GEOCHEMICAL, MINERALOGICAL AND SEDIMENTOLOGICAL APPRAISAL OF CLAY DEPOSITS IN IGUORIAKHI, OFUNMWENGBE AND ENVIRONS SOUTHWEST NIGERIA FOR INDUSTRIAL USES.

BY

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BENIN CITY.

AUGUST 2023

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A DISSERTATION IN THE DEPARTMENT OF GEOLOGY SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DOCTOR OF PHYLOSOPHY GEOLOGY (MINERAL EXPLORATION) OF THE UNIVERSITY OF BENIN, BENIN CITY.

AUGUST 2023

DECLARATION

I declare that the work in the project thesis entitled **"Geochemical, Mineralogical and Sedimentological Appraisal of Clay Deposits in Iguoriakhi, Ofunmwengbe and Environs Southwest, Nigeria for Industrial Uses."** has been performed by me in the Department of Geology, University of Benin, Benin City under the supervision of **Professor O. I. Imasuen.** The information derived from literature has been duly acknowledged in the text and list of references provided. No part of this project thesis was previously presented for any other degree or diploma at any university.

…………………………………….. **…..………………**

Samaila Bangshika BAKARI **Date**

CERTIFICATION

We certify that the thesis was carried out by **Samaila Bangshika BAKARI** in the Department of Geology, University of Benin, Benin City, Edo State, Nigeria.

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Prof. O. I. Imasuen **Date**

Thesis Supervisor

……………………………… …………………

Dr. S. A. Salami **Date**

Head of Department

DEDICATION

This Thesis is dedicated to my late Father and Role Models of blessed memories: Mr. Bakari Musa Wadumbiya, Dr. Ronald Nze Eyime, Dr. Bala Jones Takaya and Prof. W. O. Emofurieta for the roles they played in my life to get me to where I am today, may their gentle souls continue to rest in peace. Amen.

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Finally, to my wife Mrs. Queen Bakari, my daughter Princess Aaliyah Bakari and my son Prince Elgibbor Bakari thank you for your patience, love, support and prayers.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Geochemical and mineralogical determination of clay deposits with integrated sedimentological characterization of their physical properties are fundamental in bridging the knowledge gap and raw material feed for industrial processes and applications. In this study, I investigated clays at locations with relatively little or no investigations carried out to discover the untapped mineral deposits. The clay deposits situated at Iguoriakhi, Ofunmwengbe and environs were investigated using several analytical techniques; X Ray Diffractometry (XRD), X Ray Fluorescence Spectroscopy (XRF), Hydrometer Method, Wet Sieving Analysis and other geotechnical techniques. The average abundance of minerals in the samples derived from the XRD Peaks indicates that Clay minerals present include; Kaolinite, ranges between (19.52% - 22.33%) and (24.24% - 28.60%), Montmorillonite (10.49% and 4.6%), Illite (5.24% and 4.07%) and associated non clay minerals include; Mica (5.50% - 7.02%) and (4.88% - 6.03%), Feldspar (6.02% - 6.53%) and (3.03% - 3.50%), quartz (49.77% - 52.80%) and (54.11.0% - 55.99%) for Iguoriakhi and Ofunmwengbe samples respectively. Geochemical signatures Al_2O_3/TiO_2 ratio for clastic rocks used to determine origin indicates that the Al_2O_3/TiO_2 for Iguoriakhi and Ofunmwengbe clays range between (23.73 – 50.40) and (22.92 – 51.88) respectively signifying that the clays originated from intermediate to felsic igneous rocks. The high Chemical Index of Alteration (CIA) ranges between 86.14 - 93.57 and 86.05-93.47, Chemical Index of Weathering (CIW) between 93.59 - 97.71 and 93.55 - 97.67 and Weathering Index of Parker (WIP) between 10.27 - 12.02 and 10.04 - 12.1. The CIA, CIW and WIP values for Iguoriakhi and Ofunmwengbe clays respectively indicates a highly intense degree and almost complete weathering of parent rock minerals to clay. This is confirmed by the low amount of detrital feldspar and mica in the XRD peaks. The average sum of (K_2O + Na_2O) and (Fe_2O_3 + MnO + TiO_2) for Iguoriakhi (1.20% and 4.14%) and Ofunmwengbe (1.16% and 4.38%) clays respectively, are very low indicating that the clays are chemically inert and non-corrosive, signifying a high degree of leaching away of the alkali metals thus increasing the fertility of the soil for farming and agricultural purpose. The geochemistry of the clays reveals high composition of Al_2O_3 with average abundance of (28.77% and 29.01%), this indicates that the Al_2O_3 can be extracted for fertilizer and animal feeds production. The Average natural Moisture Content (AMC) values were 14.93% to 25.82%; Liquid Limits (LL) between 62.5% and 129.0%; the Optimum Moisture Content (OMC) and Maximum Dry Density (MDD) between 25.5% to 42.2% and 1.10 g/cm^3 to 1.32 g/cm^3 respectively; and Specific Gravity (SG) between 1.81 and 2.05. These indicate the characteristics of a soil composition with a significant fine content predominantly clay. The industrial potential of the clay deposits based on their physical and chemical characteristics indicates that the clays with little beneficiation compare favourably with other industrial specifications suitable for the ceramics industry, pharmaceutical, paint and agricultural industries.

CHAPTER ONE

1.1 Introduction

Clay minerals are widely encountered in industrial processes ranging from ceramics manufacturing, oil exploration and production, nuclear waste storage to management of water resources and civil engineering or soil science.

Clay minerals are found to be the most interesting class of minerals that have attracted substantial worldwide attention and investment in research and development. Clay minerals are considered as gift to mankind because of their low cost, environment friendly, easily available and non – toxic. Clay minerals are so widespread that in the world, there is hardly any country where there are no deposits of one or other kind of clay minerals. In nature, clay minerals are found with certain physical and chemical characteristics which play an important role in different fields from research to industries Kodama H. (2020). The clay minerals are a class of rock-forming minerals having porous like sheet structure with different distances between the sheets.

Clay minerals are the characteristic minerals near the earth surface environment with variable amount of ions like iron, magnesium, alkali metals, alkaline earth metals and other cations. They are considered as important constituents of soil and form by diagenetic and hydrothermal alteration of rocks in presence of water Tong W.K. (2000) which could either be residual or transported:

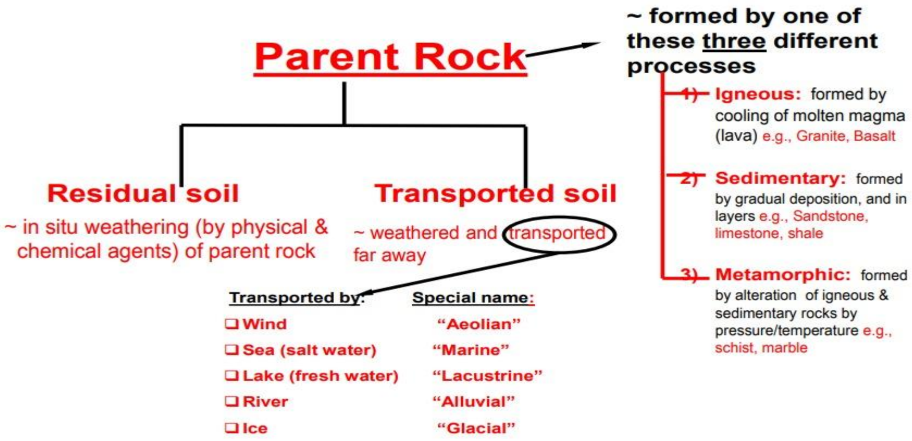


Figure 1.1. Clay formation through weathering and neoformation in soils.

From (figure 1.1) clays are formed as residual clays found in the place of origin (in situ) and formed by surface weathering which give rise to clay through; Chemical decomposition of rocks, such as granites containing silica and alumina or by solution of rocks, such as limestone containing clayey impurities which being insoluble are deposited as clay, also through disintegration and solution of shale Kerr P.F. (1952). Transported clay: also known as sedimentary clay, removed from the place of origin by erosion and deposited in a new and possibly distant position.

Clay minerals such as kaolinite, smectite, chlorite, micas are main components of raw materials of clay and formed in presence of water. They are known as hydrous phyllosilicate having silica, alumina and water with variable amounts of inorganic ions like Mg^{2+}, Na^{+}, Ca^{2+} which are found either in interlayer space or on the planetary surface.

1.1.1 Definition of Clay

Georgius Agricola (1494–1555) the founder of geology was seemingly the first who gave the definition of clay in 1546. It has been modified several times due to questions regarding the constituents and other properties. The latest effort to solve all these issues was done by the Joint Nomenclature Committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS). According to these societies, clay is defined as a naturally occurring material composed mainly of fine-grained minerals, become plastic in presence of water and hard when dried or fired. Bergaya F. and Lagaly G. (2006) and Guggenheim S. et. al. (1995).

The definition of "clay" was formalized in 1546 by Agricola Guggenheim S. et al. (1995). However, it has been revised many times since then although the fundamentals involving plasticity, particle size, and fire hardening were retained by most Ni J. et al. (2013). Clay is an earth material that is plastic when moist but hard when fired and composed mainly of fine particles of hydrous aluminum silicates and other minerals as defined by Rao K.S. (2013). Based on composition clay is a crystallized aluminum silicate which contains other impurities. Secondary components of clay can be quartz grains of and, more rarely, zircon, apatite, granite and others Saba S. et al. (2014).

Clay can incorporate with one or more clay minerals even in presence of minute quantities of quartz (SiO_2), metal oxides (Al_2O_3, MgO etc.) and organic matter Augustyn A. (2020). The plasticity of clays is due to their particle size, geometry as well as content of water and become hard, stiff, coherent and non: plastic upon drying or firing. Plasticity and hardness are greatly affected by the chemical composition of the material present in the clay. Clays are easily molded into any form that they retain when dry, and they become hard and lose their plasticity when subjected to heat.

In all definition of clays, the particle size is a key parameter, the Geologists and soil scientists usually consider a particle size of 2 μm (clays being finer than silts) for the separation, sedimentologists apply 4–5 μm, and colloid chemists use 1 μm Guggenheim S. and Martin R.T. (1995). According to Geotechnical engineers, differentiation between silts and clays can be done on the basis of the plastic characteristics of the soil, as measured by the soils' Atterberg limits. The clay can appear in different form of colours from white to dull grey or brown to deep orange and red depending on the soil's content.

1.1.2 Formation of Clay Minerals

The formation of clay minerals is due to the chemical weathering of rock Tong W.K. (2000) and Hillier S. et al. (2003). The chemical and structural composition of clay minerals are found to be similar to the primary minerals which originate from the crust of earth mainly from igneous or metamorphic rocks. Transformations may occur in ambient conditions. Although some of the most resistant primary minerals such as quartz, micas and feldspar may remain in soils whereas other less resistant primary minerals (pyroxenes, amphiboles) are susceptible to breakdown by weathering, thus forming secondary minerals. The resultant secondary minerals are formed due to either modification of the primary mineral structure (incongruent reaction) or neoformation through precipitation or recrystallization of dissolved constituents of primary minerals into a more stable structure (congruent reaction) as shown in (figure 1.2) below.

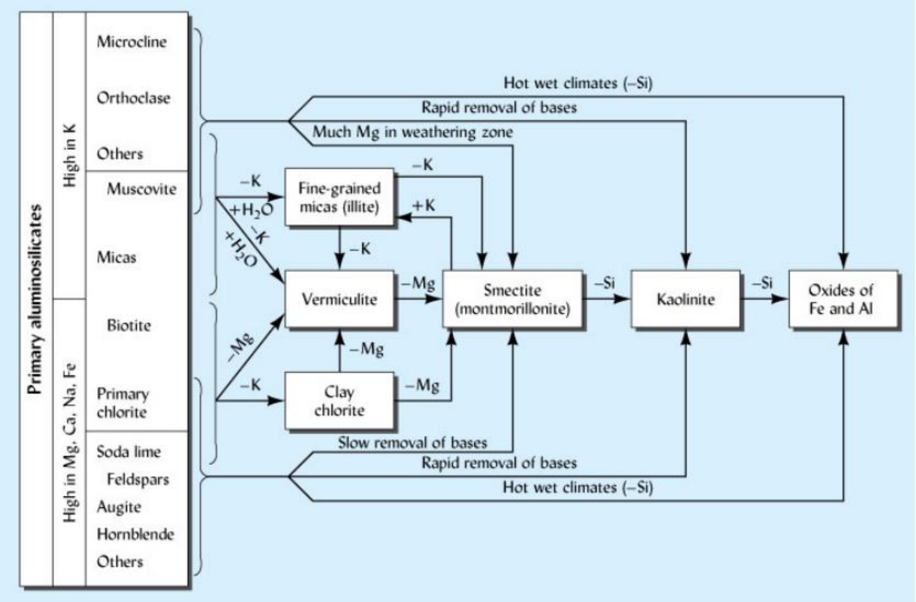


Figure 1.2 Origin of clay minerals

1.1.3 Structure and Chemical Composition of Clay

The properties that define the composition of clay minerals are derived from chemical compounds present in clay minerals, symmetrical arrangement of atoms and ions and the forces that bind them together. The clay minerals are mainly known as the complex silicates of various ions such as aluminium, magnesium and iron Benjamin K. (2004). Based on the arrangement of these ions the crystalline units of clay minerals are of two types:

a. Silicon – Oxygen tetrahedron consists of silicon surrounded by four oxygen atoms and unite to form the silica sheet as shown in (figure 1.3).

b. Aluminium or Magnesium octahedron consists of aluminium surrounded by six hydroxyl units or oxygen and combine to form gibbsite sheet (when aluminium is main dominating atom) or brucite sheet (when magnesium is main dominating atom) as shown in (figure 1.3).

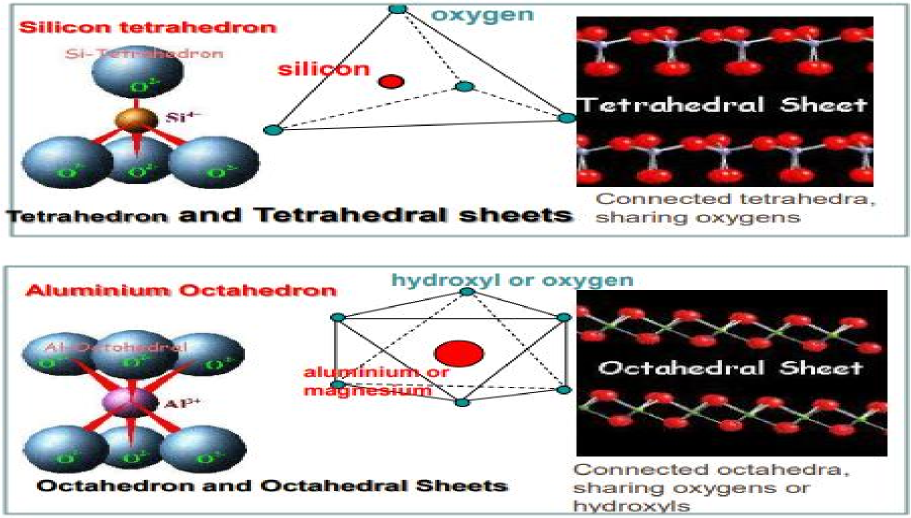


Figure 1.3. Tetrahedral and Octahedral sheets of clay minerals

1.1.3.1 Tetrahedral Sheet

The main dominating atom in the tetrahedral sheet is found in form of Si^{4+} cation. The basic building block of tetrahedral sheet is a unit of silicon (Si) atom surrounded by four oxygen (O) atom known as silica tetrahedra. The tetrahedral sheet is formed by sharing of three oxygen of each tetrahedra with three nearest tetrahedra as shown in (Figure 1.3).

These oxygen atoms are known as basal oxygen which connect pairs of all tetrahedra together (more or less) in one plane whereas the fourth oxygen atom remain free and form the bond with other polyhedral elements known as apical oxygen. Apical oxygens are all in a separate plane and provide a link between both tetrahedral and the octahedral sheet. As only one apical oxygen (O) is present per tetrahedron therefore, each tetrahedron shares a corner with an octahedron in the octahedral sheet.

The tetrahedral sheet is carrying negative charge due to the isomorphous substitution of Al^{3+} in place of Si^{4+} generating the charge deficiency in tetrahedral sheet. Common tetrahedral cations are Si^{4+}, Al^{3+}, and Fe^{3+}.

1.1.3.2 Octahedral Sheet

The main dominating atoms in octahedral sheets are Al^{3+} or Mg^{2+} surrounded by six oxygen atoms or hydroxyl units which give rise to eight-sided building block known as octahedron. Since, octahedral sheet are present in two forms: dioctahedral or trioctahedral sheet.

Di-octahedral Sheets, aluminium having three positive valences present in the octahedral sheet, only two-thirds of the sites are filled so that the charges will be balanced which results in formation of dioctahedral sheet. When magnesium having two positive charge valences is present, all three positions are filled to balance the charge which results in formation of trioctahedral sheet. Therefore, for di – octahedral sheet, Al^{3+} is the main dominating atom with $Al_2(OH)_6$ a unit cell formula and often abbreviated as the stoichiometric equivalent $Al(OH)_3$ where two Al^{3+} atoms coordinated with six oxygen/or hydroxyl ions.

Tri-octahedral sheet, Mg^{2+} is the main dominating atom where three Mg^{2+} atoms are coordinated with six oxygen/or hydroxyl ions having a unit cell formula of $Mg(OH)_2$. Gibbsite or hydrargillite (hydrous aluminum oxide, $Al_2(OH)_6$ or $Al_2O_3 \bullet 3H_2O$) and brucite (hydrous oxide of magnesium, $Mg(OH)_2$). The octahedral sheet is formed by sharing of two oxygen of each octahedra when various octahedra linked together horizontally (Figure 1.3). Schultz D.G. et. al. (1989) and Sarkar B., Singh M. et al. (2018).

1.1.4 Classification of Clay Minerals

The aluminosilicate layers comprise of the basic structural units of phyllosilicates which is formed by the combination of tetrahedral and octahedral sheets bound by shared oxygen atoms. Both the tetrahedral and octahedral sheets are the main components of phyllosilicates (due to their leaf like or plate like structure, they are known as phyllosilicates) which bound together by sharing of oxygen atoms into different layers.

Clay can be classified depending on the way that the tetrahedral and octahedral sheets are packed into layers. The major groups of clay minerals present in the soil environment include layer and chain silicates, and other inorganic minerals as shown in (figure 1.4). Pohl W.L. (2011).

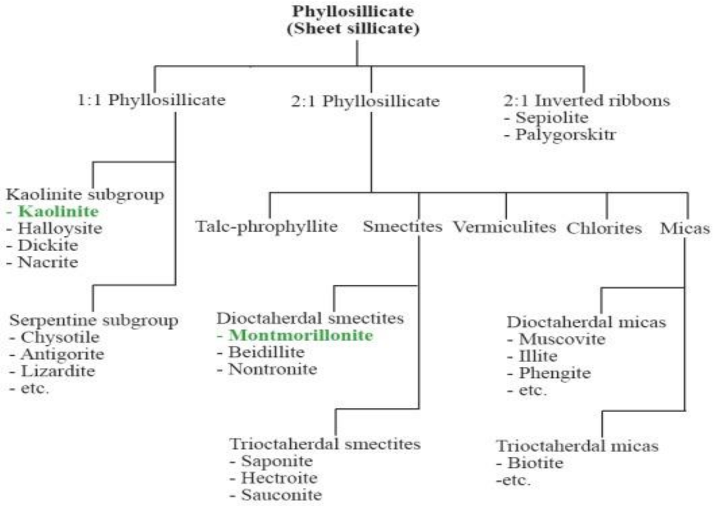


Figure 1.4. Classification of clay minerals from Pohl W.L. (2011).

1.1.4.1 Layered Silicates

A silicate comprising of planar octahedral layer bound to tetrahedral layer above and below with a distinctive repeating distance between t-o-t layers. These are the primary component of soils and are known as excellent trappers of water held between layers. Minerals within these groups are further categorized into dioctahedral and trioctahedral, Barton C.D. (2002). On the basis of number and arrangements of tetrahedral and octahedral sheets present in clay, the layer silicate is divided into three categories: 1:1 type of clay minerals, 2:1 type of clay minerals and 2:1:1 type of clay mineral as shown in (figure 1.4).

1.1.4.1.1 The (1:1) Type of Clay Minerals

Each individual layer is assembled from one tetrahedral (SiO_4) and one octahedral sheet (AlO_6). The sheets are bonded together by sharing of O^{2-} ions. Kaolinite and Halloysite are examples under this category Schroeder P.A. (2002).

Kaolinite is a 1:1 clay mineral with chemical formula $Si_4Al_4O_{10}(OH)_8$. The rocks that are found to be rich in kaolinite are identified as kaolin or China clay Perry D.L. (2011). The chemical weathering of aluminium silicate such as feldspar results in formation of a soft, usually white, earthy mineral (dioctahedral phyllosilicate clay). The dickite and nacrite are rare forms of kaolinite which are chemically similar to kaolinite but amorphous in nature.

Kaolinite is found to be electrostatically neutral having triclinic symmetry. The hydrogen bonding is found in between oxygen atoms and hydroxyl ions of the layers that are paired. The ideal structure of kaolinite has no charge. Hence, the structure of Kaolinite is fixed due to the hydrogen bonding; therefore, there is no expansion between the layers or have low shrink-swell capacity when clay is wetted. Kaolinite does not swell in water and have low surface areas and cation exchange capacity.

Dickite and Nacrite are polytypic forms of kaolinite consisting of a double 1:1 layer and have monoclinic symmetry. Dickite and Nacrite differentiate themselves by different stacking sequences of the two 1:1 silicate layers. The mineral Halloysite having 1:1 layer structure as kaolinite has a single sheet of water molecules between two layers with c-spacing/interlayer spacing 10.1Å which makes it different from kaolinite. It is illustrated by its tubular form in contrast to the platy form of kaolinite particles. Dehydration occurs on mild heating of Halloysite and will irreversibly get transformed to kaolinite. Halloysite possesses a hydrated form with a composition of $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. which irreversibly changes to a dehydrated variety mainly at relatively low temperatures (60°C) or upon being directed to conditions of low relative humidity. The dehydrated form of Halloysite has basal spacing with thickness of a kaolinite layer (approximately 7.2 Å) whereas the basal spacing of hydrated form is about 10.1 Å. The difference of 2.9 Å is due to the thickness of a sheet of water. Consequently, in hydrated form, the layers of halloysite are separated by monomolecular water layers that are lost during dehydration.

1.1.4.1.2 The (2:1) Type f Clay Minerals

Most of the layer silicate clays are commonly found in soils and based on the mica structure in which a single octahedral sheet sandwiched between two tetrahedral sheets and form an individual composite layer referred as (2:1) layer silicates in which Talc [$Mg_3Si_4O_{10}(OH)_2$] and Pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] are the trioctahedral and dioctahedral members. In dioctahedral and trioctahedral layer silicates, two and three octahedral sites are occupied respectively out of the three available sites in the half- unit cell (single Si_4O_{10}), Anthony J.W., Bideaux R.A. et al. (2000). These types of clay minerals consist of one octahedral layer sandwiched between two tetrahedral layers. They are further characterized into two categories: expanding clay minerals: Smectite group and Vermiculite and non – expanding clay minerals: Illite (mica groups).

1.1.4.1.2.1 The expanding clay minerals

This includes mainly smectite group of clay minerals and vermiculite clay minerals. They are known for their interlayer expansion which happens during their swelling behaviour when they are wet. Smectites are mainly based on either trioctahedral 2:1 (talc) or dioctahedral 2:1 (Pyrophyllite) structure and differ from these neutral structures due to the presence of isomorphous substitution in the octahedral or tetrahedral layer. The Smectite group of clay minerals are further divided into Saponites (trioctahedral) and Montmorillonite (dioctahedral). Another important member of the Smectite family is Bentonite. Bentonite clay is also known as sedimentary clay and has unique property of water retaining. The most prominent members of this group are Montmorillonite, Beidellite, nontronite, and saponite. The flake-like crystals of smectite (e.g., Montmorillonite) are consisting of an expanding lattice.

In Montmorillonite, magnesium ions are replaced by aluminium ions in some sites of octahedral sheet and likewise, some silicon ions in the tetrahedral sheet may be replaced by aluminium ions. This type of replacement is known as isomorphic substitution which give rise to a negative charge on the surface of clay minerals. The magnitude of the negative charge depends upon the number of substituted atoms/ions. These negative charges of the unit cell are typically balanced by exchangeable hydrated alkali (Li, Na, K, Rb, Cs, Fr) or alkaline earth (Be, Mg, Ca, Sr., Ba, Rd) cations. The general structural formula of smectite group of clay minerals is $(Na,Ca)0.33(Al,Mg)_2Si_4O_{10}(OH)_2.(H_2O)n$.

The structure, chemical composition, exchangeable ions are responsible for their several unique properties such as high cation exchange capacity, high surface area and high adsorption capacity. The quantity of cations required to balance the charge deficiency induced by these substitutions is referred to as the cation exchange capacity (CEC). The CEC for Montmorillonite ranges from 80 to 100 milliequivalent per 100 grams. Montmorillonite clays have very poor thermal stability. These minerals show some prominent characteristics like high cation exchange capacity, swelling and shrinkage capacity.

Bentonite: Bentonite is an impure form of aluminium phyllosilicate clay consisting 98% of montmorillonite and produced by in-situ devitrification of volcanic ash or by mechanical and chemical weathering of the parent rock, most often in the presence of water. Chemical composition of the unit cell has been represented as $(Si_{8.0})(Al_{3.02}Mg_{0.50}Ca_{0.06}Fe_{0.18}Ti_{0.02}Na_{0.22})O_{20}(OH)_4$. It is a versatile mineral due to its platelet structure. The platelet consisting of a tetrahedral silicon oxide layer in which some silicon replaced by trivalent cations sandwiched between two octahedral aluminium oxide layers with aluminium replaced by divalent cations. The hydroxide group is present on the edge of each platelet results in thixotropic nature Murray H.H. (2006). The different types of bentonites are found based on their respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al). For industrial purposes, three main classes of bentonite exist: sodium, calcium and potassium bentonite.

Sodium Bentonite: expands in wet condition where it absorbs water as much as several times its dry mass, due to its excellent colloidal properties, Sutherland W.M. (2014). It is often used in drilling mud for oil and gas wells and in boreholes for geotechnical and environmental investigations Odom I.E. (1984). Due to its swelling capacity, sodium bentonite is used as a sealant, since it offers a self-sealing, low permeability barrier. Enhancement in some rheological or sealing performance are observed after various surface modifications of sodium bentonite for example, the addition of polymers, Hosterman J.W. and Patterson S.H. (1992).

Calcium Bentonite: is considered as a useful adsorbent for ions, fats and oils Theng B.K.G. (1979) and (Robertson, 1989). It is known as the main active component of fuller's earth, probably one of the earliest industrial cleaning agents.

Potassium Bentonite: This is also known as potash bentonite or K-bentonite. Potassium bentonite is formed from alteration of volcanic ash and considered as potassium-rich illitic clay.

Vermiculite: Vermiculite also belongs to (2:1) group of clay minerals where one octahedral sheet occurs between two tetrahedral sheets. Most of the Vermiculites are Al dominated showing dioctahedral structure. Vermiculite is known as hydrous phyllosilicate mineral which undergoes substantial expansion when heated results in exfoliation and commercial furnaces can routinely generate this effect. Vermiculite formed by the weathering or hydrothermal modification of biotite or phlogopite Robertson R.H.S. (1986). Vermiculite was first described in 1824 in Millbury, Massachusetts. Its name is derived from Latin word, vermiculare, "to breed worms", for the manner in which it exfoliates when heated (Vermiculite,). In Vermiculite clay mineral, tetrahedral sheet is highly negatively charged due to the more substitution of Al^{3+} in place of Si^{4+} results in high layer charge density (in between 0.6 – 0.8 per unit formula) which is higher than smectite group of clay mineral. The chemical formula of Vermiculite is $(Mg,Fe^{2+},Fe^{3+})_3(SiAl)_4O_{10}(OH)_{24}H_2O$. The water molecules are present along with Mg^{2+} and other ions in the interlayer space instead of K^+ ion which makes it different from micas. Therefore, both the tetrahedral and octahedral units are joined together tightly rather than driving apart from each other resulting in less expansion of interlayer spacing on wetting (Wikipedia). The cation exchange capacity of Vermiculite is very high (100 –150 meq/100 g). Vermiculite clays are weathered micas where the potassium ions are replaced by magnesium and iron ions between the molecular sheets.

1.1.4.1.2.2 Non-expanding clay minerals:

This group includes mainly Mica (illite) clay mineral which is a secondary form of mineral precipitate. This group is an example of a phyllosilicate, or layered alumino-silicate. Muscovite and biotite are also found in the clay fractions which are also called fine grained Mica. Illite is considered as a modified product of muscovite and feldspar formed from weathering and hydrothermal environments; known as component of sericite. It is commonly found in soil and argillaceous sedimentary rocks as well as in some low-grade metamorphic rocks. In illite, the tetrahedral sheet has more negative charge even higher than vermiculite which is due to the presence of 20% of aluminium atoms in tetrahedral sheet in place of silicon atoms sites having considerable ion isomorphic substitution. The charge deficiency is mainly balanced by K^+ ions which are present in the interlayer space and act as bridge between the layers thus preventing the expansion of layers making them non - expanding. Therefore, the interlayer spacing is found to be 10 Å. The adsorption capacity, swelling, shrinkage capacity is less than montmorillonite and vermiculite, but more than Kaolinite interstratified layers are present. The cation-exchange capacity (CEC) of illite is smaller than that of smectite but higher than that of kaolinite, typically around 20–30 meq/100 g.

1.1.4.1.3 The 2:1:1 Type of Clay Minerals

Chlorite mainly belongs to 2:1:1 silicate group which are basically iron magnesium silicates with some aluminium atoms. The typical chlorite clay crystal composed of 2:1 layer, such as in vermiculites clay mineral alternate with a magnesium dominated tri-octahedral sheet (also known as brucite) giving rise to 2:1:1 ratio. All the octahedral positions in chlorite are occupied by magnesium ions as in the brucite layer. The negative charge of chlorites is less than smectite or vermiculites but about the same as that of fine-grained mica. There is no water adsorption between the layers responsible for the non – expanding nature of this crystal. The interlayer spacing is about 14 Å. Chlorites having a muscovite-like silicate layer and an aluminium hydroxide sheet are called donbassite and show the ideal formula of $Al_{4.33}(Si_3Al)O_{10}(OH)_8$. In many cases, the aluminium ions present in octahedral layer are partially replaced by magnesium ions as in magnesium-rich aluminium dioctahedral chlorites called sudoite. Another type of dioctahedral chlorite is Cookeite in which lithium substitutes for alumina in the octahedral sheets.

1.1.4.2 Chain Silicates

Palygorskite or Attapulgite; Palygorskite is a fibrous magnesium aluminium phyllosilicate having the formula $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ which is mainly found in a type of clay soil in the Southeastern United States. It is one of the types of fuller's earth. The structure of palygorskite consists of extended silicon-oxygen sheets results in the retention of the mineral in the layer silicate family whereas the tetrahedral SiO_4 groups forming silicon-oxygen sheets are oriented in such a manner so that extended lathlike features could be developed which create the fibrous morphology. The chain silicate mineral found in sediments from playa lakes, saline deposits in desert soils and in calcareous material.

Sepiolite: It is also known as Meerschaum, a fibrous hydrated magnesium silicate having chemical formula $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$. It is opaque and white, grey, or cream in colour. It may seem like the bones of the cuttlefish Sepia. The name of Sepiolite is derived from cuttlefish Sepia. The structures of sepiolite and palygorskite are almost similar consisting of narrow strips or ribbons of 2:1 layers that are attached to each other at the corners. One ribbon is attached to the other by inversion of the direction of the apical oxygen atoms of SiO_4 tetrahedrons; in other words, an extended rectangular box comprising of continuous 2:1 layer is enclosed to the nearest boxes at their extended corner edges. Therefore, due to the absence of silicate layers, channels or tunnels occur on the extended sides of the boxes resulting in the fibrous morphology of the minerals. Since the octahedral sheet is irregular, some of the magnesium ions present in octahedral layer are exposed at the edges and hold on bound water molecules (H_2O). In addition to the bound water molecules, variable amounts of zeolitic free water (H_2O) are included in the rectangular channels. The width of the ribbons is found to be greater in sepiolite than in palygorskite which is a major difference between these chain silicates. The width of ribbons defines the number of octahedral cation positions per formula unit. Wada K. (1989).

Sesquioxide; Sesquioxide clays are produced from heavy rainfall and leached most of the silica and alumina from alumino – silicate clay by leaving less soluble iron oxide (Fe_2O_3), iron hydroxide ($Fe(OH)_3$) and aluminium hydroxide ($Al(OH)_3$). Sesquioxide's of iron and aluminium are found in soil. A sesquioxide is an oxide comprising three atoms of oxygen and two other elements. For example, aluminium oxide (Al_2O_3) is a sesquioxide. Many sesquioxide's contain the metal atom having (+3) oxidation state and the oxide ion such as Al_2O_3, La_2O_3 except the alkali metal sesquioxide's which contain both peroxide, (O_2^{2-}) and superoxide, (O^{2-}) ions, example Rb_2O_3 is formulated $[(Rb^+)_4(O_2^{2-})(O^{2-})_2]$. They are not adhesive in nature and do not swell in presence of water. They have ability to hold large amount of phosphate as they have tendency to hold phosphorous tightly make them unavailable for absorption by plants. They have low CEC and found in both crystalline and amorphous form. Crystalline Sesquioxide are either metal oxide or hydroxide whereas amorphous Sesquioxide are Allophane and Imogolite.

Imogolite: is an aluminosilicate having the composition of $SiO_2 \cdot Al_2O_3 \cdot 2.5H_2O$. This mineral was discovered in a soil obtained from glassy volcanic ash known as "imogo." Electron-optical observations of imogolite suggest a unique morphological feature with smooth and curved threadlike tubes differing in diameter from 10 to 30 nanometers which can further extend up to several micrometers in length. The shape of imogolite is cylindrical consisting of a modified gibbsite sheet where the hydroxyl of one side of a gibbsite octahedral sheet loses protons which form bond with silicon atoms located at vacant octahedral cation sites of gibbsite. Thus, three oxygen atoms and one hydroxyl present around silicon atom make up an isolated SiO_4 tetrahedron as in orthosilicates which make a planar array on the edge of a gibbsite sheet, because of shorter bond length between silicon-oxygen bonds than aluminium-oxygen bonds sheet change into curve shape results in a tube-like structure with inner and outer diameters of about 6.4 Å and 21.4 Å, respectively, and with all hydroxyls exposed at the surface.

Allophane; are considered as a group of naturally occurring hydrous aluminosilicate minerals. They are not totally amorphous but are short-range (partially) ordered. Allophane are described by the dominance of Si-O-Al bonds where most of the aluminum atoms are tetrahedrally coordinated. Unlike imogolite, the morphology of allophane varies from fine, rounded ring-shaped particles to irregular aggregates which indicates that the ring-shaped particles may be hollow spherules or polyhedrons. Despite their indefinable structure, their chemical compositions surprisingly fall in a relatively narrow range as the SiO_2:Al_2O_3 ratios are mostly found to be in between 1.0 and 2.0. In general, the SiO_2:Al_2O_3 ratio of allophane is higher than that of imogolite Wada K. (1989).

1.1.5 Properties of Clay Minerals

The physical and chemical properties of clay minerals depend significantly on their sheet structure, cation and anion-exchange capacity and adsorption ability which mainly determines their importance in different applications, Nadziakiewicza et. al. (2019).

1.1.5.1 Cation Exchange Capacity (CEC)

The ability of clay minerals to adsorb certain cations/anions and their retention around outside of structural unit depends on positive or negative charge deficiency in their mineral structure. Cation exchange capacity (CEC) is the measurement of number of cations retained on the surface of soil particles. It has been defined as quantity of cations that are available for exchange with other cations at a given pH and usually expressed in milliequivalent/100 gram of dry clay. Negatively charged ions present on the surface of soil particle bind with positively charged ions but allow them to exchange in the surrounding soil water with other positively charged particles results in alteration of chemistry of soil, Verbung K. and Baveye P. (1994). The various aspects of soil chemistry are affected by CEC. As CEC indicated the soil capacity to retain the nutrients like K^+, NH_4^+, Ca^{2+}, therefore, the soil fertility is measured by CEC. It also indicates the capacity to retain pollutant cations like Pb^{2+}. CEC depends on particle size, crystallinity perfection and adsorbed ion therefore for a given mineral, values exist in range rather than single specific capacity. The exchange capacities also depend on pH due to the presence of hydroxyl group on the surface of certain clay minerals like allophane and kaolinite. The original negative charge layer is either replaced or exchanged by the adsorbed cations. This ability of colloidal particles such as clay minerals to maintain and exchange positively charged ions is important because it governs the mobility of positively charged chemical species both in soils and in general geochemical cycling of cations. CEC is a reversible process and normally correlated with clay minerals due to the presence of interlayer exchangeable cations such as smectites.

1.1.5.2 Swelling Capacity (SC)

The ability of dry clay minerals to adsorbe water in a controlled environment, into their interlayer space in discrete forms of layer causing swelling or expansion of the interlayer space. The swelling of interlayer space of clay minerals is due to the hydration energy forces associated with the particle's interaction. Karpinsk B. and Szkodo M. (2015).

The swelling capacity of clays depends on granularity as well as superficial activities of clay itself. The swelling properties of clay minerals play an important role in design of structures of light buildings. The mobilization of swelling capacity may result in stability concerns and foundation threats, tunnels and slopes which required certain assumption and factors like swelling potential which need to be mobilized by applying the swelling pressure. The factors affecting the swelling potential are known as internal factors (cations present in clay minerals and properties of clay minerals) and factors having significant effect on swelling potential are known as external potential (properties of ions and available pore water) Cherif M.M. et al. (2018). Swelling pressure mainly depends on the average specific surface area, more surface area, more force acting on the surface results in high volume change and high swelling pressure. The clay minerals showing more expansion belongs to (2:1) group of clay minerals with tetrahedrons and octahedrons layers where cations and water molecules are stored in the interlayer spaces. The difference between swelling and non-swelling clay minerals is the size of interlayer space. Greater the interlayer space, more change will be in swelling behaviour. The swelling clay show more interlayer spacing while non-swelling clay show less interlayer space.

1.1.5.3 Surface Charge Properties (SCP)

The surface charge of clay minerals affects various chemical properties of clay minerals by varying the quantity of electrical and surface charge density. The surface charge properties play an important role in the formation of organo-complexes of clay minerals, migration of ions, swelling and shrinkage. Based on difference in surface properties, clay minerals are categorized into two categories:

1.1.5.3.1 Clay minerals having Permanent Negative Charge

The permanent negative charge in clay minerals occurs due to the isomorphous substitution in the tetrahedral and octahedral layers. This type of charge is also known as structural charge and is pH independent. The negative charges of clay minerals are mainly balanced by the interlayer ions present in the interlayer space of clay minerals. Karak T., Das D.K. et al. (2005).

1.1.5.3.2 Clay Minerals having Variable Charge:

The charge arises due to the protonation of Si – OH group present on the edges of clay surface. This type of charge is pH dependent. It may either be positive or negative due to the protonation or deprotonation of functional group of clay minerals depending on the pH. Moghimi A.H. and Hamdan J. (2013).

1.1.5.4 Adsorptive Properties (AP)

Clay and clay-based minerals show non-covalent adsorptive behaviour in three ways to various molecules from liquid to gaseous state. Physical adsorption where non-ionic adsorption takes place onto the clay surface (larger surface area compromised in small volumes). Ion exchange adsorption which takes place either through the electrostatic interaction or exchange. Addition of small molecules in pore/cavities and partial or complete elimination of large molecules by the cavities through zeolitic adsorption action.

The adsorption capacities of clay minerals depend on various factors. The high adsorption capacities of clay minerals for metal ions, organic matters and other substances are due to large surface area, low permeability, high cation exchange capacities and high retention capabilities. There are some other factors like structure and chemical composition of clay minerals which affects their adsorption capacity. There are different active sites in the clay minerals through which adsorption takes place: exchangeable cations (Na^+, K^+, Ca^{2+}), hydroxyls of acidic/basic character (SiOH, $SiO(H^+)Al$, Al-OH, and OH or Mg-OH), coordinatively unsaturated ions of Al^{3+}, Mg^{2+}, and/or Fe^{3+}; and oxygen anions. Such active sites present on the surface and the structural elements results in physical adsorption through Vander wall interaction of hydrogen bonding which takes place through the hydroxyl group present on the surface. Secondly, chemisorption also takes place due to the formation of chemical bond formed through stronger interaction between surface and molecules. Novikova L. and Belchinskaya L. (2016).

1.1.5.5 Specific Surface Area (SSA)

Specific surface area (SSA) is defined as the surface area of soil particles per unit mass (or volume) of dry soil. Its unit is in m^2/g. The clay minerals show high specific surface area due to the high soil water contaminant interaction results in high reactivity. The reactivity is different for different clay minerals (Kaolinite<Illite< Montmorillonite). The surface area of clay minerals mainly depends on the particle size and shape of the constituents present in clay minerals. As the particle size decreases, the specific surface area increases that can be both internal as well as external. This statement is true in case of the clay minerals which have large fraction of internal surface area such as smectite, vermiculite, sepiolite and palygorskite. The specific surface area is different for different types of clay minerals. The expanding clay minerals like montmorillonite and vermiculite have high specific surface area up to 810 m^2/g (combination of both internal and external surface areas) whereas non-expanding clay minerals like kaolinite have specific surface area up to 10–70 m^2/g as they show only external surface area due to non-contribution of interlayer surface.

1.1.5.6 Plasticity

Plasticity of clay mineral is one of the important properties. It is the deformation of shape of clay minerals under the influence of finite force. It is defined as property of material which allow it to be repeatedly deformed without rupture when acted upon by a force sufficient to cause deformation and which allows it to retain its shape after the applied force has been removed. The plasticity of clay minerals is affected by their composition (types of clay minerals, proportion of non-plastic minerals etc.), organic substances, specific surface area, dispersion state of particles, particle size distribution and water characteristics (viscosity and surface tension). The other factors are pressure applied, body temperature and nature of additive used. High plasticity of clay-water system requires more force for deformation which occurs to a greater extent without any cracking as compared to clay-water system having low plasticity which easily deform and rupture.

Plasticity also known as extrudability, ductility consistency or workability. When water is added in dry clay, cohesion is increased and tend to maximum after displacing of air from the pores present between clay particles. When water reaches into the pores, formation of high yield strength body takes place results in cracking or rupturing due to the deformation. The minimum quantity of water required to make plastic clay is known as plastic limit. When the water content increases in the clay, it converts into paste where the yield strength gradually reduced. The clay become sticky to fingers. The water content corresponding to this state is known as liquid limit. With further increasing the water content, dispersed form of clay obtained. The difference in water content between these two points is expressed as plasticity index.

1.1.5.7 Dispersion and Flocculation

Dispersion is defined as a system where solid or liquid particles are dispersed into the continuous phase of liquid, solid, gas of different composition. In case of clay minerals, when they are wetted, separation of particles of clay minerals takes place which results in formation of dispersion. Flocculation is defined as when the particles such as clay minerals dispersed into the solution, they come in contact and adhere with each other to form clusters, flocks or clumps of larger size. The clay dispersion is regulated by repulsive and attractive forces at the surface of charge colloid in electrical double layer. For dispersion of clay particles, there should be balance between attractive and repulsive forces which is examined by exchangeable cations and ionic strength of the clay solution. Rengasamy P. (1991).

Table 1.1 Some properties of clay minerals adopted from Grim R.E. (1968).

S/N	KAOLINITES	MONTMORILLONITE	ILLITE
1	1:1 Layer	2:1 Layer	2:1 Layer
2	Hexagonal Flakes	Thin Flakes Elongate	Elongate
3	Low Base Exchange Capacity	High Base Exchange Capacity	Moderate Base Exchange Capacity
4	Minimal Layer Charge	High Layer Charge	Moderate Layer Charge
5	Low Surface Area	Very High Surface Area	High Surface Area
6	Largest Grain Size	Smallest Grain Size	Intermediate Grain Size
7	Lowest Dry Strength	Highest Dry Strength	Intermediate Dry Strength
8	Lowest Swelling and Shrinkage Behaviour	Largest Swelling and Shrinkage Behaviour	Intermediate Swelling and Shrinkage Behaviour

1.1.6 Industrial Classification of Clay Resources

Industrial clay resources have been classified into four categories adopted from Harvey and Murray H. (1997) and (2006).

1.1.6.1 Clays of category 1; are high-quality, high-technology clays, which require major investment for large-tonnage production to supply both local and international markets. Typical examples of this category are the sedimentary kaolins of Georgia and the SE USA, the hydrothermal kaolins of Cornwall in the UK and the bentonites from Milos, Greece.

1.1.6.2 Clays of category 2; are specialty clays, which require advanced technologies for small-tonnage specialty markets, locally and internationally. Examples of this category include the halloysite deposits of New Zealand and the hectorite deposit at Hector, California.

1.1.6.3 Clays of category 3; include low-technology clays of moderate quality, which mainly supply local markets. Typical examples are the kaolin deposits of central and eastern Europe in the Czech Republic, Ukraine and Germany and the bentonite deposits at Wyoming, USA.

1.1.6.4 Clays of category 4; justify little or no processing and may be suitable for large tonnage local markets. These clays may be of moderate to high quality but are considered to be uneconomic due to isolation from markets, politically or economically unstable locations, or unfavourable legislative environments.

1.2 Aim and Objectives of the Study

1.2.1 Aim

The study was aimed at carrying out bulk mineralogical evaluation and geochemical determination of the major oxides and trace elements and the sedimentological investigation of physical properties of the clay deposits, to appraise their economic potentials and viability for industrial uses.

1.2.2 Objectives

1. To develop an appropriate geological map and a lithologic cross section across the study area derived from field mapping.

2. To determine the bulk mineralogical composition of the samples and generate a mineral data for the inherent clay minerals in the area.
3. To determine the bulk geochemical composition of the major and trace elements, using geochemical signatures to determine clay provenance and origin.
4. To carry out sedimentological analysis of the clays to determine their geotechnical properties.
5. To correlate the clay deposits with other clay deposits of standard requirements and specifications for different industrial applications.

1.3 Scope of Study

The scope of the study follows a systematic sequence involving field work, data acquisition, preprocessing, interpretation, and industrial application. The key steps are outlined below:

1.3.1 Comprehensive Literature Review:

A detailed review of existing literature, reports, Journals (both local and International), policy documents on mineral exploration were carried out to have an in-dept knowledge of the proposed thesis and the study area.

1.3.2 Field Work:

The research started with field study: reconnaissance and detailed geologic sampling and mapping of the study area.

1.3.3 Laboratory Work:

Thirty freshly representative samples were collected adopting point sampling method and taken to the laboratory in well labelled and sealed polythene bags to prevent contamination and loss of moisture. The samples were then prepared for analyses by crushing using a jaw crusher, followed by milling which was accomplished by gently grinding the sample, so as not to destroy the structure of the constituent minerals.

1.3.4 Mineralogical Analysis:

The bulk mineralogical compositions were determined using X Ray Diffractometry (XRD). A Philips P Analytical instrument equipped with a pw 3830 X-ray generator operated at 40 kV and 25 mA was used. The samples were oven-dried at 100°C for 12 hours to remove the adsorbed water. The samples were pressed into rectangular aluminium sample holders using an alcohol wiped spatula and then clipped into the instrument sample holder. The representative clay samples were step-scanned from 5 to 85 degrees 2 theta scale at intervals of 0.02 and counted for 0.5 sec per step at Rolab Research and Diagnostic Laboratory, Challenge, Off Lagos - Ibadan Bye-Pass, Ibadan, Oyo State.

1.3.5 Geochemical Analysis:

The whole rock elemental geochemistry was determined using X Ray Fluorescence Spectroscopy (XRF), The bulk chemical compositions of the clay samples were determined by X-ray fluorescence (XRF) analysis. Samples were oven-dried at 100°C for 12 hours for adsorbed water measurements and crushed. The powdered samples were then mixed with a binder (ratio of 1:9 in grams of C-wax and EMU powder) at a ratio of 2:9 (2g binder and 9g sample). The powder mixture was then pelletized at a pressure of 15 Kbars for 1 minute. Loss on ignition (LOI) experiment was performed prior to major element analysis. at Rolab Research and Diagnostic Laboratory, Challenge, off Lagos - Ibadan Bye-Pass, Ibadan, Oyo state.

1.3.6 Sedimentological Analysis

Hydrometer method, Wet sieving analysis and other geotechnical techniques were carried out to determine the Moisture content, Specific gravity, Particle size distribution, Atterberg limits; (Liquid Limit, Plastic Limit and Plasticity Index) at Civil Engineering Department, University of Benin, Benin City, Edo State.

1.3.7 Data Analysis

The data and results obtained were analyzed, presented, and interpreted as follows:

1.3.7.1 Xray Diffractograms

The results from the XRD analysis of the samples were presented in the form of diffractograms with peaks indicating the mineral types.

1.3.7.2 Tables

The results from XRF analysis for major oxide, trace elements and rare earth elements, particle size distribution, specific gravity, moisture content, liquid limit, plastic limit are all presented in tables and figures.

1.3.7.3 Geochemical Signatures and Calculations

These includes; Nesbitt and Young (1982) proposal for weathering index (CIA) interpreted as an indicator of conversion degree from feldspars to clay such as kaolinite (CIA = $[Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)]*100$), Harnois (1988) suggested weathering index (CIW) which modified (CIA) The assumed immobility of Al and higher mobility of (Na, K, and Ca) makes CIW increases with the increase of weathering degree (CIW = $[Al_2O_3/(Al_2O_3+CaO+Na_2O)]*100$), Parker (1970) suggested weathering index (WIP) for silicate rocks based on element mobility, which was related to bond strength of each element (Na, K, Mg, and Ca) with oxygen. It is expressed by the sum of alkali and alkaline earth element composition ratio. (WIP) does not need to assume Al immobility during the weathering (WIP = $2Na_2O/0.35+MgO/0.90+2K_2O/0.25+CaO/0.7$)

1.3.7.4 Diagrams and Charts

These includes the (TiO_2/Al_2O_3) Binary Diagram as suggested by Ekosse (2001), Discriminant Diagram after Roser and Korsch (1988), Plasticity Chart using plasticity index and liquid limit after Casagrande (1948), Clay identification chart using plastic limit and plasticity index as a parameter after Bain (1971).

1.3.7.5 Discussions

The results were compared with well-established industrial standards and specifications for clay industries. The findings from this study were well documented with conclusions, recommendations and submitted as a thesis.

1.4 Justification

The dominance of oil and gas on the Nigerian economy and the sole dependence on crude oil as its mono source of deriving gross revenue is a major problem in a country like Nigeria where abundant untapped clay deposits occur, however the unavailability of more detailed research on the mineralogy and physico-chemical properties of these clay deposits for industrial use and economic viability, remains a major setback that this study attempts to address.

1.5 Location and Accessibility of The Study Area

The study area traverses through Iguoriakhi, Ofunmwengbe and environs covering about 80Km^2. The study area is accessible through the major highways (Benin Sagamu Express way) from Benin City to Ofunmwengbe and through minor local roads (Siluko road) to Iguoriakhi and earth roads (foot paths) along river channels, light forest and settlements, where samples were collected in Ovia Southwest Local Government Area of Edo State, Southwest Nigeria (figure 1.5 and 1.6). The area is geographically located between latitude 6°15'N and 6°20'N and longitude 8°05'E and 8°10'E. The Geology departmental bus and walk through footpaths during the field work were employed to aid accessibility and movement through the study area and locations where samples were collected.

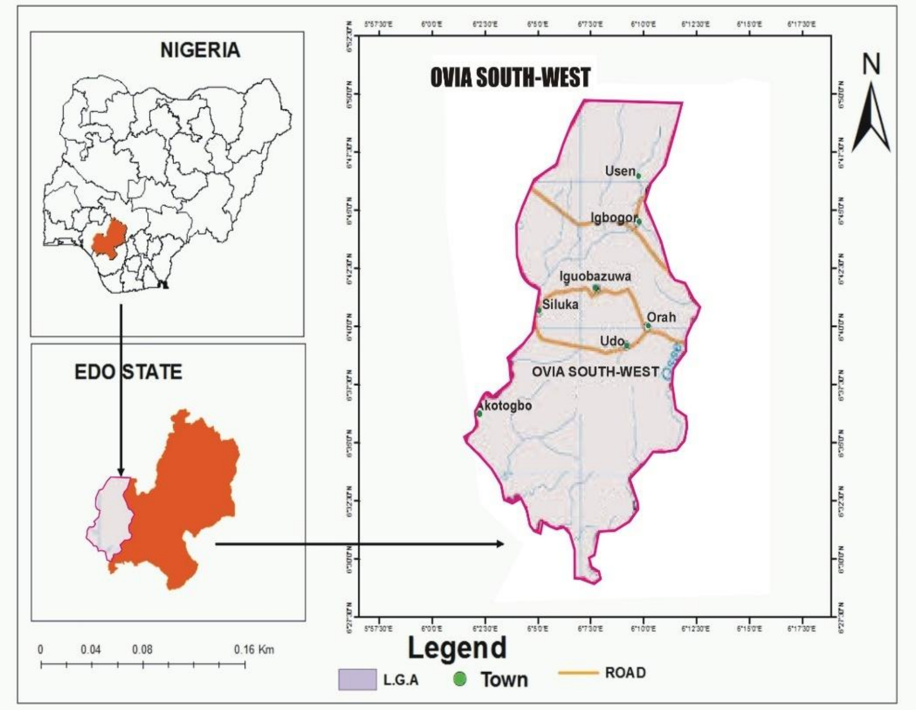


Figure 1.5. Map of Nigeria Showing Edo State and Ovia Southwest Local Government Area

1.6 Topography, Climate and Vegetation of Study Area

The study area is located at Iguoriakhi, Ofunmwengbe and environs in Ovia Southwest Local Government Area of Edo State, Nigeria. It shares borders with Ovia Northeast Local Government Area and Ondo State and the geographical coordinates are within latitudes 6º28‘‘30” N - 6º39‘‘00” N and longitudes 5º18‘‘0” E - 5º33‘‘0” E of the equator (Figure 1.6).

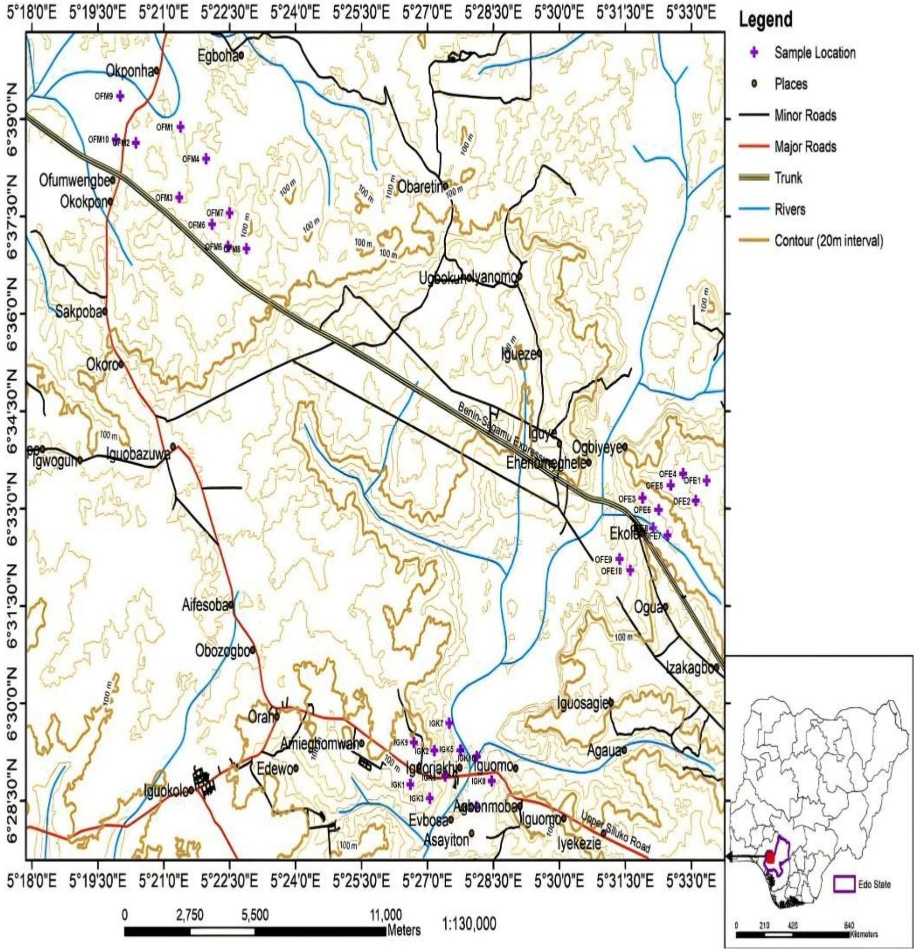


Figure 1.6. Geology map of the study area showing sample locations

The study area falls within the tropical rainforest region of Edo State Nigeria, it has a hot and humid tropical climate. The climate is characterized by seasonal rainfall, high temperature and relative humidity. The environment is noted for two distinct seasons of rainy and dry periods in a year. The Southwest trade wind predominates over the area, usually between March and November, while the Northeast

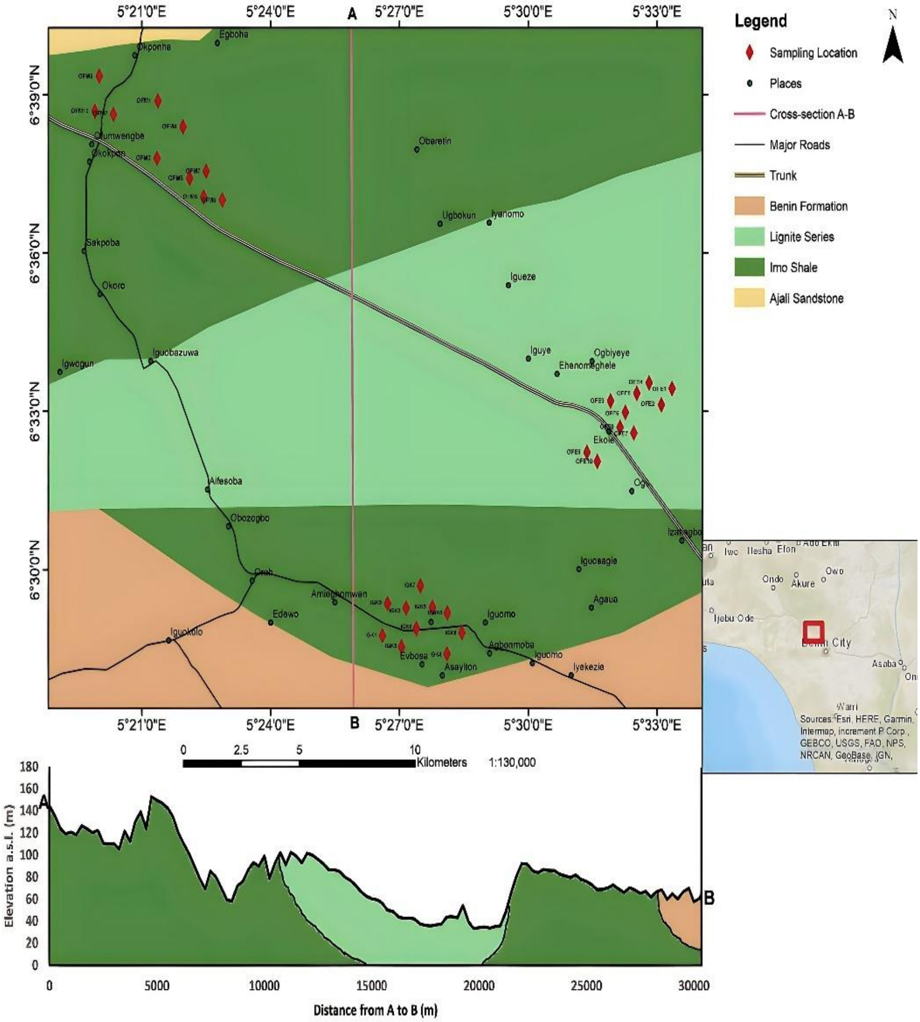


Figure 1.7. Geological map with lithologic cross section of the study area

trade wind has greater influence between December and February/March. The climatic data of rainfall, temperature and relative humidity with mean annual rainfall of >1,500 mm. with peaks in September/October, the mean air temperature ranged between 28°C to 36°C while the relative humidity ranged between 70% to 80% Pa. Oviasogie P.O. et al. (2020).

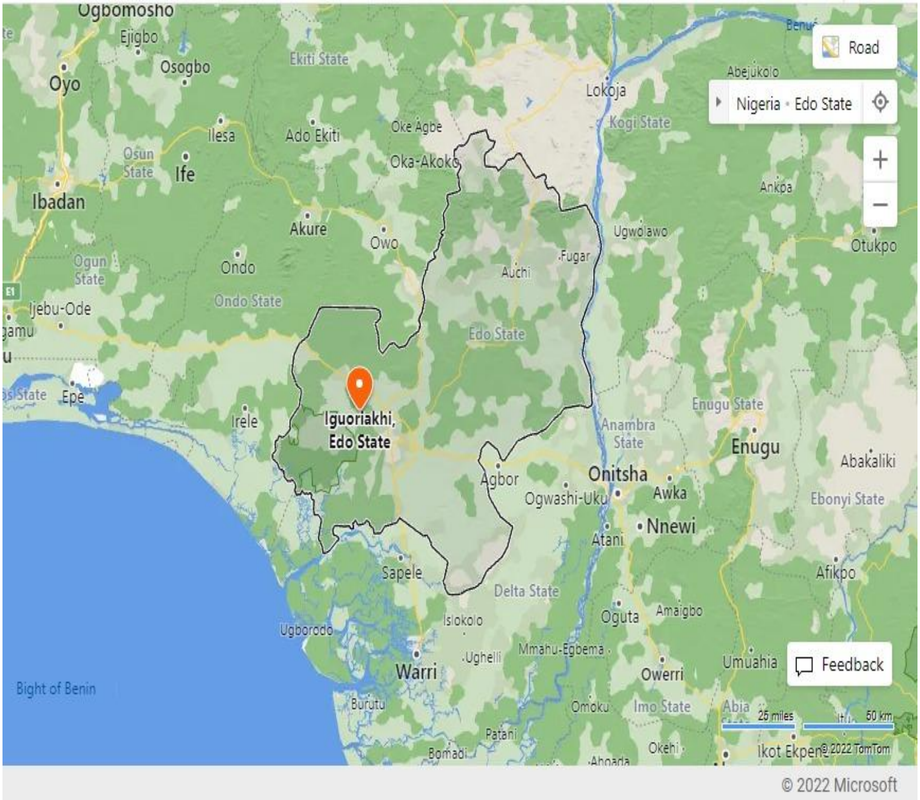


Figure 1.8. Satellite map showing the study area and environs (google map 2022).

The vegetation consists of primary forest, the topography ranged from flat to undulating / sloppy with elevation above the sea level of greater than 100 m as shown in (figures 1.6, 1.7 and 1.8). The natural vegetation consists of climbers and tall trees ranging from 20 to 30m high with continuous canopy. There were relatively high densities of oil palm trees, other naturally occurring plant species and grasses (Floyd et al., 2016). The drainage system of the study area is dendritic in pattern, as a function of lithologic control. The study area is mainly drained by rivers Siluko and Osse respectively with few minor drainage flows as shown in (figure 1.6).

CHAPTER TWO

2.0 Literature Review

Clay minerals are seldom mono-mineralic and have no genetic significance, as it is used for residual weathering products, hydrothermally altered products, and sedimentary deposits (Murray, 2007). These minerals occur under a limited range of geologic environments which include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. In general, they form where rocks are in contact with water, air, or steam and the type of clay however is controlled by the composition of pre-existing rock mineralogy Kabeto et al. (2012). Several studies show that clays preserve a geochemical 'fingerprint' specifically few trace elements of the parent rocks from which they were formed. Mosser (1980) and Mosser et al. (1991). Clays of various kinds and grades abound throughout Nigeria's sedimentary basins and on the basement. Falode et al. (2007).

Some specific physical and chemical properties of kaolin are dependent on the environment of deposition, geological origin, geographic source and the material method at the end of processing. (Murray and Kogel, 2005). Superficial clay deposit is formed from the weathering of Precambrian Basement rocks. One major progenitor of clay deposits is feldspar, which is a common mineral in many granitic rocks like granite pegmatite. Furthermore, clay deposits are common in areas where hydrothermal alteration leads to high level of kaolinization, which characterizes area where Pan-African magmatism is prevalent, (Okunlola, 2008). The type of clay that formed is not only a function of the nature of parent rock but also the intensity of weathering and the length of time during which it occurred (Akinola and Obasi, 2014). Clay deposits are widely distributed on the Precambrian Basement Complex of Nigeria (Ajayi and Agagu, 1981; Emofurieta and Salami, 1988).

Recent investigations by the Nigerian Mining Corporation (NMC) established the existence of bentonitic clay reserves of over 700 million tons in the country, with the largest single deposit at Afuze in Edo State holding 70-80 million tones. Research performed in the early 90's by the Bureau of Mines of the United States of America (U.S.A), showed that the sum of bentonite deposits in the world was about 1.36 billion tons, and the U.S.A. has more than 50.0% of the total (Apugo-Nwosu et al., 2011).

Thus, earlier workers such as (Omole et al., 1989) were able to have a pioneering study on the suitability of the black cotton clay soil of northeastern Nigeria as drilling mud. Their work evaluated the nature and geotechnical properties as well as effects of beneficiation on the clay soil. The results of their beneficiation tests showed that the beneficiated clays were still not suitable for direct use as oil drilling mud but could be used for drilling water wells.

Later researchers, such as (Mihalakis et al., 2004), observed that the rheological properties of the black cotton clays improved with addition of Na_2CO_3, such that the upgraded clay can be used as multipurpose drilling mud. Other researchers (Ezeribe and Oyedeji, 2005) added lignite to clay mud to improve its rheological and filtration properties. The lignite was activated with sodium hydroxide (NaOH) and added to freshwater mud at different concentrations. The authors concluded that the addition of lignite improved the suitability of the clay with a significant improvement observed when 3% of lignite was introduced.

The work of (Okogbue and Ene, 2008) revealed that some southeastern Nigeria natural clays possess properties that are somewhat similar to those of naturally active bentonitic clays from Wyoming and Texas which are used in the industry as drilling mud.

Ajayi and Agagu (1981) carried out mineralogical analyses of primary clay deposits from seven localities representing different rocks in the Nigerian Basement Complex and found that the deposits that weathered from granites, gneisses, pegmatites and schists consisted mainly of kaolinite and trace proportions of montmorillonite and illite while deposits weathered from calc-silicate rocks contained high proportions of montmorillonite.

Orumwense F.F. (1996) studied the removal of lead ions from water by adsorption on kaolinite (clay from Nigeria). During this experiment the effect of time (0-120 min), concentrations (5, 10, and 75 mg/dm^3), pH (3 to 9.5) and temperature (30, 40, and 50 °C) on the adsorption capacity of the clay was examined. The results showed that the adsorption capacity of the clay to remove lead increases with increasing solution temperature. The maximum adsorption capacity of lead of 6.457 mg/g was achieved at 50 °C. Adsorption of lead is reduced from 93% to 82% with the increase of the pH value of the solution. Also, it was found that the presence of negative charge on the silicon surface of the adsorbent is responsible for the adsorption of lead.

Churchman G.J. (1998) outlines the following methods to enhance or activate the properties of a natural clay or clay minerals for several industrial uses.

(i) Physical - alteration of particle size (specific surface area) mechanically.

(ii) Thermal - alteration of chemical composition and/or crystalline structure by the effect of temperature.

(iii) Chemical - This is usually limited to ionic exchange: therefore, it does not include massive chemical destruction of the clay mineral structure.

(iii) Pillaring -This may be regarded as using chemical and physical restructuring of the clay mineral structure to increase capacity for adsorption or to make spaces that encourage adsorption of specific ions.

Osadebe C.C. *et al.* (2011) carried out the evaluation of Imo clay-shale deposit (Paleocene) from Okada, Edo state, Southwestern Nigeria, as drilling mud clay and discovered that the Imo clay-shale from Okada contains appreciable amount of vermiculite, chlorite, glauconite and montmorillonite occurring as a mixed layer. It is essentially smectite dominated, with quartz as the main subsidiary non-clay mineral. The clay-shale is characterized by high loss on ignition which is an indication of high water of crystallinity. The result reveals that the Okada clay-shale and the drilling mud have close chemical composition. However, the Okada clay-shale may require beneficiation, blending and refining processes to reduce its loss on ignition and SiO_2 values. Consequently, the Okada clay-shale can serve as a good source of raw material for drilling mud.

Okorie E. et al. (2015) acknowledge that Nigeria is known to host large reserve of untapped bentonitic clay deposits and this clay is predominantly calcium 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 Souza D.J.L. *et al,* (2007), kaolin deposits in Patagonia, Argentina. Dominguez E. *et al.* (2008); and in Tanzania, the Pugu kaolin clays Bloodworth A.J. *et al.* (1989). Some known clay deposits in Africa include those found in Botswana in Makoro and Kgwakgwe localities Ekosse, G.I.E. (2005) and the clay deposit in Abu Darag, Egypt Baioumy H.M. (2014).

Nweke O.M., Igwe E. O. et al. (2015) studied the physical and chemical properties of some clays from Abakaliki formation, southeastern Nigeria and the extent to which sodium carbonate and barite properties can be improved for possible use of these clays as drilling mud.

Elakhame Z. et al. (2016) studied the mineralogical and physical properties of clay minerals at Ujogba, Edo State Nigeria. The clays were 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 fireclays. Therefore, are considered useful in refractories and ceramic applications.

Umudi E.Q. *et al.* (2017) studied clay deposit at Ozanagogo, Delta State, Nigeria with emphasis on their mineralogical composition. 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. They concluded that edible clays especially that from Baleke could be used as a potential source for iron, magnesium and a good source of food for lowering blood pressure.

Clay minerals are the most important industrial minerals whose application is dependent on its physical, mineralogical and chemical composition (Adeola et al., 2017). Interestingly, various researchers have looked at some of these clays from different perspectives (Ajayi and Agagu, 1981; Ehinola et al., 2009; Olaolorun and Oyinloye, 2010). Clay mineral composition and such physical characteristics as particle size distribution, organic matter content and geologic history also influence their agricultural productivity and engineering performance (Onyeobi et al., 2013). In agricultural terms, the soil's capacity for ion – exchange, water retention and sustained fertility are dependent on the nature and quality of clay minerals (Kronberg et al., 1979; Gillman, 1980; Fyfe et al., 1982).

Onyekuru S.O. et al., *(*2018) 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 were 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 were 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 the clay minerals were good for engineering and some economic purpose after comparison with specific standards.

Adeola A.J. et al. (2020) worked on the geochemical and mineralogical characteristics of clay deposits at Ijesha-Ijebu and its environs, Southwestern Nigeria showing that kaolinite was the dominant mineral, while quartz, albite and muscovite are the major non-clay minerals. Chemical data showed that the values of SiO_2, Al_2O_3 and Fe_2O_3 are 66.11%, 20.53% and 3.037% respectively in weathered banded gneiss, in sedimentary the values of SiO_2, Fe_2O_3 and Al_2O_3 are 42.12%, 34.43% and 7.37%. Evaluation of the clay properties and characteristics shows the industrial application of the clay to be most likely for the production of ceramics, building bricks and other structural wares.

Moses O.E. et al. (2021) reviewed the mineralogical and chemical characteristics of clays found in southern part of Nigeria, with a view to determine its usability. Findings revealed that the dominant clay minerals within the study area include montmorillonite, illite, and kaolinite. It was also observed that non-clay minerals such as feldspar, quartz, dickite and many others were found with clay. Chemical characteristics consists mainly of Al_2O_3, K_2O, CaO, SiO_2, P_2O_5, MgO, Fe_2O_3, TiO_2, MnO and Na_2O with Some trace elements such as Be, Ba, Sc, Sr, Zr, V and Y were present in clay deposits found in selected part of Ogun state. It was observed that the mineralogical and chemical characteristics of clay in the study area makes it suitable for pharmaceutical, textile, cosmetic and polymer industries, but considered to be fairly suitable for the oil and gas industry.

Ike J.C. et al. (2021) from their study pointed out that clay mineral is one of the most sorted industrial minerals. Clay is of economic importance and industrially utilized in ceramic, paint, and paper industries, petroleum, agriculture, environmental remediation and construction.

2.1.1 Industrial application of clays

The Industrial requirements for clay application includes mineral composition, content of Al_2O_3 and SiO_2, impurity content, pH value, chemical stability, swelling, fire resistance, coarseness of particles, whiteness Velde B. (1995) and Garzon E. *et al.* (2010). Depending on the application and customer requirements, clays must have certain properties: for paper production (high degree of whiteness as well as low abrasiveness is necessary), paint industry (a high degree of whiteness, large proportion of fine particles and good dispersion properties), in plastics industry (is mainly related to the particle size), ceramics industries primarily requires (good shaping ability), in production of refractory materials (bricks) requires a (high content of aluminum oxide Al_2O_3).

2.1.1.1 Heat Storage Materials

Reduction of heat losses in buildings has a significant impact on total emissions of greenhouse gases. Traditional insulation materials have been used in thin or multiple layers in order to achieve a higher thermal resistance but caused more complex construction details. For this reason, in recent years an attention has been focused on phase-change materials (e.g., hydrated salts, paraffin, fatty acids) Farid M.M. et al. (2004) and materials with good absorption properties as thingy and bentonite, which have an ability to store the thermal energy in a latent form. In this way, the capacity of heat storage per unit volume was increased compared to that of conventional building materials.

2.1.1.2 Electrical Engineering

Clay minerals can be used as insulators in electrical engineering. Bentonite gels were used as thickening agents for electrolytes, which are used in electrical capacitors. Bentonite has also been used as an excipient for the polymer batteries. Aradilla D. et al. (2014).

Rozynek et al. (2013) studied the electric-field-induced structuring of kaolinite and halloysite particles in respect to their electrorheological response in silicone oil and in paraffin dispersions. It was found that kaolinite particle dispersions have an improved electrorheological response relative to dispersions of halloysite particles.

2.1.1.3 Agriculture

Impermeability to water provides slower swelling of soluble fertilizer and thus rational use of fertilizers. The main advantage of clays in the soil is moisture retention and a slow release of fertilizing elements Tian L. et al. (2013) and Peteiro-Moure M. (2009). The presence of bentonite in the soil increases its drying and thus there is an increase in the pH of soil which is of great importance for the plants growing in such a soil. The use of bentonite was suggested for superphosphates Xiaoyu N. et al. (2013) and mixed fertilizers with a super-phosphate, nitrogen and potassium hydroxide.

2.1.1.4 Preparation of Insecticides and Fungicides

The use of particle film technologies is one of the approaches to suppress arthropod pests of crops Glenn D.M. et al. (1999). There are data on the application of kaolin particle films in a number of different crops (mainly fruit) against a range of different pests Abd El-Aziz Sh. E. (2003a) and Abd El-Aziz Sh. E. (2003b). The material is chemically inert over a wide pH range, and therefore has no direct toxicity to animals or plants. In this case, kaolin is used as an aqueous suspension which is sprayed onto the crop, forming a white particle film between the pest and its host plant Abd El-Aziz, Sh.E. (2013). This hampers insect movement in plants, prevents the feeding and other physical activities of insects.

2.1.1.5 Food Industry

Fruit and vegetable storage technologies available today consume a lot of electricity and generate more pollutants. However, recently more and more attention were paid to the design of equipment that should be a low cost technology, eco-friendly, affordable and easy to handle. Al-Arfaj A.A. et al. (2013) were focused on clay pyramid for storing household fruits and vegetables. They used two storage systems like refrigerator and room temperature as control. The efficiency of the bentonite clay pyramid is estimated by determining the physiological loss of weight, heterotrophic microbial count and organoleptic quality for the stored products such as bitter guard, chilly and orange. From the result obtained it may be concluded that the clay pyramid storage system is a more effective method than storage room and refrigerated storage. Therefore, this pyramid could be used as the best eco-friendly, electricity free, zero cost mechanisms.

2.1.1.6 Textile Industry

Gashti M.P. et al. (2013) developed a method that provides a simple and practical solution for improving the dyeability of cotton with direct and basic dyes. During the experiment, the fibres were dyed with basic and direct dyes after the nano clay pre-treatment. In this case, the nano clay was used as received. Based on obtained results, it was concluded that the basic dyes showed a higher dyeability on the clay pre-treated samples compared to raw materials. Bentonite, due to its large specific surface area and adsorption capacity increases emulsion stability, and thus extends the shelf life of the product. For example, the stability of the flax oil paint is increased by addition of bentonite and disabled by the separation of pigment (barium sulphate) from the oil. These bentonite emulsions, due to the ability to absorb water by bentonite, reduce the water permeability which results in greater protection of objects from corrosion. Also, in the paint industry, bentonite is used as a tanning agent for the dye. The cotton fabric can be coated with flame retardant intumescent formulations containing bentonite nano clay. In this way the thermal stability of cotton fabric is increased after 300 °C Nehra S. (2013).

2.1.1.7 Production of Detergents

The presence of alkaline earth metal ions or polyvalent cations Ca^{2+} and Mg^{2+} has a negative effect on the ability to wash surfactants. Adsorption of polyvalent cations reduces the electrical potential which makes it difficult to remove impurities and facilitates its re-entry to the substrate fabrics. Clay binds alkaline earth metals, and it is itself negatively charged so that the negative potential increases and thereby increases the effect of washing. Clay can replace polyphosphates in laundry detergents. Clay does not allow agglomeration of the impurity particles by reducing the Vander Walls's force of attraction that exists between them. Also, clay does not allow return of the impurities from the washing solution on the material. Bentonite was mixed with the surfactants used in ecological detergents. Therefore, detergents with bentonite were characterized by valuable benefits such as: Large contact area, formation of abundant and light foam, ability to facilitate the dissolution of detergent, to penetrate well into the fibers and to absorb the impurity, ability to soften hard water through ion exchange Jha A.K. (2011). Clay allows the integration of fatty substances, creating a stable suspension in the solution, Underwear after washing, softer and longer retains the freshness Feng-LG H. (2011) and Reyes A. (2011).

2.1.1.8 Environmental Protection

Industrial effluents are contaminated with highly toxic, non-biodegradable and cancerogenic heavy metals, which are generated by industries such as electroplating, mineral processing, galvanization plants, paints formulation, porcelain enameling, nonferrous metal and vegetable fat producing industries Meena et al. (2005). Due to the discharge of large amounts of metal-contaminated wastewater, the electroplating industry is one of the most hazardous among the chemical-intensive industries Pereira et al. (2010). If not carefully managed, however, wastewater may produce both short and long-term effects on human health and the ecological system.

Chantawong V. et al. (2003) during their study investigated the adsorption characteristics of clay in Thailand, for the removal of ions Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) in the form of nitrates. Based on the obtained results the adsorption of metal ions from solution by the individual success of the removal took place in the following order: Pb> Cr> Cd> Zn> Cu> Ni.

2.1.1.9 Biomedical, Pharmaceuticals, Spas and Aesthetic Medicine

Clays play an important role in medicine Mukherjee S. (2013). Clay therapy is based on the ability of clays and clay minerals to adsorb and retain harmful and toxic substances. Because of their properties as a high specific area and sorptive capacity, rheological properties, chemical inertness and low or null toxicity for the patient. Clay and clay minerals are extensively used in the formulation of various pharmaceutical and cosmetic products Lopez-Galindo A. et al. (2007). The therapeutic properties of clay come from its complex chemical composition and those are antitoxicity, antiseptic properties, bacteriocidity, anti-inflammatory properties, absorption, and demineralization Fratzl P. et al. (2007).

In pharmaceutical formulations, they are used as active substance orally administered (osmotic oral laxative, anti diarrehoeaics, gastrointestinal protectors) or administered topically (dermatological protectors, cosmetics) and as excipients (lubricants, delivery systems, inert bases, emulsifiers). Isabel Carretero M. (2002). The novel sun lotion was introduced with considerable Ultraviolet (UV) absorption properties compared to commercially available sunscreens. This formulation, containing bentonite and zeolite minerals, could absorb the highest level of Ultraviolet (UV) light compared to that of the commercially availab) introduced.

Due to clay properties such as absorption/adsorption capacity, high cation exchange capacity, plastic properties, rheological properties, grain size and cooling index, clay minerals have become useful in spas, geotherapy, pelotherapy and paramuds Isabel Carretero M. (2002). The mixture of clays and water in geotherapy is directly applied upon the skin to treat dermatological diseases and to alleviate the pain caused by chronic rheumatic inflammations and sport traumatism.

The desirable physical and physiochemical properties of clay minerals have led them to play a substantial role in pharmaceutical formulations. The elemental features of clay minerals which caused them to be used in pharmaceutical formulations are high specific area, sorption capacity, favourable rheological properties, chemical inertness, swelling capacity, reactivity to acids and inconsiderable toxicity, of course, these are highly cost effectual.

Table 2.1 Pharmaceutical activities of clay mineral

S/N	GROUP	PHARMACEUTICAL ACTIVITY	MECHANISM OF ACTION
1	Palygorskite-sepiolite, smectites	Gastric and duodenal Ulcer	H+ neutralizing capacity decomposition in gastric acid and bring the bowel pH to 6. Robert M.F. et al. (1991).
2	Kaolinite, palygorskite-sepiolite, Smectites	Gastrointestinal Protector	High-specific area and sorption capacity. Carretero M.I. (2006).
3	Palygorskite-sepiolite, smectites kaolinite	Antidiarrhoeaics	Astringent action of the Ca^{2+} ion, which forms nonsoluble, hydrated phosphates. Murray H.H. (2000).
4	Kaolinite-talc, smectites	Dermatological Protectors	Adhere to skin, forming a film that mechanically protects the skin. Adsorbs the skin's secretions and creates a large surface for their evaporation which promotes a gentle antiseptic action by producing a water poor medium that is unfavourable for the development of bacteria. Arab S. et al. (2012).
5	Mirabilite, epsomite, periclase brucite, magnesite	Laxatives	High solubility in water and HCl; release of Na+ or Mg2+ ions and nontoxic anions when ingested. Silva P.S.C. et al. (2011).
6	Kaolinite	Anti-inflammatories and local anaesthetics	High absorption and heat retention capacities. Parolo M.E. (2011).
7	Palygorskite, sepiolite, kaolinite, smectites, talc	Cosmetic creams, powders and emulsions	Opacity and high sorption capacity. Carretero M.I. (2010).

8	Silver and cationic surfactant modified smectites	Antibacterial activity	Heavy metals modified montmorillonites exhibit high cation exchange capacity, large specific surface and colloid properties that give rise to optimum adsorbents of organic and inorganic substances. Williams L.B. et al. (2010)
9	Halite, sylvite, melanterite, epsomite, mirabilite	Haemostatics	Smectite group of minerals have wider applications due to their high swelling and cation exchange capacity. Silva P.S.C. et al. (2011)

2.2 Geology of the Study Area

The geology of the study area is characterized by Cretaceous to Tertiary Sedimentary formations which occupies over eighty percent of Edo State (Figure 2.1). Some cretaceous sediments of Anambra Basin and tertiary sediments of Niger Delta sequences are found in the study area. These formations contain clay deposits. The Ogwashi-Asaba Formation consists of clays, sands and grits and seams of lignite alternating with gritty clays. It grades upwards into the Benin Formation (Omoruyi et al., 2022). The Ogwashi-Asaba Formation is exposed in stream channels at the northern parts of the Benin Region, west of Ekiadolor-Iwu and 4 km east of Utekon and north of Azalla (Reyment, 1965).

The Benin Formation is assigned to the Oligocene-Pleistocene period in the continent of Africa and to the Oligocene-Pleistocene to recent at the sub oceanic (Short and Stauble, 1967). The formation is characterized by top reddish to reddish brown lateritic massive indurate clay and sand. This is often marked with reticulate mud cracks as shown in (figure 2.1). This cap the underlying more friable pinkish-yellowish white often gravelly-pebble sands, clayey soils, sands and clay (Akujieze, 2004). The sedimentary sequences are poorly bedded with discontinuous clay horizons at various depths.

It is estimated to be about 800m thick under Benin City and about 1,830 m near the seashore sections of the formation. They are exposed at various erosion sites, sand quarry sites, and road cuttings. Regionally, the Imo Shale, which sits on top of the Nsukka Formation reveals a shallow marine shelf environment with preserved foreshore and shoreface sands (Petters and Ekweozor, 1981; Obirike, 2012). It also contains black shales, blue-grey clays, and marl with intersperse calcareous sandstone, marl, and limestone (Onyekuru et al., 2018).

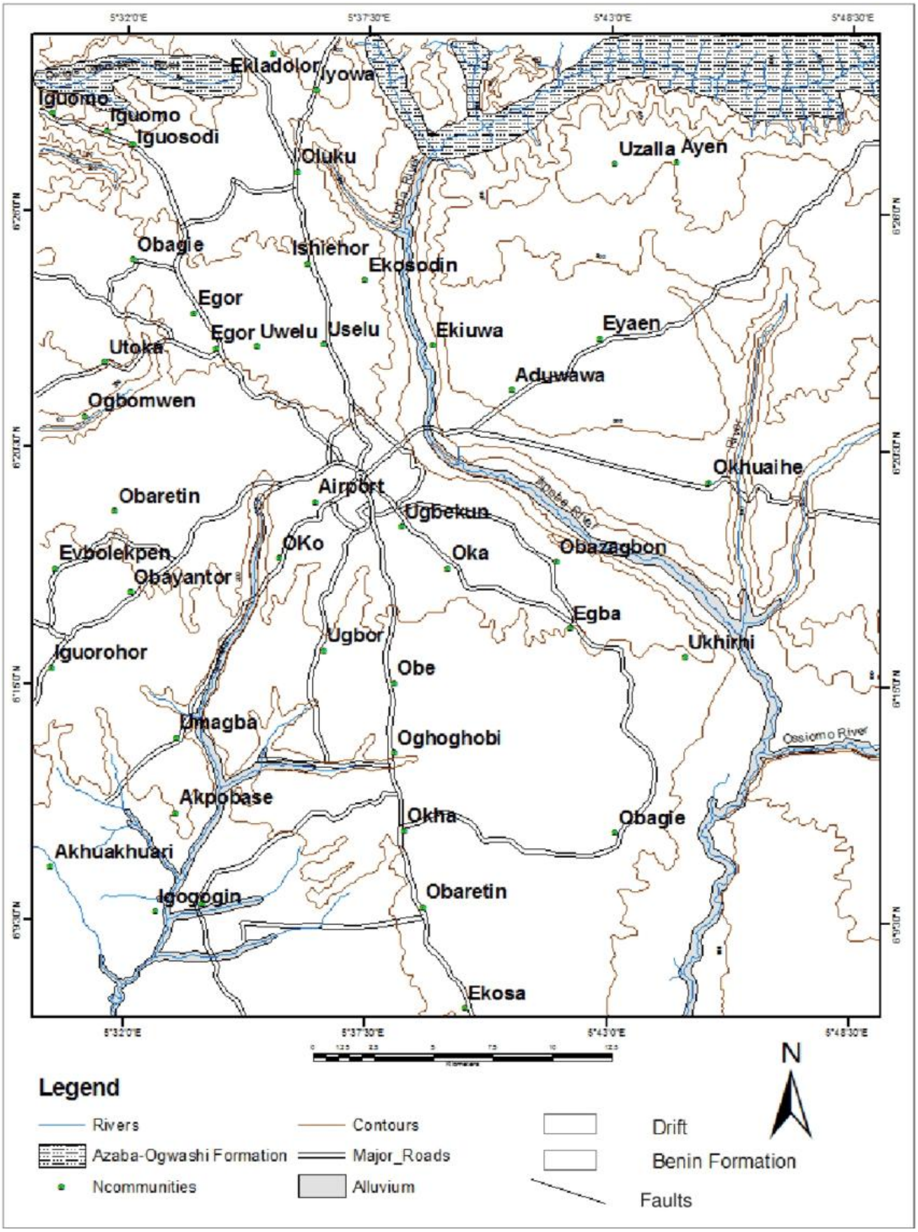


Figure 2.1. Geology of Benin Formation, Edo State (from Akujieze 2004)

According to Obirike et al. (2007) and Onyekuru et al. (2018), regression persisted throughout the Eocene and culminated in the formation of Lower and Middle Eocene deposits, which include the clastic Ameki and Nanka Formations. The transition back to regressive conditions is marked by the progradational Nanka Formation. In the northern parts of the Niger Delta, the Agbada Formation represents the subsurface deposits of the prograding shoreface and river plain, while the Akata Formation refers to the marine Imo Shale counterpart. The Oligocene-Recent Ogwashi-Asaba and Benin Formations dominate the area's uppermost lithostratigraphic units of the stratigraphic succession (Nwajide, 2005; Okoye and Obi, 2011).

Figure 2.2a. Clay deposits at Iguoriakhi sample location

Figure 2.2b. Clay deposit at Iguoriakhi showing mud cracks.

In the Miocene period, the Niger Delta sediments accumulate and prograde seawards. As a result, the sea level is lowered during the Pleistocene. The Niger River cut wide valleys through its own delta. These troughs are being filled today as the sea level gradually rises (Okoye and Obi, 2011).

Figure 2.2c Locally Mined clay deposits at Iguoriakhi

Figure 2.3a. Clay deposits with interbedded layers of shale and clayey shale layers at Ofunmwengbe sample location

Figure 2.3b. Sedimentary profile of iron cap stones, sandstones with intercalated clay layers at Ofunmwengbe.

2.3 The Regional Geology

The geology of Nigeria is made of three major litho-petrological components: the Basement Complex, the Younger Granites and the Sedimentary Basins. The Basement Complex, which is Precambrian in age, is made up of four units; the Migmatite-Gneiss Complex, the Schist Belts, the Older Granites and Undeformed Acid and Basic dykes. The Younger Granites is made up of several magmatic ring complexes cantered around Jos, Plateau state and other parts of North-Central Nigeria. The Sedimentary Basins comprising sediments fill of Cretaceous to Tertiary ages: which include the Niger Delta, the Anambra Basin, the Lower, Middle and Upper Benue Troughs, the Chad Basin, The Sokoto Basin, the Mid-Niger (Bida-Nupe) Basin and the Dahomey Basin.

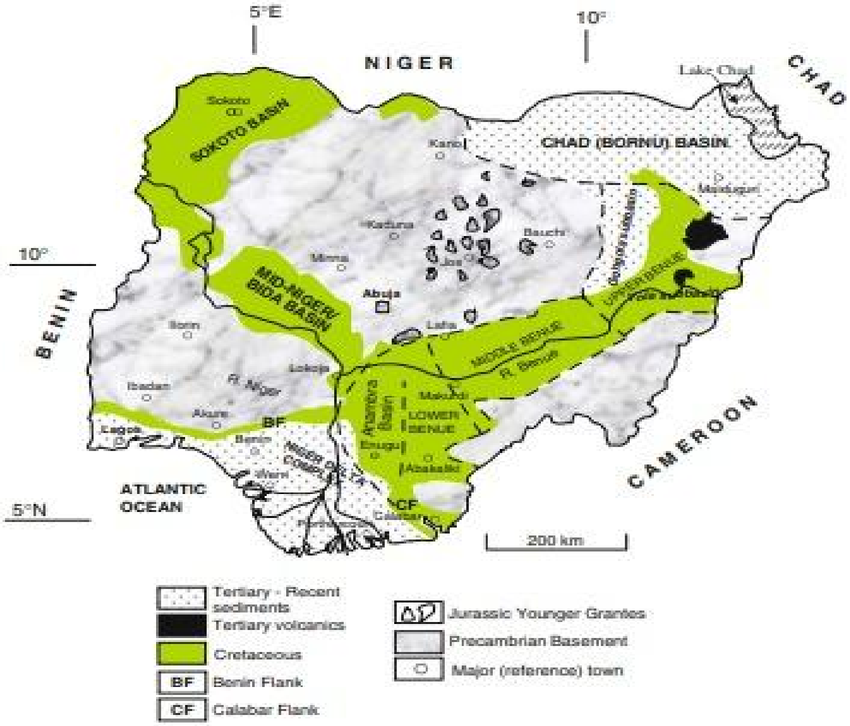


Figure 2.4. Geological sketch map of Nigeria showing the major geological components from Obaje N.G. (2009).

2.3.1 The Basement Complex

The Basement Complex forms a part of the Pan-African mobile belt and lies between the West African and Congo Cratons and south of the Tuareg Sheild (Black, 1980). It is intruded by the Mesozoic clac-alkaline ring complexes (Younger Granites) of the Jos Plateau and is unconformably overlain by Cretaceous and younger sediments. The Basement Complexes was affected by the 600Ma Pan-African Orogeny and it occupies the reactivated region which resulted from plate collision between the passive continental margin of the West African craton and the active Pharusian continental margin (Burke and Dawey, 1972; Dada, 2006).

The basement complex rocks are believed to be the results of at least four major orogenic cycles of deformation, metamorphism and remobilization corresponding to the Liberian (2,700 Ma), the Erburnean (2,000 Ma), the Kibaran (1,100 Ma), and the Pan-African cycles (600 Ma). The first three cycles were characterized by intense deformation and isoclinal folding accompanied by regional metamorphism, which was further followed by extensive magmatization. The Pan-African deformation was accompanied by a regional metamorphism, migmatization and extensive granitization and gneissification which produced syntectonic granites and homogeneous gneisses (Abaa, 1983).

Late tectonic emplacement of granites and granodiorites and associated contact metamorphism accompanied the late stages of this last deformation. The end of the orogeny was marked by faulting and fracturing (Gandu et al., 1986; Olayinka, 1992).

2.3.1.1 The Migmatite – Gneiss Complex (MGC)

The Migmatite Gneiss Complex is generally considered as the basement complex (Rahaman, 1988; Dada, 2006) and it is the most widespread of the component's units in the Nigerian basement. It has a heterogeneous assemblage comprising migmatites, orthogneisses, paragneisses and a series of basic and ultrabasic metamorphosed rocks Petrographic evidence indicates that the Pan-African reworking led to recrystallization of many of the constituent minerals of the MGC by partial melting with majority of the rock types displaying medium to upper with majority of the rock types displaying medium to upper amphibolite facies metamorphism. The MGC also termed by some workers as the Migmatite-Gneiss-quartzite complex makes up about 60% of the surface area of the Nigerian Basement (Rahaman and Ocan, 1978). These rocks record three major geological events (Rahaman and Lancelot, 1984); the earliest, at 2,500 Ma, involved initiation of crust forming process and of crustal growth by sedimentation and orogeny; followed the Eburnean, 2,000 ± 200 Ma, marked by the Ibadan type granite gneisses; this was followed by tags in the range from 900 to 450 Ma which represent the imprint of the Pan-African event which not only structurally overprinted and reset many geochronological clocks in the older rocks, but also gave rise to granite gneisses, migmatites and other similar lithological units. The close analogy in time with the development of the Birrimian of the West African Craton is striking. Definite geochemical evidence for the existence of theses rocks exists in area in northern, western and eastern Nigeria covered by rocks of the MGC; Abuja, Keffi, Bauchi, Kaduna Okene (in northern Nigeria) Ibadan, Ile-Ife, Akure, Ikere (in western Nigeria) and Obudu and the Oban Massif areas in eastern Nigeria. Lithologically similar rocks in other parts of Nigeria, especially in the northeast and southeast, have given only Pan-African ages (Tuboson, 1983).

2.3.1.2 The Schist Belt (Metasedimentary and Metavolcanic Rocks)

The Schist Belts comprise low grade, metasediment-dominated belts trending N-S which are best developed in the western half of Nigeria. These belts are considered to be Upper Proterozoic supracrustal rocks which have been in folded into the migmatite-gneiss-quartzite complex. The lithological variations of the schist, phyllites, banded iron formation, carbonate rocks (marbles/dolomitic marbles) and mafic metavolcanics (amphibolites). Some may include fragments of ocean floor material from small back-arc basins. (Rahaman, 1976) and Grant, 1978) for examples suggest that there several basins of deposition whereas (Oyawoye, 1972) and (McCurry, 1976) consider the schists belts as relicts of a single supracrustal cover. (Olade and Elueze, 1979) consider the schist belts to be fault-controlled rift-like structures. (Grant, 1978), (Holt, 1982) and (Turner. 1983), based on structural and lithological associations, suggest that there are different ages of sediments. However, (Ajibade et al., 1979) disagrees with this conclusion and shows that both series contained identical deformational histories. The structural relationships between the schists belts and the basements were considered by (Truswell and Cope, 1963) to be conformable metamorphic fronts and it was (Ajibade et al., 1979) who first mapped a structural break. The schist belt rocks are generally considered to be Upper Proterozoic. Klemm et al. (1984) have concluded that the Ilesha belt may be an Archean greenstone belt. (Olade and Elueze, 1979), (Ogezi, 1977) and (Ajibade, 1980) have favoured dominantly ensialic processes in the evolution of the schist belts while (Ajayi, 1980), (Rahaman, 1981) and (Ebuniwe, 1982) have stressed that some include oceanic materials with tholeiitic affinities. Some metallogenetic features of the schist belts are relevant to these problems; the apparent absence of subduction related mineral deposits may be indicative of a limited role for the ensimatic processes; the distribution of primary gold occurrences in some belts but its marked absence in others nay indicate that they do not represent a single supracrustal sequence. The schist belts are best developed in the western part of Nigeria, west of 8^0E longitude, though smaller occurrences are found to the east but only sporadically. The belts are confined to a NNE trending zone of about 300Km wide. The area to the west of this zone is made up of gneisses and migmatites that constitute the Dahomeyan of (Burke and Dewey, 1972). Similarly, to the east, no schist belts are known for a distance of 700km until in Cameroun where a number of schist belts, considered to be Upper Preterozoic, occur in the Pan-African granite-migmatite terrain north of the Congo Craton. The schist belts have been mapped and studied in detail in the following localities: Maru, Anka, Zuru, Kazaure, Kusheriki, Zungeru, Kusheka, Isheyin Oyan, Iwo and Ilesha where they are known to be generally associated with gold mineralization.

2.3.1.3 The Older Granites (Pan African Granitoids)

The term Older Granites was introduced by (Falconer, 1911) to distinguish the deep-seated, often concordant or semi-concordant granites of the basement complex from the high level, highly discordant tin-bearing granites of Northern Nigeria. The Older granites are believed to be pre, syn, and post tectonic rocks which cut both the migmatite-gneiss-quartzite complex and the schist belts. They range widely in age (750-450 Ma) and composition. They represent a varied and long lasting (750-450 Ma) magmatic cycle associated with the Pan-African orogeny. The rocks of this suite range in composition from tonalites and diorites through granodiorites to true granites and syenites. Charnockites form an important rock group emplaced during this period. They are generally high-level intrusions and anataxis has played an important role (Rahaman, 1981). The Older granites suite is notable for its general lack of associated mineralization although the thermal effects may play a role in the remobilization of mineralizing fluids.

The Older granites are the most obvious manifestation of the Pan-African orogeny and represent significant addition of materials (up to 70% in some places) to the crust (Rahaman, 1988). Attempt to classify the Older Granite with respect to timing during an orogenic event are valid over only short distances. Contact features between members of the Older Granites suite suggest the coexistence of several magmas. (Dada, 2006) was of the opinion that the term Pan-Afican Granitoids be used for the Older Granites not only on the merit of age which was not available at the time they were named Older Granites, but because it covers several important petrologic groups formed at the same time.

The granitoids which outcrop with the schist belts in northwestern and southwestern include biotite granites, biotite muscovite granites, syenites, charnockites, serpentinites and anorthosites. Rahaman (1988) discard the earlier classification of members of the Older Granites suite based on their texture, mineralogical composition and the relative timing of their emplacement. In its place, members of the Older Granite suite were classified as follows, based mainly on their textural characteristics; Migmatite granite, Granite Gneiss, Early pegmatites and fine-grained granite, Homogeneous to coarse porphyrytic granite, slightly deformed pegmatite aplites and vein quartz and Undeformed pegmatites, two-mica granites and vein quartz.

The Older Granites occur intricately associated with the Migmatite-Gneiss Complex and the Schist Belts into which they generally intruded. Older Granite rocks therefore occur in most places where rocks of the Migmatite Gneiss Complex or of the Schist Belt occur. However, Older Granites are particularly noteworthy in the and around Wusasa (Zaria), Abuja, Bauchi, Akwanga, Ado-Ekiti and Obudu areas.

In Bauchi area and some parts southwestern Nigeria, most of the Older Granite rocks occur as dark, greenish-grey granites with significant quantities of olivine (fayalite) and pyroxene occurring with quartz, feldspars and micas.

Charnockitic rocks constitute one of the important petrological units within the Precambrian Basement Complex of Nigeria. They usually contain quartz, plagioclase, alkali feldspar, orthopyroxene, clinopyroxene, hornblende, biotite and fayalite with accessory minerals usually zircon, apatite and iron ores (Olanrewaju, 2006). Charnockitic rocks are found in Toro-Bauchi, Ado-Ekiti, Akure, Idanre and Obudu Plateau.

2.3.2 The Sedimentary Basin

The Benue trough of Nigeria is a rift basin in Central West Africa that extends NNE-SSW for about 800km in length and 150km in width. The southern limit is the Northern boundary of the Niger Delta, while the northern limit is the southern boundary of the Chad Basin. The trough contains up to 6,000m of Cretaceous-Tertiary sediments of which those predating the mid-Santonian have been compressional folding, faulted and uplifted in several places. Compressional folding during the mid-Santonian tectonic episode affected the whole of the Benue Trough and was quite intense, producing over 100 anticlines and synclines (Benkhelil, 1989). Major deformational structures include the Abakaliki anticlinorium and the Afikpo syncline in the Lower Benue, the Giza anticline and the Obi syncline in the Middle Benue and the Lamurde anticline and the Dadiya syncline in the Upper Benue Trough. The Benue Trough is arbitrarily subdivided into Lower, Middle and Upper portions. No concrete line of division can be drawn to demarcate the individual portions, but major localities that constitute the depocenters of the different portions have been well documented (Petters, 1982; Nwajide, 1990; Idowu and Ekweozo, 1993; Obaje et al., 1999).

2.3.2.1 The Lower Benue Trough and the Anambra Basin

Sedimentation in the Lower Benue Trough commenced with the marine Abian Asu River group, although some pyroclastics of Aptian-Early Albian ages have been sparingly reported (Ojoh, 1992). The Asu River Group in the Lower Benue Trough comprises the shales, limestones and sandstones lenses of the Abakaliki Formation in the Abakaliki area and the Mfamosing Limestone in the Calabar Flank (Petters, 1982).

The marine Cenomanian-Turonian Nkalagu Formation (black shales. Limestones and siltstones) and the interfingering regressive sandstones of the Agala and Agbani Formation rest on the Asu River Group. Mid-Santonian deformation in the Benue Trough displaced the major depositional axis westward which led to the formation of the Anambra Basin. Post deformational sedimentation in the Lower Benue Trough,

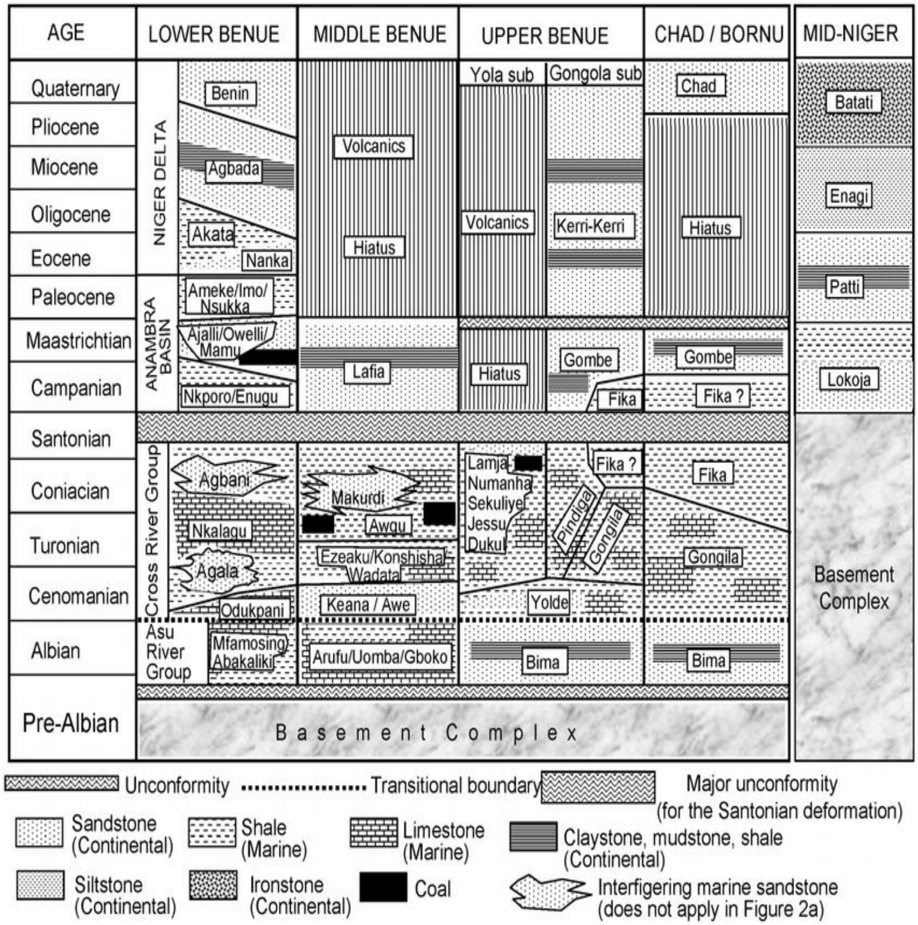
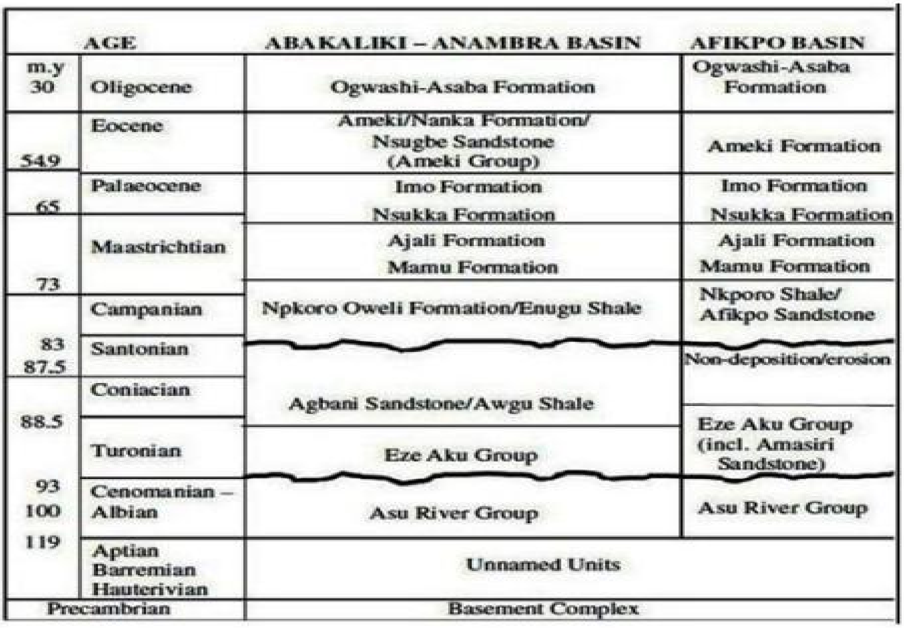


Figure 2.5. The stratigraphic succession in the Benue trough in the Nigerian Sector of the Chad Basin. (Obaje, 2009).

therefore, constitutes the Anambra Basin. Sedimentation in the Anambra Basin thus commenced with the Campanian-Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations, overlain by the coal measures of the Mamu Formation. The fluviodeltaic sandstones of the Ajali and Owelli Formation lie on the Mamu Formation and constitutes its lateral equivalents in most places. In the Paleocene, the marine shales of the Imo and Nsukka Formations were deposited, overlain by the tidal Nanka Sandstone of Eocene age.

Downdip, towards the Niger Delta, the Akata Shale and the Agbada Formation constitute the Paleogene equivalents of the Anambra Basin.

The Enugu and Nkporo Shales represent the brackish marsh and fossiliferous pro-delta facies of the Late Campanian-Early Maastrichtian depositional cycle (Reijers and Nwajide, 1998). Deposition of the sediments of the Nkporo/Enugu Formations reflects a funnel-shaped shallow marine setting that graded into channelled low-energy marshes as shown in (figure 2.5). The coal-bearing Mamu Formation and the Ajali Sandstone accumulated during this epoch of overall regression of the Nkporo cycle. The Mamu Formation occurs as a narrow strip trending north-south from the Calabar Flank, swinging west around the Ankpa plateau and terminating at Idah near River Niger.



AGE		ABAKALIKI – ANAMBRA BASIN	AFIKPO BASIN
m.y 30	Oligocene	Ogwashi-Asaba Formation	Ogwashi-Asaba Formation
54.9	Eocene	Ameki/Nanka Formation/ Nsugbe Sandstone (Ameki Group)	Ameki Formation
65	Palaeocene	Imo Formation Nsukka Formation	Imo Formation Nsukka Formation
73	Maastrichtian	Ajali Formation Mamu Formation	Ajali Formation Mamu Formation
	Campanian	Npkoro Oweli Formation/Enugu Shale	Nkporo Shale/ Afikpo Sandstone
83 87.5	Santonian	Agbani Sandstone/Awgu Shale	Non-deposition/erosion
	Coniacian		
88.5	Turonian	Eze Aku Group	Eze Aku Group (incl. Amasiri Sandstone)
93 100	Cenomanian – Albian	Asu River Group	Asu River Group
119	Aptian Barremian Hauterivian	Unnamed Units	
Precambrian		Basement Complex	

Figure 2.6 The Geology of the Anambra Basin

The Ajali Sandstone marks the height of the regression at a time when the coastline was still concave. The converging littoral drift cells governed the sedimentation and are reflected in the tidal sand waves which are characteristic of the Ajali sandstaone. The sand best exposure of the Nkporo shale is at the village Leru (Lopauku), 72km south of Enugu on the Enugu-Port Harcourt express road, while that of Enugu shale is at Enugu, near the Onitsha-Road Flyover.

The Mamu Formation is best exposed at the Milken Hills in Enugu, with well-preserved sections along the road cuts from the King Petrol station up the Milken Hills and at the left bank of River Ekulu near the bridge to Onyeama mine.

The Nsukka Formation and the Imo Shale mark the onset of another transgression in the Anambra Basin during the Paleocene. The shales contain significant amount of organic matter and may be a potential source for the hydrocarbons in the northern part of the Niger Delta (Reijers and Nwajide, 1998). In the Anambra Basin, they are only locally expected to reach maturity levels for hydrocarbon expulsion.

2.3.2.2 Local Geology of Iguoriakhi and Ofunmwengbe Areas

The local geologic setting of Iguoriakhi and Ofunmwengbe lies conformably on the Upper Senonian Abeokuta Formation (Rayment, 1965). The Imo shale is essentially thick clayey shale, dark grey to bluish grey with occasional admixtures of clay, ironstone thin sandstone beds and limestone. The shale is typically dark, very thinly laminated fissile and contains abundant pyrite crystals, but poorly fossiliferous (Ogbe, 1970). The Imo shale in the eastern part is a lateral equivalent of the Akinbo Formation in Southwestern Nigeria (Fayose and Asseez, 1972). The Imo formation outcrops at Iguoriakhi as sand and clay and at Ofunmwengbe as clay, sandstone, lignite and shale respectively as shown in (figure 2.7).

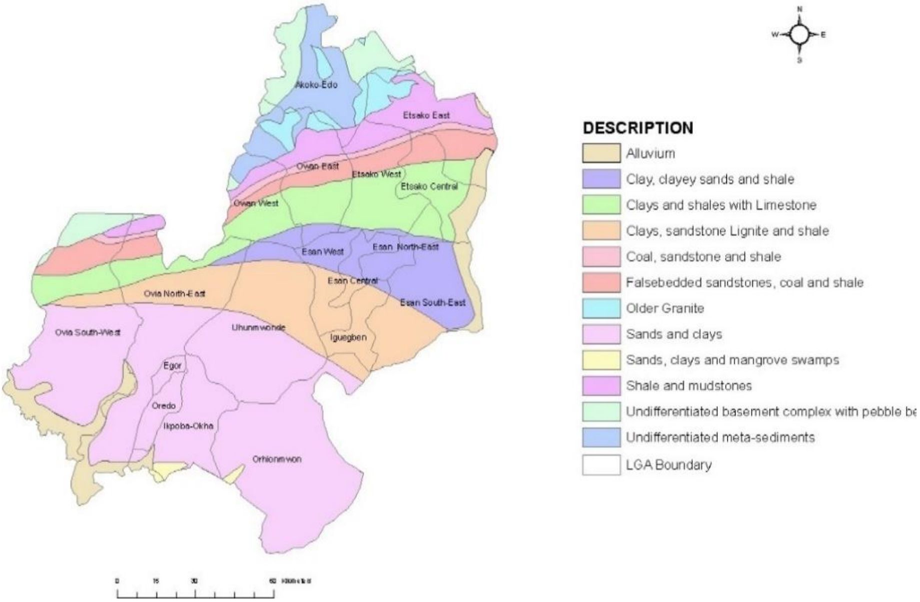


Figure 2.7 The Geology of Edo state Nigeria

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Field Study

Clay minerals are seldom mono-mineralic and have no genetic significance, as they are used for residual weathering products, hydrothermally altered products, and sedimentary deposits (Murray, 2007). These minerals occur under a fairly limited range of geologic environments which include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. In general, they form where rocks are in contact with water, air, or steam and the type of clay however is controlled by the composition of pre-existing rock mineralogy (Kabeto et al., 2012). Thirty (30) fresh samples of clays were taken from Iguoriakhi, Ofunmwengbe and environs, Southwest Nigeria. The samples are herein designated and well labelled. Care was taken when sampling to ensure that fresh samples were taken and that such samples were representative of the materials to be assessed. The sampling depth ranged from 1 to 2.5 m. The samples were subjected to preliminary treatment and physical beneficiation tests also bulk mineralogical and chemical analyses were carried out.

3.2 X-Ray Diffractometry (XRD)

X-rays are produced in a cathode ray tube by heating the filament to produce electrons and accelerating them to the target material by applying a voltage. As the sample and detector are rotated, the intensities of diffracted X-rays are recorded. When Bragg's equation is satisfied (Bragg, 1913), it means that the geometry of diffracted X-rays shows.

Figure 3.1 Representative samples collected from Iguoriakhi (IGK) clay deposit in well labelled sample bags

Figure 3.2a. Representative samples collected from Ofunmwengbe (OFM) clay deposits in well labelled sample bags.

Figure 3.2b. Representative dark grey/bluish grey samples collected from Ofunmwengbe shales deposits (OFE) in well labelled sample bags.

constructive interference and peak show up in the diffractogram. The detector, which is present inside the diffractogram, records that intensity. This intensity is then converted into a count rate, which is displayed and recorded into the monitor. The geometry of the diffractometer is such that the sample rotates the X-rays beam at an angle of θ, whereas X-rays, which are diffracted, rotates an angle of 2θ. The goniometer rotates the sample and detector.

X-ray powder diffraction analysis is the basic technique for clay mineral analysis (Moore and Reynolds, 1989). After preliminary removal of sand, clay is separated from silt by centrifugation or sedimentation from suspensions. X-ray diffraction patterns are obtained for air-dried samples and, in the case of oriented aggregates, also for samples treated with ethylene glycol vapour or heated to 350 and 550 °C. Diffraction patterns are compared with standards (Grim, 1968; Thorez, 1975; Brindley and Brown, 1980; JCPDS, 1981) for identification of minerals. Comparisons are complicated, however, by variations in diffraction patterns arising from differences in amounts of absorbed water, by the presence of imperfections in the crystal lattice structure of the minerals, and by mixed-layer structures formed by interstratification of minerals within a single particle (Grim, 1968). Approximate quantification of mineral abundance in samples containing several minerals is possible, although subject to a variety of complications and errors (Starkey et al., 1984; Salt, 1985).

X ray diffraction is the most heavily relied on technique, and the most powerful tool, in the identification of minerals. Especially in mixed-phase complexes, which is the usual situation met in the determination of clay minerals, the XRD has many applications. Mineralogical studies are very useful in determining the distribution of resources and the dispersion of minerals. Moore and Reynolds (1989) concluded from their research that among the methods of studying and identifying clay minerals such as the XRD method, the differential thermal method, the infrared spectroscopic method, the scanning electron microscopy method (SEM), and the method of using chemical tests), the XRD method had the most applications in the identification of clay minerals. Identification of clay minerals can determine the relationships between mineralogical changes and changes in climate, land use, and in the intensity of weathering. Studying the characteristics of soil minerals and the way these minerals change and transform into each other helps to understand the chemical properties of soils and the origin of their fertility too (Oliyae et al., 2009). On the other hand, clay minerals are components of all soils and the types of these minerals can significantly influence land use (Hartermink, 2006). That is why this research was conducted in an area situated at Iguoriakhi, Ofunmwengbe and environs few kilometers away from Benin City. Obtained diffractograms in the X-ray diffraction test indicated the presence of illite, Kaolinite, montmorillonite, feldspars and quartz in the clays of the studied area and, to some extent the degradation of mica minerals.

Bulk samples were mixed with acetone and ground using agate mortar and pestle. The thick slurry was spread evenly on a glass slide and let to dry at ambient temperature. Acetone was used to allow rapid drying and, consequently, diminish preferred orientation of platy sheet silicate particles. Two or three mounts were prepared of each sample because the diffractograms were used for semiquantitative evaluation of mineral composition. Most of the samples are raw material and therefore heterogeneous. MX-80 is homogenized, and Milos activated and Friedland ground to very fine-grained powder. The XRD data was collected on a Philips X'Pert diffractometer equipped with a vertical goniometer, a diffracted beam monochromator and a rotating sample holder. CuKa-radiation was used and the applied voltage was 40 kV with a 55 mA current. Each X-ray diffraction pattern has a unique set of Bragg peaks. Thus, each crystalline material has its own “fingerprint” (set of peaks). This permits x-ray diffraction to be used for phase (mineral) identification. Phase identification is done by comparison of the experimental pattern with a database of known patterns. The Powder Diffraction File of the International Centre for Diffraction Data (ICDD-PDF) contains either or both the experimentally measured and calculated digitized patterns for hundreds of thousands of compounds. It includes minerals, metals and alloys, inorganic materials, organic compounds and pharmaceuticals. Phase identification is performed either visually or by using automatic searches but generally a combination of both is used. Automatic search/match is rapid, uses multiple Bragg reflections and searches the database available (many hundred-thousand entries). Critical search/match parameters include: The number of Bragg peaks that match in position and in relative intensity (to a lesser extent). The tolerance or difference in positions between the observed and database peaks as long as the deviation remains within the tolerance, peaks are considered to match. Automatic searches usually generate a large number of matches. The correct solution should be selected manually by the user. This may involve simple visual matching, or an understanding of the sample.

3.3 X Ray Fluorescence Analysis

The bulk chemical compositions of the clay samples were determined by X-ray fluorescence (XRF) analysis. Samples were oven-dried at 100°C for 12 hours for adsorbed water measurements and crushed. For the total chemical analysis, all samples were pulverized in a tempered carbide-steel grinding vessel and dried at 40°C in a forced air oven. Pressed powder pellets were prepared and the elemental composition determined using X-ray fluorescence spectroscopy (XRF). The powdered samples were then mixed with a binder (ratio of 1: 9 in

Figure 3.3. Soaked samples during sample preparation.

Figure 3.4. Homogeneous grinding and blending of samples.

Figure 3.5. Well packaged Iguoriakhi samples ready for analysis

Figure 3.6. Ofunmwengbe samples ready for XRF analysis.

grams of C-wax and EMU powder) at a ratio of 2: 9 (2gram binder and 9gram sample). The powder mixture was then pelletized at a pressure of 15 Kbars for 1 minute. Loss on ignition (LOI) experiment was performed prior to major element analysis. The XRF analyses were, carried out at the Geology department of the University of the Western Cape, South Africa. A Phillips PANalytical PW1480 X-ray fluorescence spectrometer using a Rhodium Tube as the X-ray source was used. The technique reports concentration as % oxides for major elements and ppm for minor elements.

3.4 Sieve Analysis

This analysis was carried out to determine the particle-size distribution curve of the clay (soil) samples and to also determine the coefficient of uniformity (Cu) and coefficient of concavity (Cc) of the samples.

Each sample was mounted and basically shaken through a set of sieves that have progressively smaller openings. Sieves that are taken for the process are U.S. standard sieves. Sieve analysis was categorized to determine the size range of particles present in a soil expressed as a percentage of the total dry weight. Sieve analysis can only be implemented for the soils with particle sizes larger than 0.075 mm in diameter (passing through No. 200 sieve). Where a large portion of the soil particles is smaller than 0.075 mm, hydrometer analysis is used to define the particle – size distribution.

3.4.1 Theory

Weight of soil retained = (weight of soil + sieve) – (weight of sieve)

Percentage retained on any sieve = (Weight of soil retained/Total soil weight) x 100

Cumulative percentage retained on any sieve = sum of the percentages retained on the sieve Coefficient of uniformity (Cu); an indication of the spread of particle size, which is calculated as,

$Cu = D_{60}/D_{10}$ ………………………………………… (1)

Coefficient of concavity (Cc); a measure of the shape of the curve between D_{60} and D_{10} grain size and is defined as;

$Cc = D_{30}/ (D_{10} \times D_{60})$ ……………………………… (2)

where D_{10}, D_{30} and D_{60} are the soil diameters, at which 10%, 30%, and 60% soil weights are finer, respectively.

3.4.2 Apparatus

Set of sieves (2.36mm, 1.18mm, 0.85mm, 0.6mm, 0.425mm, 0.25mm and 0.075mm) – U.S Standard, Sieve shaker, Sample splitter larger evaporation dishes, Spatula, Brush, Balance sensitive to 0.1 g, Mortar and pestle.

3.4.3 Procedures

Preparation of soil sample: The air-dried soil was used and aggregation of lumps were thoroughly broken up with the fingers, large soil samples were divided using the sample splitter to preserve their grain size distribution.

Testing procedure: Soil sample were oven dried and allowed to cool. Weight of the sample was measured. Weight of each of the sieve was recorded. Stack of sieves was arranged so that the largest mesh opening is at the top and the smallest is at the bottom with Pan attached to the bottom of the sieves. The sample was poured on the top sieve and a cover plate was added to avoid any loss of particles while shaking. The stack of sieve was placed on the mechanical shaker and stack was shaken horizontally for about 10min.

3.5 Hydrometer Analysis

This method was used to determine the particle size distribution of the samples where the particle size is smaller than 0.075mm in size. Hydrometer analysis is governed by the principles of sedimentation of soil grains in water. The settlement of a diffused soil sample in water which depends on the shape, size and weight of the soil particles and the viscosity of the water.

Throughout the analysis soil particles were assumed to be spheres and the velocity of soil particles is expressed by stoke’s law.

3.5.1 Theory

“Stokes Law” provides the relationship among the terminal velocity of fall of sphere in a fluid, the diameter of a sphere, the weights of the sphere, and the viscosity of the fluid.

Hydrometer reading is a measure of soil mass in suspension at the level of the bulb. The grams of soil still in suspension after elapsed time (t) can be obtained from the actual hydrometer reading (Ra). To determine the correction (Cd) due to the dispersing agent on hydrometer readings, readings were obtained within a sedimentation cylinder with distilled water and same amount dispersing agent as that used in soil-water suspension. Meniscus error (Cm) occurred while readings were taken to the top of the meniscus due to the invincibility of bottom of the meniscus as it is surrounded by coloured water. Hence, correction of meniscus (Cm) is applied to the hydrometer readings prior to calculating the percentage finer of soil.

Corrected hydrometer reading (Rc) = Ra – (Cd – Cm) where, Ra is the actual reading of the hydrometer.

Percentage finer (P) = (Rc x a x 100)/W% where, W is the weight of soil in suspension and value of a = 1.

Weight of soil finer than a particular particle size in given soil fraction (W1) passing through No 200 sieve = (W1 x P)g

Percentage finer than particular particle size of the soil sample used in sieve analysis.

= ((W1 x P)/W2) x 100 where, W2 is the total weight of the sample used for sieve analysis.

3.5.2 Apparatus

Hydrometer, Mixer, Dispersing agent, Graded cylinders (1000 ml), Thermometer, Timer, Measuring Cylinder, Distilled water, Drying oven, Desiccator, Syringe, Large evaporation dishes and Spatula.

3.5.3 Procedures

50g of soil sample was accurately weighed. Weighted soil was placed in a beaker and 125 ml of Sodium Hexametaphosphate solution (40g/liter) was added. The mixture was stirred using a mixer and kept soaking for 16hours. Base solution of 1000 ml and the same amount of dispersing agent was prepared in a separate measuring cylinder.

The soaked soil sample was transferred to the cup of mixer and water was added to half fill the cup and stirred for 3 minutes. Soil water slurry was then transferred to the glass sedimentation cylinder and distilled water was added until the water is 1000ml. The cylinder was shaken vigorously by turning it upside down and back using the palm of the hand over the open end of the cylinder, for a period of 1 minute or more until a uniform suspension is formed. The hydrometer was inserted carefully into the soil water suspension and hydrometer readings were taken at different time intervals (George, 2005).

3.6 Atterberg Limits

Atterberg limits are a basic measure of the critical water contents of a fine-grained soil, such as its shrinkage limit, plastic limit, liquid limit and plasticity index. The samples were analyzed in accordance with

ASTM D4318: (Standard Test Methods) for Liquid Limit, Plastic Limit and Plasticity Index to determine its type based on the Unified Soil Classification System (USCS).

3.6.1 Apparatus

The following materials were used for Liquid Limit Test: Liquid Limit Device (Casagrande Cup), Flat Grooving Tool, Guage, Water Content Container, Mixing and Storage Container and Balance. Materials used for Plastic Limit Test include Sieves (Number 40), Glass Plate, Drying Oven and Containers with Lid.

3.6.2 Procedure

The Liquid Limit Test: The samples were sieved in a 425um (No. 40) sieve. A portion of the retained sample was mixed with distilled until smooth consistently. The Casagrande cup was well calibrated. The base of the cup was filled with the soil water mixture until the surface is 10 mm away from the deepest point smoothen out the surface and then tap the cup to eliminate the air bubbles inside the mixture. A groove was formed in the soil using the grooving tool while ensuring that the separation between soils is in the required dimensions. The cup was lifted and dropped at the rate of two (2) drops per second using the crank of the device until the two parts of the mixture came together at the distance of 13mm. The number of drops were counted until it reaches this stage and then recorded.

The Plastic Limit test: More soil was added to the soil water mixture left until it formed into clay without sticking to the hands. 2grams of the clay sample were measured and rolled until it formed into a cylindrical rod with 1/8’ diameter. For the samples that break at 1/8’ diameter the samples were placed in a container of known mass and sealed. The mass of the sample and the container were measured and left inside the oven for 24hours. While the samples that break before the 1/8’ diameter more soils were added in the sample and those that did not break at the 1/8’diameter more water was added to the sample. Samples were left inside the oven for 24hour, and each sample’s moisture content was calculated.

CHAPTER FOUR

4.0 Results, Discussions and Appraisal of Analyzed samples.

4.1 Mineralogical Analysis Results and Appraisal of Samples

The X-ray diffractograms showing the mineral composition for the analysed samples are shown in Figure 4 (a, b and c).

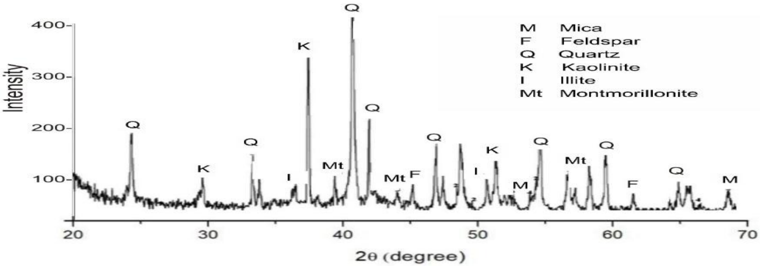


Figure 4.1a. X-ray Diffractograms for Iguoriakhi clay sample (IGK) shows a mineralogical assemblage of Kaolinite,

Montmorillonite, Illite as major clay minerals with quartz, feldspars and micas. It was observed that Quartz was the dominant mineral followed by kaolinite as indicated by the high intensity of its numerous peaks in the x-ray diffractogram. The presence of kaolinite and illite suggests the chemical decomposition of the Iron bearing ferromagnesian minerals such as micas and feldspars.

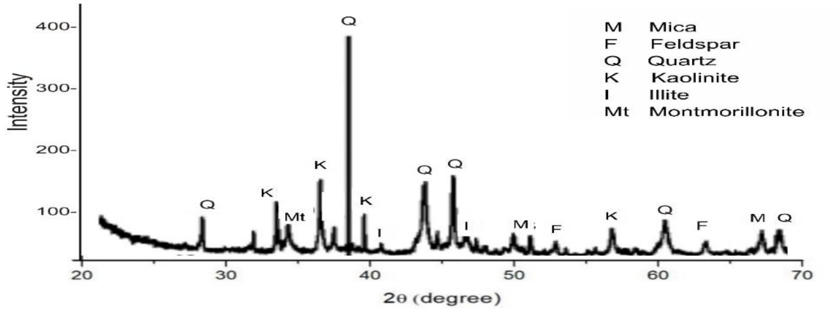


Figure 4.1b. X-ray Diffractograms for Ofunmwengbe clays samples (OFM) shows mineralogical assemblage of Kaolinite, Montmorillonite and illite as major clays with quartz, micas and feldspars occurring as accessory non clayey minerals in the samples. The prominent peaks show the abundance of kaolinite and quartz resulting from the chemical weathering of feldspar minerals.

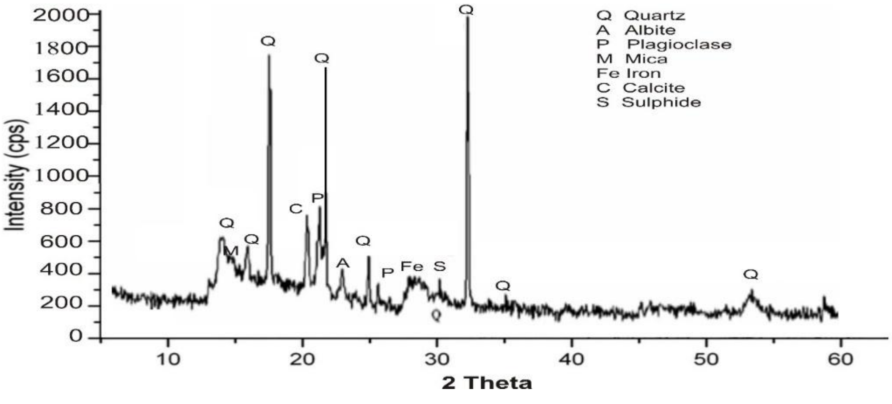


Figure 4.1c. X-ray Diffractogram for Ofunmwengbe shales samples (OFE) shows mineral assemblages of quartz, albite, plagioclase, mica, calcite, sulphide and iron. Quartz was observed as the dominant mineral indicated by the high intensity of its numerous peaks in the X-ray diffractogram. The presence of albite and plagioclase is an indication that the weathering process is still at the incipient state. The presence of iron, sulphide and other carbonaceous minerals may be responsible for its dark colour which lies within the lignite series conforming to the geology of the study area.

4.1.1 X ray Diffractogram characterization of the clay mineral deposits

Kaolinite is the dominant clay mineral in the samples and represents about 26% overall as shown in (Figures 4a and b) and table 4.1. Illite and montmorillonite occur in small quantities in both Iguoriakhi and Ofunmwengbe clay deposits but were completely absent in Ofunmwengbe shales. The investigation shows that the average kaolinite contents.

Table 4.1. Mineralogical composition of the clay samples (* representative values for 10 samples from each location)

Minerals (%)	Iguoriakhi* (IGK)		Ofunmwengbe* (OFM)		Ofunmwengbe Extensions* (OFE)	
	Range	Mean	Range	Mean	Range	Mean
Quartz	44.83 - 53.23	50.83	51.80 - 57.37	55.80	62.44 - 72.11	68.97
Kaolinite	15.88 - 24.21	20.01	20.50 - 29.97	26.10	---	---

Calcite	---	---	---	---	5.74 - 8.03	6.81
Illite	4.30 - 9.52	5.24	3.88 - 5.04	4.07	---	---
Sulphide	---	---	---	---	1.20 - 3.88	2.90
Montmorillonite	8.2 1 - 13.83	10.49	3.23 - 5.68	4.60	---	---
Mica	5.45 - 8.02	6.89	4.69 - 6.15	5.80	3.42 - 5.76	4.54
Plagioclase	---	---	---	---	8.84 - 10.01	9.98
Feldspar	5.44 - 7.98	6.23	2.85 - 3.99	3.40	---	---
Albite	---	---	---	---	3.00 - 4.12	3.63

were higher in Ofunmwengbe clays with 26.10% higher than in Iguoriakhi with 20.01%. Quartz was the major non clay mineral present in all the samples with Ofunmwengbe shales higher with about 68.97% with Ofunmwengbe clays at 55.80% higher than Iguoriakhi with 50.83%. Mica was present in all the samples in the range between 4.54% - 6.89% as well as feldspar in the range between 3.4% - 6.23% though occur as albite and plagioclase in Ofunmwengbe shales.

Typical diffractogram of the Iguoriakhi clays (IGK), Ofunmwengbe clays (OFM) and Ofunmwengbe shales (OFE) as shown in (figures 4a, b and c) and in table 3 shows prominent quartz, kaolinite and mixed layer peaks of minerals. The prominent basal reflections of the mixed layer clay minerals quartz, kaolinite, illite and montmorillonite as indicated by the strong peaks are indications of moderate to well crystalline mineral components.

The clay mineral assemblage therefore comprises of kaolinite, illite and montmorillonite mixed layer clay. Quartz, feldspars (albite and plagioclase), micas, calcite, sulphides and iron are the main nonclay minerals detected from the XRD peaks.

4.2.1 Chemical Characterization of the Major Oxides in Samples

An overview of the chemical analysis from tables (4.2, 4.3 and 4.4) shows the chemical composition of the samples from the study area. The dominance of SiO_2, Al_2O_3 and Loss on Ignition (LOI) of the clay samples clearly defines them as hydrated aluminosilicates. The Iguoriakhi clay deposits have an average composition values of SiO_2 (54.55%), Al_2O_3 (28.77%) and LOI (10.52%) and Ofunmwengbe clay deposits have average composition values of SiO_2 (54.36%), Al_2O_3 (29.01% and LOI (10.52%) and Ofunmwengbe shales have average composition values of SiO_2 (54.99%), Al_2O_3 (26.30%) and LOI (10.46%). These shows that the samples from Ofunmwengbe shales have higher content of SiO_2 compared to Iguoriakhi clays and Ofunmwengbe clays but less content of Al_2O_3 and lower values of LOI as compared to Iguoriakhi and Ofunmwengbe clays deposits respectively. A close observation of the chemical composition reveals that the Iguoriakhi and Ofunmwengbe clay deposits are geochemically similar due to their similar origin (Imo shale formation) as shown in (figure 1.7) with little or less variations as a result of their environmental conditions of formation.

The average ratio of SiO_2:Al_2O_3 shows average values of (1.82) for Iguoriakhi clays, (1.83) for Ofunmwengbe clays and (1.89) for Ofunmwengbe shales. This shows approximately a (1:1) layer to (2:1) layer type of clay deposits in the study area. The average composition of silica and alumina in the samples constitute about 83% of the total chemical composition of the samples. The ratio of alumina to silica is low (0.53 and 0.54) suggesting that the quantity of free quartz is higher in the samples.

The relatively low average composition of CaO (1.23%, 1.32% and 1.13%), Na_2O (0.28%, 0.24% and 0.32%) and MgO (0.40%, 0.38% and 0.42%) in the clay compositions for Iguoriakhi clays and Ofunmwengbe clays is as a result of leaching from the breakdown of biotite, augite and other ferromagnesium minerals of the precursor rocks (micas and feldspars) of granites and gneisses suggesting a neutral to acidic environment of formation. However, the Ofunmwengbe shales show associated carbonates with dolomitization by the presence of calcite and iron in the XRD peaks attributed to the associated carbonates and dolomitization process in various portions of the Lower Benue Trough (Akande et al., 1999).

The relative high values of K_2O compared to Na_2O are in indication of the presence of illite and in contrast the low values of Na_2O are probably consequent upon the relatively low occurrence of sodic feldspars and sodic rich clays in the analysed samples.

Furthermore, the average values for the sum of (K_2O + Na_2O) and (Fe_2O_3 + MnO + TiO_2) in the clay samples (1.20%, 1.16% and 1.08%) and (4.14%, 4.38% and 3.95%) for Iguoriakhi clays, Ofunmwengbe clays and Ofunmwengbe shales respectively were very low, this indicates that the clays are chemically inert, non-corrosive and further indications of the purity of the clays in both Iguoriakhi and Ofunmwengbe.

Geochemical signatures of Al_2O_3 ratio increases from 3 to 8 for mafic igneous rocks, 8 to 21 for intermediate rocks and 21 to 70 for felsic igneous rocks (Hayashi et ai., 1997). This indicates that the analysed clay deposit shows that the calculated Al_2O_3/TiO_2 ratios ranged from for (23.73 – 50.40) and (22.92 – 51.88) Iguoriakhi and Ofunmwengbe respectively shows that the clays originated from intermediate to felsic igneous rocks. Ekosse (2001) also used of TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks as shown in figure 4.8. This shows that the clays originate from Ryolite granite source rock.

The high Chemical Index of Alteration (CIA) ranges between 86.14 - 93.57 and 86.05-93.47, Chemical Index of Weathering (CIW) between 93.59 - 97.71 and 93.55 - 97.67 and Weathering Index of Parker (WIP) between 10.27 - 12.02 and 10.04 - 12.1. The CIA, CIW and WIP values for Iguoriakhi and Ofunmwengbe clays respectively indicates a highly intense degree and almost complete weathering of parent rock minerals to clay. This is confirmed by the low amount of detrital feldspar and mica in the XRD peaks.

4.2 Geochemical Analysis Results and Appraisal of Samples

Table 4.2 Geochemical Composition of Major Elements (Oxides) for Iguoriakhi (IGK) clay samples

Major Element Oxides (%)	IGK1	IGK2	IGK3	IGK4	IGK5	IGK6	IGK7	IGK8	IGK9	IGK10	MEAN
SiO_2	52.90	56.38	55.70	54.54	50.90	56.40	55.68	55.80	52.68	54.50	54.55
Al_2O_3	28.49	29.24	29.20	27.70	30.47	29.22	29.20	29.22	27.20	27.72	28.77
Fe_2O_3	3.65	3.65	2.50	2.82	3.65	3.65	2.50	3.30	2.80	2.84	3.14
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.08	0.46	0.50	0.55	0.08	0.45	0.50	0.42	0.45	0.55	0.40
CaO	1.90	1.45	1.30	0.20	1.90	1.45	1.30	1.25	1.35	0.20	1.23
Na_2O	0.05	0.28	0.25	0.47	0.05	0.28	0.25	0.38	0.35	0.45	0.28
K_2O	0.99	0.94	0.90	0.85	0.99	0.95	0.90	0.95	0.90	0.85	0.92
TiO_2	1.18	1.04	1.23	0.55	1.20	1.04	1.22	1.09	1.02	0.55	1.01
P_2O_5	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.05	0.02
LOI	10.20	10.55	10.24	11.30	10.20	10.55	10.24	10.25	10.40	11.30	10.52
Total	99.46	104.01	101.36	99.02	99.46	104.01	101.81	102.68	97.17	99.02	100.80
SiO_2/Al_2O_3	1.86	1.93	1.91	1.97	1.67	1.93	1.91	1.91	1.94	1.97	1.90
Al_2O_3/SiO_2	0.54	0.52	0.52	0.51	0.60	0.52	0.52	0.52	0.52	0.51	0.53
Al_2O_3/TiO_2	24.14	28.11	23.73	50.36	25.39	28.10	23.93	26.81	26.67	50.40	30.76
Na_2O/K_2O	O.05	0.30	0.28	0.55	0.05	0.29	0.28	0.40	0.39	0.53	0.31
K_2O/Na_2O	19.80	3.36	3.60	1.81	19.80	3.39	3.60	2.50	2.57	1.89	6.23
K_2O+Na_2O	1.04	1.22	1.15	1.32	1.04	1.23	1.15	1.33	1,25	1.30	1.20
$Fe_2O_3+MnO+TiO_2$	4.84	4.70	3.74	3.38	4.86	4.53	3.73	4.40	3.83	3.40	4.14
CIW	93.59	94.41	94.96	97.64	93.99	94.41	94.96	94.72	94.12	97.71	95.05
CIA	86.14	87.73	88.69	93.31	86.92	87.69	88.69	88.22	87.23	93.57	88.82
PIA	88.64	90.18	91.12	96.18	89.33	90.17	91.12	90.75	89.72	96.46	91.37
MIA	86.56	85.73	86.06	89.73	87.26	85.76	86.06	86.32	84.99	89.96	86.84
WIP	11.01	11.70	11.04	10.38	11.01	11.77	11.04	12.02	11.63	10.27	11.19
RBL	9.43	9.34	9.90	13.38	10.09	9.34	9.90	9.74	8.92	13.52	10.36

Table 4.3. Geochemical Composition of Major Elements (Oxides) for Ofunmwengbe (OFM) clay samples

Major Element Oxides (%)	OFM1	OFM2	OFM3	OFM4	OFM5	OFM6	OFM7	OFM8	OFM9	OFM10	MEAN
SiO_2	52.54	55.35	55.70	54.72	50.60	55.40	55.64	54.50	52.80	56.35	54.36
Al_2O_3	28.85	30.27	28.20	27.50	30.77	30.22	29.24	27.27	28.50	29.25	29.01
Fe_2O_3	3.65	3.60	3.50	2.82	3.65	3.63	2.50	2.84	3.63	3.65	3.34
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.08	0.44	0.50	0.60	0.08	0.45	0.50	0.55	0.08	0.49	0.38
CaO	1.94	1.45	1.30	0.20	1.90	1.48	1.30	0.20	1.90	1.48	1.32
Na_2O	0.05	0.30	0.25	0.47	0.09	0.28	0.25	0.45	0.05	0.23	0.24
K_2O	0.95	0.98	0.90	0.80	0.95	0.90	0.92	0.85	0.99	0.92	0.92
TiO_2	1.17	1.05	1.23	0.53	1.20	1.09	1.20	0.55	1.20	1.05	1.03
P_2O_5	---	0.01	---	0.03	---	0.01	---	0.05	---	0.01	0.02
LOI	10.20	10.55	10.24	11.30	10.20	10.50	10.20	11.30	10.20	10.50	10.52
Total	99.44	104.01	101.83	98.98	99.44	103.97	101.76	98.57	99.35	103.96	101.13
SiO_2/Al_2O_3	1.82	1.83	1.98	1.99	1.64	1.83	1.90	2.00	1.85	1.93	1.88
Al_2O_3/SiO_2	0.55	0.55	0.51	0.50	0.61	0.55	0.53	0.50	0.54	0.52	0.54
Al_2O_3/TiO_2	24.66	28.82	22.92	51.88	25.64	27.72	24.36	49.58	23.75	27.86	30.72
Na_2O/K_2O	0.05	0.31	0.28	0.59	0.09	0.31	0.27	0.53	0.05	0.27	0.28
K_2O/Na_2O	19.00	3.27	3.60	1.70	10.56	3.21	3.68	1.89	19.80	3.68	7.04
K_2O+Na_2O	1.00	1.28	1.15	1.27	1.04	1.18	1.17	1.30	1.04	1.17	1.16
$Fe_2O_3+MnO+TiO_2$	4.83	4.66	4.74	3.36	4.86	4.73	3.72	3.40	4.84	4.71	4.38
CIW	93.55	94.53	94.79	97.62	93.93	94.50	94.97	97.67	93.60	94.42	94.96
CIA	86.15	87.90	88.27	93.44	86.92	88.05	88.58	93.47	86.08	87.77	88.88
PIA	88.52	90.39	90.75	96.16	89.20	90.34	91.05	96.40	88.58	90.18	91.16
MIA	86.56	86.05	85.86	89.47	87.26	86.13	85.96	89.82	86.50	85.60	86.92
WIP	10.75	12.11	11.04	10.04	10.92	11.41	11.20	10.27	11.01	11.45	11.02
RBL	9.55	9.55	9.56	13.29	10.19	9.72	9.85	13.30	9.44	9.32	10.38

Table 4.4 Geochemical Composition of Major Elements (Oxides) for Ofunmwengbe (OFE) shale samples

Major Element Oxides (%)	OFE1	OFE2	OFE3	OFE4	OFE5	OFE6	OFE7	OFE8	OFE9	OFE10	MEAN
SiO_2	55.7	54.54	50.70	56.40	55.48	54.90	55.75	54.70	55.45	56.25	54.99
Al_2O_3	29.20	27.70	30.67	29.20	29.50	27.32	29.52	30.45	30.12	28.50	26.30
Fe_2O_3	2.50	2.82	3.60	3.67	2.50	2.64	2.85	3.65	3.53	2.55	3.03
MnO	0.01	0.01	---	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.50	0.55	0.08	0.45	0.50	0.55	0.55	0.08	0.45	0.50	0.42
CaO	1.30	0.20	1.90	1.45	1.30	0.20	0.20	1.95	1.45	1.30	1.13
Na_2O	0.25	0.47	0.07	0.28	0.25	0.45	0.48	0.37	0.32	0.25	0.32
K_2O	0.90	0.85	0.99	0.95	0.80	0.85	0.85	0.98	0.95	0.80	0.89
TiO_2	1.23	0.55	1.23	1.04	1.22	0.75	0.55	1.22	1.09	1.20	1.01
P_2O_5	---	0.03	---	0.01	----	0.05	0.01	0.01	0.01	0.01	0.02
LOI	10.24	11.3	10.20	10.55	10.24	10.30	10.30	10.20	10.55	10.20	10.41
Total	101.83	99.02	99.44	104.01	101.8	98.02	101.07	103.62	103.93	101.57	101.4
SiO_2/Al_2O_3	1.91	1.97	1.65	1.93	1.88	2.01	1.89	1.80	1.84	1.97	1.89
Al_2O_3/SiO_2	0.52	0.51	0.60	0.52	0.53	0.50	0.53	0.56	0.54	0.51	0.53
Al_2O_3/TiO_2	23.74	50.36	24.93	28.08	24.18	36.43	53.67	24.96	27.63	23.75	
Na_2O/K_2O	0.28	0.55	0.07	0.29	0.31	0.53	0.56	0.38	0.34	0.31	0.36
K_2O/Na_2O	3.60	1.81	14.14	3.39	3.20	1.89	1.77	2.65	2.97	3.20	3.86
K_2O+Na_2O	1.15	1.32	1.06	1.23	1.05	1.30	1.33	1.35	1.27	1.05	1.08
$Fe_2O_3+MnO+TiO_2$	3.74	3.38	4.83	4.72	3.73	3.40	3.41	4.88	3.63	3.76	3.95
CIW	94.96	97.64	93.96	94.41	95.01	97.68	97.75	92.92	95.45	94.84	95.46
CIA	88.62	93.31	86.86	87.68	89.01	93.48	93.51	85.44	87.85	88.74	89.45
PIA	91.05	96.18	89.24	90.16	91.17	96.41	96.20	87.68	90.26	90.95	91.93
MIA	86.00	89.73	87.19	85.75	86.37	89.80	90.11	85.87	85.92	86.06	87.28
WIP	11.04	10.38	11.12	11.77	10.24	10.27	10.44	12.83	12.00	10.24	11.03
RBL	9.90	13.38	10.09	9.33	10.35	13.33	14.19	9.01	9.50	10.00	10.91

Table 4.5. Comparison of the average chemical composition of Iguoriakhi clays (IGK), Ofunmwengbe clays (OFM) and Ofunmwengbe shales (OFE) of the study area with average chemical composition of other clays as Standard References (A) and Industrial Specifications (B)

Oxides (%)	Study Samples			References (A)					Industrial Specifications (B)							
	IGK*	OFM*	OFE*	i	ii	iii	iv	v	i	ii	iii	iv	v	vi	vii	viii
SiO_2	54.55	54.36	54.99	44.98	55.49	52.92	46.88	57.67	49.88	47.00	44.90	45.00	67.50	46.07	47.90-48.30	51.00-70.00
Al_2O_3	28.77	29.01	26.30	37.54	18.63	9.42	37.65	24.00	37.65	40.00	32.33	38.10	26.50	38.07	37.90-38.40	25.00-44.00
Fe_2O_3	3.14	3.34	3.03	2.35	9.67	3.65	0.88	3.25	0.88	---	0.43	0.60	0.50	0.33	13.40-13.80	0.20-0.70
MnO	0.01	0.01	0.01	0.007	0.04	---	---	---	----	---	---	----	1.20	---	---	---
MgO	0.40	0.38	0.42	1.72	1.25	0.08	0.13	0.30	0.13	---	---	----	0.19	0.01	0.20-0.30	0.20-0.70
CaO	1.23	1.32	1.13	0.09	0.77	1.91	0.03	0.70	0.03	---	---	----	0.30	0.38	0.03-0.25	0.10-0.20
Na_2O	0.28	0.24	0.32	0.19	0.46	0.03	0.21	0.20	0.21	---	0.14	----	1.50	0.27	0.20-0.35	0.80-3.50
K_2O	0.92	0.92	0.89	1.01	1.84	0.98	1.60	0.50	1.60	---	0.28	---	3.10	0.43	0.10-0.40	---
TiO_2	1.01	1.03	1.01	1.42	---	---	0.09	---	0.09	---	1.80	1.70	---	0.50	---	---
P_2O_5	0.02	0.02	0.02	---	---	0.02	---	---	---	----	---	---	---	---	0.02	---
LOI	10.52	10.52	10.41	12.60	10.18	10.19	12.45	10.50	12.45	13.00	14.20	14.70	12.51	13.47	---	---
Total	100.80	101.13	101.4	99.91	98.33	79.20	99.92	97.10	99.92	---	----	---	----	99.93	---	---
K_2O/Na_2O	6.23	7.04	3.86	1.20	4.00	---	1.81	0.70		---	0.02	---	2.06	1.59	---	---
K_2O+Na_2O	1.20	1.16	1.08	1.20	2.30	1.01	1.01	0.70						0.83		
$Fe_2O_3+MnO+TiO_2$	4.14	4.38	3.95	5.49	10.92	3.73	0.30	3.53								

REFERENCES (A)

i. Ibadan Kaolin (Emofurieta and Salami, 1988)
ii. Isan Brown Clay (Elueze and Bolarinwa, 1995)
iii. Florida Active Kaolinite (Huber, 1985)
iv. China Clay (Huber, 1985)
v. Plastic Fire Clay (Huber, 1985)

INDUSTRIAL SPECIFICATIONS (B)

i. Agricultural (NAFCON, 1985)
ii. Pharmaceutical (Todd, 1975)
iii. Rubber (Keller, 1964)
iv. Textile (Keller, 1964)
v. Ceramics (Singer and Sonja, 1971)
vi. Fertilizer (NAFCON, 1985)
vii. Paints (Paine, 1961)
viii. Refractory Bricks (Parker, 1967)

Table 4.5. shows the comparison between the average chemical composition of Iguoriakhi clay (IGK), Ofunmwengbe clay (OFM) and Ofunmwengbe shale (OFE) with some industrial clays and some notable clay samples. The average silica and alumina values of the Iguoriakhi clays, Ofunmwengbe clays were similar to the Plastic fire clay of St. Louis (Huber, 1985) and Refractory bricks (Paker, 1967). However, the average silica values for Iguoriakhi clay and Ofunmwengbe clays were slightly similar to those of Florida active kaolinite (Huber, 1985) and Isan brown clay (Elueze and Bolarinwa, 1995) but the average value for alumina is higher than Isan brown clay (Elueze and Bolarinwa, 1995) and very high compared to Florida active kaolinite (Huber, 1985).

Table 4.6 Average Trace Elements (ppm) Composition of the Analysed Samples

Trace Elements (ppm)	Iguoriakhi (IGK)		Ofunmwengbe (OFM)		Ofunmwengbe Extension/Environs (OFE)	
	Range	Mean	Range	Mean	Range	Mean
Ba	657.62 - 673.60	667.35	650.40 - 679.40	666.38	655.62 - 675.60	668.19
Cu	25.65 - 28.53	27.11	20.45 - 28.34	26.99	23.45 - 28.25	26.61
Cr	100.30 - 122.20	113.04	11.20 - 120.20	100.46	100.20 - 120.20	112.27
Ni	26.30 - 32.52	30.01	22.33 - 32.55	29.50	22.30 - 32.65	28.82
Zn	210.25 - 222.46	214.35	210.22 - 220.44	213.00	210.25 - 220.46	215.77
Pb	10.20 - 14.40	12.04	10.20 - 16.20	11.63	10.20 - 12.80	11.60
Rb	6.40 - 8.40	7.98	5.60 - 8.40	6.86	5.30 - 8.50	7.77
La	0.20 - 0.28	0.23	0.20 - 0.24	0.22	0.20 - 0.28	0.24
Nb	---	---	---	---	5.54 - 6.70	6.13
Th	5.12 - 6.50	5.90	3.22 - 6.50	5.52	---	---
Ta	---	---	---	---	0.20 - 0.22	0.21
U	0.20 - 0.22	0.21	0.20 - 0.22	0.21	---	---
Zr	---	---	---	---	0.20 - 0.35	0.27
V	0.20 - 0.34	0.28	0.20 - 0.34	0.28	---	---
Co	---	---	---	---	6.20 - 8.62	7.73

Sc	6.20 - 8.64	8.18	2.20 - 8.50	4.45	---	---

4.2.2 Chemical Characterization of Trace Elements in samples

From table 4.5 above the average concentration of Barium (Ba: 666.38 - 668.19 ppm) is very high with relatively high values of Zinc (Zn: 213.00 – 215.77 ppm) and Chromium (Cr: 100.46 – 113.04 ppm) in Iguoriakhi and Ofunmwengbe respectively and present in all (30) samples analysed from the study area. The relatively low concentration of Cupper (Cu: 26.61 – 27.11 ppm), Nickel (Ni: 28.82 – 30.01), Lead (Pb: 11.60 – 12.04 ppm), Rubidium (Rb: 6.86 – 7.98 ppm), were present in all the (30) samples while other trace elements with very low concentration Thorium (Th: 5.52 – 5.90 ppm), Niobium (Nb: 6.13 ppm) Tantalum (Ta: 0.21 ppm) Uranium (U: 0.21 ppm) Zirconium (Zr: 0.27 ppm), Vanadium (V: 0.28 ppm) Cobalt (Co: 7.73 ppm) and Scandium (Sc: 4.45 – 8.18 ppm) occur in very little concentration only in some and absent in some of the samples.

The trace elements concentration in the samples can be extracted with appropriate beneficiation processes for use in medical and pharmaceutical industries. From table 4.6 the average Barium (Ba) concentration value in the clays is approximately 61%. The clays can serve as chief source of raw materials for the extraction of barium for various industrial applications. Which can be used as spark plug electrodes and as a drying and oxygen removing agent in vacuum tubes, barium compounds can be used in oil and gas industries for the production of drilling mud which simplifies drilling through rocks by lubricating the drill, barium compounds are also used in paints, bricks, tiles, glass and rubber production. Chromium (Cr) is the most important mineral for overweight people. In addition is one of the key minerals in controlling both blood sugar and fat levels. As the main component of Glucose Tolerance Factor (GFT), Chromium assists insulin in reducing blood glucose, by stimulating glucose uptake by the muscles and other tissues. Cupper (Cu) in its many forms is the third most mineral in the body. Cupper is found throughout the Musculo-skeletal system, with the largest amount found in the brain and liver. Zinc (Zn) is necessary for a healthy immune system and is also important in fighting skin problems such as acne and sore throats.

Table 4.7. Trace elements (ppm) composition for Iguoriakhi clay (IGK) samples

Trace Elements (ppm)	IGK1	IGK2	IGK3	IGK4	IGK5	IGK6	IGK7	IGK8	IGK9	IGK10	MEAN
Ba	662.61	672.67	662.60	670.57	665.60	670.63	657.62	672.30	665.26	673.60	667.35
Cu	28.33	28.36	27.35	28.24	28.53	26.32	25.85	26.20	25.65	26.22	27.11
Cr	100.30	112.20	110.22	120.20	105.30	112.20	114.20	116.35	117.25	122.20	113.04
Ni	31.60	31.65	30.60	28.45	30.40	32.62	28.50	32.52	27.50	26.30	30.01
Zn	210.45	210.45	214.25	220.34	212.40	213.45	210.25	214.25	215.25	222.46	214.35
Pb	11.00	10.20	12.80	12.50	12.20	12.50	14.40	12.25	12.40	10.20	12.04
Rb	8. 10	7.60	6.40	7.80	8.32	8.30	8.25	8.40	8.35	8.32	7.98
La	0.20	0.22	0.22	0.20	0.24	0.22	0.28	0.25	0.26	0.22	0.23
Th	5.12	5.74	5.59	6.22	6.20	5.54	6.40	5.45	6.20	6.50	5.90
U	0.21	0.20	0.20	0.20	0.22	0.20	0.22	0.20	0.20	0.20	0.21
V	0.28	0.33	0.34	0.28	0.20	0.33	0.25	0.30	0.27	0.23	0.28
Sc	8.20	8.30	8.60	6.20	8.64	8.50	7.60	8.55	8.60	8.62	8.18

Table 4.8. Trace element (ppm) composition for Ofunmwengbe clay (OFM) samples

Trace Elements (ppm)	OFM 1	OFM 2	OFM 3	OFM 4	OFM 5	OFM 6	OFM 7	OFM 8	OFM 9	OFM10	MEAN
Ba	670.60	662.60	660.60	650.40	670.60	670.60	660.62	679.40	669.61	669.37	666.38
Cu	28.25	28.30	29.30	28.20	28.20	26.30	20.45	28.20	24.35	28.34	26.99
Cr	95.30	112.20	120.20	120.20	112.30	112.20	110.20	11.20	100.60	112.20	100.46
Ni	30.40	29.95	30.20	22.33	30.50	32.55	30.50	25.30	31.60	31.65	29.50
Zn	212.45	214.40	210.22	220.30	210.50	210.55	210.25	220.44	210.45	210.45	213.00
Pb	10.20	10.20	11.40	12.20	12.20	12.50	16.20	10.20	11.00	10.20	11.63
Rb	6.70	5.60	6.33	4.80	6.30	8.30	8.25	6.30	8.40	7.60	6.86
La	0.20	0.24	0.22	0.20	0.24	0.22	0.22	0.20	0.20	0.22	0.22
Th	3.22	5.70	5.60	5.2	6.20	5.54	6.40	6.50	5.12	5.74	5.52

U	0.20	0.20	0.20	0.20	0.22	0.20	0.22	0.20	0.21	0.20	0.21
V	0.22	0.30	0.34	0.30	0.20	0.33	0.25	0.20	0.28	0.33	0.28
Sc	2.20	4.30	5.60	6.5	5.6	8.50	5.50	7.60	8.20	5.40	4.45

Table 4.9. Trace element (ppm) composition for Ofunmwengbe shale (OFE) samples

Trace Elements (ppm)	OFE1	OFE2	OFE3	OFE4	OFE5	OFE6	OFE7	OFE8	OFE9	OFE10	MEAN
Ba	662.60	670.57	668.60	670.60	655.62	670.60	672.10	665.50	675.60	670.12	668.19
Cu	27.35	28.24	28.23	26.32	25.45	24.22	28.20	28.25	26.35	23.45	26.61
Cr	110.22	120.20	100.20	112.62	117.20	120.20	115.20	100.50	111.20	115.20	112.27
Ni	30.60	28.45	30.40	32.62	28.40	26.30	22.30	30.45	32.25	26.40	28.82
Zn	214.25	220.34	212.40	220.45	210.25	220.46	220.40	218.40	210.25	210.50	215.77
Pb	12.80	12.50	12.20	12.50	10.40	10.20	10.20	12.25	12.40	10.50	11.60
Rb	6.40	7.80	8.32	5.30	8.25	8.32	8.50	8.25	8.33	8.25	7.77
La	0.22	0.20	0.25	0.22	0.28	0.22	0.22	0.25	0.22	0.28	0.24
Nb	5.59	6.22	6.20	5.54	6.40	6.50	6.70	6.10	5.55	6.45	6.13
Ta	0.20	0.20	0.22	0.20	0.22	0.20	0.20	0.22	0.22	0.22	0.21
Zr	0.34	0.28	0.20	0.33	0.25	0.23	0.20	0.25	0.35	0.25	0.27
Co	8.60	6.20	8.20	6.50	7.60	8.62	7.60	8.10	8.40	7.50	7.73

4.3 Sedimentological Analysis Results and Appraisal of samples

Different geotechnical test parameters were investigated to assess the sedimentological characteristics of the clays deposit at Iguoriakhi (IGK) and Ofunmwengbe (OFM) and environs. They include natural moisture content (MC), specific gravity (SG), particle size distribution (PSD), Compaction, Atterberg limits: liquid limit (LL), plastic limit (PL) and plasticity index (PI). These tests were performed in accordance with the American Standards for Testing Materials (ASTM) and British Standards (BS).

4.3.1 Natural Moisture Content

The natural moisture content of a soil is the percentage of water available in the soil pore spaces. This geotechnical index property is interdependent on the sedimentology of a soil material. The natural moisture content of a soil content predicts the type of texture, structure and organic matter in the soil. Soil with smaller particles (clay, silt) have a larger surface area than those with larger sand particles and a large surface area allows a soil to hold more water.

Table 4.10. Results from two test samples evaluated for moisture content, one each for Iguoriakhi and Ofunmwengbe clays.

Samples	Iguoriakhi (IGK1)	Ofunmwengbe (OFM1)
Can no.	C10	M6
Can Wt(g)	17.60	16.50
Can + Wet Soil (g)	30.80	34.10
Can + Dry Soil (g)	28.10	31.80
Wt of Water (g)	2.70	2.30
Wt of Dry Soil (g)	10.50	15.30
Moisture Content or water Content: (Wt of H_2O/Wt of Dry Soil) x 100	(2.7/10.5) x100	(2.3/15.30) x 100
MC	25.71%	15.03%

Table 4.10. shows a representative experimental procedure for the analysed samples with one sample from each study area. Similarly, other samples were evaluated as seen in Table 4.12 and 4.13 showing the complete natural moisture content results for all the samples analysed.

The range of the average moisture content values shows that Iguoriakhi clays (23.52% - 25.82%) have more water content retention capacity than those of the Ofunmwengbe clays which were relatively low (14.93% to 15.04%). The results shows that the samples of the study area are clayey soil with organic matter (Bowles, 2012; DD ENV 1997-2, 2000; AASHTO M145-91, 2012)

Table 4.11. Results of four test samples evaluated for Specific Gravity, two samples each of Iguoriakhi (IGK) and two of Ofunmwengbe (OFM) clays

Samples	Bottle No.	$M_{1=}$ Bottle Wt (g)	$M_{2=}$ Bottle + Soil (g)	$M_{3=}$ Bottle + Soil + Water (g)	$M_{4=}$ Bottle + Water (g)	A = M_4-M_1	B = M_3-M_2	C = M_2-M_1	D = A-B	SG = C/D
IGK1	NO	22.10	49.70	88.80	74.30	52.20	39.10	27.60	13.10	2.11
IGK2	EL	25.60	53.20	92.30	78.60	53.00	39.10	27.60	13.90	1.99
OFM1	VC	24.40	49.40	87.50	76.40	52.00	38.10	25.00	13.90	1.80
OFM2	IT	20.80	45.70	87.00	75.70	54.90	41.30	24.90	13.60	1.83

Where Specific Gravity (SG) = $$\frac{(M_2 - M_1)}{(M_4 - M_1) - (M_3 - M_2)}$$

Table 4.12: Results of Liquid Limit (LL), Plastic Limit (PL) Plasticity Index (PI), Specific Gravity (SG), Loss on Ignition (LOI) and Average Moisture Content (MC) for Iguoriakhi Clays

Iguoriakhi (IGK)											
Samples	IGK1	IGK2	IGK3	IGK4	IGK5	**Mean (IGKu)**	IGK6	IGK7	IGK8	IGK9	IGK10	**Mean (IGKv)**
LL (%)	60.01	61.02	64.10	65.40	62.00	**62.50**	68.40	66.30	67.10	66.40	66.80	**67.00**
PL (%)	33.50	32.60	31.20	30.40	30.10	**31.56**	30.20	29.80	29.20	28.80	28.40	**29.28**
PI (%)	26.51	28.42	32.90	35.00	31.90	**30.94**	38.20	36.50	37.90	37.60	38.40	**37.72**
SG (%)	2.11	1.99	2.03	2.05	2.03	**2.04**	2.07	2.03	2.05	2.04	2.05	**2.05**
LOI	10.20	10.55	10.24	11.30	10.20	**10.45**	10.50	10.20	11.30	10.20	10.50	**10.54**
AMC	25.71	24.03	22.04	22.74	23.40	**23.58**	25.77	26.83	26.90	25.01	24.58	**25.82**

Table 4.13: Results of Liquid Limit (LL), Plastic Limit (PL) Plasticity Index (PI), Specific Gravity (SG), Loss on Ignition (LOI) and Average Moisture Content (MC) for Ofunmwengbe Clays

Ofunmwengbe (OFM)												
Samples	OFM1	OFM2	OFM3	OFM4	OFM5	**Mean (OFMu)**	OFM6	OFM7	OFM8	OFM9	OFM10	**Mean (OFMv)**
LL	178.30	179.25	180.79	183.20	183.48	**181.00**	131.31	130.40	127.22	128.08	128.00	**129.00**
PL	49.96	50.75	50.46	51.83	50.52	**50.70**	43.49	40.70	41.66	41.37	40.63	**41.57**
PI	128.34	128.50	130.33	131.37	132.96	**130.30**	87.82	89.70	85.52	86.71	87.37	**87.43**
SG	1.80	1.83	1.79	1.81	1.82	**1.81**	2.01	1.96	1.95	1.88	2.03	**1.97**
LOI	10.20	10.55	10.24	11.3	10.20	**10.50**	10.55	10.24	10.25	10.40	11.3	**10.55**
AMC	15.03	14.94	14.80	14.86	15.02	**14.93**	15.51	15.21	14.91	14.46	15.20	**15.04**

4.3.2 Specific Gravity

The specific gravity test was carried out on the samples to determine the ratio of its unit weight to an equal weight of water. This geotechnical index property determines the mineral classification and history of weathering of the soil material. In terms of mineral classification, the magnitude of specific gravity values of an iron mineral is more than that of the silica minerals (Bowles, 2012). While in terms of history of weathering, soil composition with more of the fine grain content have a larger value of specific gravity than the coarse grain content (DD ENV 1997-2,2000).

The results from table 4.11. Shows the specific gravity of four test samples analysed with two samples from Iguoriakhi and two samples from Ofunmwengbe, Similarly the test results for all the other samples are presented in tables 4.12 and 4.13 respectively. The results show that the average specific gravity values for iguoriakhi clays (2.04 – 2.05) are higher than those of the Ofunmwengbe clays (1.81 – 1.97) similar to the natural moisture content result, this result shows a clayey soil with significant organic matter (Bowles, 2012; DD ENV 1997-2,; AASHTO M145-91, 2012).

4.3.3 Particle Size Distribution (PSD)

Particle size distribution represents the relative proportions of the grain sizes in the soil material. The proportion of different sizes of soil particles coarser 75micrometers were determined by sieve analysis while that less than 7micrometer were determined by hydrometer analysis.

The geotechnical index property was used in the prediction of soil water movement and the gradation of the soil, that is whether the distribution of the different grain sizes present is well graded or poorly graded through the sub-analysis of Coefficient of uniformity (Cu) and Coefficient of curvature (Cc).

A value of Cu greater than 4 or 6 classifies the soil as well graded and when Cu is less than 4, it is classified as poorly graded or uniformly graded soil. While a soil with Cc between 1 and 3 is well graded if the Cu is also greater than 4 for gravels and 6 for sands. For cases where the Cc of soil is less than 1 or greater than 3, the soil is poorly graded. A well graded soil consists of a representative of all grain sizes in a complementary proportion and in a more grain to grain area contact. However, a poorly graded soil shows a closely packed soli in terms of quantity of particle sizes leaving relatively large voids due to the missing or small quantity of some intermediate particle sizes and less grain-to-grain area contact as compared to a well graded soil (DD ENV 1997-2, 2000).

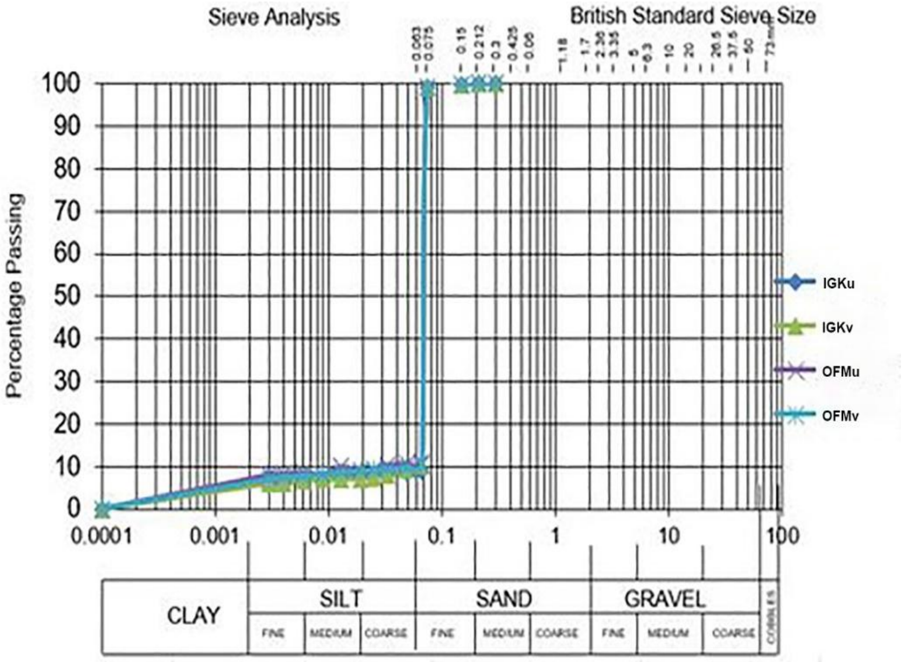


Figure 4.2. Particle size distribution curve for the average ten values of Iguoriakhi clays (IGKu and IGKv) and average of ten values of Ofunmwengbe clays (OFMu and OFMv) respectively.

The gradation curve obtained from the sieve and hydrometer analysis showed a soil containing fine sand, (coarse, medium and fine grain size) silt and clay as shown in figure 4.2 above. The average percentage of fine sand as observed from the graph above is approximately 90%, silt has an average percentage of 4% of the soil composition while clay contains the remaining 6% of the soil composition for all the samples analysed.

The average effective size of the soil, D_{10} was approximately evaluated as 0.02micrometer showing the corresponding grain size at 10% percentage passing as seen from the graph above. Similarly, D_{30} and

D_{60} were evaluated as 0.07micrometer and 0.071micrometer respectively.

$Cu = D_{60} / D_{30}$

$Cu = 0.0071 / 0.02$

$Cu = 3.55$ ………………………………………………………… (1)

$Cc = (D_{30})^2 / (D_{10} \text{ x } D_{60})$

$Cc = (0.07)^2 / (0.02 \text{ x } 0.071)$

$Cc = 0.0049 / 0.00142$

$Cc = 3.45$ ………………………………………………………… (2)

From the calculation above equation (1) and (2) shows the value of Cu less than 4.0 and Cc value greater than 3 which signifies that both Iguoriakhi clays and Ofunmwengbe clays were poorly graded soil. It also shows that some grain fractions were either missing or in very small or excess quantity compared to the others (BS 1377: Part 2, 1990).

In conjunction with the percentage fine passing through sieve size 0.075micrometer, the analysed samples of the clay deposits were grouped according to American Association of State Highway and Transportation Officials (AASHTO) classification as seen in Figure 4.3 below.

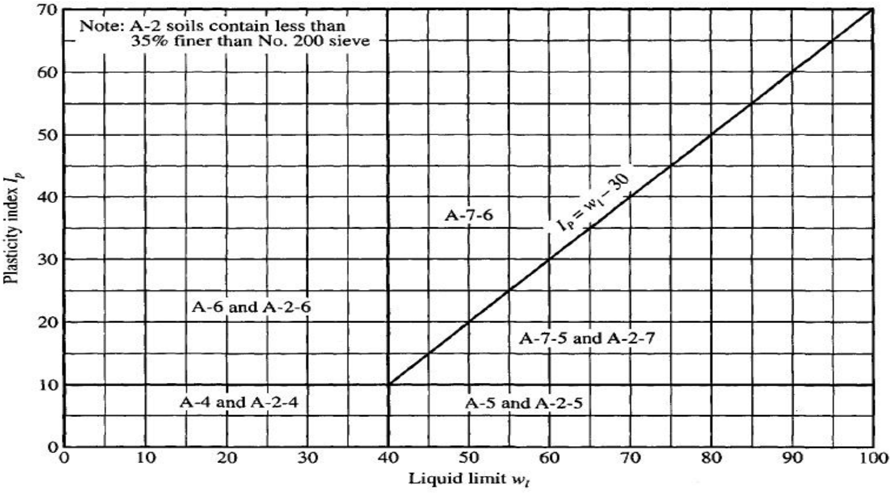


Figure 4.3. AASHTO Classification of Soil

The readings from the AASHTO chart classified the clay deposits from Iguoriakhi and Ofunmwengbe as obtained from the corresponding liquid limit (LL) and plasticity index (PI) taking into cognizance of the percentage fine passing through the 75micrometers, the clays fell into the A-7-6 class. The types of significant constituent materials in an A-7-6 class are clayey soils with fair to poor subgrade rating in pavement design.

4.3.4 Atterberg Limits

The consistency of a soil composition of majorly fine grain is greatly influenced by the water content of the soil. A gradual decrease in the water content causes the fine-grained soil slurry to pass from the liquid state to plastic state known as the Liquid Limit (LL), from the plastic state to a semi-solid state known as the Plastic Limit (PL) and finally to the solid state. The range of the plastic state is given by the difference between Liquid Limit and Plastic Limit and is defined as the Plasticity Index (PI). The Liquid Limit (LL) was obtained as the corresponding moisture content at 25 number of blows as seen figure 4.4 below.

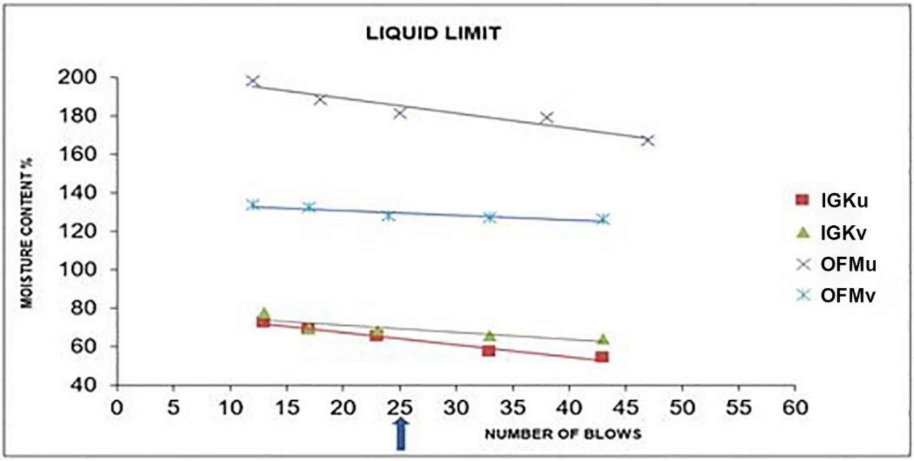


Figure 4.4. Liquid Limit Analysis

The LL values were determined from the average percentage of the samples as seen in Table 4.11 and 4.12 also in figure 25 as (IGKu: 62.5%) and (IGKv: 67.0%), for Iguoriakhi clays and (OFMu: 181.0%) and (OFMv: 181.0%) for Ofunmwengbe clays respectively. While average Plastic Limits (PL) were evaluated as 31.56%, 29.28%, 50.70% and 41.7% for IGKu, IGKv, OFMu and OFMv clays respectively. The difference between LL and PL which is the PI were evaluated as 30.94%, 37.72%, 130.3% and 87.43% for IGKu, IGKv, OFMu and OFMv clays respectively.

From the plasticity chart of plasticity index (PI) against liquid limit (LL) in (figure 4.5) below, the plasticity level of the analyzed samples from the clay deposit is CH and CV (DD ENV 1997-2, 2000). The result shows that Iguoriakhi clays grouped into (IGKu and IGKv) falls within the CH level with high plasticity while those of Ofunmwengbe clays grouped into (OFMu and OFMv) falls within the CV level with very high plasticity. Both Iguoriakhi clays and Ofunmwengbe clays from the plasticity chart shows that they were susceptible to a very high compressibility (BS 1377: Part 2, 1990; AASHTO M145-91, 2012).

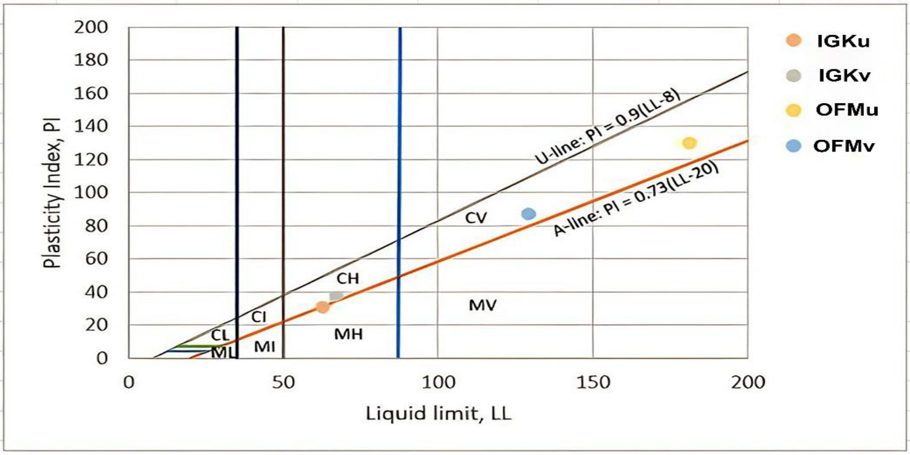


Figure 4.5. Plasticity Chart of the average values of Iguoriakhi clays grouped into (IGKu and IGKv) clays and Ofunmwengbe (OFMu and OFMv) clays respectively for the classification of clay deposits (Casagrande, 1948).

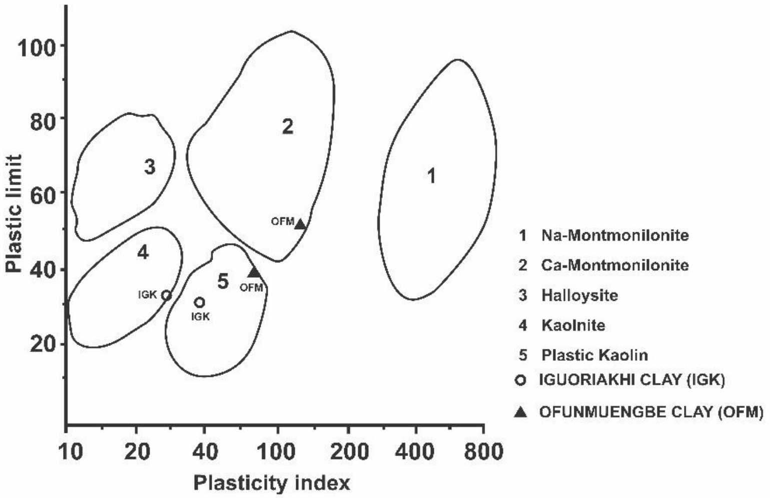


Figure 4.6 Clay identification chart for mineral classification (Bain, 1971).

Figure 4.7 shows the classification of the clay minerals into five clsses of minerals; sodium montmorillonite, calcium montmorillonite halloysite, kaolinite and plastic kaolinite (Bain 1971). The chart shows that Iguoriakhi clays falls within the Kaolinite and plastic kaolinite minerals while Ofunmwengbe clays fall within the plastic kaolin and calcium montmorillonite minerals. However, the Ofunmwengbe clay minerals that fall within the calcium montmorillonite class may be attributed to the high content of organic matter in the clay deposit.

4.3.5 Compaction

The results of the proctor compaction test (table 4.14) were obtained from the dry density versus average moisture content relationship of the British Standard, B.S. 1377 (light) compaction test, 2.5kg rammer method as seen in (figure 4.7). Below.

Table 4.14. The Dry Density and Moisture Content of Iguoriakhi and Ofunmwengbe clay deposits.

Iguoriakhi Clays (IGK)	IGK1	IGK2	IGK3	IGK4	IGK5	IGK6	IGK7
Dry Density (g/cm^3)	1.02	1.07	1.10	1.09	1.03	0.94	---
Moisture Content (%)	37.20	39.40	42.20	43.20	46.80	48.40	---
Ofunmwengbe Clays (OFM)	OFM1	OFM2	OFM3	OFM4	OFM5	OFM6	OFM7
Dry Desity (g/cm^3)	1.14	1.19	1.24	1.30	1.32	1.26	1.22
Moisture Content (%)	18.40	19.90	21.40	23.00	25.50	28.60	29.30

From table 4.14 and figure 4.7 curve below shows the average values of the Maximum Dry Density (MDD) and Optimum Moisture Content (OMC) for Iguoriakhi clays MDD: 1.1g/cm^3 and OMC: 42.2% respectively while that of Ofunmwengbe clays were MDD: 1.32 and OMC: 25.5% respectively According to the British and European standard code of practices, the range of evaluated for MDD and OMC classified the clays as inorganic clayey soil with high organic content (BS 1377: Part 2, 1990; DD ENV 1997-2, 2000).

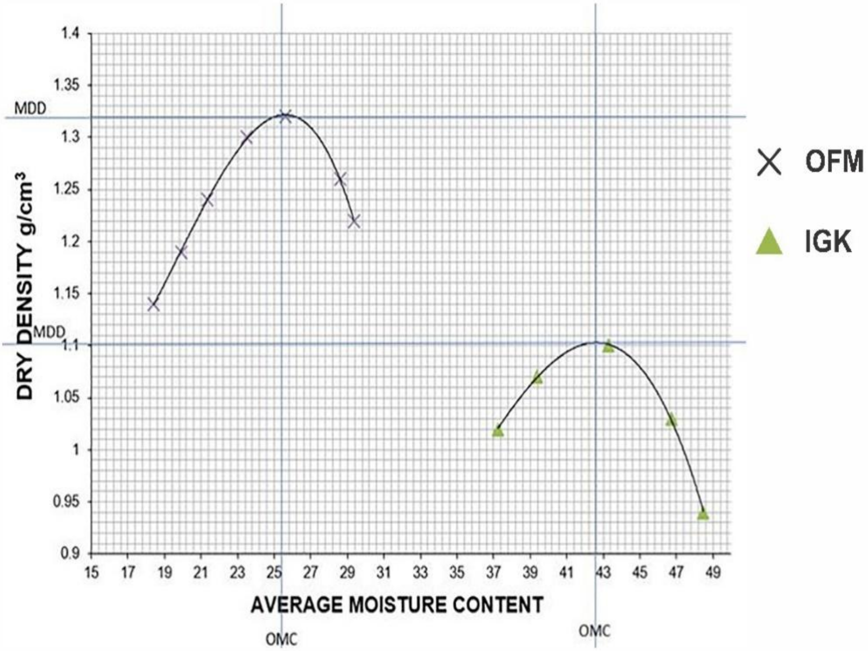


Figure 4.7. Compaction curve of the analysed samples Iguoriakhi and Ofunmwengbe clay deposits.

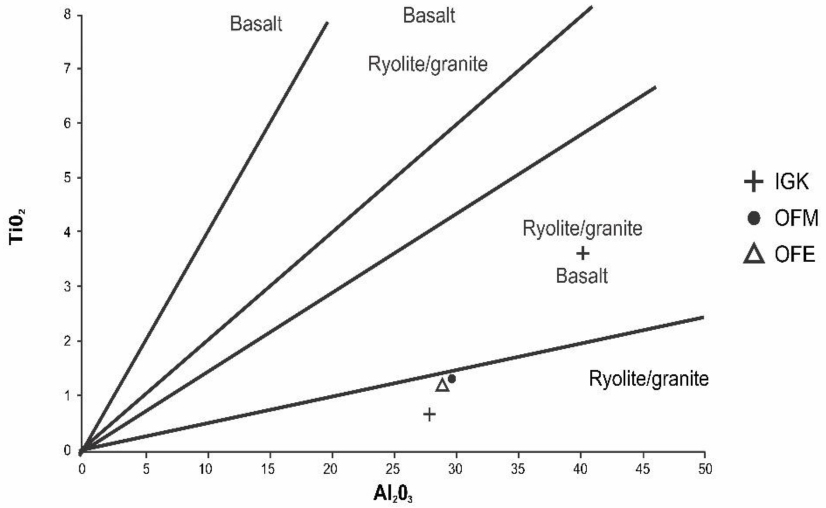


Figure 4.8 TiO_2/AlO_3 binary plots of some clays in the study areas source (modified after Ekosse 2001).

4.4 Potential Industrial Uses

A simple comparison of the mineralogical compositions of the clays with those of some well-known kaolin deposits indicate that the investigated clay deposits were relatively similar to some notable ones (Table 4.5).

The Iguoriakhi and Ofunmwengbe clays are similar to Isan brown clay (ii) Florida active kaolinite (iii) and Plastic fire clay (v) with little variations in Al_2O_3 and Fe_2O_3 respectively.

The average SiO_2:Al_2O_3 values of 1.82 and 1.83 for Iguoriakhi and Ofunmwengbe clay deposits respectively. The ratio of silica alumina in clays in relation to bleaching has been studied and was applied by

Amozie et al. (1993), they established that kaolinitic clays whose silica:alumina ratio is 3 and above were fairly good bleaching agents while those with ratio between 2.0 and 2.7 bleach poorly, and those with 2.0 and below bleach very poorly. The ratio of SiO_2: Al_2O_3 of both Iguoriakhi and Ofunmwengbe were less than 2 indicating that the clays at their natural state are poor bleaching agents. However, can be improved with little beneficiation process.

In view of the physical, chemical and mineralogical investigations of these clays, their use in manufacture of high-temperature general-purpose porcelain products is recommended. The Iguoriakhi and Ofunmwengbe clays have very little amount of montmorillonite and illite that often contain alkali and alkaline earth ions capable of reducing refractory property. At very high temperature, kaolinite is converted to mullite and cristobalite which are very good refractory minerals. In view of the characteristics of Iguoriakhi and Ofunmwengbe clay, a good mix of the clays will be suitable for refractory products which are used for lining furnaces and kilns to withstand high temperatures.

Oyinloye (1997) had reiterated the need to produce refractories in large quantities to meet the robust demand of Nigerian Steel Industries in order to reduce importation of refractories and thereby conserve foreign exchange earnings. This will in turn encourage the development of local industries. Other products for which the Iguoriakhi and Ofunmwengbe clays could serve as raw material are electronic appliances such as switch base, spark plug, cup, jug and toilet wares etc.

Abundance of kaolinite in the samples indicates dominant contribution of Al_2O_3 as the presence of alumina and silica contents is the direct reflection of general purity of the clay deposits.

The general low contents of TiO_2 (average 0.55% - 1.23%), MgO (average 0.08%-0.55%), Na_2O (average 0.05%-0.47%), P_2O_5 (average 0.01%-0.04%) and K_2O (average 0.85%-0.99%) for Iguoriakhi clays and low contents of TiO_2 (average 0.53% - 1.23%), MgO (average 0.08%-0.55%), Na_2O (average 0.05%-0.47%), P_2O_5 (average 0.01%-0.05%) and K_2O (average 0.80%-0.99%) respectively are further indications of the purity of clays in both Iguoriakhi and Ofunmwengbe; these values fall within reasonable limits of those of China clay.

The kaolinitic clays possess certain specific properties: plasticity (where present), appropriate shrinkage to avoid cracks during drying and great strength to permit handling which make them suitable for ceramics and poetry products.

A raw mix with right proportion of the two clays Iguoriakhi and Ofunmwengbe can fulfil specific requirements for the ceramics industry which include aesthetic colourations, plasticity, drying strength with the addition of feldspar for fluxing and vitreous binding effect.

Murray (2002) observed that 45% of the world production of kaolin goes into paper filling and coating. According to Murray (2002), kaolin which consists mainly of the mineral kaolinite, is uniquely suited for this use because of its fine particle size, good viscosity, low abrasion, good opacity, white colour, high brightness and good print quality. The Iguoriakhi and Ofunmwengbe clays with minimum beneficiation process to remove non clayey and coarse fractions are obviously suitable for this application considering, among other qualities their high percentage of kaolinite, purity and low average specific gravity of (1.8).

The Iguoriakhi and Ofunmwengbe clays (Kaolinitic clay) forms slurry when added to water because it distributes itself evenly throughout the water suitable for the paint industry in the evenly dispersion of pigment (colour) throughout the paint. Without the clay to act as a carrier, it would be difficult to evenly mix the paint base and colour pigment. The unique purity of the Iguoriakhi and Ofunwengbe clays makes it attractive to the pharmaceutical industry as raw material for the preparation of certain drugs, notably those that are used in the treatment of stomach disorders and those for which it could serve as carrier because it is non-corrosive and chemically inert.

The average aboundance of montmorillonites in Iguoriakhi and Ofunmwengbe clays are suitable because of a net charge deficiency that exists in its structure that makes it an important medium for transporting and dispersing contaminants and most especially good carriers of pesticides.

The geochemistry of the clays reveals high composition of alumina with average aboundance values (28.77% and 29.01%) in Iguoriakhi and Ofunmwengbe clays respectively can be extracted for the production of fertilizer and animal feeds and other products in which high alumina content is desired.

The studied clays were poorly graded, fine grained and characterized by high proportion of clay size fraction with little silt and missing portion of sand showing high plasticity index value and plots on the region of inorganic clays of high plasticity on the Casagrande plasticity chart (figure 4.5). The high liquid limit values are indicative of soils with clays of high compressibility. The plasticity can be reduced by base exchange treatment. This can be done by the addition of lime to the clay in form of blending or injected as slurry.

CHAPTER FIVE

CONCLUSION, FINDINGS AND CONTRIBUTIONS TO KNOWLEDGE

5.1 Conclusion

The results from the investigated samples show that mineralogically the samples from Iguoriakhi have kaolinite as the predominant clay while the samples from Ofunmwengbe have kaolinite as the major clay minerals and a kaolinite mixed layer clay-shale samples with quartz as the major non clay mineral also iron, sulphide and limestone/calcite occur as accessory minerals mainly at Ofunmwengbe.

Chemically the investigated samples show major element concentration of the following oxides: SiO_2, Al_2O_3 and Fe_2O_3, constitute more than 86% while Na_2O, MnO, K_2O, CaO, MgO, P_2O_5 and TiO_2 relatively low values approximately 4%, with Loss on ignition approximately 10% showing that the samples are predominantly hydro aluminosilicates.

The mineralogical, chemical composition and sedimentological (physical) properties were the parameters used in appraising the suitability of the studied samples for use in various industrial applications as compared with some industrial specifications.

From the reference clays (A) average chemical composition of the clays from Iguoriakhi and Ofunmwengbe compared favourably with the Plastic fire clay (Huber, 1985) and relatively similar to that of Florida active kaolinite (Huber, 1985) with relatively higher alumina content.

From the industrial specification clay (B) average chemical composition of the clays from Iguoriakhi and Ofunmwengbe compared favourably and meets the industrial specifications for Refractory Bricks (Parker, 1967), Ceramics (Singer and Sonja, 1971), with relatively little beneficiation for either silica or alumina or both to meet up the industrial requirements for use as raw material for Agriculture (NAFCON, 1985), pharmaceutical (Todd, 1975) and Paints (Paine, 1961). Industries.

The investigated sedimentological (physical) parameters shows a considerable amount of silt in the fines as evidenced by the SiO_2 values (approximately 55%), Loss on ignition (LOI) of (approximately 10.5%) and Optimum moisture content (OMC) of 42.2% and 25.5% shows that the clays from the study area are of low porosity and indicates that finished products would show relatively low or no cracks or damages on firing, thus, rendering these clays suitable for ceramics wares and pottery production.

The plasticity coupled with general fineness and highly compressible, highly pure and non-corrosive properties meets the industrial specification for their application as raw materials for paint and pharmaceutical (cosmetics) industries (Elueze et al., 1999) as fillers and coating materials.

5.2 Findings

The findings from these studies are as follows:

The geology of the sampled area was found to fall within the Imo Shale/Imo Formation extending into the Lignite series of the Benin

Formation composed mainly of sand and clays as confirmed by the derived geologic map.

The mineral data of the study area were found to be clay minerals such as Kaolinite, Illite and Montmorillonite with non-Clayey minerals, quartz, feldspars and micas.

The geochemical signatures from the summation and ratios of the major oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, K_2O, Na_2O, TiO_2), determined the provenance and origin of the clays to be grading from intermediate to felsic igneous environment.

The physico-chemical properties indicate that the clays are inorganic clays with high plasticity, moderate compressibility and intense toughness with the presence of organic matter.

The clays were found to compare favourably with industrial specifications for ceramics, pharmaceuticals, Paints, agriculture and for lining of kilns though a little beneficiation is required.

5.3 Contributions to Knowledge

The study has contributed to knowledge in the following ways:

This study has bridged the gap existing in the mineral data base of Edo State, Southwest, Nigeria.

The study has contributed to knowledge by creating awareness of the untapped clay deposits lying in the studied area as major source of raw materials for industrial application and economic growth.

The Shaly component of the laminated sedimentary clastic rocks in the study area consisting mainly of silty-clays high organic matter may be recommended for further investigation, for the possibility of a hydrocarbon reservoir for oil exploration.

5.4 Recommendations

The clay minerals from the studied area were highly recommended for the refractory and bricks industries, ceramics, paint and cosmetics industries as feed for raw material needs. However, further processing and appropriate beneficiation is recommended to improve the quality of the clays to meet other industrial specifications.

The clays from the studied area are abundant and can be recommended locally for use as raw material feed to meet industrial needs both locally and internationally.

The clay deposit in the study area were appraised to have vast economic potential, thus, more studies and exploration is recommended in order to determine the quantity and tonnage of these deposits which can be harnessed by sitting industries in the study area to mine and process the clay and clay-shale deposits for application and exportation.

The clayey shale deposits from the study area were classified as kaolinite, plastic kaolin and calcium montmorillonite from Casagrande plasticity chart. Therefore, a more detailed study is required to the possibility of bentonite clay deposits in the study area which could be utilized as drilling mud in the oil and gas industries.

The highly characterized clay-shale component of Ofunmwengbe with high organic matter content indicated by almost all the investigated parameters may be recommended for further investigation for the possibility of hydrocarbon reservoir for oil exploration.

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