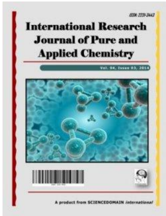

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Chemical Analysis of Itobe Limestone Deposit for Potential in Cement Manufacturing

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Authors' contributions

This work was carried out in collaboration between all authors. Authors TEA and DJ designed the study, carried out the statistical analysis, wrote the protocol and the first draft of the manuscript and also managed literature searches. Authors AV, ED, JB and FDU managed the analyses of the study and also did literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this research, the assessment of the chemical composition of the Itobe marble deposit for comparison with the general limestone requirements for cement making was investigated. Six pits were dug and carefully studied in the area. The research work is aimed at determining the suitability of the Itobe marble deposit in the manufacturing of cement, establish the nature, size and type of the deposit and to estimate the various impurities present and at what concentrations. The soil samples collected were analysed for their chemical properties. Samples were also obtained from river channels and from outcrops of the deposits. The result showed that an appreciable amount of the marble deposit, with CaO in the range of 32.95% to 50.05% and Silica ranging from 1.40% to 7.20%. From these chemical analyses, Itobe limestone showed a great potential in cement production to augment cement availability for building and civil engineering construction in Nigeria.

Keywords: Marble deposit; cement; outcrops; river channels.

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1. INTRODUCTION

Limestone is a sedimentary rock formed from the skeletons and shells of ocean organisms that consists chiefly of calcium carbonate. It is a primary raw material that is required in the manufacturing of cement and it is of high demand all over the world [1]. Limestone is a general term used to describe sedimentary rock composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate. There are numerous forms and types of limestone differing in chemical composition, mineralogy, crystallinity, colour, texture and hardness. Calcium and dolomite limestone are the two most fundamental types of limestone. Pure high calcium limestone is 100% calcium carbonate [2]. Limestone may contain varying amounts of impurities, the most common of which are Silica and alumina. Others are iron, phosphorous and sulphur. Clay, silt and sand that may have become incorporated in the limestone when it was first deposited or may have accumulated later in crevices and between strata. In some cases, iron, phosphorous and sulphur may also occur as impurities while trace substances such as manganese, copper, titanium, sodium, arsenic and fluorine can also be present [3].

Cement, on the other hand is a fine gray powder of calcined limestone and clay. It can be defined as a calcareous sedimentary rock composed of the mineral calcite ($CaC0_3$) which upon calcination yields lime (CaO) for commercial use. In its broadest definition the term ‘cement’ includes any calcareous material such as marble, chalk, travertine, tufa, lime shell, coral and marl, each possessing different distinct physical characteristics. The crystalline equivalents of limestone having the same chemical composition are calcite and aragonite [4]. Cements are finely ground powders that when mixed with water set to a hard mass. Setting and hardening which are as a result of hydration, is a chemical combination of the Cement compound with water which yields gel – like material with a high surface area. Due to the hydrating properties, constructional cements which will sets and hardens under water are often called hydraulic

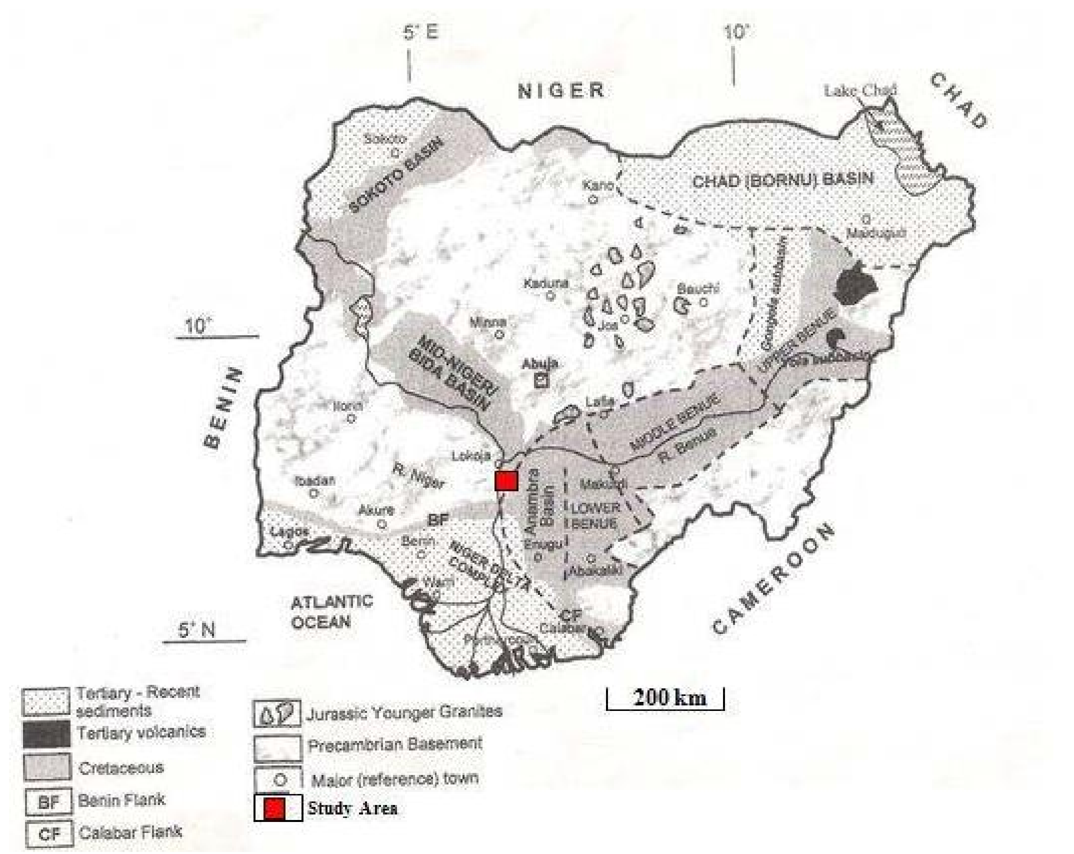

Fig. 1. Geological sketch map of Nigeria showing the location of the study area

cements. Cement is produced from raw materials such as limestone, chalk, shale, clay, and sand. These raw materials are quarried, crushed, finely ground, and blended to the correct chemical composition, the most important of these is Portland cement. Other types of Cements are processed slag containing high Silica and alumina [5]. Cement is mainly used in civil and building constructions. It can be used directly ("neat" as grounding materials) but the normal use is in mortar and Concrete in which the cement is mixed with inert material known as aggregate.

The availability of cement to meet the construction requirements of the country has been a great challenge over the years, and this has been responsible for increase in production of cement through importation as well as increased number of cement plants. However, despite these efforts, the available cement has still remained insufficient. It is based on this that this study is conducted with the aim of evaluating the Itobe for potential production of cement to augment the current cement production in the country.

The Itobe marble deposit is located near Allo village, just after Itobe, about 70km North East of Lokoja or about 25km East of Ajaokuta, within Latitude 07' 25.655'N and Longitude 006' 45' 111E/006.45.506'E within the basement complex of North Central Nigeria. The area is characterised by flat lowland with the marble deposit extending as ridge at an elevation of above 575 m. The climate has distinct wet and dry seasons with an annual rainfall of about 1300mm while the mean temperature is about 300ºC.

2. MATERIALS AND METHODS

2.1 Sampling

A Total of seven marble samples, adequately representing the deposits which stretched out to about 1km were obtained from six dug pits. This is in addition to those from river channels and from outcrops of the deposit.

Pit 1: Marble deposits were obtained at a depth of 1.8m. The pit is elevated at about 366ft. and at a distance of about 20 meter North East of the massive deposit. The top soil is thin, 0.1mm (dark in colour).This is followed by brown lateritic soil that extends to a depth of 1.8m. The marble is crystalline, ash and relatively free from alteration.

Pit 2: Marble deposits were obtained at near surface, occurring in the form of boulders increasing in massiveness. The marble sample was obtained at a distance of about 10m eastward of the massive deposit.

Pit 3 & 4: The general profile of this pit is of top humus soil, dark in colour, extending to about 0.2-0.3m. This is followed by sand silted intercalation. At depth of 3.0m, no marble deposit was found.

Pit 5: Sample was collected at the surface and at a depth of 2.5m. The area is highly weathered with the marble turning to light brown in colour with whitish fine particle dust. The pit area is at an elevation of 450ft, and at a distance of 30m southward.

Clay; Pit 6: In order to obtain suitable clay material within 10km of the marble deposit, 3 pits at 3m depth were dug, however, at that depth, two of the pits showed only silt and sandstone intercalation, thus samples were not obtained at the points. Sampling was done at the third pit located behind the marble ridge at depths of 1m and 2m.

2.2 Experimental

The following chemical parameters were analysed for comparison of the general limestone requirement for cement making using the analytical procedures in line with the standards for chemical analysis [6]. They are CaO, MgO, Cl, SiO_2 and Al_2O_3, while K_2O, SO_3, and Na_2O were analysed. Alumina; (Al_2O_3), Sodium oxide; (Na_2O) and Potassium oxide; (K_2O) were analysed using X-Ray Fluorescence Spectrometer while classical method was used for calcium oxide; (Cao), sodium oxide; (NaO) and chloride; (Cl^-).

There are many different types of cements of which Portland cement, Siliceous Fly Ash, Calcareous Fly ash, slag cement, and silica fume are the major types [7, 8]. They only differ in their chemical composition [9]. Depending on the type of cement being produced, required proportions of the crushed clay, lime stones, and any other required materials are then mixed by a process known as pre-homogenization and milled by grinding the material. After pulverization, it is homogenized again and calcined at 1400°C, in rotary kilns for the raw material to be transformed to a clinker, which is discharged from the lower end of the kiln while red-hot, cooled by various

Table 1. Chemical composition of the Itobe lime stone deposits

S/N	Sample code	Tested Parameters							
		CaO %	MgO %	SO_3 %	Cl %	SiO_2 %	Al_2O_3 %	K_2O %	Na_2O%
1	Pit 1(1.8)	50.05	2.32	1.972	ND	2.60	ND	0.22	0.14
2	Pit 2(surface)	46.27	5.34	1.798	ND	2.80	0.60	0.53	0.06
3	Pit 2B(2.5m)	48.51	3.43	1.623	ND	1.40	1.00	0.23	0.10
4	Massive Deposits (surface)	47.11	2.72	2.397	ND	7.20	0.60	0.16	0.10
5	River channel Exposure	32.95	Trace	2.147	ND	4.10	0.80	0.22	0.20
6	Pit 5A (surface)	0.42	0.50	1.623	ND	66.40	20.00	2.20	0.30
7	Pit 5B (2.5m)	0.42	0.30	1.898	ND	60.40	21.20	2.57	0.09
8	Clay (1m)	0.70	1.71	1.398	ND	55.75	-	1.63	0.02
9	Clay (2m)	0.84	0.50	2.0437	ND	54.00	-	1.54	0.04

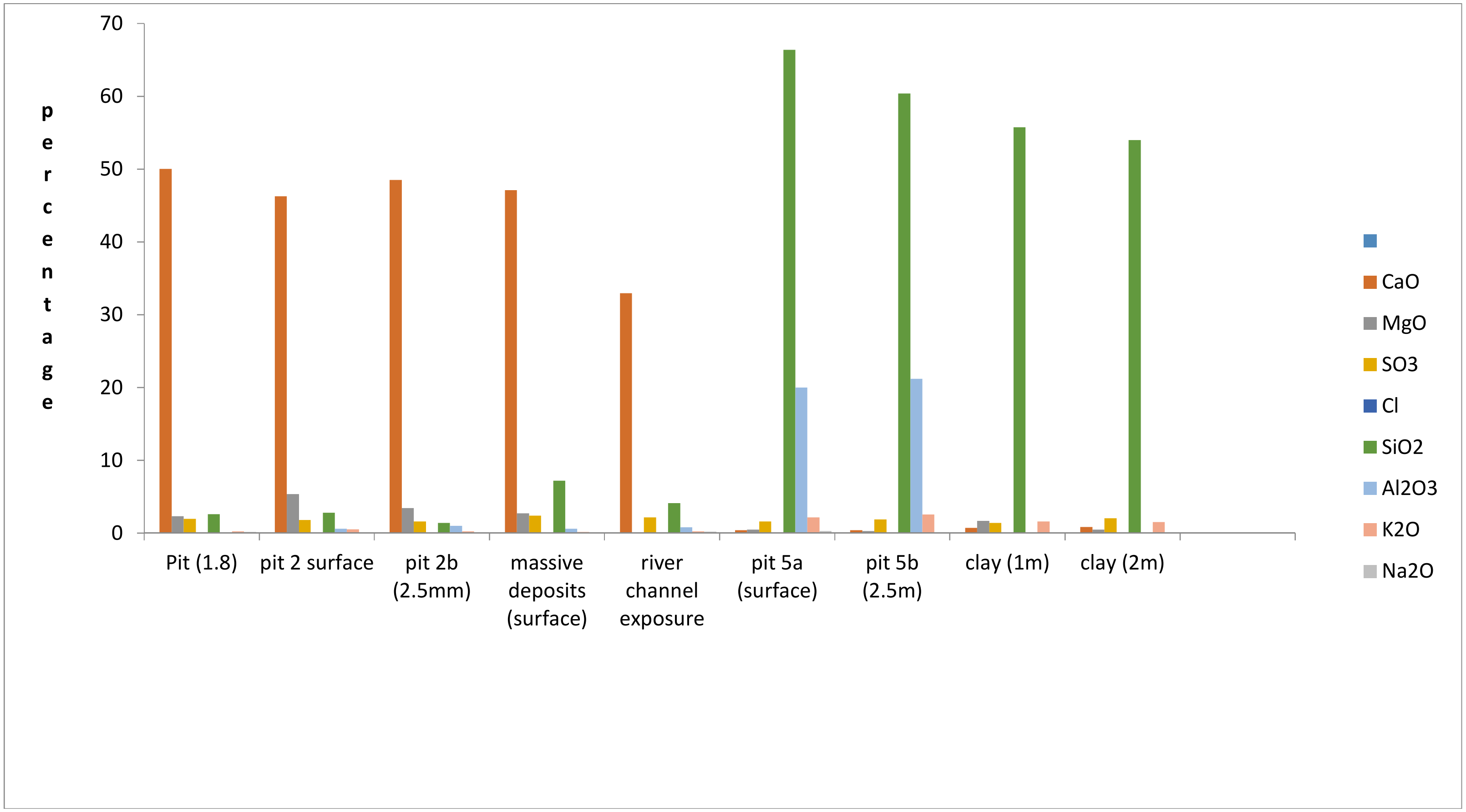

Fig. 2. Chemical Composition of Itobe Limestone deposit

Table 2. Representative chemical analysis (percentage composition) of different types of limestone (Boyton, 1980)

S/N	%CaO	%MgO	% SiO_2	% Al_2O_3	% Fe_2O_3	% Na_2O
1	54.54	0.59	0.70	0.68	0.08	0.16
2	38.90	2.72	19.82	5.40	1.60	-
3	41.84	1.94	13.44	4.55	0.56	0.31
4	31.20	20.45	0.11	0.30	0.19	0.06
5	29.45	21.12	0.14	0.04	0.10	0.01
6	45.65	7.07	2.55	0.23	0.20	0.04

Table 3. Percentage composition of some typical raw materials used for the manufacture of Portland cement (Britanica online encyclopedia, 2011)

Raw material	%CaO	%SiO_2	%Al_2O_3	%Fe_2O_3	%MgO	%LOI
Limestone	52	3	1	0.5	0.5	42
Chalk	54	1	0.5	0.2	0.3	43
Cement rock	43	11	3	1	2	36
Clay	1	57	16	7	1	14
Slag	42	34	15	1	4	0

steps, ground and mixed with small amounts of gypsum and limestone, and very finely ground to produce cement [10]. There are well over ten different types of cements that are used for construction purposes. They only differ in their composition and are manufactured for different uses [11,18]. In general, Portland cement, Siliceous Fly Ash, Calcareous Fly Ash, slag cement, and silica fume are used in concrete as primary binder, cement replacement, and property enhancer, respectively [12]. Concrete is the most common construction material used in building industry while cement is a major component of concrete used for building and civil engineering construction. Limestone and marble exists throughout Nigeria in both Basement rocks and in the Sedimentary Basins. The Sedimentary limestone, which is of Cretaceous and Tertiary ages is often associated with shale, siltstone, and fine grained sandstone [13,14]. Limestone is formed either by direct crystallization from water (usually seawater) or by accumulation of shell and shell fragments. All limestone are formed from the precipitation of calcium carbonate from water. Calcium carbonate precipitates from solutions in many ways and each way produces a different kind of limestone. All the different ways are either with or without the aid of a living organism (that is, either by organic or inorganic processes) [15]. Marble deposits are of great economic value being used for various purposes such as raw materials for a variety of products like fillers, glass, papers, lime, pesticide and sewage treatment, decorative construction, monuments, paint making and most of all very suitable for cement production [16]. The role of small scale mineral exploitations in providing sources of livelihood for millions of the rural and semi-urban African communities cannot be underestimated as seen in the areas job creation, road construction, infrastructural development and urban expansion and so on [17]. These desirable effects are however, overshadowed by the corresponding adverse effects that often accompanies mineral explorations. Some of these include ecological disturbance, destruction of natural flora and fauna, pollution of air, land and water, instability of soil and rock masses, landscape degradation and radiation hazards [18,19]. A plan of action to ameliorate some of these effects can only be effective if there is information on the elemental composition of the mineral deposit that is being mined [20].

3. RESULTS AND DISCUSSION

All the values of the elements analysed in the marble samples based on their total metal contents expressed in percentages are presented in Table 1 and are within acceptable range as reported worldwide in marble and limestone samples. Although pit 5 shows a rather high Silica content and a much lower values of CaO and MgO content. The results of these preliminary chemical analyses gave CaO in the range of 32.95% - 50.05% with silica ranging from 1.40% - 7.20% for all marble samples with the exception of pit 5 samples. The results in Table 1 is within the range reported by (Boynton, 1980) as shown in Table 2, and that of Britannica encyclopaedia (2011) in Table 3 for typical limestone materials for different parts of the world which are being used for cement manufacturing. Although, the result in Table 1 is a little lower than those of Portland cement by (Brandes, 1983) and (Messaoudene and Jauberthie 2010), the results obtained showed an appreciable percent content that is required for any quality cement production. The results of the analysis in Table 1 also show rather lower impurity content expressed in percentages. The impurity content reported by Boynton (1980) are much higher than those of the analysed samples. Also, those of Murray (1954) are also of higher percent content compared to those of the analysed samples. The percent silica content of the analysed clay samples is within the range reported by Britannica Encyclopaedia (2011).

Tables 2 and 3 show a comparative representation of different types of limestone and their chemical compositions. Table 3 presents typical percentages of impurities in limestone raw materials for cement production and Tables 5, 6 and 7 show typical chemical composition of cement from different parts of the world.

Table 4. Major impurities in high calcium limestone (Murray, 1954)

Element	percentage
SiO_2	0.10 -2.89
Al_2O_3	0.13 -0.92
Na_2O	0.00 - 0.16
MgO	0.12 - 3.11

Table 5. Chemical composition of cement (Dunuweera and Rajapakse, 2018)

Element	Percentage
SiO_2	21.5
Al_2O_3	5.20
Fe_2O_3	2.8
CaO	65.6
MgO	1.53
K_2O	0.73
Na_2O	0.15
SO_3	2.53
LOI	1.58

The sample numbers in Table 2 corresponds to the followings:

1 - Indiana high calcium stone
2 - Lehigh valley cement rock
3 - Pennsylvania, cement rock
4 - Illinois Niagara dolomite stone
5 - North-western Ohio Niagara stone
6 - New York Magnesium stone

Other impurities in raw material that must be strictly limited are fluorine compounds, phosphorus, metal oxides and sulphide and excessive alkaline.

Table 6. Chemical composition of Portland cement (Brandes, 1983)

Element	Percentage
SiO_2	5.5
Al_2O_3	39
Fe_2O_3	10
MgO	5.82
CaO	7.62
FeO	6
LOI	1.13

Table 7. Chemical composition of cement (% by weight) (Messaoudene and Jauberthie, 2010)

Element	Percentage
CaO	66.60
MgO	0.95
SiO_2	22.40
Al_2O_3	2.96
Fe_2O_3	2.33
SO_3	2.13
Na_2O	0.10

4. CONCLUSIONS

From the results of tests conducted and analysed on the Itobe limestone for potential use in cement production, the following conclusions are made

(i) The analysed marble samples showed an appreciable metal content that is adequate for a good and quality cement production.
(ii) The results of the total metal contents analysis of the clay sample are within the range required for cement manufacturing.
(iii) The mineral composition of the Itobe marble is essentially calcite with little

dolomite and quartz which is quite good for a quality cement production.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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