving Vermiculite-Chlorite-Kaolinite Differentiation. In A. Swineford (Ed.), Clays and Clay Minerals (pp. 274–286). Pergamon. https://doi.org/10.1016/B978-0-08-009351-2.50028-3

Earle, S., & Earle, S. (2015). 2.4 Silicate Minerals. https://opentextbc.ca/geology/chapter/2-4-silicate-minerals/

Ekosse, G.-I. E. (2010). Kaolin deposits and occurrences in Africa: Geology, mineralogy and utilization. Applied Clay Science, 50(2), 212–236. https://doi.org/10.1016/j.clay.2010.08.003

Elakhame, Z. U., Bello, S., Agunsoye, J., I., P., & O., O. (2017). Characterization of Ujogba Clay Deposits in Edo State, Nigeria for Refractory Applications. Kathmandu University Journal of Science, Engineering and Technology, 12, 71–82. https://doi.org/10.3126/kuset.v12i2.21523

Galos, K. (2011). Composition and ceramic properties of ball clays for porcelain stoneware tiles manufacture in Poland. Applied Clay Science, 51(1), 74–85. https://doi.org/10.1016/j.clay.2010.11.004

Gilchrist, J. D. (1977). Fuels, furnaces, and refractories. Pergamon Press. http://archive.org/details/fuelsfurnacesref0000gilc

Grimshaw, R. W. (1971). The Chemistry and physics of clays and allied ceramic materials (4th ed., rev.). Benn.

Hoogsteen, M. J. J., Lantinga, E. A., Bakker, E. J., & Tittonell, P. A. (2018). An Evaluation of the Loss-on-Ignition Method for Determining the Soil Organic Matter Content of Calcareous Soils. Communications in Soil Science and Plant Analysis. https://doi.org/10.1080/00103624.2018.1474475

Kagonbé, B. P., Tsozué, D., Nzeukou, A. N., & Ngos, S. (2021). Mineralogical, physico-chemical and ceramic properties of clay materials from Sekandé and Gashiga (North, Cameroon) and their suitability in earthenware production. Heliyon, 7(7), e07608. https://doi.org/10.1016/j.heliyon.2021.e07608

Manning, D. A. C. (1995). Industrial clays: Kaolin (china clay), ball clay and bentonite. In D. A. C. Manning (Ed.), Introduction to Industrial Minerals (pp. 35–71). Springer Netherlands. https://doi.org/10.1007/978-94-011-1242-0_3

Musa, U., Aliyu, A., Sadiq, M. M., Mohammed, I. A., Isah, A., & Mohammed, A. D. (2012). A Comparative Study of the Refractory Properties of Selected Clays in Niger State, Nigeria. Advances in Biotechnology and Chemical Processes - World Open Access Journals, 2, 1–5.

Nnaneme, F., Onuegbu, T., Agbo, S., & Okwute, E. S. (2020). The Characterization of Local Clay from Anambra State Nigeria for Its Potential Applications in the Production of Ceramic Whitewares. Asian Journal of Chemical Sciences, 22–33. https://doi.org/10.9734/ajocs/2020/v8i219038

Nnuka, E. E., & Agbo, U. J. E. (2000). Evaluation of the Refractory Characteristics of Otukpo Clay Deposits. Nigerian Society of Engineers (NSE) Technical Transaction, 35(1), 34–41.

Nwajide, C. S. (2013). Geology of Nigeria's Sedimentary Basins. CSS Bookshops Limited Brood Street.

Obinegbu, I. R., & Chiaghanam, O. I. (2019). Reserve Estimations and Economic Potentials of Exposed Kaolin Outcrops in Parts of South- Eastern Anambra Basin, Anambra State, Nigeria – CJPS. Journal of Physical CJPS Sciences, 2(8), 84–91.

Ode, J. U., Najagu, C. O., & Nnuka, E. E. (2009). Ezebunagu clay deposit and its potential for Industrial application. Journal of Metallurgical and Material Engineering, 4(2), 31–37.

Omowumi, O. J. (2000). Characterization of some Nigerian clay as refractory materials for furnace lining. Nigerian Journal of Engineering Management, 2, 1–4.

Onyeaguocha, A. C. (1980). Petrogrophy and Depositional Environment of the Benin Formation. Journal of Mining Geology, 17(2), 147–151.

Onyemesili, O. C., & Odumodu, C. F. R. (2019). Pebble Morphometric Study of the Ogwashi-Asaba Formation at Ubakala and Environs in Southeastern Nigeria. Journal of Natural Sciences Research, 9(6), 36.

Perkins, D. (1998). Mineralogy (2nd edition). PHI Learning Private Ltd.

Ryan, R. (2013). Cochrane Consumers and Communication Review Group. Cochrane Consumers and Communication Review Group: data synthesis and analysis. https://cccrg.cochrane.org/sites/cccrg.cochrane.org/files/public/uploads/AnalysisRestyled.pdf

Saikia, Dr. N., Bharali, D., Sengupta, P., Bordoloi, D., Goswamee, R., Saikia, P., & Borthakur, P. (2003). Characterization, beneficiation and utilization of a kaolinite clay from Assam, India. Applied Clay Science - APPL CLAY SCI, 24, 93–103. https://doi.org/10.1016/S0169-1317(03)00151-0

Shuaib-Babata, Y., Ambali, I., Ibrahim, H., Kabiru Suleiman, A., Elakhame, Z. U., Aremu, N., & Odeniyi, O. (2019). Assessment of Physico-Mechanical Properties of Clay Deposits in Asa Local Government Area of Kwara State Nigeria for Industrial Applications.

Supandi, S., Zakaria, Z., Sukiyah, E., & Sudradjat, A. (2019). The Influence of Kaolinite—Illite toward mechanical properties of Claystone. Open Geosciences, 11, 440–446. https://doi.org/10.1515/geo-2019-0035

Ugada, U., Opara, A. I., Emberga, T. T., Ibim, F. D., Omenikoro, A. I., & Womuru, E. N. (2013). Delineation of Shallow Aquifers of Umuahia and Environs, Imo River Basin, Nigeria, Using Geo-Sounding Data. Journal of Water Resource and Protection, 05(11), 1097–1109. https://doi.org/10.4236/jwarp.2013.511115

Vardanega, P. J., Haigh, S. K., & O'Kelly, B. C. (2022). Use of fall-cone flow index for soil classification: A new plasticity chart. Géotechnique, 72(7), 610–617. https://doi.org/10.1680/jgeot.20.P.132

Weir, A. H., Ormerod, E. C., & Mansey, I. M. I. E. (1975). Clay mineralogy of sediments of the western Nile Delta. Clay Minerals, 10(5), 369–386. https://doi.org/10.1180/claymin.1975.010.5.04

Wilson, M. J. (1999). The origin and formation of clay minerals in soils: Past, present and future perspectives. Clay Minerals, 34(1), 7–25. https://doi.org/10.1180/000985599545957

Yami, A., Hassan, M., & Umaru, S. (2007). Evaluation of The Refractory Characteristics of Dukku Clay Deposit. Continental Journal of Engineering Sciences, Vol.2., Pp. 15-21.

Yami, A., & Umaru, S. (2007). Characterization of Some Nigerian Clays as Refractory Materials for Furnace Lining. Continental Journal of Engineering Sciences, Vol. 2., Pp. 30-35.

Zhang, B., Yu, T., Guo, H., Chen, J., Liu, Y., & Yuan, P. (2022). Effect of the SiO2/Al2O3 Molar Ratio on the Microstructure and Properties of Clay-based Geopolymers: A Comparative Study of Kaolinite-based and Halloysite-based Geopolymers. Clays and Clay Minerals, 70(6), 882–902. https://doi.org/10.1007/s42860-023-00223-x