

Petrographic And Geochemical Studies of IGBETI Marble Southwestern Nigeria in Relation to It's Economic Potential

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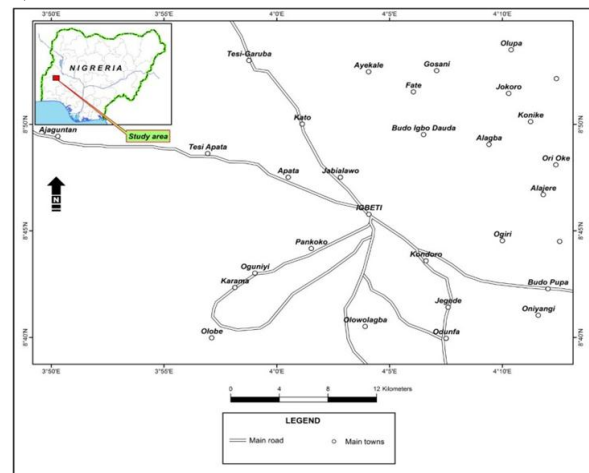
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Abstract- This work reports the results of the investigation carried out on Igbeti marble to determine its economic potential and suitability for cement production. Previous studies on the meta-sedimentary rocks of Igbeti area made no reference to the suitability of the marble as a potential cement raw material. The study area lies within latitude 8° 41'N and 8°42'N and longitude 4°05'E and 4°10'E of the Southwestern Basement Complex of Nigeria. Six fresh samples of marble were collected from old and current quarries. Thin sections were made and representative samples prepared for geochemical analysis using the Inductive Coupled Plasma Atomic Emission Spectrometric (ICP-AES) method. The mineralogy and modal analysis indicated the composition of the marble as calcite 88.49%vol, dolomite 4.71%vol, pyrite 1.97%vol, muscovite 1.44%vol, tremolite 0.78%vol, quartz and albite 2.81%vol. Result of geochemical analysis revealed the elemental composition, in part per million, of the marble as SiO₂ (0.76-0.001), Al₂O₃ (0.16-0.001), Fe₂O₃ (0.47-.007), Na₂O (0.47-.007), K₂O (0.03-.001), P₂O₅ (0.02-.001), MnO (0.04-.02), silica and alumina ratios (0.906, 0.231) with relatively high MgO (21.81-.20.92), CaO (30.85-30.55) and LOI 46.7-47.4. Igbeti marble manifests dolomitic character with silica and alumina ratios falling below Ordinary Portland Cement recommended values of SR (2.28) and AR (2.41). Variation plot of Na₂O/Al₂O₃ vs. K₂O/Al₂O₃ indicated a meta-sedimentary origin for the marble. The marble is not suitable for cement production but can be upgraded to meet acceptable raw mix composition for cement production.

Index terms- Meta-sedimentary, Silica Ratio (SR), Alumina Ratio (AR), Dolomitic, Calcitic, Ordinary Portland Cement (OPC).

INTRODUCTION

The study area, Igbeti, lies within Latitude 8° 41'N and 8°42'N and Longitude 4° 05'E and 4°10'E. (Figure 1)



The area is generally low lying but occasionally interrupted in some places by hills and ridges of the Older Granite rocks. The marble deposit occurred in the area as a low-lying medium to fine-grained white and grey colored intrusive bodies within the Migmatite gneiss complex terrain.

Traditionally, limestone is a major raw material in the commercial production of Ordinary Portland cement but the use of marble as cement raw material has recently become popular in the Nigeria cement manufacturing sector with Ukpilla, Jakura, Obajana and Ibeshi marble deposits being mined currently for cement production.

Marble is a metamorphosed limestone whose occurrence in Nigeria is reported to be associated with the Younger metasedimentary sequence of the Precambrian Complex found within the migmatite-gneiss-schist-quartzite terrains [1, 2]. Marble deposits have been reported in Igbeti, Elebu, Kwakuti-Okpella, Jakura, Igarra, Ikpeshiu, Ubo Ukpilla,

Ososo, Atte, Idoani and Osara. Other known marble occurrence in Nigeria include Isale-Osin, Okelute, Oro (Kwara State), Takalafia in the Federal Capital Territory, Toto- Muro Hill in Nasarawa, Kankata (Kaduna State), Itobe (Benue State) [3].

Igara marble does not meet the required standard for the production of Ordinary Portland Cement (OPC) because of low values of CaO, SiO₂, Al₂O₃, Fe₂O₃, and MgO and the Ikpeshe marble was also considered not suitable for cement production for the same reason [4]. The MgO, silica ratio (SR) and lime saturation factor (LSF) are significantly higher in Ikpeshe marble than the specified standards for cement production and considered not suitable for cement production. The pre-metamorphosed limestone of Igarra and Ikpeshe areas were of greywacke, litharenite and archaistic sand class. Despite the abundance of marble occurrence in Nigeria, only the deposits in Ukpilla, Obajana and Ibese areas are presently being exploited for cement production.

Cement is a fine-grayish powdered material produced by grinding about 95% calcined limestone with 5% of gypsum (CaSO₄.2H₂O) to standard fineness. The gypsum is a binding force that enables the cement to produce standard paste when water is added to the mixture with sand. Basically, there are two types of raw materials for the production of cement namely lime-containing materials such as limestone, marble, oyster shells, marl, chalk and secondly, clay and clay-bearing materials like shale, slag from blast furnaces, bauxite, iron ore, silica, and sand. These materials, though considered suitable for cement production, require the addition of appropriate materials at a required mixing ratio to achieve acceptable raw mix composition suitable for cement production.

The chemistry of cement is controlled primarily by the proportion of major oxides in the raw mix, which include CaCO₃ of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, and Na₂O A good cement raw mix therefore must have these oxides in optimum amounts. This is the essence of blending of the crushed limestone while clay and or marl are usually added as additives in the event of a short fall in the chemical components of any of the major oxides in the raw mix. If the raw mix is properly grounded, a raw meal with a compositional range within recommended values, suitable enough to give the desired Silica Ratio (SR), Alumina Ratio (AR) and Lime Saturation

Factor (LSF) that meets Ordinary Portland Cement standard is produced. The raw meal that meets the OPC standard is then allowed to pass through kiln where, by calcinations under high temperature, a solid solution reaction process takes place.

The product of this process produces cement minerals like Dicalcium silicate (C₂S), Tricalcium silicate (C₃S) and Tricalcium Aluminoferrite (C₄AF). Any material that is capable of producing these cement minerals can as well be used for cement production. The preliminary geochemical appraisal of Igbeti marble in this work is to assess its potential as raw material for cement production.

REGIONAL GEOLOGICAL SETTING

The Precambrian Basement Complex of Africa (Figure 2) is defined by three large cratonic land masses namely Kalahari craton, Congo craton and West African craton. These cratonic land masses are separated each from the other by mobile belts that are active in the Proterozoic (2500Ma). The Nigerian Pan African Basement Complex lies within the Pan-African mobile belt, east of the West African and Congo – Gabon Craton and south of the Touareg shield [5, 6, 8].

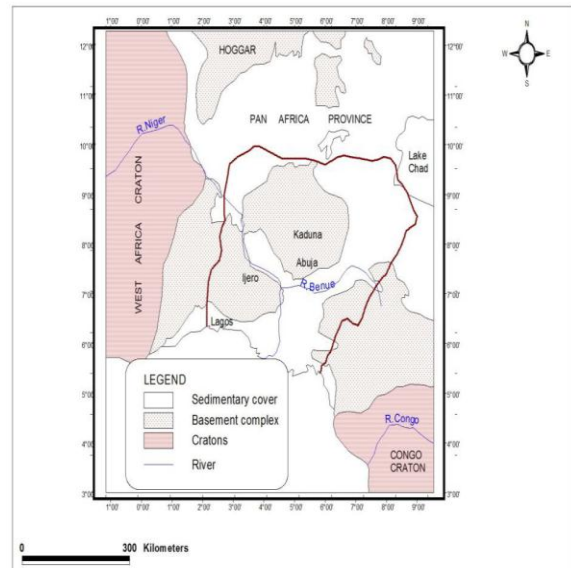


Figure 2: Map Showing Nigeria in the Pan African Province Located Between the West African and Congo Cratons (After Black, 1980)

The geology of Nigeria is lithologically classified as crystalline and sedimentary rocks. The sedimentary

rocks of Nigeria occupy about half of her land mass and they are scattered within the seven depositional basins, the oldest being of Lower Cretaceous age (about 145Ma).

The crystalline rocks of Nigeria are referred to as the Basement Complex and this covers the other half of the Nigerian land mass. The Nigerian Basement Complex occurs within the Pan African mobile belt lying between the West African and Congo cratons. The basement complex rocks in Nigeria are grouped into three broad lithological units namely the migmatite-gneiss complex, the schist belt and the Pan-African granitoids. The Migmatite-gneiss-complex is believed to be the product of a long polycyclic evolutionary process [3]. Migmatite is a mixed rock comprising of granite, biotite and banded gneiss intricately intermeshed in a light-dark color arrangement. An heterogeneous origin was proposed for the Migmatite-gneiss-complex on the basis of the varied chemical composition [9]. The age of the Migmatite-gneiss –complex has been put at between 2.8 – 2.0Ga but older ages of 3.0Ga have also been recorded [10].

The schist belt is a low-grade metasediments and metabasic rocks which is reported to be a N-S synformal troughs unfolded into the Migmatite-gneiss. The Southwestern Nigeria schist belt is well represented in Iseyin, Ilesha, Egbe-Isanlu and Igara [9, 11]. The Igbeti marble occurs within the Iseyin schist belt.

GEOLOGY OF STUDY AREA

Igbeti town is located on a pediment surrounded by granite inselbergs. The major rock types in the area are the gneisses, the granites and meta-sedimentary rocks, principally the amphibolites schist, quartz schist and marble. The granite gneiss occurring at the west of the study area forms the border of the amphibole schist. A NE-SW trending quartz schist parted by porphyritic and biotite-hornblende granite mark the contacts with the marble to the east. The occurrence of amphibole schist as low-lying, highly fissile and weathered bodies was observed around the north-western part of the study area. Coarse to porphyroblastic granite and biotite hornblende granite bodies are widespread in the study area (Figure 3).

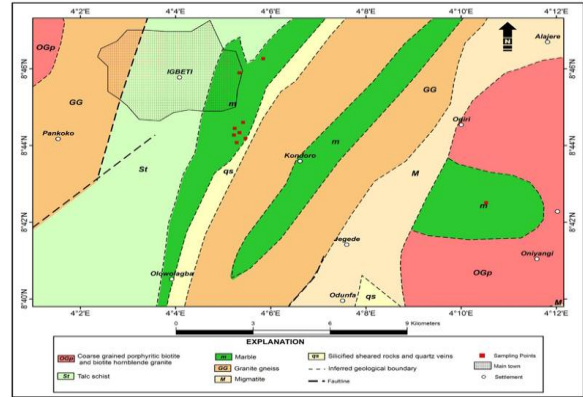


Figure 3: Geological Map of the Study Area Modified After NGS, (1965)

Showing Sample Locations

The marble occurrence is a north-south trending lenses, delimited in the east and west by the porphyritic gneiss and the migmatite-gneiss. The fine-grained granoblastic marble occur in white and grey colour variety, forming distinctively low-lying physiographical features in the area. Careful observation of some of the quarry sites shows that the occurrence of the marble is at a relatively shallow depth below poorly consolidated gritty sand. However, field observations did not reveal exposure of any feasible contact of the marble deposit with older basement rocks except along some river channels.

MATERIALS AND METHODS

The study involves geological mapping and random sampling of marbles from existing mining quarries (Figures 4 and 5). Sample locations were identified by the global positioning system (GPS) and coordinates recorded for each of the sample points.



Figure 4: Typical Marble Mining Sites in the Study Area



Figure 5: Typical Marble Mining Sites in the Study Area

Six representative marble samples were collected and prepared in the laboratory for microscopic studies and for major and trace element geochemical analysis. The pulverized samples were packaged and sent to Activation Laboratories in Ontario, Canada for analysis using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) method. The samples were dried at 60°C, crushed and sieved to -80 mesh (-177µm). 0.5gm of the pulverized samples are weighed into platinum crucible and 3-4 drops of water added to produce a wet paste and a ratio of 3-25ml of nitric/perchloric acid (HClO₃), trioxonitrate (V) HNO₃ and 15mls of hydrofluoric acid (HF) are subsequently added. The solution was properly stirred and heated at low temperature for some hours to allow it evaporate and 4mls of hydrochloric acid (HCL) then added and washed to dissolve the salts. The cooled solution was diluted to 50mls with distilled water and introduced into the ICP touch as aqueous aerosol. The emitted light by the ions in the ICP is converted to an electric signal by a photomultiplier in the spectrometer. The intensity of the electric signal from the emitted light

Table 1: Major Oxides and Trace Elements in Igbeti Marble (Wt. %).

Oxides/Locations	L1	L2	L3	L4	L5	L6	Average	Range.
SiO ₂	0.76	0.06	0.1	0.001	0.76	0.06	0.29	0.76-0.001
Al ₂ O ₃	0.16	0.03	0.001	0.001	0.16	0.03	0.064	0.16-0.001
Fe ₂ O ₃	0.47	0.24	0.08	0.07	0.47	0.24	0.262	0.47-.007
MgO	20.92	21.5	21.31	21.81	20.92	21.5	21.327	21.81-20.92
CaO	30.55	30.59	30.73	30.85	30.55	30.59	30.643	30.85-30.55
Na ₂ O	0.01	0.001	0.001	0.001	0.01	0.001	0.004	0.01-.006
K ₂ O	0.02	0.03	0.001	0.001	0.02	0.03	0.017	0.03-.001
TiO ₂	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
P ₂ O ₅	0.02	0.02	0.01	0.001	0.02	0.02	0.015	0.02-.001
MnO	0.02	0.02	0.03	0.04	0.02	0.02	0.025	0.04-.02
Cr ₂ O ₃	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001-.001
LOI	46.7	47.1	47.4	46.9	46.7	47.1	46.983	47.4-46.7

was compared with a standard or control previously recorded from a measured concentration of the elements. Quality control is ensured carrying out a sample prep blank as first sample and pulp duplicate to monitor analyzed precision and this is carried out at all the stages from preparation to analysis.

RESULTS AND DISCUSSION

Geochemical results of major and trace elements in the Igbeti marble are presented in Tables 1 and 2 below. A relatively low values of SiO₂ (0.26 wt%), Al₂O₃ (0.064 wt%) , Fe₂O₃ (0.26 wt%) , and MnO (0.03 wt%) are recorded for the marble but comparable with values of Ikpeshi marble; SiO₂ (1.95 wt%), Al₂O₃ (1.76 wt%), Fe₂O₃ (1.23 wt%) and MnO (0.04 wt%). The values of CaCO₃ and MgCO₃ equivalents of CaO and MgO indicated that Igbeti marble has CaCO₃ of 54.65 wt% and MgCO₃ of 44.79 wt%. This is moderately lower than CaCO₃ of 85.81wt% in Ikpeshi marble and CaCO₃ of 83.76 wt% in Obajana marble but higher than the value for Zambezi belt marble (43.76wt%). The MgCO₃ content of 44.79wt% in Igbeti marble is higher than 7.07wt% in Ikpeshi marble, 1.58wt% in Igara marble and 4.98wt% in Obajana marble. The relative percentage of carbonate in marble determines whether the marble is calcitic or dolomitic. Marbles with greater than 40wt% of MgCO₃ are dolomitic while marbles with less than 11% MgCO₃ are calcitic (Brown, 2007). The geochemical results (Tables 1) backed by micrographic expressions (Figures 6, 7, 8 and 9) affirm that Igbeti marble is predominantly dolomitic with some isolated crystals of calcitic minerals.

(Na ₂ O+ K ₂ O)	0.03	0.031	0.002	0.002	0.03	0.031	0.021	0.031 – 0.002
MgCO ₃	43.93	45.15	44.73	45.80	43.93	45.15	44.73	45.15- 43.93
CaCO ₃	54.56	54.63	54.88	55.10	54.56	54.63	54.73	55.10 – 54.56
Trace Metals								
Ba	37.0	4.0	42.0	0.90	169.9	0.9	42.45	169.9 – 4.0
Ni	1.5	0.7	0.5	0.9	248.8	0.3	42.117	248.8 – 0.3
Sr	67.9	54.3	99	43.1	835.1	30.1	188.25	835.1 – 30.1
Rb	0.3	2.5	4.8	0.001	57.1	0.001	10.784	57.1 – 0.001
Co	1.2	0.1	1.2	0.1	50	0.1	8.783	50 – 0.1
Be	0.9	0.9	15	0.9	2	0.9	3.433	15 – 0.9
Cu	1.7	47.4	6.9	1.3	58.7	1.2	19.533	58.7 – 1.2
Pb	3.8	31.2	17.5	5.1	5.7	1.1	10.733	31.2 – 1.1
Ga	0.4	0.4	21.3	0.4	17.1	0.4	6.666	21.3 – 0.4
Nb	0.001	0.2	15.4	0.001	7	0.001	3.767	15.4 – 0.001
Zn	7.0	45.0	9.0	14.0	55.0	12.0	23.666	55 – 7.0

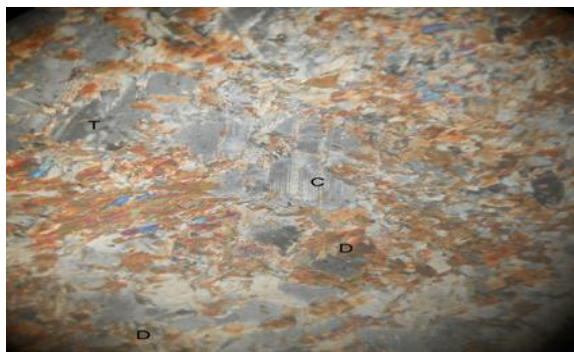


Figure 6: Photomicrograph (x40) of sample showing predominantly Dolomite (D) and calcite (C)



Figure 7: Photomicrograph of marble sample showing Calcite (C), Dolomite (D) (x40)



Figure 8: Photomicrograph of marble sample showing Calcite (C), Dolomite (D) (x40)



Figure 9: Photomicrograph of marble sample showing Calcite (C), Dolomite (D) (x40)

The total alkali content (Na₂O+K₂O) in marble is a good indicator of the depositional and lithification condition of the environment before the metamorphism of the carbonate material. When salinity of a depositional environment increases, the Na and K concentration tends to decrease in that environment [12]. The low values of the total alkali content in the Igbeti marbles is an indication that the environment of deposition of the original carbonate materials must have been a shallow highly saline environment. The high MgO coupled with low SiO₂, Na₂O and K₂O values suggests possible argillaceous matter deposited in a fluctuating energy regime during formation [13].

High Loss on ignition (LOI) with values ranging between 47.4- 46.7% suggests the presence of some clay minerals and gas in the marble, which has the characteristic of losing its water content and gas (CO₂) when subjected to high temperature..

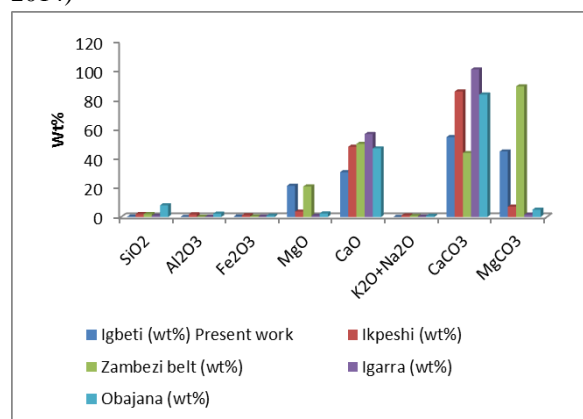
Table 2 shows the comparison among major oxides content (wt %) in four marble deposit locations in the

Southwestern Nigeria and the Zambezi belt. The variation of oxide composition in marble deposits of some locations in the Southwestern Nigeria and the Zambezi belt is presented. The dolomitic character of Igbeti marble is revealed in the magnesium carbonate content ($MgCO_3 = 44.79\%$) and this is comparable to the marble from Zambezi belt ($MgCO_3 = 89.32\%$). In the other deposits the magnesium carbonate value is less than 10wt%. The histogram in Figure 10 shows the comparative oxide composition in marble deposits at the respective locations.

Table 2: Comparative Results of Major Oxides in Four Locations in the Southwest (wt %).

Oxides	*Igbeti(Present work) (wt%) A	Ikpeshi(wt%) B	Zambezi belt(wt%)C	Igarra(wt%) D	Obajana (wt%) E
SiO ₂	0.29	1.94	1.98	0.814	7.99
Al ₂ O ₃	0.06	1.76	0.13	0.205	2.31
Fe ₂ O ₃	0.26	1.23	0.36	0.329	0.88
MnO	0.03	0.04	0.03	0.018	0.02
MgO	21.33	3.67	20.84	0.753	2.37
CaO	30.64	48.05	50.01	56.7	46.90
Na ₂ O	0.004	0.40	-	0.24	0.33
K ₂ O	0.017	0.62	0.07	0.028	0.47
TiO ₂	0.001	0.15	0.01	0.042	0.12
P ₂ O ₅	0.015	0.06	-	0.065	0.09
CaCO ₃	54.65	85.81	43.76	100.92	83.76
MgCO ₃	44.79	7.07	89.32	1.58	4.98
(Na ₂ O+K ₂ O)	0.021	1.02	0.07	0.268	0.80

*A - Oxides in Igbeti marble from present work (wt%) B - Ikpeshi marble (Romanus and Fredrik, 2012), C - Zambezi belt marble (Munyanyiwa and Hanson), D - Igarra (geoworks) marble (Romanus and Fredrik, 2012), Obajana marble (Jimohet *et al.*, 2014)



Deposits of some locations in the southwestern Nigeria

ECONOMIC POTENTIAL OF IGBETI MARBLE

Refractory Bricks

For refractory lime, that is dead burned dolomite for open hearth lining, the requirements are Magnesium oxide (MgO) not less than 18%. Silica (SiO₂), ferric oxide (Fe₂O₃) and alumina (Al₂O₃) not exceeding 1% each, but lower grades sometimes acceptable. The Igbeti marble is a suitable raw material for the production of refractory bricks especially for high magnetite bricks.

Paints and Fillers

In paints and fillers industries, it is required that calcium carbonate content exceed 96% but magnesia limestone containing as much as 8% magnesium oxide occasionally are tolerated—the MgCO₃ content generally is 1%. Other maxima are; Fe₂O₃ (0.25%), SiO₂ (2.0%) and SO₂, (1%). Paint manufacturing requires marble of white or pink color, small particle sizes (98% passing through 325 mesh) and absence of hard particles. Standard chemical specification provides that Al₂O₃ ≥ 2%, MgO + SiO₂ > 75% and LOI within the range of 4-8% is acceptable. The Igbeti marble is chemically below the required standard (Table 1). The marble is therefore unsuitable for use for Paint production.

However, paint manufacturers have their individualized specifications so much so that they establish their peculiar standards as long as their brands of paint satisfy their quality, their customers and in conformity with their production formulations. In line with this, many paint industries in Nigeria source their raw materials for production from the Igbeti marble.

Glass Manufacturing

In glass manufacturing Ferric oxide (Fe₂O₃) not more than 0.05%, preferably not more than 0.02% for colorless glass, rock having up to 0.1 % Fe₂O₃ is sometimes accepted for colored container glass. Calcium carbonate (CaCO₃) should exceed 96% in case of marble, or 96% calcium-magnesium carbonate in case of dolomite. Amounts of silica, alumina, magnesia etc., must not vary from shipment to shipment. Igbeti marble meets these specifications and thus can be used in glass manufacturing.

Sewage Treatment

The lime products is a useful ingredient in sewage treatment, neutralization of acid water, silica and

phosphate removal from sewage effluents. The specification required in these industries are similar to that for water softening and purification. If processed well, the Igbeti marble lime products could be useful in sewage water treatments.

Construction

For concrete aggregate, road base material the general requirements are concrete aggregate of low alkalis and free surface organic matter. Presence of opal silica is highly undesirable in concrete aggregate. Other qualities of materials suitability for aggregate in construction work are durability, toughness and low porosity. CaO and MgO of about 70%, CO₂ < 50% by ASTM standard (1976), is a pre-requisite for materials suitable for construction purposes. In terms of fineness, it must leave little or no residue and compressive strength of > 20Mpa, tensile strength > 2Mpa and shear strength > 7Mpa are requirements. Igbeti marble could be used as road stabilizers, aggregates material, ornamental stones and building blocks.

Agriculture

Soil liming is one of the oldest uses of raw and calcined marble. The marble function as a neutralizer of acids and soil enhancer when the pH >8 and grittiness is low. The pH of 8.3 for Igbeti marble meets this requirements and thus useful as soil ameliorants and nutrients status enhancer.

Pesticide production

In pesticide production, calcium arsenate, arsenic acid is reacted with a milk of lime forming calcium arsenate, CaO > 60% is required, also for varnish, the marble must be very low in iron and magnesium content. Igbeti marble can be used for varnish but cannot be used for pesticide production because the MgO is greater than 20%.

CONCLUSION

The results of this study revealed that Igbeti marble is not suitable for cement production in its present form, but it has some other application areas that can be of economic interest to investors in the solid mineral business. However, all hope is not lost in the possibility of its use as cement raw material. Having this fulfilled will provide windows of opportunities to

investors in mini-cement production, which will be a booster to the economic value of the area, the state and Nigeria in particular.

REFERENCES

- [1] McCurry P (1976). The Geology of the Precambrian to lower Paleozoic rocks of Northern Nigeria- a review In C. A. Kogbe (ed.) Geology of Nigeria. Elizabethan Publishing Lagos 15-39.
- [2] Folami S.L. and Ojo, J.S., 1991. Gravity and magnetic interpretation over Marble deposit in the Igara area. Bendel State. Journal of Mining and Geology. 27(1). P49 - 54
- [3] Emofurieta, W.O. & Ekuajemi, V.O., J. (1995); ; Lime Products And Economic Aspects Of Igbetti, Ososo And Jakura Marble Deposits In S. W Nigeria. Journal Of Mining And Geology, 31(1) 89-97.
- [4] Obasi and Isife (2012). Geochemistry and economic potential of marble from Ikpesi, southwestern, Nigeria
- [5] Kennedy. W.O., 1964. The structural differentiation of Africa in the Pan African (± 500 M.Y) episode. Research Inst. For African Geol. (Leeds) 8th Annual Report pp48 – 49
- [6] Ajibade, A.C. (1980). Geotectonic evolution of the Zungeru Region, Nigeria. Unpublished Ph.D. Thesis, University of Wales, Aberystwyth.
- [7] Black, R. (1980). Precambrian of West Africa. Episode, 4, 3-8. Chemical characterization of Isale-osin marble, Kwara state. Geoscience Consultancy Report for Ministry of Commerce and Industry, Ilorin, Kwara state,
- [8] Elueze AA (1981). Geochemistry and petroectonic setting of Meta sedimentary rocks of the schist belt of Ilesha area S.W Nigeria. *Precambrian Research*, 19 167-177.
- [9] Dada S.S, Briquet L & Brick JL (1996). Pb-Pb and Sm-Nd isotopic study of meta-igneous rocks of Kaduna: implication for the Archean mantle in Northern Nigeria in 32nd *proceedings of the Annual Conference of Nigeria Mining and Geoscience Society Benin City, Abstract 57.*
- [10] Rahaman, M.A (1973) The geology of the district around Iseyin Western State , Nigeria. PhD Thesis University of Ibadan (unpublished) 268pp

- [11] Annor, A.E.; Olobaniyi, S.B., and Mucke, A. (1996). A note on the Geology of Isanlu area, in the Egbe-Isanlu schist belt S.W. Nigeria. *Jour. Min. Geol.* Vol. 32 (1), pp 47 – 52.
- [12] Clarke FN 1924. *The Data of Geochemistry* (2nd ed.) Washington Government Printing Office: 782p.
- [13] Oluwatoyin O. Akinola, Anthony T. Bolarinwa and Oladimeji L. Ademilua. (2014); *Lithologic Features and Petrochemical Characteristics of Metasedimentary Rocks of Igbetti Area, Southwestern Nigeria*