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GEOCHEMICAL COMPOSITION, MINERALOGY, GEOTECHNICAL CHARACTERISTICS OF SOME CLAY DEPOSITS IN PARTS OF THE SOUTHERN NIGER DELTA, NIGERIA

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ABSTRACT

Clay soil samples from the Afo-Okpella and Okpekpe in parts of the southern Niger Delta were analyzed for their geochemical composition, mineralogical and geotechnical characteristics. X-ray fluorescence analysis, x-ray diffraction analysis and index property tests were carried out to determine elemental composition, mineralogical nature and geotechnical attributes of the clay. The XRF reveals that SiO_2 and Al_2O_3 are the predominant oxides. The XRD analysis shows that kaolinite is the predominant clay mineral with varying amount of quartz also traces of illite, smectite. The geotechnical index test shows that the clay soil samples studied also contains considerable amounts of silt-size particles (18%-70%) which makes them unsuitable in their raw state for use as fillers, raw materials in the paint industries. The clays were generally of medium to high plasticity and medium to high compressibility, however the classification of degree of expansion as regard to percentage linear shrinkage places the entire clay bodies studied in the critical degree of expansion. The study reveals that they are good for the production of quality bricks, ceramics and other industrial usage such as rubber, paper and paint industries.

KEYWORDS: Geochemical, mineralogical, geotechnical, kaolinite, clay

INTRODUCTION

There is a demand to speed up the exploration and exploitation activities of the different solid mineral deposits in Nigeria for sustainable diversified economy of the country. This will improve industrial techniques and technological advancement needed to take care of the increasing population of our people. The present monolithic petroleum driven economy is not the best giving to the unstable and occasionally decreasing oil revenue coupled by international politics of trade. This study will hopefully lead to the unveiling of new mineral deposits which will form an economic basis for future industrial diversification of southern Nigeria.

The nature of clay and its composition determine not only its quality and commercial value but also, to a large extent, its engineering behaviour. Among the characteristics of clays that influence their engineering performance are clay mineral composition, physical properties such as particle size distribution, plasticity, shrinkage, non-clay mineral composition, amorphous components (e.g organic matter, content) and geologic history (Grim, 1968). Deposits of clay raw material are widely distributed in Nigeria. In order to determine the financial gain of clay materials from a particular deposit, it is of paramount to examine the morphology, micro structure, determine the mineralogical composition in such clay deposit.

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This study addresses the geochemical, mineralogical and geotechnical character of two clay deposits in the southern Niger Delta in view of their industrial application and utilization. Similar studies have been out by many researchers.

Detailed information on clay mineralogy and chemistry has been provided by (Weaver and Pollard, 1973; Dixon and Weed, 1989; Brindley and Brown, 1980; Barshad, 1966; Biscaye, 1965; Moore and Reynolds, 1997).

Interestingly, various researchers have looked at some of these clays from different angles. For example, Ajayi and Agagu, (1981) carried out mineralogical studies of clay deposits from different areas representing different rocks from parts of the Basement complex and concluded that the deposit weathered from gneisses, granites, schists and pegmatites consist mainly of kaolinite and small proportions of montmorillonite and illite. Emofurieta et al., (1992) established that many clays occur as extensive cover of allochthonous units within Cretaceous and Tertiary sedimentary succession. Onyeobi et al., (2013) noticed the Iyuku clay are product of in situ weathering of rocks within the Basement Complex of Nigeria. Lucas et al., (2020) and Itiowe et al. (2021) carried out quantitative mineralogical analysis on samples from the Northern Delta and Greater Ughelli Depobelts and noticed the depobelts consisted predominantly of kaolinite, followed by illite/muscovite, chlorite and sepiolite.

In spite of this research precedence, there is need for more clays studies in Southern Nigeria as this would broaden the clay resource database of the Nation, which is the drive behind this study.

This work attempts to audit the compositional and basic geotechnical attributes of two clay deposits at Afo-Okpella and Okpekpe in southern Niger Delta, Nigeria, with a view to establishing their industrial relevance, as a contribution to the nation's economic development

The study area has a latitude of 7°10'0"N to 7°20'00"N of the equator and longitude 6°21'30" to 6°27'0"E of the Greenwich Meridian with an elevation of 167m high above the sea level (Fig.

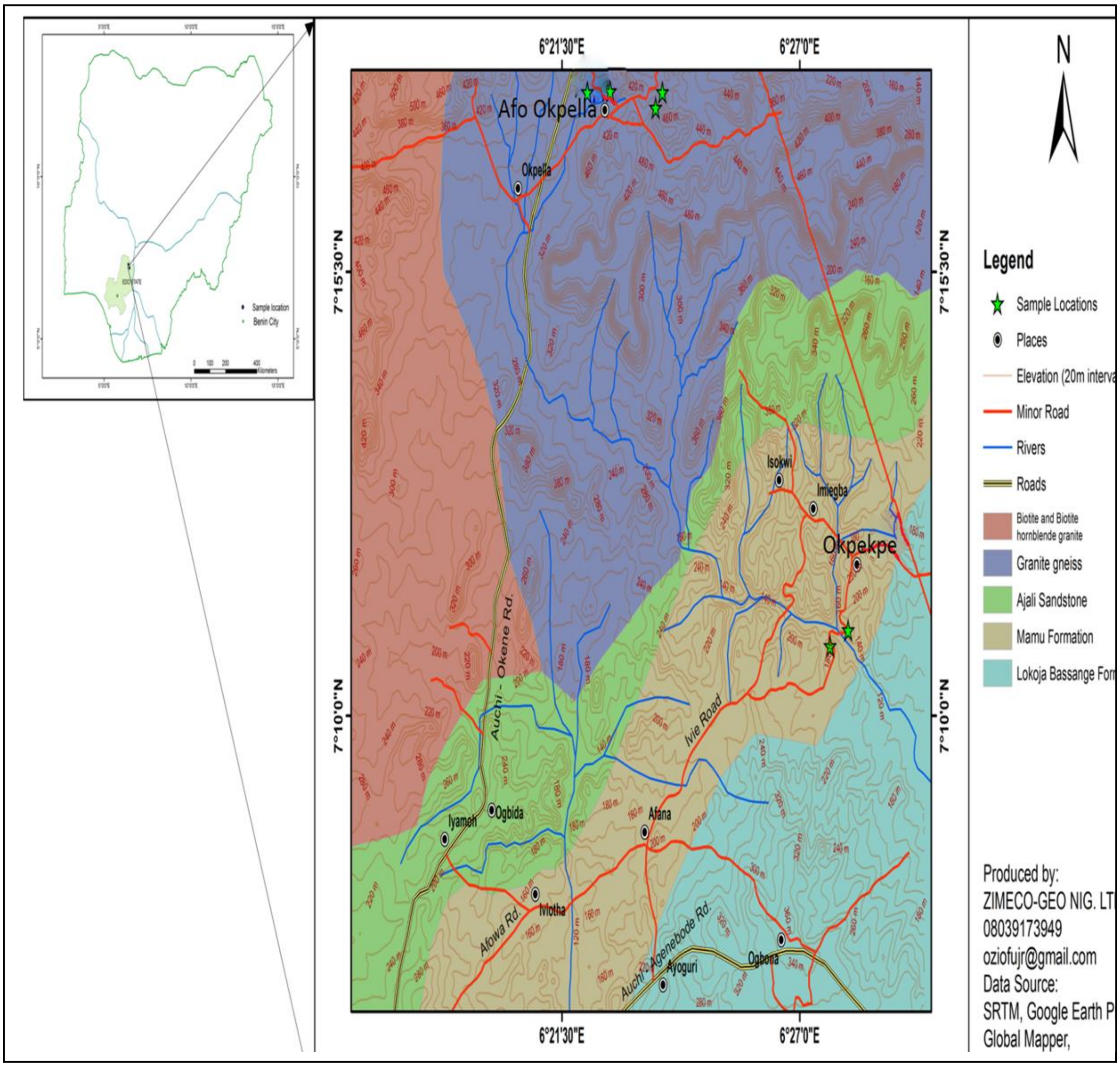

Fig. 1: Geological map of the sampled areas.

MATERIAL AND METHODS

Soil sampling

Four representative clay samples from Afo-Okpella and Okpekpe deposits were collected from good exposures and kept in a sealed polythene bags to prevent moisture loss and contamination. These samples were taken to laboratory for analysis.

Analytical methods

In clay characterization studies, several methodologies are applied to determine mineralogy, geochemical composition and geotechnical behaviour of the clay deposit. Some of these methodologies include: x-ray fluorescence analysis for the determination of the geochemical composition of the clay. A quantitative determination of the mineralogical properties of the clay samples using X-ray diffraction were carried out at Rolab Research and Diagonistic Laboratory Challenge, Ibadan. Powdered samples were pelletized and sieved to 0.074mm. These were later taken in an aluminium alloy grid (35mm x 50mm) on a flat glass plate and covered with a paper. Wearing hand gloves, the samples were compacted by gently pressing them with the hand. Each sample was run through the Rigaku D/Max-lllC X-ray diffractometer developed by the Rigaku Int. Corp. Tokyo, Japan quipped with an x-ray tube capable of producing a beam of monochromatic x-ray, a sample holder, inbuilt standards, Peak/width, goniometer and x-ray detector and set to produce diffractions at scanning rate of 20/min in the 2 to 500 at room temperature with a CuKa radiation set at 40kV and 20mA. The angles and intensities of diffractions for each mineral are recorded electronically using a detector. After the scan of the sample the x-ray intensity can be plotted against angle 2Ө to produce a chart. The angle 2Ө for each diffracted peak can be converted to d-spacing using bragg's equation. ($n\lambda=2d\sin\theta$). The diffraction data (d value and relative intensity) obtained was compared to that of the standard data of minerals established by Brown (1951), Carrol (1971) and the JCPDS (Joint Committee on Powder Diffraction Standard) the mineral powder diffraction file (1980), which contained and includes the standard data of more than 3000 minerals.

Furthermore, X-ray fluorescence analysis was used for the determination of the geochemical composition of the clay. XRF is a rapid, relatively non-destructive process that produces chemical analysis of rocks. Its purpose is to identify the elemental abundances of the sample i.e. Identification of both major and trace elements. The samples were analysed for major element oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O and MnO) in percentages while Mn, Ni, Co, Cr, and Zn were analysed in part per million using a Phillips PW1606 X-ray Fluorescence Spectrometer.

The geotechnical test and laboratory testing was carried out according to the procedure stated in British Standard: BS 1377 1990) and ASTM. 1992. The samples were later tested for grain size analysis, plastic limit, liquid limit, plasticity index, specific gravity, moisture content and linear shrinkage.

RESULTS

Chemical composition

For the clay body studied, the major oxides composition of the soils is shown in Table 1 and Table 3. SiO_2, Al_2O_3 and Fe_2O_3 are the dominant oxides in the soil (Table 1 and 3), the variation in the silica content is apparently clear where the Okpekpe 1 has a value of (54.82%) lower than Okpekpe (56.70%), Afo-Okpella 1(56.39%) and Afo-Okpella 2 (56.46%) (Table 1). However from the table the alumina contents, are moderately high as compared to a typical china clay and florida non- active kaolinite (Table 3), the values ranges from (29.02% to 31.23%) while china clay has a value of (37.65%) and florida non-active kaolinite (38.45%). The Fe_2O_3 concentration in the clay samples shows little variations with Okpekpe 1 having a value of (4.98%), Okpekpe 2 (4.06%), Afo-Okpella 1 has a value of (4.66%), while Afo-Okpella 2 has a of (4.75%). The relative high Fe_20_3 is probably due to superficial oxidation and contamination by Fe-rich percolating water from the highly ferruginous facies capping the clay deposit. TiO_2 contents is less than 2% in all the locations where okpekpe1 has a value of (1.23%), Okpekpe 2 (1.34%), Afo- Okpella 1 has a value of (1.13%), Afo-Okpella 1(1.25%). The alkalis (K_2O, Na_2O) as well as CaO and MnO occur in fairly low proportion and it is indicative of the high degree of weathering under tropical conditions from which the clay bodies were formed. The samples shows a very low concentration of P_2O_5 were Okpekpe 1 has a value of (0.04%), Okpekpe 2 (0.05%) and Afo-Okpella 2 has a value of (0.04%) while Afo-Okpella 1 is depleted of P_2O_5.The studied samples have a fairly high concentration of MgO when compared with bricks clay with a value of (8.50%) (Murray, 1960).

Table 2 present the results of chemical analysis showing the different trace element contained in the clay samples and are expressed in part per million (ppm). This includes Cu, in the range of (20.22-23.30), Cr (12.20-48.20), Ni (10.40-21.52), Zn (10.42-44.25), Co (10.15-13.15) etc. the concentration of colourant such as Co, Ni, and Cu are low which implies that they will not impact any colouration on the finished product. Others includes Sr (10.00-44.28), Pb (20.13-20.45), Sc (8.15-30.25), Cd (0.04-0.21).

Table 1: Chemical analysis of the clay samples (elemental oxide concentration in percentage)

ELEMENTAL OXIDES	AFO-OKPELLA 1 (%)	AFO-OKPELLA 2 (%)	OKPEKPE 1 (%)	OKPEKPE 2 (%)
SiO_2	56.39	56.46	54.82	56.70
Al_2O_3	29.60	29.02	31.23	30.22
Fe_2O_3	4.66	4.75	4.98	4.06
TiO_2	1.13	1.25	1.23	1.34
CaO	1.66	1.75	1.61	1.66
P_2O_5	-	0.04	0.04	0.05
K_2O	0.89	0.98	0.85	1.01
MnO	0.07	0.08	0.08	0.07
MgO	4.69	4.75	4.29	5.08
Na_2O	0.87	0.90	0.83	0.87
LOI	0.04	0.02	0.04	0.05

Table 2: Chemical analysis of the clay samples (trace element concentration in PPM)

TRACE ELEMENTS	AFO-OKPELLA1	AFO-OKPELLA 2	OKPEKPE 2	OKPEKPE 1
Ba	990.61	862.62	862.30	956.60
Cu	23.30	21.31	21.32	20.22
Cr	22.40	48.20	35.20	12.20
Ni	21.52	10.40	16.60	20.22
Zn	10.42	40.45	44.25	12.20
Co	12.18	11.30	13.15	10.15
Sr	10.00	42.11	32.13	44.28
Pb	20.45	20.30	20.24	20.13
Sc	30.25	8.15	8.44	10.25
Cd	0.21	0.08	0.12	0.04

The results of the chemical analysis was compared with typical composition of Average clay-shale, Afam clay (AFC), China clay (SCC), Florida non-active kaolinite as shown in Table 3.

Table 3: Comparison of the average chemical composition of the studied clays with average chemical composition of other types of clay

ELEMENTAL OXIDES	AFO-OKPELLA 1 (%)	AFO-OKPELLA 2 (%)	OKPEKPE 1 (%)	OKPEKPE 2 (%)	I(AVC)	ii(AFC)	Iii (CC)	Iv(FNK)
SiO_2	56.39	56.46	54.82	56.70	58.10	42.20	46.88	45.57
Al_2O_3	29.60	29.02	31.23	30.22	15.40	38.45	37.65	38.45
Fe_2O_3	4.66	4.75	4.98	4.06	4.24	0.75	0.88	0.75
TiO_2	1.13	1.25	1.23	1.34	-	0.01	0.09	0.01
CaO	1.66	1.75	1.61	1.66	3.1	-	0.03	-
P_2O_5	-	0.04	0.04	0.05	-	-	-	-
K_2O	0.89	0.98	0.85	1.01	3.24	0.06	1.60	0.06
MnO	0.07	0.08	0.08	0.07	-	-	-	-
MgO	4.69	4.75	4.29	5.08	2.44	0.05	0.13	0.05
Na_2O	0.87	0.90	0.83	0.87	1.30	-	0.21	-
LOI	0.04	0.02	0.04	0.05	-	-	-	-

I. Average clay-shale (Pettijohn, 1957) AVCS
II. Afam clay (Jubril &Amajor, 1991) AFC
III. China clay GTY (Huber, 1985) SCC
IV. Florida non-active kaolinite (Huber, 1985)

Mineralogical characteristics

The mineralogical composition shows that kaolinite, illite, smectite, chlorite, mica was found to be the preponderant clay minerals. Other minerals include quartz, plagioclase feldspar, albite, muscovite, biotite and accessory minerals such as apatite, magnesite, siderite and lastly pyrite. Table 4 shows the result of the minerals present in each of the sample analysed for mineralogy.

Table 4: Mineralogical composition of clay deposits from the different locations

AFO-OKPELLA 1	AFO-OKPELLA 2	OKPEKPE 1	OKPEKPE 2
Kaolinite	Kaolinite	Kaolinite	Kaolinite
Quartz	Quartz	Illite	Plagioclase
Mica	Magnesite	Quartz	Quartz
Plagioclase	Albite	Smectite	Albite
Illite	Plagioclase	Siderite	Apatite
	Muscovite	Plagioclase	Magnesite
	Biotite	Illite/smectite	Mica
	Illite	Chlorite	illite
		Pyrite	

The diffractograms indicate that kaolinite and illite were present in all the clay deposits (Figs. 2-5) but only Okpekpe was found to contain variable amount of smectite, illite/smectite and chlorite (Figure 4 and 5). From the diagonostic peaks the quartz content are far higher than the kaolinites in all the clay deposits. The diffractograms of Afo-okpella1,Afo-okpella2 and Okpkepe 2 are characterised by broad kaolinite and Quartz peaks. The morphology of these peaks is indicative of distorted crystallinity of the minerals which is suggestive of intense weathering. The high dominance of quartz in the clay deposit explains it grittiness and also suggest the clay to be of residual origin.

The presence of plagioclase, albite, mica and its associated mineral such as muscovite, biotite as indicated against the diagnostic peaks as shown in the diffractograms of Afo-Okpella 1and 2 is an indication that they are of granitic origin because mica and plagioclase feldspar are important component in most igneous rocks such as granite and are often well developed in pegmatitic rocks and this conform to the geological setting of Okpella been part of the migmatite-gneiss-quartzite complex of the basement complex. Hence, during physical or chemical weathering and also possibly hydrothermal alterations of these crustal rocks, the elements present break down to form clay minerals and also infiltrate and integrate into the clay forming process, so micaceous minerals such as biotite, muscovite, chlorite and illite may be formed.

The plagioclase feldspar present in Okpekpe 1and 2 may possibly be deposited by ground water solution during formation of clay minerals and the sandstone section of the Mamu Formation is enriched in feldspar. Furthermore presence of minerals such as siderite and magnesite are found to occur in Okpekpe 1 and 2 and absent in Afo-Okpella 1and 2, this shows that the samples thus indicate associated carbonates or dolomitisation. Siderite is a mineral that occurs in thin beds with shale, clay and coal seam and this is attributable and common in the Mamu Formation of the Anambra Basin. Pyrite is not common and it is found to be present only in Okpekpe 1 and absent in the other clay deposit. Pyrite in this context is probably considered to be formed by oxidation of iron present in magnesite and siderite. But pyrite is also formed in oxygen poor environment in the presence of sulphur and iron and where decaying organic material consume oxygen and release sulphur and this conform to the clay deposit at Okpekpe 1 which is dark carbonaceous shale-clay with brownish patches attributable to oxidation.

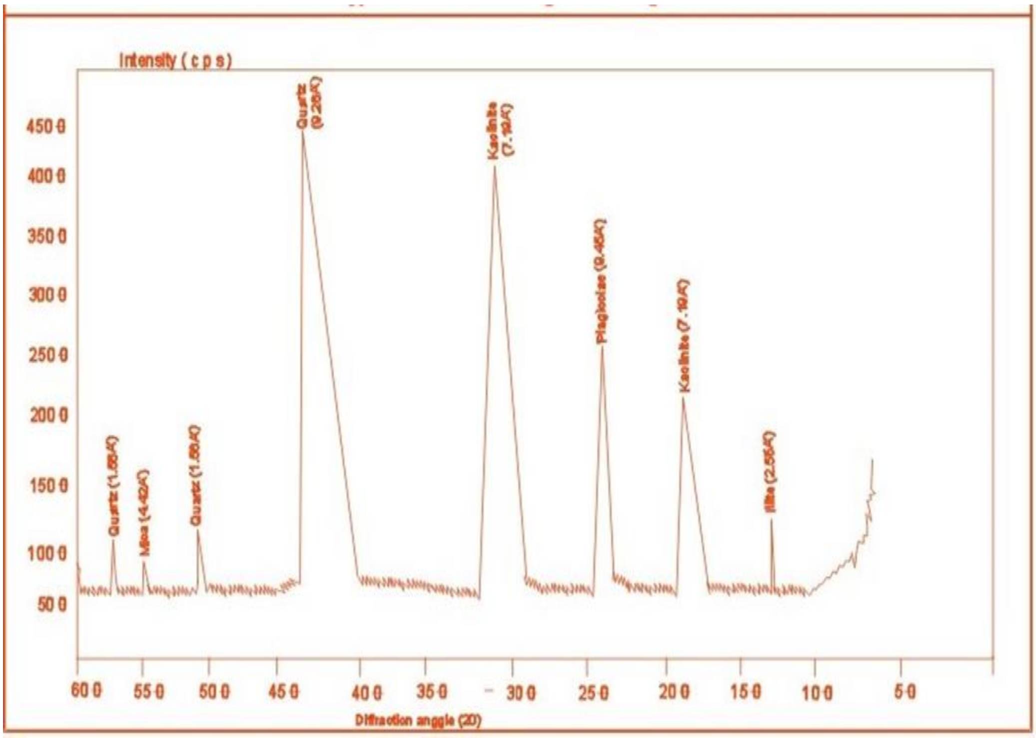

Figure 2: X-ray diffractogram of Afo-Okpella 1 clay

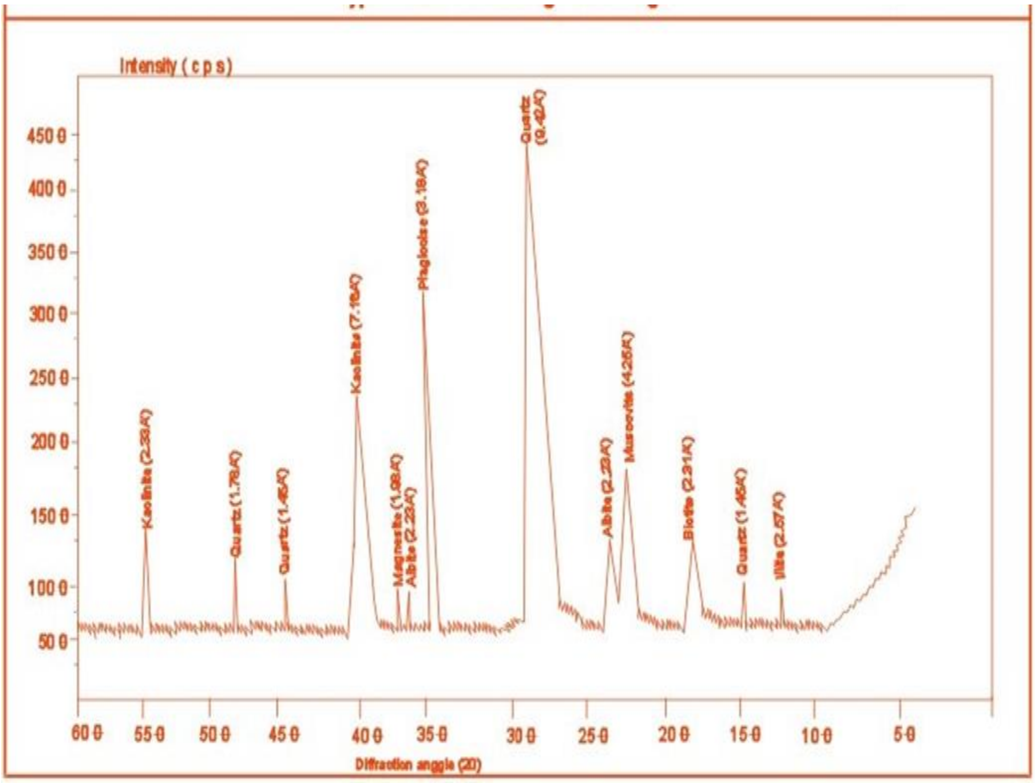

Figure 3: X-ray diffractogram of Afo-Okpella 2 clay

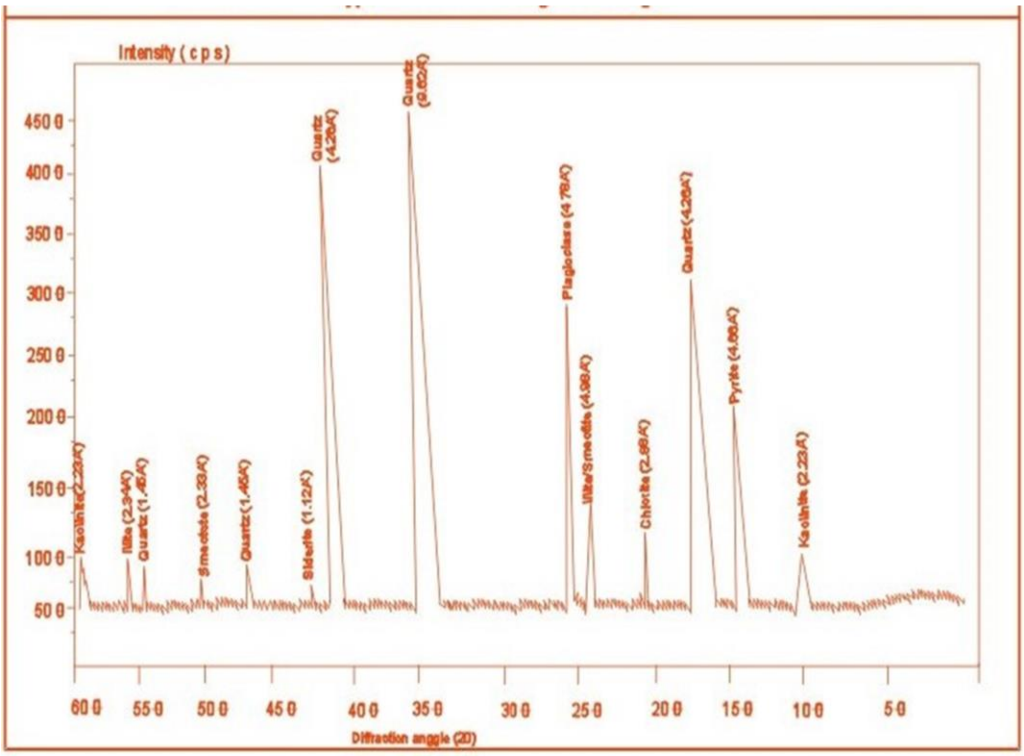

Figure 4: X-ray diffractogram of Okpekpe 1 clay

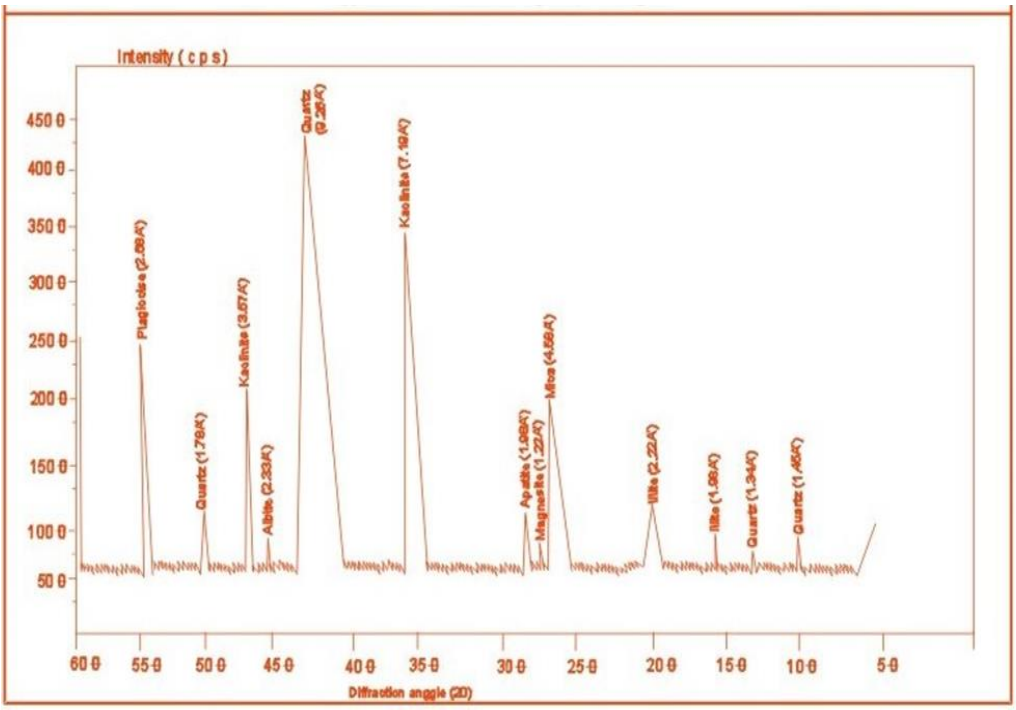

Figure 5: X-ray diffractogram of Okpekpe 2 clay

GEOTECHNICAL CHARACTERISTICS

Geotechnical characteristic of clayey soil and their associated chemical and mineralogical composition determines and influences the end use or market value of clay. The results of the basic geotechnical characteristic of the studied clay samples are presented in table 5.

Table 5: The basic geotechnical characteristics of the studied clay samples

Property	AFO-OKPELLA 1	AFO-OKPELLA 2	OKPEKPE 1	OKPEKPE 2
PSD-Clay (%)	10	37	30	37
PSD-Silt % (%)	38	28	70	18
PSD-Sand (%)	52	35	0	45
Fine (%)	48	65	100	55
Liquid limit (%)	29	43	53	54.5
Plastic limit (%)	13.17	14.78	20.47	19.2
Plasticity Index %	15.83	28.22	32.53	35.3
Clay activity	1.58	0.76	1.08	0.95
Moisture Content (%)	2.06	10.92	22.24	11.25
Liquidity Index	-0.70	-0.14	0.05	-0.23
Specific Gravity	2.61	2.63	2.00	2.62
Linear shrinkage (%)	10.20	10.50	12.60	12.70

The particle size distribution of the studied clays indicated that Afo-Okpella 1and 2 and Okpekpe 2 have similar range of particle size with percentage fine fraction between 48% & 65% while the Okpekpe 1 is fine-grained with 100% fines which confirms to a low energy environment. Afo-Okpella 2 and Okpekpe 1 & 2 has moisture content between 10.92% & 22.24%, a much lower value of 2.06 was recorded for the Afo-Okpella 1. Liquidity indices are mostly negative as values Afo-Okpella1&2 range from -0.70 to -0.14, while that of Okpekpe 1&2 range from -0.23 to 0.05. This implies the clays (Afo-Okpella1,2 &Okpekpe2) were predominantly in a hard and brittle state at the time of sampling except for Okpekpe1 which was in its plastic state. The plasticity index values ranges from 28.22% to 35.3% except for the Afo-Okpella 1 clay with a rather lower plasticity index of 15.83% and an equally low liquid limit value of 29%. Generally, the plasticity indices are indications of slightly medium to high swelling potentials which is due to mixed kaolinite/illite presence and amorphous components (such organic matter) in the clays (Okogbue and Onyeobi 1999, Avwenagha 2021).The liquid limit of the other samples range from 43% to 54.5%, which indicate that they are clay of medium-slightly high compressibility (Smith, 1978, BS5930,1999). The clay studied has plastic limit of about 13.17 to 20.47 with the Afo-Okpella 1 having the lowest value. Casangrande plasticity chart (Figure 6) identifies the four clays (Afo-Okpella1,2 &Okpekpe1,2) as inorganic clays of low to high plasticit

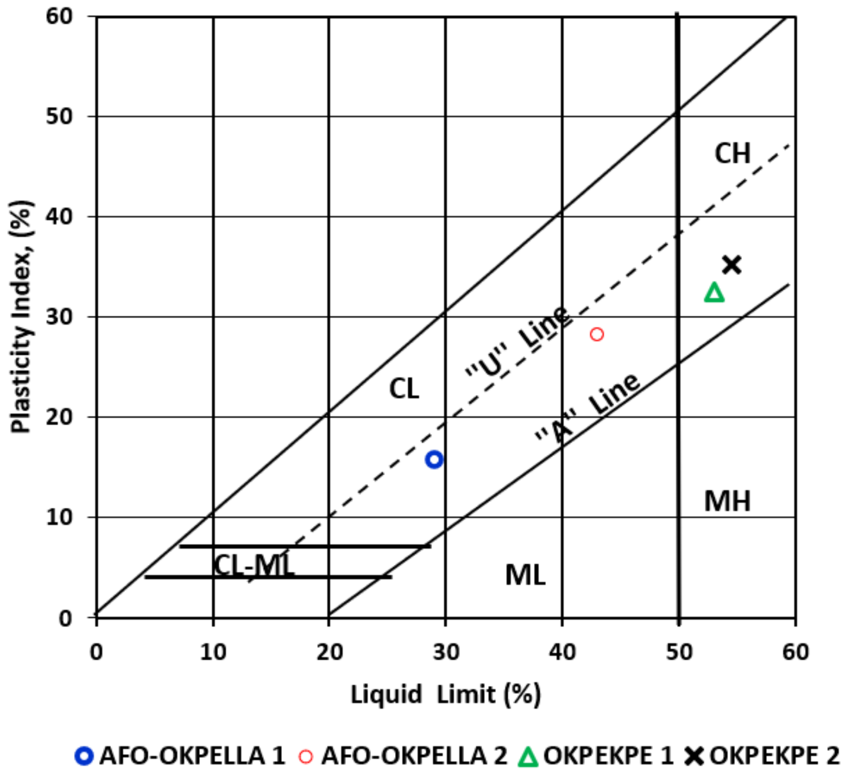

Figure 6: Casangrande Plasticity classification of clays samples.

However, the specific gravity ranges from 2.00 to 2.63 with the Okpekpe 1 having the lowest value (2.00). This implies Okpekpe1 has the highest organic matter content which is evidenced by dark carbonaceous appearance coupled with its highest fines content (100%) relative to other clays. Clay activity of Afo-Okpella 1 &2 ranges 1.58 to 0.76 while Okpekpe 1& 2 between1.08 to 0.95. These values suggest that the clays are mostly normal clays except for Afo-Okpelle1 which is indicative of active clay (Skempton 1953). This clay activity classification conforms to Onyeobi et al., 2013, but partly conforms to the results of the diffractograms (Figure 1-4) which is dominated by inactive clays minerals (e.g kaolinite) and normal clay minerals (e.g. illite). Altmeyer's (1955), classification of degree of expansion in terms of percentage linear shrinkage places the entire clay sample studied in the critical degree of expansion.

INDUSTRIAL APPLICATION

The geochemical, mineralogical, and physical characteristics constitute crucial parameters in the assessment of the suitability of clays as industrial raw materials. Evaluation of the industrial utilization of the clays is based on their geotechnical and geochemical characteristics and comparison with chemical specification of some industrial clay. Table 4 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, their alumina content of the clays corresponds to the refractory industrial specification (Parker, 1967) and ceramics (Singer and Sonja, 1971). 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 (Keller, 1964).

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. 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. 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. 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 Afo-Okpella 1 and 2 clay which is typically pinkish and whitish in colour and which is of low plasticity to medium plasticity, low compressibility will probably have similar properties with those of china and beneficiation/processing of the clay to remove the silty/sandy quartz particles that make it gritty would reduce the silica percentage, thereby enhancing the alumina content and successive blending with good quality clay with high alumina content will add to its refractory nature.

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.

CONCLUSION

A comprehensive appraisal of the geochemical, mineralogical and geotechnical characteristics of the Afo-Okpella clay and Okpekpe clay deposit reveals the clay are essentially kaolinitic with variable amount of quartz also traces of illite, smectite were recorded in Okpekpe 1 clay. The study of these kaolinitic clay bodies also indicates that they are composed of non-clay minerals such as feldspar, albite, pyrite, and siderite etc which is amenable to beneficiation to yield good quality kaolinite in the finished product.

Geochemically SiO_2 and Al_2O_3 are the predominant oxides, the clay bodies studied have similar range of silica and Alumina but the Afo-Okpella 1 is less hydrophilic than the others.

Geotechnical audit shows that the plasticity, swelling potentials, compressibility of Afo-Okpella clays and Okpekpe clay deposits are of slightly medium to high degree. However the classification of degree of expansion in terms of percentage linear shrinkage places the entire clay bodies studied in the critical degree of expansion. These geotechnical attributes preclude their usability for ceramics production.

On the bases of chemical and mineralogical assessment, the clays are suitable several industrial utilities (such as ceramics, refractory bricks) but are unviable for ceramic production from the geotechnical perspective unless after appropriate beneficiation.

RECOMMENDATION

In the past decades, the procurement of clay especially kaolin to meet the industrial needs of the country have been done through the importation of millions of tons of the product from overseas countries thereby biting into the meagre foreign reserve of the nation. This wrong aberrant practise was aided by improper investigation and documentation of the clay deposits in the country.

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. However, improvement in both the chemical and mineralogical of the clays after processing are proof to the fact that the raw product is amenable to beneficiation which when effectively executed, can yield a pure kaolinite in the finish product to service our industries such as the modern ceramic company at Umuahia. The added cost of processing cannot however be equated to the financial involvement inherent in the importation of kaolin from overseas countries to meet our industrial needs.

It is recommended that further investigations of the clay deposit studied in estimating and quantifying the accurate reserves of the deposits be urgently carried out as a follow up for purposes of their development and exploitation.

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