*Quest Journals*
*Journal of Research in Environmental and Earth Science*
*Volume 2~ Issue 5 (2015) pp: 01-12*
*ISSN(Online) : 2348-2532*
www.questjournals.org

**Research Paper**

# The Physico-Chemical and Mineralogical Compositional Characteristics of Limestone and Shale Sediments around Yewa River, South Western Nigeria

Popoola Samuel Olatunde[1], Appia Youpele Juliano[2], Oyeleke Peter Olaoye[3].

[1]*Department of Physical and Chemical Oceanography, Nigerian Institute for Oceanography and Marine Research PMB, 12729, Victoria Island, Lagos.*
[2]*Department of Marine geology and geophysics, Nigerian Institute for Oceanography and Marine Research PMB, 12729, Victoria Island, Lagos.*
[3]*Department of Science Laboratory Technology, Federal College of Animal Health and Production Technology, Moor Plantation, Ibadan, Oyo state, Nigeria.*

**R**eceived 03 Oct, 2014; **A**ccepted 11 June, 2015 © The author(s) 2015. Published with open access at **www.questjournals.org**

***ABSTRACT: -*** This study presents detailed compositional characteristics (physical, chemical and mineralogical properties) of limestone and shale deposits for possible industrial uses and specifications. The study area is about 36km$^2$ and falls within the eastern Dahomey basin, south western Nigeria. Core sediment samples were collected from fourteen boreholes at a depth of approximately 30 meters each in communities around Yewa lagoon: Alagbe, Andrew, Alaran, Erin, Irogun akere,Idogo,Araromi papanla, Igbobe, Oke odan, Owode, Ado-odo, Ipokia, Idi-iroko and Ibatefin, Ogun state; southwestern Nigeria. Lithological units were observed in the following sequences -: topsoil with an average thickness of 0.382m, clay 2.99m, limestone, 2.94m, shale, 6.01m and sandstone 20.42m respectively. Fifteen limestone and shale samples were isolated from the borehole for physical analysis (specific gravity, hardness and moisture content), chemical/mineralogical analysis (Xray diffraction and major/minor element analysis).The chemical analyses on the limestone and shale were carried out using inductively coupled Plasma Atomic Emission Spectrometry (ICPAES) at Acme analytical laboratory, Vancouver, Canada. The result of the Xray diffraction analysis revealed the shale beds to be made up of quartz as the dominant non clay minerals and clay minerals such as; montmorillonite with diffuse peaks of illite, microcline feldspar and kaolinite .The average hardness of limestone and shale is 6.5 kg/cm$^3$ and 2.43kg/cm$^3$, its average specific gravity is 2.50 and 2.00, while the average moisture content of limestone and its associated shale is 3.5% and 30.43% respectively. The results of the chemical analyses of limestone shows a range value of; $SiO_2$, 3.71-8.53%, $Al_2O_3$, 0.83-8.53%, $Fe_2O_3$,1.47-7.32%,MgO, 0.84-1.67%, CaO, 43.84-50.20%, $Na_2O$, 0.01-0.20%, $K_2O$, 0.05-0.35%, $TiO_2$, 0.67-1.09%, $P_2O_5$, 0.13-7.67%, MnO, 0.19-0.52%, $Cr_2O_3$ ,0.01-0.02%, loss on ignition, 29.00-41.70% , while the result of chemical analysis of shale show a range of $SiO_2$, 39.21-48.80%,$Al_2O_3$,9.87-18.00%,$Fe_2O_3$,3.68-8.75%,MgO,0.66-3.51%,CaO,0.86-19.34%,$Na_2O$,0.05-0.10%,$K_2O$,0.57-1.05%,$TiO_2$,0.67-0.80%,$P_2O_5$,0.05- 0.47%,MnO,0.19-0.52%,$Cr_2O_3$0.01-0.03%,loss on ignition, 21.30-26.00%. However, the limestone and shale beds of the study area were compared with other standard physicochemical industrial specifications and various chemical mixing ratios. The study revealed that the limestone and associated shale of the communities around Yewa lagoon satisfies the physical and chemical factors for Portland cement production, but slightly falls below the standard chemical specifications for other industrial uses-: steel, ceramics, paper mills, refractory bricks and plastics productions.

***Keywords:-*** Limestone and shale sediments, physical analysis, x-ray diffraction, major and minor element analysis, chemical mixing ratio, Portland cement

*Corresponding Author: Popoola Samuel Olatunde
[1]*Department of Physical and Chemical Oceanography, Nigerian Institute for Oceanography and Marine Research PMB, 12729, Victoria Island, Lagos.*

# I. INTRODUCTION

The most important physical and chemical components from limestone and shale are the specific gravity, hardness and moisture contents quicklime (CaO), silica ($SiO_2$) and alumina ($Al_2O_3$), and other minor chemical constituents such as iron ($Fe_2O_3$),magnesium oxide(MgO),total alkali($K_2O$) and ($Na_2O$).These constituent determines the diversity and industrial uses of the limestone, shale and clay beds.

Detailed physical and chemical compositional characteristics of limestone, shale and clay sediments of some localities: Odukpani and Mfamosing, Cross River state, South-South Nigeria, Nkalagu, Ebonyi state, South-Eastern Nigeria, Yandev, Benue state, North-central, Nigeria (RMRDC,2010).Moreover in the southern part of Nigeria, Okada, Edo state, South-South, Nigeria (Obrike *et. al*.,2007) and Sagamu, Oke Ate, Papa alanto, Ewekoro, Ibese, Owode, Igana Egugu and Ijeun, Ogun state, South western Nigeria (Ako *et. al.*,1980). has all been known and documented.

Ewekoro limestone and shale are being exploited both at Sagamu and Ewekoro, by the West-African Portland cement company. Mfamosing and Odukpani limestone/shale are being exploited by the united cement company of Nigeria limited, Nkalagu limestone and associated shale are being exploited by Bulk cement limited and Ibeto cement company, while the Yandev limestone and associated shale had once been under exploitation by Benue cement company on account of their respective and well documented physical/chemical compositional characteristics.

Large reserves of limestone and shale have been reported in the neighbouring communities around Yewa lagoon but detailed physical, chemical and mineralogical characteristics for Portland cement productions and other industrial uses such as: fertilizer, mortar, filler, steel, oil and white cement, concrete, ceramics, paper mills, refractory bricks and plastic productions have not been documented.

Yewa lagoon, one of the nine lagoon in the south western Nigeria,(kusemiju, 1998, Nwankwo 2004, Onyema 2008, Onyema and Nwankwo 2009, Onyema & Emmanuel, 2009,Onyema 2009,)with adjoining communities: Alagbe, Andrew, Alaran, Erin, Irogun akere, Idogo, Araromi papanla, Igbobe, Oke odan, Owode, Ado-odo, Ipokia, Idi-iroko, Ibatefin, Ogun state, south western Nigeria and several other farming and fishing settlements. The study area lies within the latitude 6°49'N to 6°51' and longitude 2°55'E and 3°00' (fig 1&2). Samples were taken towards the Northeastern and Northwestern part of River Igbin which drains in a dendritic flows pattern into the Yewa lagoon (Jones and Hockey, 1964) around Ebute Adewale .The sediments around the study area have been known to be of sufficient quantities of; sand, shale, clay and limestone.

This study presents the compositional characteristics of the limestone and shale sediments around the Yewa lagoon in south-western Nigeria, using its physical, chemical and mineralogical compositions to determine, whether the limestone and shale beds around the Yewa lagoon can be a desirable pointer for industrial applications-: filler, concrete, mortar and cement, plastic, refractory blocks, ceramics, steel and other documented chemical compositions.

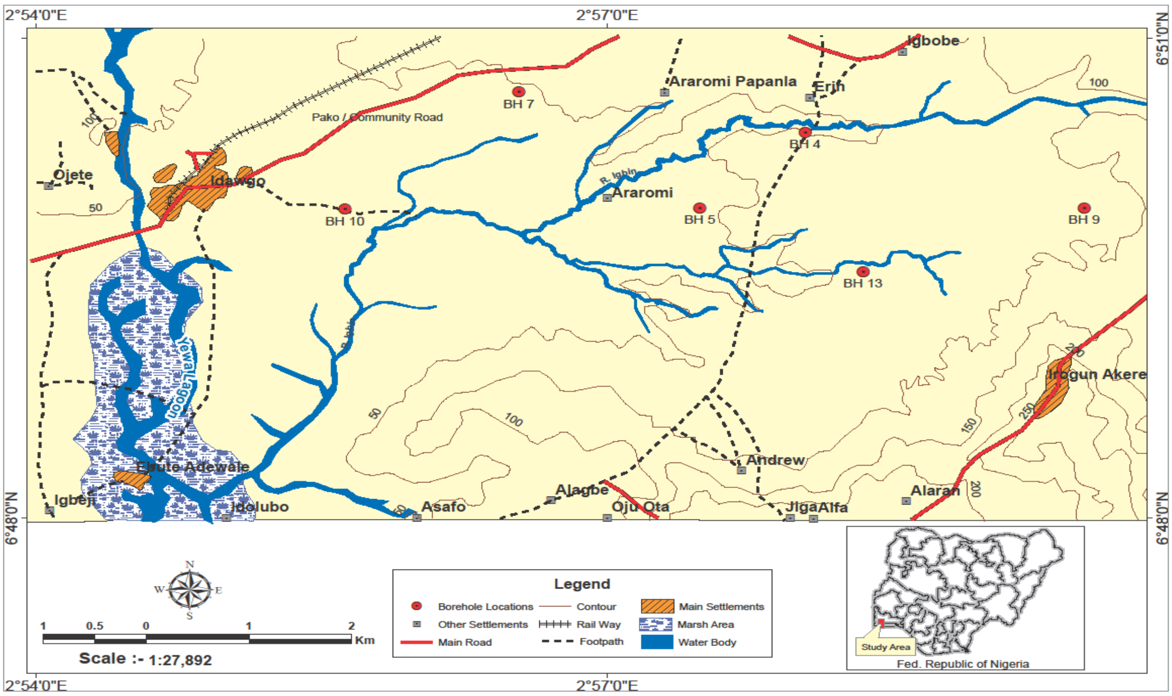


**Fig 1: Sampling Location Stations**

## II. MATERIAL AND METHODS

Field work was carried out in the month of February to June 2009. Core sediments samples were collected from fourteen boreholes using rotary drilling method in order to reveal the underlying lithology, after pitting processes have demarcated the area of concentration of the limestone and shale sediment.

Sample was taken as soon as there is a change in lithology with relation to depth during the drilling operations. Detailed lithologic description of the core samples were carried out with column for; depth, rock types and colour. These processes were followed by logging and documentation of exposures with standard form containing information, such as; texture, colour and core recoveries. Samples were then collected into well labeled sample bags for storage and laboratory analysis. The contaminated surfaces were removed by hammering and samples were then crushed to gravel size using a chip munk jaw crusher. The chips were further pulverized to fine powder in a disc mill to promote dissolutions. The mortal was later cleaned with metylated spirit in order to avoid contamination after each pulverization process. The samples were then passed through a 212um sieve mesh and each sample weighing about 5g was collected in sample sachets. The sachets were properly labeled and stored for chemical analyses.

Fifteen limestone and shale representative samples from the core sediments were subjected to physical tests (hardness, specific gravity and moisture contents) at the Lagos State material testing laboratory, Ojodu, Berger, Lagos state. The hardness of the limestone and shale were determined by comparing them with Mohr's scale of hardness, while the specific gravity of the limestone and shale were determined by subtracting the sample weight in air from the sample weight in water. The moisture content was calculated by sun-drying the limestone and shale samples for a period of seven days. Ten grams each of four limestone and seven shale samples were placed in a porcelain crucible and dried in an oven for 5 hours at $105^0$C.The crucible was cooled and weighed the difference in weight was recorded as the moisture content.

The chemical analyses were carried out via; X-ray Diffraction studies to determine the shale sediments mineralogy and inductively coupled Plasma Activation Emission Spectrometer (ICP-AES) to determine the limestone and shale sediments' chemical compositions.

The X-ray Diffraction studies was carried out at the Engineering Materials Development Institute (EMDI) Akure, Ondo State and Center for Energy Research and Training (CERT), Obafemi Awolowo University,Ile-Ife, Osun-state (fig4&5) with the aid of Philiph X-ray diffractometer model 1800 fitted with copper anode with a scanning rate of $2^0$/2q/minute (Brown 1951).The interpretation of the diffactogram was done by comparing the peaks obtained with those of standard minerals established by Carrol (1971) and joint committee on powder diffraction standards while the abundance was calculated using the area method (IJCPS, 1980).

The major, minor and trace elements were determined using inductively coupled plasma activation emission spectrometer (ICP-AES) on limestone and shale sediments at the Activation Laboratories Limited) Ontario Canada, detailed results are presented in table v and vii.

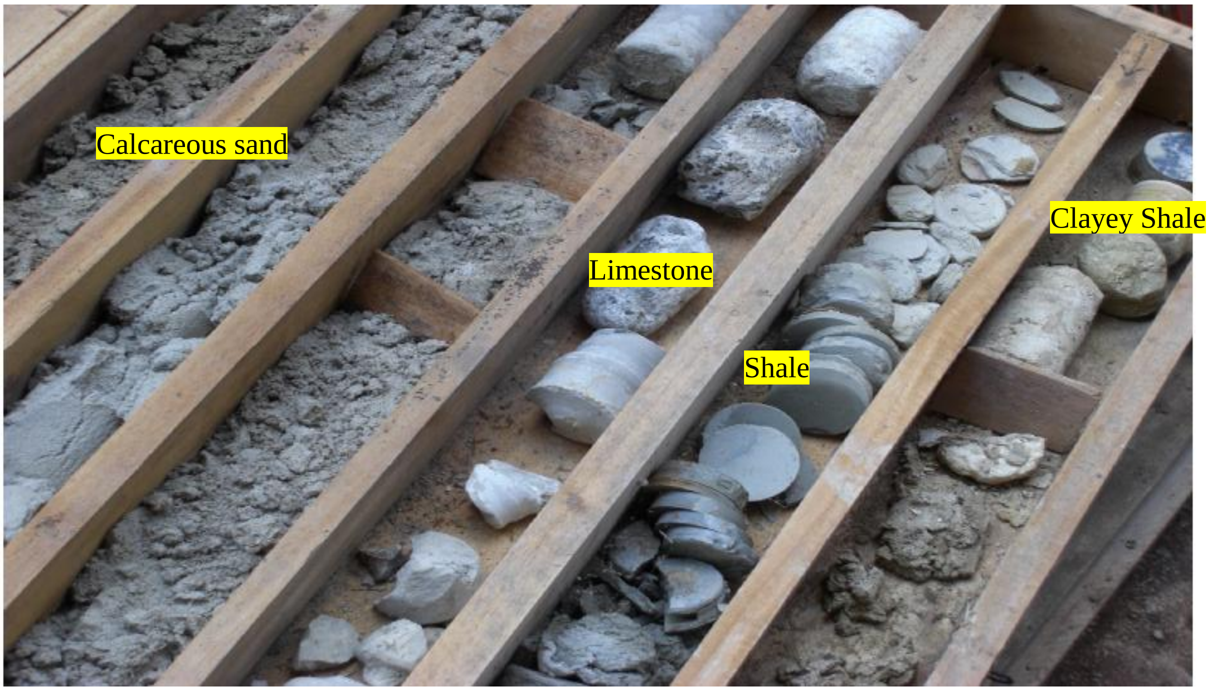


**Plate 1: The core sediments**

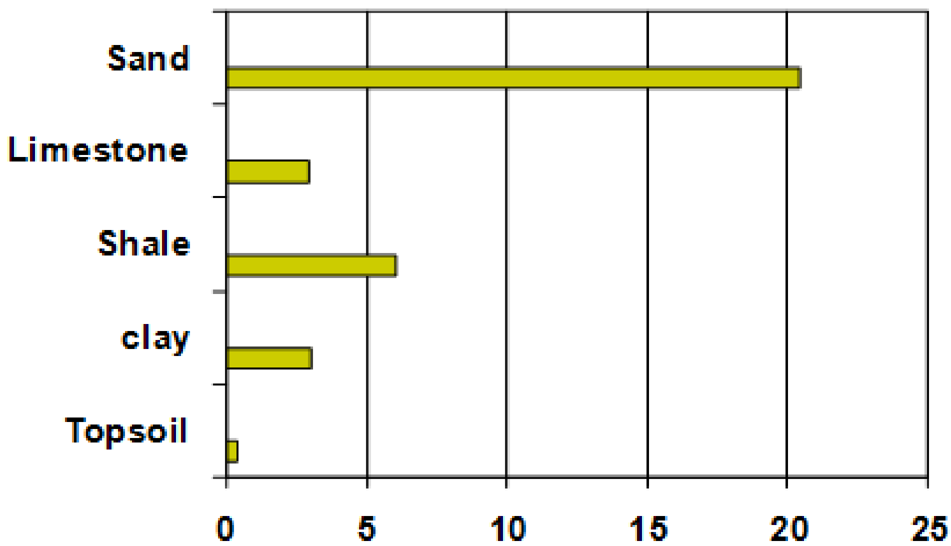


**Fig 2: Average thickness of cored samples depth (meters)**

## III. RESULTS

**Physical Characteristics of Limestone and Shale Sediments Hardness and Specific Gravity**

The hardness of limestone and shale fall within 6.0 and 7.0 and 2.0 and 3.0, with average of 6.5 and 2.5 when both were compared with Mohr's scale of hardness, while, the specific gravity of limestone sediments range between 2.55 and 2.58 with an average of; 2.56 and shale, with a specific gravity of; 1.56 to 2.42 with an average of 2.00 respectively.

**MOISTURE CONTENT**

The result of the moisture content carried out on limestone sediments show a range between 2.5% to 4.45% with an average of 3.57% and shale sediments ; 25% to 35% with an average of 30.43% respectively.

**MARL(IMPURED LIMESTONE)**

The hardness of marl range between 3.6 to 4.0 with an average value of 3.8 and its specific gravity ranges between 2.5 to 3.2 with an average value of 2.77 respectively. However, its moisture content ranges between 2.56 to 4.45 with average of 21.66.

**TABLE i: THE PHYSICAL PROPERTIES OF LIMESTONE SEDIMENTS**

| BOREHOLE | DEPTH(M) | HARDNESS | SPECIFIC GRAVITY | MOISTURE CONTENT (%) |
|---|---|---|---|---|
| **BH4** | I.6-4.0 | 6.0 | 2.56 | 3.02 |
| **BH5** | 8.0-10.3 | 7.0 | 2.65 | 3.56 |
| **BH7** | 10.0-12.8 | 7.0 | 2.58 | 2.56 |
| **BH10** | 4.0-7.0 | 7.0 | 2.55 | 3.05 |
| **BH13** | 12.8-16.0 | 6.0 | 2.56 | 4.45 |
| **BH14** | 8.2-11.0 | 6.0 | 2.57 | 4.35 |
| **BH15** | 6.0-9.0 | 6.5 | 2.55 | 4.0 |
| **AVERAGE** | | **6.5** | **2.56** | **3.57** |

**TABLE ii: THE PHYSICAL PROPERTIES OF SHALE AND MARL SEDIMENTS**

| BOREHOLE | DEPTH(M) | HARDNESS | SPECIFIC GRAVITY | MOISTURE CONTENT (%) |
|---|---|---|---|---|
| **BH5** | 5.-8.0 | 3.0 | 1.56 | 28.0 |
| **BH7** | 6.2-10.0 | 2.0 | 1.58 | 32.0 |
| **BH7** | 5.4-6.0 | 3.0 | 1.80 | 30.0 |
| **BH9** | 16.5-30.0 | 3.0 | 2.25 | 25.0 |
| **BH9** | 6.1-9.8 | 2.0 | 2.40 | 35.0 |
| **BH10** | 3.2-4.0 | 2.0 | 2.42 | 30.0 |
| **BH13** | 8.0-12.0 | 2.0 | 2.02 | 33.0 |
| **AVERAGE** | | **2.43** | **2.00** | **30.43** |
| **MARL SEDIMENTS** | | | | |
| **BH7** | 6.0-6.2 | 4.0 | 2.50 | 22.0 |
| **BH5** | 11.9-14.1 | 3.8 | 3.20 | 18.0 |
| **BH9** | 9.8-11.5 | 3.6 | 2.60 | 25 |
| **AVERAGE** | | **3.8** | **2.77** | **21.66** |

**TABLE iii (a): STANDARD PHYSICAL PROPERTIES OF LIMESTONE SEDIMENTS**

| Physical Properties | Study area | ASTM 1976 | Neville,1935 |
|---|---|---|---|
| **Specific gravity** | 2.56 | 2.5-2.7 | SG,3.15 |
| **Hardness(kg/cm3)** | 6.5 | >4 | >3-4 |
| **Moisture content (%)** | 3.57 | 1.9-3.0%, | >2 |

**TABLE iii (b) STANDARD PHYSICAL PROPERTIES OF SHALE SEDIMENTS**

| Physical Properties | Study area | ASTM | Okada shale |
|---|---|---|---|
| **Specific gravity** | **2.00** | 2.5-2.8 | 2.45-2.48 |
| **Hardness(kg/cm3)** | **2.43** | <3 | <3 |
| **Moisture content (%)** | 30.43 | 10-30% | >12 |

## IV. GRAIN SIZE, COLOUR AND TEXTURAL DESCRIPTION

The lithologic description of the core sediments were based on their grain size, texture, colour and fossil contents, aided by the use of a typical hand lens. The topsoil is generally loose, dark brown, soft clayey, humic soil while, clay is generally plastic, brownish to yellow with phosphatic nodules. The shale are generally grey to brown thinly laminated and fissile beds (plate1), while the limestone are generally grey to dark grey, fossiliferous rock. The sands are generally fine to medium grain grey to brownish grey in colour, (see plate 2, 3 and 4).Detailed lithologic and pectrographic description of the sediments around River Yewa; its provenance and environment of depositions were described in Popoola etal., (2014).


**Plate 2: Clay**


**Plate 3: Sand**


**Plate 4: Limestone**

**Chemical Characterisics of Limestone and Shale Sediments**

**TABLE IV: X-RAY DIFFRACTION ANALYSES**

| BH | DEPTH (M) | I % | Q % | MF % | M % | K % |
|---|---|---|---|---|---|---|
| **BH5** | 11.9 - 14.1 | 4.3 | 37.87 | 12.09 | 31.31 | 14.02 |
| **BH13** | 8.0 - 12.0 | 20.22 | 57.48 | - | 22.25 | - |

Note: I= illite, Q= quartz, MF=microcline feldspar, M= montmorillonite, K= kaolinite

Three important chemical components quicklime (CaO), silica ($SiO_2$) and alumina ($Al_2O_3$) compositions were used to calculate the following chemical ratios: Lime saturation factor (LSF), Silica Ratio (SR) and Alumina Iron Ratio (AIR) using the standard formula according to Carvalho M. De O. Madivate, 1999.

Lime saturation factor: $$\frac{100CaO + 0.75MgO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

Silica Alumina Iron Ratio: $$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Alumina iron ratio = $$\frac{Al_2O_3}{Fe_2O_3}$$

The results of the chemical ratio are presented in table x.

**TABLE v: CHEMICAL ANALYSIS (MAJOR AND MINOR ELEMENTS) OF LIMESTONE**

| | | **BH4** | **BH5** | **BH7** | **BH10** |
|---|---|---|---|---|---|
| **OXIDE%** | **DEPTH(M)** | 1.60-4.00 | 8.0-10.30 | 10.0-12.80 | 4.00-7.00 |
| **$SiO_2$** | | 3.71 | 4.32 | 6.93 | 8.53 |
| **$Al_2O_3$** | | 1.10 | 0.84 | 1.89 | 1.46 |
| **$Fe_2O_3$** | | 1.78 | 2.02 | 7.32 | 1.47 |
| **MgO** | | 0.85 | 1.30 | 1.67 | 0.84 |
| **CaO** | | 50.20 | 48.74 | 43.84 | 45.97 |
| **$Na_2O$** | | 0.01 | 0.07 | 0.20 | 0.05 |
| **$K_2O$** | | 0.05 | 0.17 | 0.35 | 0.17 |
| **$TiO_2$** | | 0.07 | 0.59 | 0.37 | 1.09 |
| **$P_2O_5$** | | 0.13 | 1.10 | 7.67 | 0.49 |
| **MnO** | | 0.34 | 0.19 | 0.52 | 0.22 |
| **$Cr_2O_3$** | | 0.01 | 0.02 | 0.02 | 0.01 |
| **LOSS ON IGNITION** | | 41.70 | 40.50 | 29.00 | 39.60 |
| **SUM%** | | **99.50** | **99.86** | **99.78** | **99.80** |

**BH-Borehole**

**TABLE VI: CHEMICAL ANALYSIS (MAJOR AND MINOR ELEMENTS) OF LIMESTONE SEDIMENTS OF THE STUDY AREA WITH SOME SELECTED SPECIFICATIONS**

| Deposit | CaO | MgO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O/K_2O$ | $P_2O_5$ | $Cr_2O_3$ | LOI | EQUIV $CaCO_3$ | EQUIV $MgCO_3$ | Source |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Limestone Study area** | 47.19 | 1.17 | 5.87 | 1.32 | 3.15 | 0.45 | 2.35 | 0.02 | 37.7 | 85.68 | | |
| **Marl study area** | 29.83 | 6.38 | 27.02 | 1.37 | 1.92 | 0.25 | 0.79 | 0.01 | 6.63 | 15.07 | | |
| **Odukpani** | 54.18 | 0.57 | | | | 0.31 | | | 42.58 | 96.60 | 1.20 | RMRDC,2010 |
| **Mfamosing** | 50.43 | 1.53 | 1.05 | | | | | | | | | RMRDC,2010 |
| **Yandev** | 53.10 | 0.61 | 2.25 | 0.94 | 0.49 | | 0.06 | 0.06 | 43.07 | 98.80 | 1.30 | RMRDC,2010 |
| **Nkalagu** | 49.90 | 0.70 | 5.90 | | | | | | 40.57 | 89.10 | | RMRDC,2010 |
| **Fertilizer** | 53.50 | >6.00 | >5.00 | 1.50 | >5.00 | | | | 42.41 | >90.00 | 3.43 | ASTM,1976 |
| **Standard PC** | 51.94 | 0.72 | 2.49 | 1.25 | 1.06 | 0.10 | 0.10 | 0.09 | 42.22 | 95.95 | | ASTM,1976 |
| **Standard PC** | >55 | <0.6 | 0.64-0.04 | <0.1 | <0.05-0.08 | <0.6 | <0.1 | | 43.0-43.7 | 97.7 | | ASTM,1976 |
| **Steel** | 54.28 | 3.0 | >5.0 | 0.002 | 0.002 | | 1.0 | | | | | ASTM,1976 |
| **Slag cement** | 40.0 | | 35.0 | 12.00 | 1.00 | | | | | | | ASTM,1976 |

Note: Pc = Portland cement

**TABLE vii: CHEMICAL ANALYSIS (MAJOR AND MINOR ELEMENTS) OF SHALE SEDIMENTS**

| | | **BH5** | **BH7** | **BH7** | **BH9** | **BH9** | **BH10** |
|---|---|---|---|---|---|---|---|
| **OXIDES%** | **DEPTH** | 5.30-8.00 | 5.40-6.00 | 6.20-10.0 | 6.10-9.80 | 16.50-30.0 | 3.2-4.0 |
| **$SiO_2$** | | 48.88 | 47.22 | 48.22 | 39.89 | 45.21 | 39.21 |
| **$Al_2O_3$** | | 16.74 | 15.89 | 18.00 | 12.33 | 17.24 | 9.87 |
| **$Fe_2O_3$** | | 5.57 | 6.11 | 5.59 | 4.41 | 8.75 | 3.68 |
| **MgO** | | 3.41 | 2.91 | 3.51 | 1.86 | 2.52 | 0.66 |
| **CaO** | | 1.53 | 1.15 | 0.86 | 13.34 | 1.48 | 19.34 |
| **$Na_2O$** | | 0.10 | 0.10 | 0.05 | 0.06 | 0.05 | 0.04 |
| **$K_2O$** | | 0.91 | 0.57 | 1.05 | 0.70 | 0.79 | 0.11 |
| **$TiO_2$** | | 0.67 | 0.77 | 0.71 | 0.68 | 0.70 | 0.80 |
| **$P_2O_5$** | | 0.10 | 0.05 | 0.04 | 0.47 | 0.07 | 0.46 |
| **MnO** | | 0.05 | 0.15 | 0.06 | 0.02 | 0.05 | 0.04 |
| **$Cr_2O_3$** | | 0.01 | 0.02 | 0.04 | 0.02 | 0.03 | 0.01 |
| **Loss on ignition** | | 21.90 | 24.90 | 21.30 | 26.00 | 23.00 | 25.60 |

Note:- BH-Borehole

**TABLE viii: CHEMICAL ANALYSIS (MAJOR AND MINOR ELEMENTS) FOR MARL**

| | | **BH5** | **BH7** | **BH9** | **BH13** | **BH13** |
|---|---|---|---|---|---|---|
| **OXIDES%** | **DEPTH (M)** | **5.30-8.00** | **5.40-6.00** | **6.20-10.0** | **6.10-9.80** | **16.50-30.0** |
| **$SiO_2$** | | 8.22 | 40.53 | 400.26 | 5.95 | 40.05 |
| **$Al_2O_3$** | | 2.20 | 1.02 | 1.01 | 1.62 | 1.00 |
| **$Fe_2O_3$** | | 3.09 | 1.42 | 1.35 | 2.44 | 1.32 |
| **MgO** | | 15.25 | 0.38 | 0.39 | 15.53 | 0.38 |
| **CaO** | | 28.38 | 29.97 | 30.04 | 30.61 | 30.16 |
| **$Na_2O$** | | 0.02 | 0.06 | 0.06 | 0.02 | 0.05 |
| **$K_2O$** | | 0.14 | 0.20 | 0.19 | 0.11 | 0.19 |
| **$TiO_2$** | | 0.12 | 0.36 | 0.51 | 0.09 | 0.50 |
| **$P_2O_5$** | | 0.04 | 1.32 | 1.27 | 0.04 | 1.29 |
| **MnO** | | 0.26 | 0.14 | 0.14 | 0.25 | 0.1 |
| **$Cr_2O_3$** | | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| **Los on Ignition** | | 42.00 | 24.50 | 24.70 | 43.80 | 24.80 |

**BH-Borehole**

**TABLE ix: CHEMICAL ANALYSIS (MAJOR AND MINOR ELEMENTS) OF SHALE SEDIMENTS OF THE STUDY AREA WITH SOME SELECTED SPECIFICATIONS**

| OXIDE | Study area | Ceramics(Singer and Sonja,1971) | North American Shale Composite (Gromet *et. al.*,1984) | Paper (Keller, 1964) | Plastic fire clay (M.O Huber,1985) | Refractory bricks (Parker,1967) | Average shale, (Pettijohn, 1957) |
|---|---|---|---|---|---|---|---|
| **$SiO_2$** | 44.77 | 67.50 | 64.82 | 45.90 | 57.67 | 51-70 | 51.80 |
| **$TiO_2$** | 0.72 | 0.1-1.0 | 0.80 | 0.0-1.70 | - | 1.0-2.80 | 0.6 |
| **$Al_2O_3$** | 15.01 | 26.50 | 17.05 | 33.50-36.10 | 24.0 | 25.44 | 15.4 |
| **$Fe_2O_3$** | 5.69 | 0.50-1.20 | 5.7 | 0.3-0.60 | 3.23 | 0.50-2.40 | 6.90 |
| **MnO** | 0.06 | - | - | - | - | - | Trace |
| **MgO** | 2.48 | 0.10-0.19 | 2.83 | - | 0.30 | 0.20-0.70 | 2.40 |
| **CaO** | 6.28 | 0.18-0.30 | 3.51 | 0.0-0.50 | 0.70 | 0.10-0.20 | 3.10 |
| **$Na_2O$** | 0.07 | 0.20-1.50 | 1.13 | | 0.20 | 0.80-3.50 | 1.30 |
| **$K_2O$** | 0.69 | 1.10-3.10 | 3.97 | 0.0-1.60 | 0.50 | - | 3.20 |
| **$P_2O_5$** | 0.20 | - | 0.15 | - | - | - | 0.20 |
| **LOI** | 24.78 | - | | - | - | - | - |

**NASC-North American Shale Composite**

## V. DISCUSSIONS

The results of the physical tests carried out on limestone and shale sediments are presented in table i and ii. The average physical properties (hardness, specific gravity and moisture content) of the limestone sediments are-: 6.5, 2.56 and 3.57 while, those of shale sediments are 2.43, 2.00 and 30.43 respectively. These values, when compared with American Society for Testing Material (ASTM.,1976) and Okada shale Obrike *et al.*, 2007 (table iii(a) & iii(b) all satisfies the physical requirements for cement and other constructional uses, except the impure limestone (marl) cored towards the eastern part of the study area (fig 2). According to ASTM grade on the moisture content of limestone -: A,<1%,B,1-5%,C,5-15%,D,15-35%,e,35-100%,F,>100,the limestone sediments of the study area falls within grade B, this further satisfies the standard requirements for cement ,concrete, filler and other industrial applications. The result of the chemical properties as shown in the typical diffactogram of the representative shale sediments of part of Yewa lagoon shows prominent of non clay minerals, quartz 37.87% and 57.48% and clay minerals, montmorillonite, 31.3% and 22.25% with diffuse peaks of illite, microcline feldspar and kaolinite respectively (table iv), this further indicate that the limestone and the shale sediments around yewa lagoon are thinly distributed (Jones and Hockey, 1964).

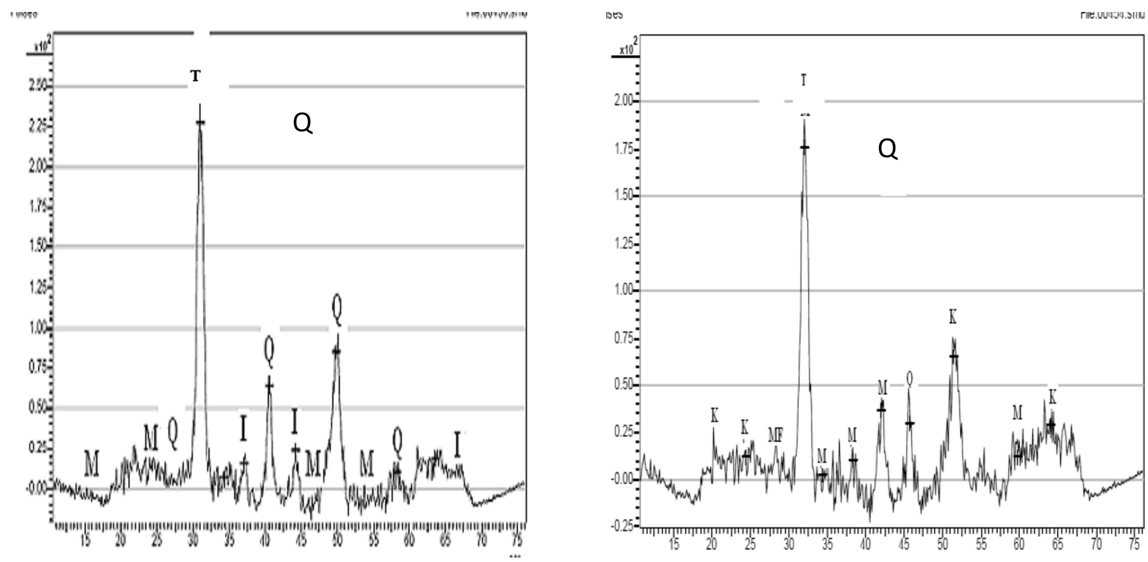


**Fig 3 & 4: X-ray diffactogram of representative samples of shale BH5&BH13**

M-montmorillonite, Q-quartz, I-illite, MF-microcline feldspar, K-kaolinite,

Table v, gives the chemical analyses of the major and minor element from the four limestone samples, while table vi summarises the average major and minor element wt% data for the study area. These were then compared with the average limestone of Odukpani, Mfamosing, Yandev, Nkalagu and some industrial chemical specifications -: fertilizer, standard portland cement, steel and slag cement (RMRDC,2010).

Based on ASTM $CaCO_3$ grade of very high purity limestone 98.5%, high purity limestone , 97.0-98.5%, medium purity limestone, 93.5-97%, low purity limestone, 85.0-93.5%, impure limestone <85%. The limestone of the study area falls within the low purity grade, while the limestone sediments of Yandev has the highest percentage of calcium carbonate content, 98.80% and falls within very high purity grade.

The average quicklime (CaO) of 47.19% and Calcium carbonate ($CaCO_3$) 85.05% at the study area are closer to the concentrations of Nkalagu limestone (RMRDC, 2010) and also closer to the standard specifications for Portland cement (ASTM, 1976), meanwhile the average magnesium oxide, (MgO) values of the study area is less than the 6.00(%) standard specification for fertilizer production. The iron($Fe_2O_3$) content of the study area is higher than the standard specification for the production of steel, oil well cement and white cement,($Fe_2O_3$ <0.01). The silica ($SiO_2$) and Alumina ($Al_2O_3$) content of the limestone of the study area is too low when compared to the standard specification for steel production (table vi).

Table vii and viii gives the chemical analyses major and minor element of six representative shale samples and five representative impure limestone(marl) samples of the study area. The impure limestone sediment (marl) of the study area does not fit into any industrial specification based on its low; Calcium oxide (CaO) and loss on ignition (LOI), high magnesium oxide (MgO) and silica($SiO_2$) content. Table ix summarises the average major and minor element wt% of the study area,these were compared with; North American Shale composite NASC (Gromet etal., 1984) standard specifications for ceramics(Singer and Sonja,1971), standard specifications for refractory bricks(Parker1967) standard specifications for Paper production(Keller,1964) and the average shale concentrations of (Pettijohn 1957). The average shale compositions of the study area is equivalent to the average shale concentrations of the North American shale composite and the average shale of Pettijohn,1957(table ix),but,has a slightly lower sillica($SiO_2$) and higher quicklime(CaO).The average iron($Fe_2O_3$) concentration of the study area is slightly higher,but the alumina($Al_2O_3$)concentration is lower than the standard specification for ceramics,paper mills and refractory brick productions.

Various chemical ratios -:of lime saturation factor(LSF),sillica ratio(SR) and Alumina-Iron Ratio (AIR),were calculated to arrive at the cement clinker ratio(table x).

**TABLE x: THE CEMENT CLINKER RATIO OF MIX 1-7 OF THE STUDY AREA**

| RAW MIX | LIMESTONE+SHALE | LSF | SR | AIR |
|---|---|---|---|---|
| **STANDARD** | | **90-102** | **1.5-4.0** | **1.4-3.5** |
| **MIX1** | 5(8 - 10.3) + 5(5.3 - 8) | 98.95 | 1.94 | 1.39 |
| **MIX2** | 7(10.0-12.8)+7(6.2-10.0) | 95.02 | 1.06 | 0.51 |
| **MIX3** | 10(4.0-7.0)+10(3.2 – 4.0) | 98.62 | 2.90 | 1.54 |
| **MIX4** | 10(4.0-7.0)+7(5.4-6.0) | 100.77 | 2.54 | 1.54 |
| **MIX5** | 4(1.6-4.0)+7(6.2-10.0) | 97.31 | 1.05 | 0.50 |
| **MIX6** | 4(1.6-4.0)+9(16.5-30.0) | 98.98 | 1.60 | 1.36 |
| **MIX7** | 10(4.0-7.0)+9(16.5-30.0) | 97.43 | 2.27 | 1.43 |

The limestone and shale of the study area satisfies the standard requirements for cement clinker compositions (LSF, AIR and SR).

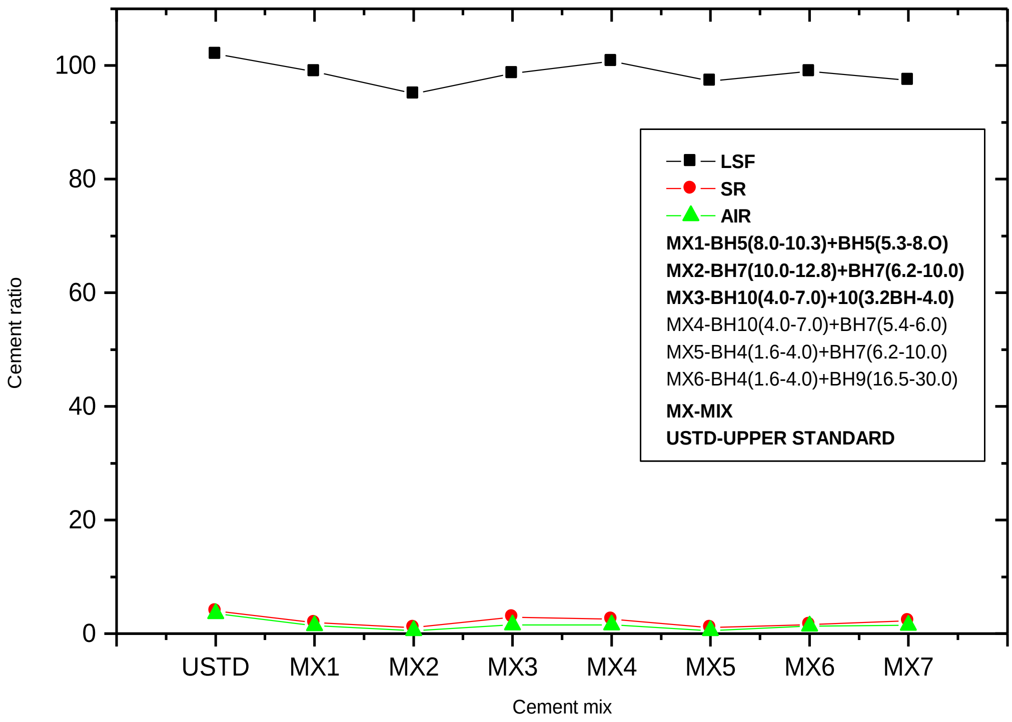


**Fig 5: Cement clinker composition of the study area**

## VI. CONCLUSIONS

The limestone sediment of the study area is generally hard with yellowish tints, light, shaly, slightly weathered or fragmented, fossillferous, dark grey and occasionally intercalated with phosphate nodules and marl which corroborate the work of Odigi and Brown-Awala (1992). However, the chemical composition of marl does not measure up to all the standard specifications. Therefore, it was eliminated in the calculation of the chemical mixing ratio.

The results of the compositional characteristics of the limestone and shale beds around Yewa lagoon reveal that the limestone shale beds satisfy the physical compositional specifications for cement, concrete, filler, mortar and other industrial uses based on its specific gravity, moisture content and hardness.

The result of the chemical/mineralogical composition of the shale samples based on the x-ray diffraction analysis identified non clay mineral, quartz as the dominant mineral, this further confirms that the limestone and the shale of the study area is thinly distributed in association with sand as the dominant lithology in the study area.

The limestone sediments of the study area are of low purity when compared with the American Society for Testing Material (ASTM, 1976) specifications using calcium carbonate ($CaCO_3$) grade. The chemical compositions of the limestone around Yewa lagoon is similar to the Nkalagu limestone (RMRDA, 2010) and also satisfies the standard specifications for Portland cement and cement clinker composition ratios-: lime saturation factor (LSF), Aluminum iron ratio (AIR) and silica ratio (SR).

The limestone of the study area does not satisfied the specifications for other industrial uses such as: fertilizer, steel, oil well cement, white cement and mortar productions, based on its low magnesium oxide(MgO) and silica($SiO_2$) composition.

The average shale composition of the study area is closer to the average shale composition of Pettijohn, 1957 and average shale of the North American shale composite (Gromet *et al*., 1984), see table (ix). The chemical composition of the shale sediments of the study area also satisfies the chemical requirements for portland cement production and chemical clinker ratio compositions (table x) but slightly falls below the specifications for ceramics, plastics production, paper mills, constructions and refractory blocks, as a result of its slightly higher iron ($Fe_2O_3$) compositions and slightly lower alumina ($Al_2O_3$) composition.

Based on these slight variations in chemical compositions with the aforementioned industrial purposes, it may be improvised for some of the industrial uses with details geotechnical investigations.

## ACKNOWLEDGEMENT

The author acknowledge late Professor A.F Abimbola of the university of Ibadan, for his guidance on this project, may his gentle soul rest in perfect peace .My appreciation goes to Dr Akinade Olatunji of the university of Ibadan, you are a source of inspiration

## REFERENCES

[1]. American Society for Testing Materials (1976): Standard specifications for limestone building stone ASTM C568-89
[2]. Brown.G.1951. The X-RAY identification and crystal structures of clay minerals Min. Soc.London. pp 489-614.
[3]. Carrol, D, 1971. Clay Minerals: A guide to their X-ray identification. Geological Society of America special paper 126,USA.
[4]. Carvalho M. De O,. Madivate,1999. Cement and Concrete Research, , Volume 29, Issue Pages 695-698,850pp cenozoic deposits. Ibadan. University press.133pp.
[5]. Gromet L.P., Dymek,R.F,. Haskin,L.A,.Korotev R.L.,1984. The North American shale composite. Its compilation, major and trace element characteristics. Geochim.Cosmochim.Acta 48,2469-2482
[6]. Joint committee on powder diffractionstandard'(www.edumine.com/sgtables.htm,www.uky.edu last accessed Dec, 2013.
[7]. Jones H. A., Hockey R. D. (1964). The geology of part of south-western Nigeria Geological survey of Nigeria, explanation of 1:250,000 sheets, Nos 59-68.
[8]. Huber, J.M.1985.Kaolin clays.Huber cooperation(clay division division),Georgia,USA,64p.
[9]. Keller W.D., 1964. Kird-Othmer Encyclopedia of chemical Technology,vol 5,John Wiley and sons, Inc.New York,pp.541-585.
[10]. Kusemiju, K. (1988). Strategies for effective management of water hyacinth in the creeks and
[11]. Lagoons of south-western Nigeria. Proceedings of the international on water Hyayacinth, Lagos 7 – 12 August, 1988. 39 – 45.
[12]. Obrike S.E., Osadebe E.E., Onyeobu T.U.S. 2007. Mineralogical, geochemical, physical and industrial characteristics of shale from Okada area, South western Nigeria. Journal of Mining and Geologist, Vol 43(2) 2007, PP 109-116
[13]. Onyema., I.C. (2008). A checklist of phytoplankton species of the Iyagbe lagoon, Lagos. Journal of Fisheries and Aquatic Sciences. 3(3): 167 – 175.
[14]. Onyema., I.C. and Emmanuel, B.E. (2009). Fishing impairment and *Spirogyra africanum.*
[15]. Onyema., I.C. and Nwankwo, D.I. (2009). Chlorophyll a dynamics and environmental factors in a tropical estuarine lagoon. Academia Arena. 1(1): 18 – 30.
[16]. Pettijohn, F.J (1957).Sedimentary Rocks (2nd Ed) Harper and Row, New York (Publ.) 628p
[17]. Parker, E.R.,(1967). Materials data book for engineers and scientist.
[18]. Popoola S.O, Oyatola O.O and Appia,Y.J ,(2014). Pectographic Study of Carbonate Sediments around Yewa River, Eastern Dahomey Basin, South Western Nigeria. Scientific Research Journal (SCIRJ), Volume II, Issue VII,PP 56-69.
[19]. Popoola S.O, Appia, Y.J and Oyatola O.O (2014). The Depositional Environments and Provenance Characteristics of Selected Sediments, South of Yewa River, Eastern Dahomey Basin, South Western Nigeria. International Organisation of Scientific Research (IOSR) Journal of Applied Geology and Geophysics (IOSR-JAGG).PP12-107.
[20]. RMRDC 2010: Non metallic mineral endowments in Nigeria 26-28, pp103.
[21]. Singer F.Sonja, S.S.1971.Industrial ceramics publ. Chapman and Hall London, 56p.

**Geographic Coordinates of sampled Borehole locations**

| Location | Latitude | Longitude |
|---|---|---|
| **BH 10** | 6° 49' 55.92" | 2° 55' 36.84" |
| **BH 5** | 6° 49' 55.92" | 2° 57' 29.16" |
| **BH 7** | 6° 50' 40.56" | 2° 56' 32.28" |
| **BH 4** | 6° 50' 25.08" | 2° 58' 2.64" |
| **BH 13** | 6° 49' 32.88" | 2° 58' 20.28" |
| **BH 9** | 6° 49' 55.92" | 2° 59' 30.84" |