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REVIEW

A Synoptic Review of Mineralogical and Chemical Characteristics of Clays in the Southern Part of Nigeria

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ARTICLE INFO

Article history
Received: 6 April 2021
Accepted: 28 April 2021
Published Online: 18 May 2021

Keywords:
Clay
Montmorillonite
Kaolinite
Illite
Oxide
Nigeria

ABSTRACT

This paper reviews the mineralogical and chemical characteristics of clays found in southern part of Nigeria, with a view to determine its usability. The usability of clays, depends on its chemical and mineralogical charactertics, the end product of clay after it is been processed is also based on it's charactertics. From reviewed literature, it was observed that sampled clay within the study area were analyzed using the XRD, XRF and ICP-MS method. Further findings also revealed that the dominant clay minerals within the study area include montmorillonite, illite, and kaolinite. On the other hand, it was observed that non-clay minerals such as feldspar, quartz, dickite and many others were found with clay as revealed by several scholars. While chemical charactertics of clay consists mainly of Al_2O_3, K_2O, CaO and SiO_2, with other major oxides such as P_2O_5, MgO, Fe_2O_3, TiO_2, MnO and Na_2O. Some trace elements such Be, Ba, Sc, Sr, Zr, V and Y were reported to be present in clays deposit found in selected part of Ogun state. From reviewed articles, it was observed that mineralogical and chemical charactertics of clay make it suitable for pharmaceutical, textile, cosmetic and polymer industries, but considered to be fairly suitable for oil and gas industry.

1. Introduction

[1] defined clay mineral as a sheet-structured alumino-silicate mineral that primarily occur in the grain size of about 2 μm fraction of soil, sediment, sedimentary rock, weathered and altered rock. It is composed of basically of silica, alumina and water, with significant concentrations of iron and alkalis. The mineralogical composition of clay relies solely on the environment that is been deposited. Several scholars were of the view that clay in open marine environment consist mainly of illites, chlorites and montmorillonites [2]. There are some charactertics of clay such as plasticity, chemical makeup, refractoriness, strength and shrinkage that determine its suitability for several industries. From chemical point of view, clay is hydrous aluminum silicates which contain small amount of Fe, Mg, Ca, K, Na and Ti. Though, clay mineral might have general physio-chemical characteristics, individual clay minerals have certain charactertics

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DOI: https://doi.org/10.30564/re.v3i2.3057

that determine their distinct properties. [3] suggested that variation in physio-chemical attribute of clay determine its application in different field. [4] reported that clay is found in Delta, Kebbi, Kastina, Enugu, Abia, Ogun, Imo, Kano Kogi and Kwara states in its pure form. Clay is known to be plastic based on the fact that it looses certain amount of water content, becomes hard, brittle and non-plastic when subjected to drying or firing. It is broadly used for different scientific and industrial purposes hence understanding its chemical, mineralogical, and physical charactertics is considered necessary [5; 6; 7] further pointed out that clay mineral is one of the most sorted mineral in industry. Clay is of economic importance utilized industrially in ceramic, paint, and paper industries, petroleum, agriculture, environmental remediation and construction industries. Although the process involved in formation of clay determined its group/type. [6] were of the view that clay mineral is formed from the disintegration of pre-existing rocks during the process of diagenesis and also due to hydrothermal alteration. [8] further reported that clay mineral is an abundant fine textured earthly powder produced by the weathering and disintegration of granite and feldspathic rocks. [9] acknowledge that Nigeria is known to host large reserve of untapped bentonitic clay deposits and this clay is predominantly Ca based. Studies have been carried out on clay mineral occurrence at global scale, which is highly needed in construction, plastic, agricultural and oil industries. In terms of global scale, some of the world-known and most utilized clay were found in Capim River, Brazil [10]; kaolin deposits in Patagonia, Argentina [11]; and kaolins in Georgia, USA [12]; deposits of kaolin in Cornwall, England [13]; and in Tanzania, the Pugu kaolin clays [14], used as standards for identifying kaolinite (29-1488) in X-ray diffraction [15]. Some known clay deposits in Africa include those found in Botswana in Makoro and Kgwakgwe localities [16] and the clay deposit in Abu Darag, Egypt [17]. Studies by [18] suggested that approximately more than eighty clay deposits have been identified across various parts of Nigeria. From detail literature review it was observed mineralogical and chemical charactertics of clay has not been reviewed from regional points of view point of view. Hence this study was aimed evaluating the mineralogical and chemical attribute of clay in southern Nigeria. Furthermore, this paper tends to proffer the quality of clay mineral and suitability for various purpose based on their aforementioned charactertics.

According to [19] four major groups of clay exist namely:

i. Kaolinite

This type of clay is formed from decomposition of orthoclase feldspar. Kaolinite, this mainly comprises of kaolin, it is formed from the gradual disintegration of rocks. In most cases, the colour is pure white to grayish-white. [20] reported that kaolinite is composed of thin, flexible sheets which are pseudohexagonal, having a triclinic crystal structure and a diameter ranging from 0.2–12 μm while the cation exchange capacity (CEC) of kaolinite is less than that of montmorillonite; values within the limits of 2–10 meq/100 g, based on the size of the kaolinite particle, but the rate of the cation exchange reaction is quite rapid.

ii. Illite

It is formed from decomposition of mica and feldspar, in most cases in marine clay and shale. It is the most common type of clay mineral. [20] also stated that illite can be formed under several conditions According to [21], illite mineral display substantially no expanding lattice attribute and is known to show intense peaks of 1.0-nm 001 and 0.33-nm 003 which cannot be altered by ethylene glycol solvation, heating to 550 °C or potassium saturation.

iii. Smectite/montmorillonite

This clay mineral is the result of the product of weathering of mafic silicates, but known to be stable in arid, semi-arid, or temperate climates. It was previously referred to as montmorillonite. It is formed from alteration of mafic igneous rocks, in most scenario rich in Mg and Ca; weak linkage by cations in most cases it leads to high swelling/shrinking potential.

iv. Chlorite

Chlorites do not necessarily fall under the group of clay minerals; hence classified under the phyllosilicate group. The members in chlorite group include cookeite, chamosite, mesite,and daphnite. According to [22] chlorites do not have a general formula and structures.

2. Literature Review on Clay Mineral across Southern Part of Nigeria

Various scholars have carried out extensive research on the mineralogical and chemical attribute of clay and its usability for various purposes. [23] evaluated the suitability of clay for industrial uses, they studied physical properties of clay such as plasticity index, particle size, firing attribute. They further determine mineralogical makeup of clay. Their findings revealed that clay mineral is composed mainly of Illite and Quartz. Findings from geochemical assessment suggested that it contains low Al_2O_3 content and that clay was considered to be of low grade (non refractory) due to low Al_2O_3 content and it was observed that the clay is fine grain. [24] studied chemical,

 DOI: https://doi.org/10.30564/re.v3i2.3057

mineral and geotechnical properties of Iwo and Ijebu clay in Ogun State southwest Nigeria using X-ray, XRD, AAS, wet sieve analysis and Atterberg limits. Findings from their mineralogical study, suggested that the clay consists of kaolinite, illite and montmorillonite in trace amounts, with presence quartz, feldspar and goethite. They concluded that the clays could serve as industrial raw materials for structural wares, colored ceramics and refractoriness industry. [3] studied the clay samples in selected part of Delta state using XRD and XRF, results from their study suggested that the chemical composition of clay was CaO K_2O, MgO, Na_2O, Fe_2O_3, Al_2O_3, SiO_2 and structural water and pointed out heamatite as the major impurity. They concluded that the sampled clays were considered fit for various manufacturing purposes. In the same light, [7] appraised the clay samples in Ifon, Ipetumodu and Iseyin, Ondo, Osun and Oyo states respectively. The study was carried out to identify the physico-chemical properties of clays in the aforementioned towns. Results from there finding revealed that main minerals contained in the clay samples are kaolinite, quartz, microcline, plagioclase/albite and muscovite/illite. The mineralogical composition of clay at Ifon, Ipetumodu and Iseyin makes it suitable for glass and iron making industry. [25], used revealed that X-ray diffraction, ICP-MS and thermal properties was used to study the mineralogical, elementary composition and degree of weathering of clay at Papalanto, Ifo, and Imoto all in Osun state. Result obtained from their study showed that dominant mineral is kaolinite while the accessory minerals include quartz, hematite and anatase, the geochemical composition of clay minerals consist mainly of major oxides such as SiO_2, Al_2O_3, and Fe_2O_3. Finally, they concluded that Papalanto clays possess high plasticity and mouldability. Tests carried out on the clays include firing, water absorption capacities, atterberg limits, and shrinkage values. The results revealed that the Ifo and Papalanto kaolinitic clays could be utilized as raw materials for building bricks, ceramics and other structural wares. Reported by [26] showed that the chemical composition of clays in Bendel and Abia state Nigeria, consists mainly of SiO_2, Al_2O_3, Fe_2O_3 , Na_2O, K_2O, MgO, and CaO. The results of the firing and shrinkage tests depicted values of about 34.40% at 1,250 °C. In summary, they concluded that the clays can be used in industry for the manufacture of ceramics and fired bricks. The mineralogical and physical properties of clay minerals at Ujogba, Edo State Nigeria was evaluated for their possible use in refractories and other applications, findings obtained from mineralogical assessment suggested that the clay minerals consist of mainly SiO_2 and Al_2O_3. While findings from physical property such as refractory property suggested that the clays are good fire-clays. Therefore are considered useful in refractories and ceramic applications [27]. [28] studied clay deposit at Ozanagogo, Delta State, Nigeria with emphasis on their mineralogical composition and further compared it to AOAC standard. Results revealed that iron is the most predominant mineral with Na, K, Ca, Mg, P, Cu, Zn in mg/100g found in significant concentration in the edible clays. He concluded that edible clays especially that from Baleke could be used as a potential source of iron, magnesium and a good source of food for lowering blood pressure. The residual clay deposits are situated at Orin, Igbara odo, Ikere and Ado- Ekiti were studied using mineralogical and geochemical analyses. Findings suggested that the kaolin deposit was formed as a result of hydrothermal alteration and in-situ weathering of granite and aplite. The clay deposit being composed of quartz, phosphates, potassium, iron and aluminum oxides [29]. [30] studied clay minerals in Calabar flank , Niger Delta Basin based on mineralogical, chemical and diagenesis process using ABS. From the result obtained from the study, it was seen that there are five major clay minerals namely, kaolinite, illite, smectite, and chlorite alongside proportions of mixed-layer (illite/smectite), while major oxide analysis indicated significant concentrations of SiO_2, AI_2O_3, Fe_2O, CaO, Na_2O, K_2O and MgO and that diagenesis of the clays resulted in the occurrence of alternating sequences of sandstones/shales. [31] evaluated the mineralogical, physicochemical (Ec, pH and PSD) and chemical charactertics of clay in parts of Eastern Dahomey and Niger Delta Basins, Nigeria using X-ray, SEM and DTA methods. From their findings it was observed that the clays have low Ec and pH values. It was also noted that the major oxides in the clay are SiO_2, Fe_2O_3, Al_2O_3 and TiO_2. Based on comparison with specifications and standards, the kaolins cannot be used for industrial purpose. However, they recommended that the Cretaceous Lakiri kaolins can be used in the paper and ceramic industry (except for kaolins having high TiO_2 and K_2O content). [32] used XRD to evaluate the suitability of clay mineral as raw material in Ikpankwu, Okigwe down to Ohiya in the Okigwe-Umuahia axis. Results from the study showed that the clays are mainly kaolins; with traces of bentonite and dickite, non clay mineral content included quartz and iron. They also observed that chemically the clay within the study area is made up of SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O and MnO. They were of the view that clay mineral that was compared to specific standard was considered good for some engineering and economic purpose. A study carried out by [33] on the characterization of clay deposits within the Abakaliki Formation in the Southern Benue Trough Nigeria, revealed that the clay

DOI: https://doi.org/10.30564/re.v3i2.3057

was made up mainly of montmorillonite and illite with traces of kaolinite, major oxide analysis suggested the presence of high content of calcium and potassium oxides. [34] also assessed bentonite clays from the Niger Delta Basin. Results showed that the clays consist mainly of montmorillonites rich in calcium and chemically stable. It was also observed that beneficiation of the clay samples with sodium carbonate will improve their rheological properties, which is indicative of a good functional application in drilling mud application.

2.1 Overview of Clay Deposit in Nigeria

Reports from RMRDC and NMC showed that deposits of clays in Nigeria was projected to be slightly above 700 million metric tons[35, 36, 37,38, 39], with large percentage of it is deposited at Afuze, Edo state south-south, Nigeria having a tonnage of about 70–80 million metric tons of bentonite clay [33,40]. [41] reported that apart from the above mentioned proven reserve of bentonite deposits, there are other localities with bentonite deposits in Nigeria. Hence, there is need for further investigation to ascertain estimated reserves, and possible characterization of the clays to determine their functional applications. [42,39,45,46] reported that barite deposit in Nigeria has been identified in states like Taraba and Bauchi which have about 7.5 million metric tons. Other parts of Nigeria with significant concentration of bentonite deposits are the NE region including Gombe, Adamawa and Borno states. In the same vein, [33,40] reported that barite deposit in Nigeria have been indentified in states like Taraba and Bauchi which have about 7.5 million metric tons, other parts of Nigeria with significant concentration of bentonite deposits is the north-east region of Nigeria these include Gombe, Adamawa and Borno states. In the same vein, [33, 40] reported the presence of bentonite clays in Abakaliki Formation SE, Nigeria with substantial quantities. [46] reported the occurrence of clay deposit in Abia, Anambra and Lagos states for more on this see Table 2. On the other hand, [46] acknowledged that bentonite can be found across all the states of Nigeria. Studies from various scholar suggested that clay deposit can out rightly be a major source of foreign exchange earnings if it is properly harnessed [5], [9], [25], [47, 48]. reported that Niger Delta region of Nigeria has a proven reserve estimated to be approximately 4 billion tons of clay deposits alone, while the north eastern parts of Nigeria have estimated value of 700 million tons in its pure untreated state. RMRDC has previous carried out research to estimate bentonite in Nigeria, [49] proposed estimated value and the location of proven reserves of bentonite clays across various part of Nigeria as presented on Table 1.

Table 1. States were clay deposit in Nigeria and their reserve estimate [49]

State	Area	Estimated reserve	Remarks
Abia	Bende, Isiukwuato and Ikwuano Arochukwu Umuahia,	5.8-7.5 Million tones	Generally, subsequent investigation is required.
Adamawa/Taraba	Gujbai (Mutai)	Not yet quantified	
Akwa Ibom	Itu	-	
Anambra	Awka	-	
Borno	Gamboru, Marte, Ngala, Dikwaand Mongunu	700 million tones	
Cross River	Ogurunde	-	
Ebonyi	Ohaozara, Edda and Abakaliki	-	Product of Afikpo-Sub Basin and Asu River Group of Southern Benue Trough
Edo	Akoko-Edo, Afuze, Esan, Etsako,o Okpebhio and Owan	-	
Delta		-	
Imo	Isu, Okigiwe, Orlu and Oru	5.8-7.5Million tones	
Kebbi	Jega	Not yet quantified	Discovered in Benin Formation
Gombe	Gombe, Akko and Yamaltu-Deba	-	-

Table 2. Village and town where there is clay southern Nigeria. Modified after [50]

Location	State
Alige,Betukwe, Behuabon, Mba, Ogurude	Cross River State
Itu, Ntok, OpkoMbiafum, Ikot Ekwere,	Akwa Ibom state
Ohaozara, Afikpo, Amuvi, Okobo, Obotme, Nkana, Amakaofia	Ebonyi state
Awka, Okija	Anambra state
Enugu East, Enugu North, Enugu South, Ezeagu Igboeze North, Isi-Uzo, Uzo-UwaniNsukka, Udi, Oji, Nkanu West	Enugu state
Aniochia South, Ughelli South, Ndokwa East, Eku, Nzu, Ubulu-Uku	Delta
Ubiaja, Ujogba	Edo
Agbaja	Kogi
Bendel, Umuahia South, Ikwuano, Isiukwato, Nnochi	Abia
Okpokwu, Ogbadibo, Apa, Vandikya	Benue
Irewole, Ilfe-Ife, Ede, Odo-Otin, Ilesha	Osun
Alakia, Iwo	Oyo
Mbano, Ehime, Mbaise, Orlu, Ahiazu, Okigwe, Oru, Okpalla, Awo-Omama	Imo
Omifun, Ewi, Abusoro, Abusoro, Odo-Aye	Ondo
Ikere-Ekiti, Isan Ekiti, Orin, Igbara, odo	Ekiti
Onibode, Ibeshe, Lakiri, Iwo, Ijebu, Ekuru	Ogun

 DOI: https://doi.org/10.30564/re.v3i2.3057

2.2 Use of Clay Mineral

Clay mineral is used for the following:

i. Drilling mud, animal feeds, waste water treatment;

ii. Making filters, seizing, in purifying sewage;

iii. Domestic and commercial wares [51,52,53];

iv. Pharmaceuticals, paint, catalysts used for cracking in petroleum industries and manufacture of auto exhaust emission catalyst control devices and cosmetics [54];

v. Iron casting;

2.3 Method used in Determining Mineralogical, Chemical and Suitability of Clay for Various Purposes

These methods include the following:

i. Cation Exchange Capacity (CEC) is used to determine the rate of exchange of reaction;

ii. X-ray diffraction (XRD) analysis is used for determination of mineralogical properties;

iii. Morphological analysis is used for determination of crystal structure;

iv. X-ray fluorescence (XRF) analysis is used for determining the major oxide presence in clay;

v. Statistical methods for determination of variable on the bulk chemical data from XRF analysis;

vi. Atterberg test is used to determine plasticity limit, liquid limit, and shrinkage;

vii. Electron diffraction, energy-dispersive;

viii. Differential thermal analysis, electron microcopy and infrared spectroscopy [55];

ix. Electron microscopy (EM) is used for employed for complementary mineral characterizations;

x. Loss on Ignition is used loss in weight after the clay was heated and it was expressed as percentage of the original weight;

3. Geology/Chemical Processes Involve in the Formation of Clay

From geological point of view the study area cuts across part of sedimentary (Niger Delta Basin, Anambra Basin, Benue Trough) hard rock terrain (Precambrian Basement Complex). The gradual disintegration of silicate bearing rocks by chemical action (carbonic acid and other dissolved solvents) over a long period of time results in the formation of clay minerals. Clays have a particle size of less than 2 μm, it is plastic with some water content, expands on wetting, but shrinks upon drying and hardens when fired [56, 57, 58]. Clay mineral is known to be formed through hydrothermal activity. Clays are argillaceous alteration products due to hydrothermal action. Argillaceous products from hydrothermal alteration are usually associated with hot springs. There is normally a zonal arrangement of the clay minerals; kaolin and mica are close to the source while montmorillonite and kaolinite are more distant. Generally, clays are classified into two primary and secondary clay deposits. Primary clays are formed as residual deposits (due to weathering) and remain at the site of formation, while secondary clays are clays that have been ransported from their site of formation by water erosion and deposited in a new sedimentary terrain. Clay deposits are usually located in very low energy depositional environments such as large lakes and marine basin [59]. [22,60] discussed that clay is made up of minerals with tiny particles and a complex structure having a high specific surface area which permits porosity. The nature of the parent material, vegetation, topography, climate, vegetation and time help to determine the characteristics of the clay mineral [61]. The character and direction of movement of water through the alteration zone helps to influence its weathering. The nature of the parent material is more important in the early stages of weathering than when the weathering has continued for long periods of time. When the dominant movement of water is downward through the alteration zone, any alkalis or alkaline earths found in the parent material are likely to be leached out. Primary minerals having concentrations of these compounds are broken down; in the case of micas, they are broken down. If there is intense leaching after the removal of the alkalis and alkaline earths, alumina or silica are depleted from the zone of alteration depending on the pH of the downward seeping waters [45]. The pH of such water is influenced by the climate and vegetation cover. When there is a warm, humid condition with long wet and dry period the surface organic material is completely oxidized hence, the downward seeping waters are neutral or slightly alkaline. In such situations, SiO_2 is removed, while Al_2O_3 and Fe are left behind and concentrated.

3.1 Clay Deposit in Precambrian Basement

The weathering of Precambrian Basement rocks leads to the generation of superficial clay mineral deposits. A major progenitor of clay deposits is feldspar, which is a constituent mineral in granitic rocks. Clay deposits are found in areas where there is high level of kaolinization due to hydrothermal alteration, which is a major feature in areas where Pan-African magmatism is prevalent [62]. The clay formed is not only due to the nature of parent rock but also due to the degree of weathering and the length of time during which it formed [63]. Clay deposit is widely distributed in the Precambrian Basement Complex of Nigeria [64,65]. Several researchers have studied some of these clays from various

DOI: https://doi.org/10.30564/re.v3i2.3057

perspectives [64,67,68]. For example, [64] studied primary clay deposits from seven localities representing different rocks in the Nigerian Basement Complex. Findings from their study suggested that weathered rocks such as granites, pegmatites, gneisses, and schists consisted mainly of kaolinite and trace concentrations of illite and montmorillonite, while deposits that weathered from calc-silicate rocks contain high concentrations of montmorillonite.

3.2 Clay Deposit in Niger Delta State

Previous scholars reported the deposit of clay in Niger Delta region of Nigeria. It was observed that clay its estimated reserve is estimated to be approximately about 4 billion tons, while the NE region of Nigeria has a total of 700 million tons in its pure untreated state [47,48].

3.3 Study Area/Climate and Physiography

The study covers southern part of Nigeria; it comprises the following states namely; Delta, Edo, Anambra, Enugu, Ebonyi, Kogi, Benue, Cross River, Abia and Ekiti states as shown in Figure 1. The study area falls within tropical rainforest belt of Nigeria with temperature ranging from 28^0 C to 30^0 C. It is characterize by two main season the dry and wet season, the dry season that spans from the month of November to March. It is also has an average rainfall of about 60 mm. [69] reported that the highest rainfall is recorded around highlands based on convectional and orographic nature of the rain received. [70] stated that rainfall pattern is highly influenced by the movement of ITCZ is characterized by a wet season from April to July, a short dry season in August, followed by a short dry season in August followed by a short wet season from September to October.

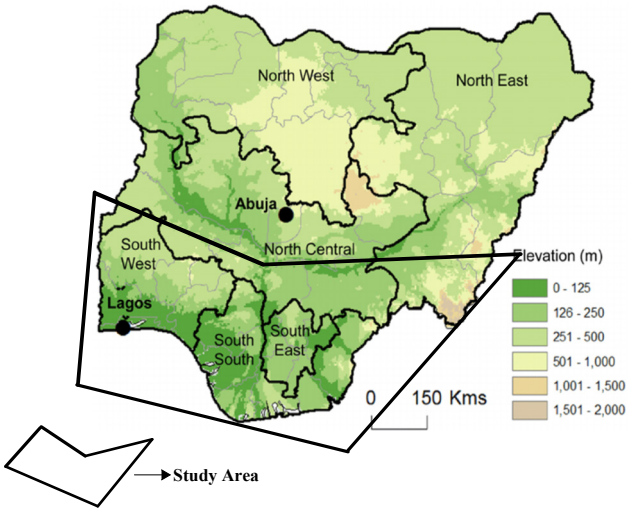

Figure 1. Map of Nigeria showing selected part of the study area (Modified after [71]).

4. Discussion

Results from the reviewed article, suggested that montmorillonite is one of the major mineral that is found in clays across the study area. Several authors suggested that montmorillonite is commonly found but at low concentrations in soil,sediment load of natural waters, and in airborne dust. [2,72] reported that kaolinite is the most abundant clay mineral found in clay in Ogun, Edo and Delta State, Nigeria as shown in Table 3. From their study, one could conclude that kaolin clay is a major clay found within the area they studied any clay that consist mainly of kaolinite with presence of other mineral is referred to as ball clay. Although, [73] were of the view that Kaolin clay in most situation is found associated with some mineral impurities such as quartz, hematite, montmorillonite, mica, illite, ilmenite, feldspar, zircon, graphite, bauxite, rutile, titaniferrous, silliminate, halloysite, attapulgite and carbonaceous materials, which might impair their industrial use. The chemical structure of kaolin as clay mineral is $Al_4(Si_4O_{10})(OH)_8$. [5] reported that the pH of 3 and high leaching environment is considered for the formation of kaolinite and halloysite. On the contrary, relatively low or no leaching environment and conditions under neutral to low alkaline pH favor the generation of montmorillonite and three layer clay minerals [6]. [74] pointed out that kaolinitic clays classification according to technological use is based on possible application to differentiate between brick clays, ball clays, fire or refractory clays, flint clays, under clays and bloating clays. [75] further stated that other classification comprises of several classes like low-grade kaolins, high-grade kaolins, light-firing clays, kaolinitic loams, raw kaolins, dark-firing clays and ball clays. From reviewed literature it was observed that one major clay mineral that is found in clay across southern part of Nigeria is montmorillonite and illite as reported by for more this see Table 3. [22] stated that illite is a common type of clay mineral, with general formula $(K, H)Al_2(Si, Al)_4O_{10}(OH)_2 \cdot XH_2O$. Generally, illite is considered as rock forming mineral that mainly consists of shale. The structure of illite group is same as that of montmorillonite group with presence of SiO_2 layer and Al_2O_3 layer in the same stacking pattern. lllite group is one of the major component in clay that is useful for making cooking pots, plates, tiles and bricks [77]. In the same vein the general formula for montmorillonite is $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2 \cdot XH_2O$, There are several reports that montmorillonite is a good insulator of heat and heat resistant effect make its useful for additive in any substance, the inclusion of montmorillonite in material,

 DOI: https://doi.org/10.30564/re.v3i2.3057

polymer, and products may lead to a significant enhancement. There have been a series of reports that montmorillonite is used to aid resistance to nausea and diarrhea, supportive to health and growth, resistance to tooth decay, drug delivery system, adsorption of dyestuff, adsorption of toxic heavy metals and polymer industry [22,78]. [76] reported that clay in selected parts of Ogun state is found associated with some mineral impurities such quartz, biotite, calcite, and feldspar. Several scholars reported the presence of chlorite in clay [79,80], chlorite is one of the main component of clay but from reviewed literature is observed that chlorite is not largely found in studied clay across Nigeria. Study conducted by [3] revealed that clays in open marine environment contains mainly of illites, montmorillonite and chlorites with illites and an increase in chlorite concentration seawards and reduction in kaolinites concentration seawards. Chlorite is formed the disintegration of mafic silicates in a cool, dry temperature, although there have been report that is found in most metamorphic rocks; ranging from low-grade to high-grade metamorphic rocks. Clays are also known to occur in shales. Findings from [79,80] revealed that chlorite mineral was found in sedimentary terrain in Nigeria. The general formula of chlorite $(Si.Al)_8(Mg.Al)_6O_{20}(OH)_4.(Mg.Al)_6(OH)_{12}$. [22] were of the opinion that each member of this mineral (amesite, chamosite, cookeite, nimite, etc) has its own separate formula. [81] identified halloysite with chemical formula as $Al_2Si_2O_5(OH)4.2H_2O$ as an important clay mineral found in clay in Edo State, Nigeria. They also reported the presence of other minerals such as muscovite, phlogopite, seipolite, hydrobiotite, and osumulite. They went further to report the presence of other clay and non-minerals such as quartz, feldspar, mica, muscovite, illite, montmorillonite and kaolinite respectively [82]. It was observed that studied clays at Uzebba, Edo State Nigeria consist mainly of sepiolite, chlorite and kaolinite. They further stated that all clay fractions are dominated by kaolin, either kaolinite, halloysite, or a mixture of both. Previous research by [83] in Niger Delta part of Nigeria showed that mineral found in clay are kaolinite, illite/mica, mixed-layer illite/smectite, but the major clay mineral is kaolinite, but mixed-layer (illite/smectite) is composed of ordered interstratified clay, the chemical property of clay was not studied. Further stated that clay volume tends to decrease in samples with increased carbonate and/or quartz. Study carried out by [84] showed that clays from selected part of southeastern Nigeria have properties that similar to those of the naturally active bentonites found in Wyoming and Texas which are utilized in the industry as drilling mud. Rheological and physical attributes of the clay were however, said to be poor. [40] were of the opinion attributes of the Abakaliki is considered useful in pharmaceutical, textile, cosmetic and polymer industries. In, the same vein [84]; [40] were of the view that clay mineral in southern eastern Nigeria is considered poor in terms of quality for use as drilling mud in oil industry. [85] studied the chemical properties of clay at Obukpa, Nsukka Local Government Area of Enugu state using AAS method sampled clay was collected at Ajona-Obukpa randomly. Findings from their study showed that clay is chemically composed of AI_2O_3, CaO, MgO, Na_2O, MnO, Fe_2O_3 and K_2O see Table 3. They further pointed out that the presence of alkali oxides such as Na2O K_2O, CaO in clay denotes that sampled clay shows good fluxing ability during firing at low temperature to form glasses of diverse compositions thereby making its good structure to the ceramic product and that Fe_2O_3 in clay was slightly higher than the above required for refractory bricks and ceramics, but the required standard for paper production, the high Fe_2O_3 content in clay makes it reddish in colour. Although by [86] reported the presence of Fe_2O_3 in clay mine at Nkpologu at Uzo- Uwani Local Government Area of Enugu state with negligible amounts. They further reported that SiO_2 content in studied clay was higher than other oxide such as Al_2O_3, Na_2O, CaO, MgO, K_2O, with the least oxide as MnO. From their findings, it was observed that studied clay was confirmed suitable for moulding sand.

5. Conclusions

Nigeria is projected to have over 700 million metric tons of clay deposit. This huge amount of clay deposit is believed to meet the increasing demand for clay mineral. Based on this it is important to evaluate the chemical and mineralogical charactertics of clay at a regional scale, for

Table 3. Related research on clay mineral deposit in southern part of Nigeria and their mineralogical findings

Researcher(s)	Study area	Experiment used	Geochemical Findings	Mineralogical findings
[87]	----	XRD(mineralogical composition),	--	**MINE:** montmorillonite
[76]	Abia state	XRD(mineralogical composition),	--	**MINE:** montmorrillonite, kaolinite biotite, calcite **Non Clay Mineral:** feldspar, quartz,
[88]	Akwa Ibom state	XRD(mineralogical composition),		

DOI: https://doi.org/10.30564/re.v3i2.3057

Researcher(s)	Study area	Experiment used	Geochemical Findings	Mineralogical findings
[4]	Enugu state	XRD(mineralogical composition),	--	**MINE:** montmorillonite
[89]	Edo state	XRD(mineralogical composition),	--	**MINE:** montmorillonite, quartz, kaolinite,
[91]	Niger Delta	XRD(mineralogical composition)	--	**MINE:** kaolinite, montmorillonite, illite
[33]	Ebonyi State	XRD(mineralogical composition), chemical properties and geotechnical test	**CEO:** Al_2O_3, SiO_2, Fe_2O_3, MgO, K_2O, MnO, Na_2O, CaO , TiO_2	**MINE:** montmorillonite, kaolinite, biotitie, lllite, calcite **Non-clay Mineral:** quartz, feldspar,
[40]	Ebonyi State	XRD(mineralogical composition), Chemical and geotechnical test	**CEO:** Na_2O, CaO , K_2O	**MINE:** Illite, montmorillonite, Kaolinite
[91]	Akwa Ibom	XRD(mineralogical composition),	--	**MINE:** kaolinite **Non-clay mineral:** quartz and trace amounts of goethite
[72]	Ogun State	XRD(mineralogical composition), ICP-MS (chemical Properties)	**CEO:** Al_2O_3, Fe_2O_3, SiO_2	**MINE:** kaolinite is the most abundant mineral in clay
[92]	Enugu State	XRD(mineralogical composition),	--	**MINE:** montmorillonite
[93]	Anambra State	XRD(mineralogical composition),	**CEO:** SiO_2	--
[94]	Edo, Ekiti, Ondo, Ogun state	XRD(mineralogical composition),	**CEO:** Al_2O_3, SiO_2, P_2O_5, Fe_2O_3, MgO, K_2O, MnO and TiO_2	--
[2]	Delta state	XRD(mineralogical composition),	**CEO:** CaO, Al_2O_3, SiO_2	**MINE:** kaolinite
[95]	Kogi state	XRD(mineralogical composition),	**CEO:** MgO, K_2O, Al_2O_3, SiO_2	
[7]	Osun state	XRD(mineralogical composition),		**MINE:** Kaolinite, muscovite/illite, microcline, plagioclase/albite **Non-clay mineral:** quartz
[59]	Ogun State	XRD(mineralogical composition),	**CEO:** SiO_2, Al_2O_3, Fe_2O_3	**MINE:** hematite **Non-Clay mineral:** quartz, anatase
[26]	Abia	XRD(mineralogical composition),	**CEO:** Fe_2O_3, Na2O, K2O, SiO_2, Al_2O_3, CaO , LOI	
[82]	Edo state	XRD(mineralogical composition),	**CEO:** SiO_2, Al_2O_3	**MINE:** kaolinite, halloysite, illite, **Non-clay mineral:** Mica, quartz, feldspar
[81]	Edo State	XRD(mineralogical composition),	**CEO**: SiO_2, Al_2O_3	**MINE:** kaolinite, illite, Halloysite, Hydrobiotite, Phogopite, Osumulite, Sepiolite, Muscovite **Non-clay mineral:** quartz, mica, feldspar,
[68]	(Okija) Anambra and (Ubiaja) Edo State	XRD(mineralogical composition),	**CEO:** MnO, Na_2O, K_2O, MgO, CaO, Fe_2O_3, TiO2, SiO_2,	**MINE:** kaolinite, illite
[27]	Edo	XRD(mineralogical composition),	**CEO:** SiO_2, Al_2O_3	**MINE:** kaolinite,
[29]	Ekiti	XRD(mineralogical composition),	**CEO**: MnO, Na_2O, K_2O, MgO, CaO, Fe_2O_3, TiO_2, SiO_2, P_2O_5, SO_3	**MINE**: kaolinite **Non Clay mineral:** quartz
[31]	Delta, Ogun State	XRD, DTA, SEM was used to determine mineralogical properties,	**CEO**: SiO_2, Al_2O_3, Fe_2O_3, TiO_2	**MINE:** muscovite, anatase, goethite **Non-clay mineral:** quartz,
[96]	Ebonyi	XRD(mineralogical composition),	**CEO:** SiO_2, Al_2O_3	MINE: --
[6]	Ebonyi	XRD(mineralogical composition),	CEO:--	**MINE:** kaolinite, illite, smectite

 DOI: https://doi.org/10.30564/re.v3i2.3057

Researcher(s)	Study area	Experiment used	Geochemical Findings	Mineralogical findings
[97]	Ogun	XRD(mineralogical composition), FTIR analyses	CEO: ---	**MINE:** hematite, goethite **Non-clay mineral:** quartz
[40]	Ebonyi	XRD(mineralogical composition),	**CEO** SiO_2, Al_2O_3, CaO, K_2O, Na_2O, TiO_2, MgO, Fe_2O_3, MnO	**MINE:** Kaolinite, montmorillonite, illite, biotite, IIIite, calcite, **Non-clay mineral:** feldspar, quartz
[72]	Ogun	XRD(mineralogical composition),	**CEO:** SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, MnO **TE:**Ba, Sr, Y, Sc, Be, Zr, V	**Mine:** Kaolinite **Non-clay mineral:** quartz
[79]	Calabar	XRD(mineralogical composition),	**CEO:** SiO_2, AI_2O_3, MgO, Fe_2O_3, CaO, Na_2O, K_2O	**Mine:** illite, kaolinite, Chlorite, smectite
[80]	Akwa Ibom	XRD(mineralogical composition) and chemical test	**CEO:** SiO_2, Fe_2O_3, MgO, CaO, Na_2O, K_2O AI_2O_3	**Mine:** smectite, illite, kaolinite, chlorite
[90]	Niger Delta	XRD(mineralogical composition),	**CEO:** SiO_2, CaO, AI_2O_3,MgO, Fe_2O_3, CaO, Na_2O, TiO_2, K_2O	**Mine:** Kaolinite, montmorillonite, Illite
[32]	Abia	XRD (mineralogical composition), geochemical	**CEO:** SiO_2, Al_2O_3, Fe_2O_3,TiO_2, CaO, MgO, Na_2O, MnO	**Mine:** Kaolinite,
[83]	Niger Delta	XRD(mineralogical composition)	CEO: --	**Mine:** Kaolinite, illite/mica, mixed-layer illite/smectite
[5]	Ebonyi	XRD and XRF	**CEO:** SiO_2, AI_2O_3, MgO, Fe_2O_3, CaO	**MINE:** illite, montmorillonite, kaolinite **Non-clay** mineral: quartz, feldspar
[85]	Enugu	AAS	**CEO:** AI_2O_3, CaO, MgO, Na_2O, MnO, Fe_2O_3, K_2O	--
[86]	Enugu	XRF	**CEO:** Al_2O_3, Na_2O, CaO, MgO, K_2O, Fe_2O_3, MnO	--

possible use in the industry. Clay clay mineral is highly needed across various industries such as oil and gas, pharmaceutical, steel, ceramics and other industries, hence it needs to continually evaluate and determine the quality and quantity of clay mineral across the country. The most common approach used in determination of chemical properties of clay is XRD, although DTA, SEM method was used to determine chemical properties. Some other approach used to determine clay mineral include XRF, ICP-MS, DTA and SEM. The study reviewed previous literature of clay mineral in southern Nigeria, with emphasis on their mineralogical and geochemical properties. Findings from the study showed that montmorillonite is the major clay mineral, with emphasis on their mineralogical and chemical properties. Findings from the study showed that montmorillonite is the major clay mineral, with some other minerals such as illite, kaolinite, with other non clay minerals. Findings from the study revealed that clay mineral in southern part of Nigeria is considered suitable for various use except for drilling purpose in oil and gas sector. It is advised that regional additional information on particle size analysis of clay mineral is needed to determine the suitability of clay mineral for manufacturing industries.

Nomenclature

CEO = Chemical analysis
TE = Trace element
MINE = Mineralogical analysis
Fe_2O_3 = Hematite
Na_2O = Sodium Oxide
K_2O = Potash
SiO_2 = Quartz
Al_2O_3 = Alumina
CaO = Quick Lime
LOI = Loss on Ignition
RMRDC= Raw material Research and Development Council
XRD = X-Ray Diffraction Analysis
XRF = X-Ray Fluorescence Analysis
AAS= Atomic Absorption Spectroscopy
ICP-MS = Inductively Coupled Plasma Emission Mass Spectrometer
AOAC = Association of Official Analytical Chemist
SEM = Scanning Electron Microscopy
DTA = Differential Thermal Analysis
PSD = Particle Size Distribution
CEC = Cation Exchange Capacity
NMC = Nigerian Mining Corporation

DOI: https://doi.org/10.30564/re.v3i2.3057

FTIR = Fourier Transform Infrared
TE = Trace Element

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