

## **Short Research Article**

# **SUITABILITY OF ITOBE LIMESTONE DEPOSIT IN CEMENT MANUFACTURING: A COMPARATIVE ANALYTICAL APPROACH**

### **ABSTRACT**

In this research, the assessment of the chemical composition of the Itope marble deposit for comparison of the general limestone requirements for cement making was investigated. Six pits were dug and carefully studied in the area, 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 shows 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%. The research work is aimed at determining the suitability of the Itope 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.

Key words: Marble deposit, cement, outcrops, river channels.

### **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 [7]. 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 [5]. 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 gathered 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 [6].

Cement, on the other side is a fine gray powder of calcined limestone and clay. It can be defined as a calcareous sedimentary rock composed of the mineral calcite ( $\text{CaCO}_3$ ) which upon calcination yields lime ( $\text{CaO}$ ) 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 [10]. 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 Cements. The most important of these is Portland cement. Other types of Cements are processed slag containing high Silica and alumina [13]. 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 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 30°C.

## 2. MATERIAL 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.

**Comment [ME1]:** There should be map showing sampling points with co-ordinate

**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.

### 2.3 Experimental

The following 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 [1]. They are CaO, MgO, Cl, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, while K<sub>2</sub>O, SO<sub>3</sub>, and Na<sub>2</sub>O were analysed. Alumina; Al<sub>2</sub>O<sub>3</sub>, Sodium oxide; Na<sub>2</sub>O and Potassium oxide; K<sub>2</sub>O were analysed using X-Ray Fluorescence Spectrometer while classical method was used for calcium oxide; Cao, sodium oxide; NaO and chloride;Cl

## 3. RESULTS AND DISCUSSION

All the calculated 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 preliminary analysis result 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 result on Table 1 is within the range reported by (Boynton, 1980) on table 2, and that of Britannica encyclopaedia (2011) on table 3. Although, the result on Table 1 is a little lower than those of Portland cement by (Brandes, 1983) and (Messaoudene et al,2010), the obtained results show an appreciable percent content that is required for any quality cement production. The results of the analysis on 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 to those of the analysed samples. The percent silica content of the analysed clay samples is within the range reported by (Britannica Encyclopaedia, 2011).

**Table 1: Chemical composition of the Itohe Lime stone deposits**

S/N	Sample code	%	%	%	%	%	%	%	%
		CaO	MgO	SO <sub>3</sub>	Cl	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
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

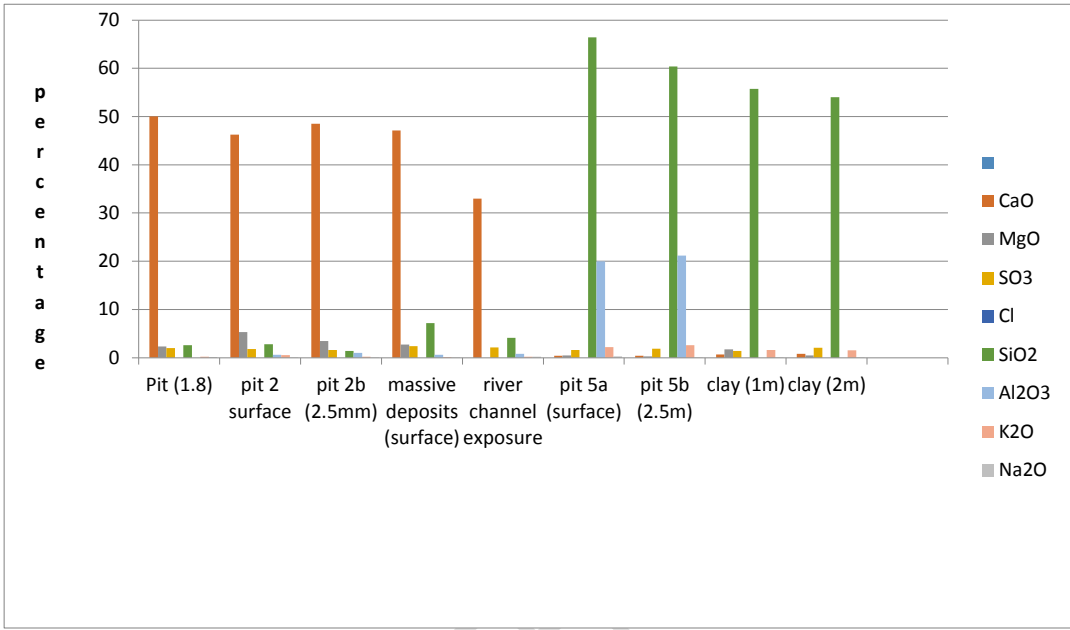


Fig. 1. Chemical composition of Itohe Limestone deposit

Below is a comparative tabular representation of different types of limestone and their chemical compositions.

**Table 2:** Representative chemical analysis (percentage composition) of different types of limestone

S/N	%CaO	%MgO	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% Fe <sub>2</sub> O <sub>3</sub>	% Na <sub>2</sub> O
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

Boynton, 1980

The numbers above corresponds to those below

- 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

**Table 3:** Percentage composition of some typical raw materials used for the manufacture of Portland cement.

Raw material	%CaO	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>	%Fe <sub>2</sub> O <sub>3</sub>	%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

Source: (Britanica online encyclopedia, 2011)

**Table 4: Major Impurities in high calcium limestone**

Element	percentage
SiO <sub>2</sub>	0.10 -2.89
Al <sub>2</sub> O <sub>3</sub>	0.13 -0.92
Na <sub>2</sub> O	0.00 - 0.16
MgO	0.12 - 3.11

(Murray, 1954)

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

**Table 5:** Chemical composition of cement

<b>Element</b>	<b>Percentage</b>
<b>SiO<sub>2</sub></b>	20.6
<b>Al<sub>2</sub>O<sub>3</sub></b>	5.07
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.9
<b>CaO</b>	63.9
<b>MgO</b>	1.53
<b>K<sub>2</sub>O</b>	0.73
<b>Na<sub>2</sub>O</b>	0.15
<b>SO<sub>3</sub></b>	2.53
<b>LOI</b>	1.58

Source: (Paul .D.Tennis, 2007)



**Table 6:** Chemical composition of Portland cement

<b>Element</b>	<b>Percentage</b>
<b>SiO<sub>2</sub></b>	<b>5.5</b>
<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>39</b>
<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>10</b>
<b>MgO</b>	<b>5.82</b>
<b>CaO</b>	<b>7.62</b>
<b>FeO</b>	<b>6</b>
<b>LOI</b>	<b>1.13</b>

Source: Blondes, 1983

**Table 7:** Chemical composition of cement (% by weight)

<b>Element</b>	<b>Percentage</b>
<b>CaO</b>	66.60
<b>MgO</b>	0.95
<b>SiO<sub>2</sub></b>	22.40
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.96
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.33
<b>SO<sub>3</sub></b>	2.13
<b>Na<sub>2</sub>O</b>	0.10

Source: Messaoudene et al, 2010

## CONCLUSIONS

1. 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<sup>6</sup>.
2. Limestone, being a sedimentary rock is composed largely of mineral calcite and aragonite which are of different crystal forms of Calcium carbonate ( $\text{CaCO}_3$ ).
3. Limestone often contains variable amount of Silica in the form of chert (Chalcedony, flint, jasper etc.) or siliceous skeletal fragment (sponge spicules, diatom, radiolarian), and varying amounts of clay, silt and sand (terrestrial detritus) brought in by rivers<sup>7</sup>.
4. Due to its various impurities, such as clay, sand, organic remains, iron oxide and other materials, limestones exhibit different colours especially on weathered surfaces. Limestone may be crystalline, classic, granular or massive, depending on the method of formation.
5. The primary source of the calcite in limestone is most commonly marine organisms. It may also form in both lacustrine and evaporate depositional environments<sup>16</sup>.
6. Coastal lime stones are often eroded by organisms which bore into the rock by various means. This process is known as bio erosion and it is most common in the tropics<sup>14</sup>.
7. Bands of limestone emerge from the earth surface in mostly spectacular rocky outcrops and islands<sup>9</sup>. The world largest limestone quarry is at Michigan Limestone and chemical company in Rogers's city Michigan.

The analysed marble samples showed an appreciable metal content that is adequate for a good and quality cement production. The results of the total metal contents analysis of the clay sample are within the range obtained from the Britannica Encyclopaedia on Table 3. The mineral composition of the Itohe marble is essentially calcite with little dolomite and quartz which is quite good for a quality cement production.

## REFERENCES

1. Annual books of ASTM standards; 1990, section 3, vol. 03-05
2. Brandes. 1983. Smith ells Metal reference book, 6<sup>th</sup> edition, Butterworth and co. Ltd.
3. Boynton RS. 1980. Chemistry and Technology of Lime and Limestone. Second Edition. John Wiley and sons.

4. Britannica online Encyclopaedia. Cement(Building material) 2011
5. Dexter P. 2001. Mineralogy 2<sup>nd</sup> ed. Pg. 142- 143
6. <http://en.wikipedia.org/wiki/Limestone>. "calcite" 2008/02/13
7. <http://en.wikipedia.org/wiki/Limestone>. "Limestone (mineral)". Archived from the original on 2009/10/3. Retrieved 2008/02/13
8. <http://en.wikipedia.org/wiki/Limestone>. "Isle of Wight, mineral" (PDF). Retrieved 2006/10/08.
9. <http://en.wikipedia.org/wiki/Limestone>. "Welcome to the Limestone city". Retrieved 2008/02/13.
10. <http://www.infomine.com/properties/Exchange>. "Mineral zone world mining Exchange". 2005
11. Messaoudene I, Jaubertie R, Molez L. 2010. Marble Filler:
12. Murray JA. 1954. Shrinkage of high Calcium Limestone during burning.  
Journal of America Ceramic. Society vol.37, page 323 – 328
13. <http://en.wikipedia.org/wiki/portlandcement>.Portland cement 2011/05/11
14. Taylor PD. and Wilson MA. 2003. Paleocology and evolution of marine hard substrate communities. Earth – science Reviews 62: 1-103.
15. Tennis .D. 2007. Composition of Cement and changes over past 50 years, pp 6.
16. Trewin NH & Davidson RG. 1999. Lake level changes, sedimentation and faunas in a middle Devonian basin – margin fish bed, Geological society, 156, 535 – 548.