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Physicochemical Characterization of Limestone Deposits at Ewekoro, Ogun State, South-West of Nigeria and the Environment Impact

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Abstract
Limestone is the primary constituent raw material for cement manufacture. While most limestone deposits are suitable for cement making, there are some characteristics of limestone which need to be defined in order to establish a usable raw material supply. These relate to compositional requirements and also the consistency of the deposit in chemical and physical terms. Limestone makes up about 10% of the total volume of all sedimentary rocks. The solubility of limestone in water and weak acid solutions leads to karst landscapes, in which water erodes the limestone over thousands to millions of years. The density and porosity of samples from the various locations vary from 2.61g/cm^3 to 2.72g/cm^3 and 2.70% to 3.80%. The Schmidt hammer rebound number of samples from Ewekoro quarry varies from 32.1 to 33.6. The uniaxial compressive strength of samples from Ewekoro quarry varies from 60.5 MPa to 63.5 MPa thereby classifying the rock as moderate to high strength. The point load strength index is obtained from the LAFARGE laboratory results and varies from 1.239 MPa to 2.185 MPa. The strength classifications fall within the range of moderate to high strength class. Also, the tensile strength, obtained from point load strength ranges from 1.862 MPa to 3.086 MPa. The staining process induces a reaction on the surface of a particular mineral species which results in coloured precipitate characteristic of that mineral. Alizarin red S in NaOH stained the samples purple indicating the presence of magnesium in the carbonate while Alizarin red S in HCL stained the samples red. Physical observation of Ewekoro limestone deposit reveal the rock is highly fossiliferous with the identified fossils indicating deposition in an open shelf environment. Moreover, the limestone deposit was equally observed to be principally mud supported which is indicative of rocks deposited in quiet water and a low energy environment.
Keywords: Limestone, Solubility, Ewekoro, Physical and Chemical.

1. INTRODUCTION

Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$). Many limestones are composed of skeletal fragments of marine organisms such as coral or foraminifera. Limestone makes up about 10% of the total volume of all sedimentary rocks. The solubility of limestone in water and weak acid solutions leads to karst landscapes, in which water erodes the limestone over thousands to millions of years. Most cave systems are through limestone bedrock. Limestone is a very common sedimentary rock consisting of more than 50% calcium carbonate. Although it occurs in many different forms, its origins can be traced back to either chemical or biochemical processes that occurred in the geological past, often tens to hundreds of millions of years ago. Many different types of marine organisms have developed the ability to precipitate calcium carbonate from seawater to serve as a protective shell or exoskeleton. For example, scallops have a two-piece outer shell that can be opened to allow the scallop to feed and closed to give protection, whereas bryozoans produce an outer casing within which they live. When these organisms die, their shells accumulate on the seafloor. The soft parts decay, leaving only the hard shells (exoskeletons or tests), which typically become broken down by current action and biological predators. Over long periods of time, the loose skeletal sediments are transformed into bioclastic limestone by the addition of a chemically precipitated carbonate cement between the shell fragments. In the warm low-latitude waters of the tropics, these are called tropical bioclastic limestones, while in the cooler waters, at mid to high latitudes, they are known as temperate bioclastic limestones. In the case of large congregations of tropical marine organisms, like reef-building corals, the normally very large structure remains intact as it is transformed into tropical limestone reef rock. Limestone is the primary constituent raw material for cement manufacture (Fig 1). While most limestone deposits are suitable for cement making, there are some characteristics of limestone which need to be defined in order to establish a usable raw material supply. These relate to compositional requirements and also the consistency of the deposit in chemical and physical terms which therefore motivated the current study to characterize the physico-chemical parameters of the limestone deposits at the study area.

Fig. 1: Limestone formation in a quarry (Wikipedia.com/limestone 2013)

As limestone, and other raw materials are required to manufacture cement clinker which include clay or shale, sand and iron oxide. However, not all these are required in all cases but their availability needs to be known to determine what qualities of cement can be made from the limestone deposits. In many plants, these materials can be made available from the by-products from other industries, such as fly ash from power stations to replace partly or wholly the clay component or waste materials from the steel industry including slags and oxide rich sludges.

Hence the primary aim of the research is to study the physical and chemical characteristics of limestone samples collected at the Ewekoro quarry in Ogun State of Nigeria. This shall help to determine the quality and/or quantity of the type of cement marketable to the public for their education.

2. STUDY AREA

Ewekoro is one of the sites of the West African Portland Cement Company (WAPCO) blessed with large deposits of limestone - the major raw material in the production of cement. The Ewekoro plant of WAPCO LAFARGE is located in Ewekoro local government area of Ogun State in the South-west Nigeria. The local government area is bounded in the North by Abeokuta, in the East by Obafemi - Owode, in the West by Yewa South and in the South by Ado-Odo Ota. Moreover, Ewekoro cement factory is on a latitude 5°.50'N and longitude 3°.17'E. Also it is approximately 64 kilometers north of Lagos and 42 kilometers south of Abeokuta. Majority of the inhabitants are farmers and the area is largely rural. Most of these farmers engage in the planting of sugar cane, cassava, maize and vegetable. Cash crops such as cocoa, kolanut and oil palm are also cultivated. These farmers also engage in the rearing of livestock like small ruminants, poultry and pigs.

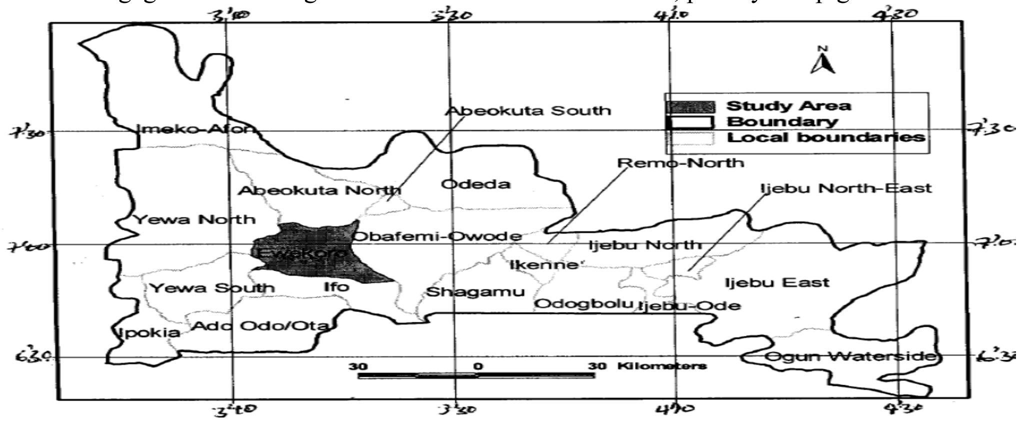

Fig 2: Map of the Study Area

3. MATERIALS AND METHODS

3.1 Collection of Samples

Courtesy of the quarry King, the authors were driven some 2km from the WAPCO main office to the quarry in an Sport Utility Vehicle (SUV). Various samples of limestones were collected at 8m depth and below at different parts of the quarry, Samples of the shale overburden overlying the limestone deposit were also collected. All the authors were kitted up in Personal Protective Equipment (PPE) which consists of a pair of goggles, safety helmet, safety vest and stilted boots to ensure safety during the collection of samples in the quarry as a heavy fine was always levied on defaulters who did not adhere to quarry safety rules and regulations.

3.2 Determination of Flakiness Index

This procedure discusses how the number of flat or elongated particles in a coarse aggregate material were determined. The following materials were used:

♦ Standard U.S. sieves which meet the requirements of Test Method "Tex-907-K, Verifying the accuracy of wire Cloth Sieves" in the following sizes:

- 22.4 mm (7/8 in.)
- 16.0 mm (5/8 in.)
- 9.5 mm (3/8 in.)
- 6.3 mm (1/4 in.)

♦ A 'Metal Thickness Gauge' made of 12 gauge carbon steel sheet
♦ Scoop, brass wire brush, bristle brush, and other necessary laboratory equipment
♦ Sample-splitter, quartering cloth or quartering machine
♦ Forced-draft oven capable of maintaining the temperatures specified in the test procedure.

The procedure adopted to determine the flakiness index was as tabulated in Table 1

Table 1: Steps adopted in determining the Flakiness Index

Step	Action
a.	Obtained a representative sample of processed aggregates according to Test Method "Tex-221-F, Sampling Aggregate for Bituminous Mixtures, Surface Treatments, and Limestone Rock Asphalt."
b.	Placed aggregate sample in an oven and dry at a temperature between 38 - 150 °C (100 - 300 °F) until sufficiently dry for testing.
c.	Quartered the aggregate sample until a minimum of 200 particles passing the 22.4 mm (7/8 in.) sieve and retained on the 6.3 mm (1/4 in.) sieve are obtained.
d.	♦ Sieved the quartered sample through the 22.4 mm (7/8 in.), 16.0 mm (5/8 in.), 9.5 mm (3/8 in.), and 6.3 mm (1/4 in.) sieves. ♦ Discard the material retained on the 22.4 mm (7/8 in.) sieve and passing the 6.3 mm (1/4 in.) sieve.
e.	♦ Counted the aggregate particles obtained from Step 4. ♦ The total sample count must be more than 200 particles.
f.	♦ Tried to pass each particle of the 22.4 mm (7/8 in.) to 16.0 mm (5/8 in.) sample through the 9.5 mm (3/8 in.) slot of the thickness gauge. ♦ Separate the particles passing through the gauge from those retained on the gauge.
g.	♦ Tried to pass each particle of the 16.0 mm (5/8 in.) to 9.5 mm (3/8 in.) sample through the 6.3
h.	♦ Tried to pass each particle of the 9.5 mm (3/8 in.) to 6.3 mm (1/4 in.) sample through the 4.0mm (5/32 in.) slot of the thickness gauge.
i.	♦ Combined all particles retained on the gauge and counted. ♦ The total is the 'Retained Sample.'
j.	♦ Combined all particles passing through the appropriate slots and counted. ♦ The total is the 'Passing Sample.'

Calculation to determine flakiness index was as follows

$$\text{Flakiness index} = \frac{Passing\ \ Sample\ \ Count}{Retained\ \ Sample\ \ Particle\ \ count + Passing\ \ Sample\ \ particle\ \ count} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Determination of Density

Four in-situ rock samples of each from the locations were collected, weighed and recorded. The determination of the density (ρ) was carried out according to the procedures suggested by ISRM (1989).

$$\rho = M/\Delta V \text{ (g/cm}^3\text{)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where M is the mass (g) and V is the volume (cm^3)

3.3 Determination of Porosity

Porosity refers to the amount of void (or open space) within a volume of sediment. The value of porosity is measured as a fraction or percentage. The equation to determine porosity is

$$n = V_v/V_t, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where "n" equals porosity, "V_v" equals volume of the pores, and "V_t" equals total volume of the saturated sediment.

Procedural steps taken to obtain porosity was as adopted by *Odunaike et., al.(2013)*

3.4 Determination of Bulk Density

Bulk density is a property of powders, granules, and other "divided" solids, especially used in reference to mineral components (soil, gravel), chemical substances, foodstuff, or any other masses of corpuscular or particulate matter. It is defined as the mass of many particles of the material divided by the total volume they occupy.

Procedural steps taken to obtain Bulk Density was as adopted by *Odunaike et., al. (2013)*

3.5 Determination of Hardness

The determination of the hardness of the samples involved the use of Schmidt hammer on lump of the rock samples. The rebound value of the Schmidt hammer was used as an index value for the intact strength of the rock material. The measured test values for the samples were ordered in descending order. The lower 50% of the values were discarded and the average upper 50% values obtained as the Schmidt Rebound hardness. The procedures followed the standard suggested by ISRM (1989).

3.6 Determination of Uniaxial Compressive Strength

The Schmidt hammer was first used on the samples to determine the rebound number. The values obtained were arranged then correlated using Deere and Miller (1966) chart to determine the uniaxial compressive strength of the rock.

3.7 Determination of Tensile Strength

The tensile strength of the rock samples was estimated based on the relationship suggested by ISRM (1989) which shows the general relationship between the point load strength (I_s) and the tensile strength (T_o) as expressed below:

$$T_o = 1.5I_s50$$

3.8 Testing Procedure for Aggregates

3.8.1 Acid Etching.

Several reagents are available for etching carbonate minerals but cold dilute hydrochloric acid (about 5 - 10% by volume) is appropriate for general petrographic study:

1.Pour the etching solution in a large glass or plastic tray and place the rock slice face up in the solution.
2.Gently agitate the acid with a glass rod to prevent formation of bubbles.
3.The etching time may be varied from 1 minute to over 5 minutes but about 2 minutes is the recommended time.
4. Flush the etched rock slice in cold water (in a bucket or sink).
5.The etched surface is now ready for examination by binocular microscopy.

3.8.2 Limestone Staining Procedure.

Potassium Ferricyanide and Alizarin Red S in 1.5% HCI.

1.Immerse sample in etching solution (dilute HC1 at room temperature) for approximately 15 seconds.

NB : the success of the staining depends on the quality of the etch; cold solutions give poor results; weak etching gives a patchy stain; and over-etching produces a very dense stain.

2.Immerse sample in combined staining solution. This consists of 3:2 mixture of dye (0.2g Alizarin Red S dissolved in 100 ml 1.5% HCl) and Ferricyanide (2g of potassium Ferricyanide dissolved in 100 ml 1.5% HCl) for 30-35 seconds.

NB: Solutions must be freshly made for each staining session.

3. Wash stained sample gently in distilled water and dry in a stream of warm air.

4.0 RESULTS AND DISCUSSION

The results of the physical test carried out on the samples are depicted in Table 2.

Table 2: Experimental results of physical and strength characterization of Limestone samples from Ewekoro quarry.

Rock Code	Porosity (%)	Density(gcm^{-3})	Rebound Hardness	Point Load Strength(MPa)	Tensile Strength(MPa)	Uniaxial Compressive Strength (MPa)
SA01	3.1	2.72	32.2	2.048	3.086	63.3
SA02	3.2	2.78	33.6	2.185	3.271	63.5
SA03	3.8	2.60	32.1	1.604	2.404	61.5
SA04	2.7	2.61	32.4	1.239	1.862	60.5

The results of the chemical test on the samples are as follows,

NAOH TEST

- Alizarin red S in 30% NaOH stains all the samples purple.

HCL TEST

- Alizarin red S in 1.5% HC1 stains calcite and aragonite red. Stains Ferroan dolomite and calcite purple.
- Potassium Ferricyanide in dilute HC1. Stains all carbonates dark blue if they contain iron. Most

dolomite are iron-rich, therefore this is a useful stain for distinguishing dolomite from calcite.

- Potassium Ferricyanide and alizarin red S in 1.5% HCl. Stain calcite pink or red and ferroan calcite purple.

5.0 DISCUSSION

The density and porosity of samples from the various locations respectively vary from 2.61g/cm^3 to 2.72g/cm^3 and 2.70% to 3.80% as shown in Table 2. The Schmidt hammer rebound number of samples from Ewekoro quarry varies from 32.1 to 33.6.The uniaxial compressive strength of the samples was estimated from the chart named after Deere and Miller, (1966). The uniaxial compressive strength of samples from Ewekoro quarry varies from 60.5 MPa to 63.5 MPa thereby classifying the rock as moderate to high strength. The point load strength index varies from 1.239 MPa to 2.185 MPa. The strength classifications fall within the range of moderate to high strength class. Also, the tensile strength, obtained from point load strength ranges from 1.862 MPa to 3.086 MPa. The results gotten thus far are in reasonable agreement with (Okewale, and Olaleye, 2013) who worked on "Characterization of Some Selected Limestone Deposits in Ogun State, Nigeria for Prediction of Penetration Rate of Drilling". The staining of limestones to determine their carbonate mineralogy is a well-established technique (Dickson, 1965; Friedman, 1959). This technique is used primarily to determine the presence of carbonate and ferroan carbonate (Iron- containing carbonate). The staining process induces a reaction on the surface of a particular mineral species which results in coloured precipitate characteristic of that mineral. Alizarin red S in NaOH stained the samples purple indicating the presence of magnesium in the carbonate while Alizarin red S in HCL stained the samples red. Had it stained it purple would have proven the existence of iron in the carbonate. Potassium ferricyanide and Alizarin red S in 1.5% HCL stains all samples of the carbonate reddish pink and would also have stained the carbonate samples purple had they contained iron. From the physico-chemical analysis of Ewekoro limestone it is shown that it is perfect for the manufacture of Ordinary Portland Cement (OPC) . Physical observation of Ewekoro limestone deposit reveal the rock is highly fossiliferous with the identified fossils indicating deposition in an open shelf environment. Moreover, the limestone deposit was equally observed to be principally mud supported which is indicative of rocks deposited in quiet water and a low energy environment. From the aforementioned textural characteristics, Ewekoro limestone deposit can be classified as Wackestone according to Dunham, 1962. Limestone mining in Ewekoro has resulted in conversion of farmlands into quarry sites. The West Africa Portland cement according to the management made frantic effort at re-settling the landowners in the estate built very close to the factory. But since this was rejected, a programme of gradual takeover of the old farm site had started. In the course of using the quarry, farmers had been stopped from the site and the cutting/felling of the trees continued, resulting into a large Expanse of land exposed to rain water and wind. The lake created as a result of blasting of limestone and release of water from within the Limestone deposit ordinarily should serve as habitat to fresh water fish, this has however not been developed. The ammonium compound washed into the lake from its primary source (explosive materials) may serve as manure and may encourage the growth of plankton, algae and aid the liming of the lake and encourage fish production. Silica exposure is an ancient hazard which has remained a serious threat to many workers including sand blasters, stone crushers, those involved in drilling, quarrying and tunneling through the earth crust. Diseases associated with the inhalation of silica-containing dust include silicosis, chronic airways obstruction and bronchitis, tuberculosis and lung cancer. Many workers including those in high-risk settings are exposed to crystalline silica. Wetting of the site road with water is carried out to reduce only the fugitive dust. Empirical observation reveals that while most of the workers are protected, the residents in the community are exposed to the dust during production process.

6.0 RECOMMENDATION

It is recommended that the latter technique (potassium ferricyanide and Alizarin red S in 1.5% HCL) is adopted for routine evaluation of carbonate deposits. It is a valuable dual staining technique that allows for differentiation between ferroan phases in calcites and dolomites to be carried out in one operation. (Dickson, 1965). It is also recommended that the carbonate samples before physical examination be pulverized, dried, sieved and even weighed before physical tests are carried out so as to get accurate results. It is of primary necessity to evaluate the air quality around any industrial unit in order to emphasize the adverse effects to ecological system and human health. For cement production activity, the dust deposition network should be set up in the surrounding of cement plants. It is also recommended that complete analysis of cement dust containing all the toxic pollutant should be carried out in detail, eventually, with such types of study, It would be possible to recommend plants for use as screen or green belts in industrial areas and adverse urban locations in order to mitigate dust and improve air quality. It is important that the industry expands its work to harmonize incident reporting requirements so that data can be collected and analyzed to identify the underlying causes of accidents and ill health. This will provide a better basis for industry benchmarking and enable health and safety improvements to be targeted where they will be most effective. Moreover there is the need for the government to intensify effort in the implementation of Environmental impact assessment of cement industries now and in the future considering the nature of its impact on all the facets of human life Aside from that the excavated area should be properly filled to forestall the contamination of groundwater, surface water and aquatic lives, the original state of the excavated area should be attained. Considerable effort must also be geared towards preventing particulates from going into the atmosphere, as its effect in unpredictable in the environment, special devices to arrest and mop up particulates should be provided. Since lots of noise would be generated as a result of the cement production and mining activities there is the need to find a way of muffling the noise and to shield the site. Moreover large volume of vehicles would be attracted to the cement factory and mining site resulting into soil surface compaction hence there is need to develop appropriate highway and widened to reduce hazards on the environment. Moreover the government the industry and the community should be encouraged to be partners in progress. They can jointly be involved in monitoring environmental resources depletion, especially the compliance level of the plant to minimum standards for sustainable and pollution free society.

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