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# The Chemical Composition and Possible Industrial Uses of the Marble Body in Itobe Area, Central Nigeria

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## ABSTRACT

Chemical analyses involving determination of major element composition and PH values were carried out on two marble outcrops (described as mass I and mass II) of the Itobe marble body in Itobe area, Kogi State, central Nigeria, with a view to determining the possible industrial uses of the marble body based on chemical composition only. The result shows that mass II is suitable for the manufacture of pesticide and cement, although for the manufacture of cement it may have to be blended with the appropriate quantity of shale and laterite to adjust the Silica Ratio (S.R.) to meet up with the requirement for typical cement Kiln feed. Masses I and II are suitable for the manufacture of sodium alkalis and as grit for the manufacture of poultry feed. Mass I, because of its relatively high MgO content is suitable for use as flux in the manufacture of steel and as refractory lime in the metallurgical industry.

**Keywords:** *Marble, Chemical, Composition, Industry, Itobe and Mass*

## I. INTRODUCTION

The present economic difficulty in Nigeria and the attendant unemployment of able bodied youths has created the need for urgent industrialization based on the development of local raw materials. In cases where some of the raw materials for industries are still being imported into the country, effort needs to be made to evaluate the economic viability of mineral raw materials for industrial use.

Marble, a major raw material for industries, is a crystalline, non – foliated metamorphic rock which is widespread in occurrence within the Precambrian basement terrain of Nigeria. It is formed from limestone or dolostone due to the action of heat and pressure. The industrial uses of a marble body are determined largely by its chemical composition as well as the size of the deposit.

Scott and Durham (1984) identified about 204 end uses of raw marble and lime (the calcined form of marble). The specifications for the use of marble as an industrial raw material vary considerably in line with the different end uses of the marble and the country using it. Broadly, however, the economic values of marble can be classified under six main groups namely; metallurgical, chemical, environmental, construction, refractory and agriculture (Boynton, 1979). Each of these groups requires some chemical specifications for the marble to be useful.

The Itobe marble deposit is located about 1 kilometer from Itobe town, along the Ajaokuta - Anyigba Road, Kogi State, in the central part of Nigeria.

The study area lies between longitudes $6^0$ 40′N and $6^0$48′ E and latitudes $7^0$21′N and $7^0$31′N (Fig. 1)

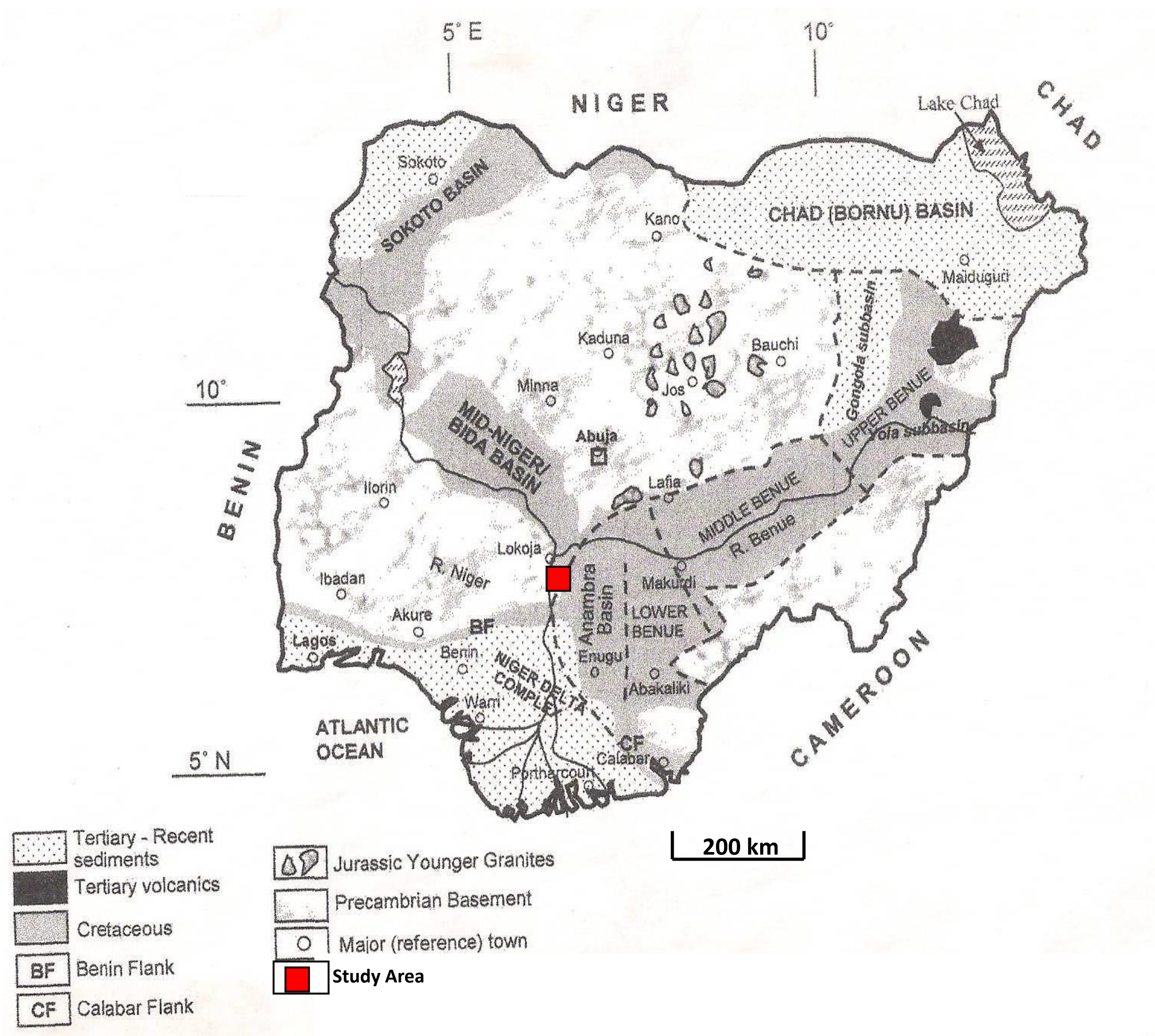


**Fig.1: Geological sketch Map of Nigeria Showing the Location of the Study Area (After Obaje, 2009)**

Present knowledge of the chemical composition of Itobe marble deposit is inadequate for economic appraisal of the deposit. Previous studies on the marble deposit include the regional study of the Lokoja – Auchi area (Hockey et al, 1986) which simply described the marble body as a dark grey, fine – medium grained narrow band of marble. Akoh (2004) based on limited chemical data, described the Itobe marble as a dolomitic marble.

This study seeks to determine the chemical composition of the Itobe marble deposit and its

possible industrial uses.

## II. GEOLOGY OF THE STUDY AREA

Two-third of the study area is underlain by crystalline metamorphic rocks assigned to the Precambrian basement complex of Nigeria. These rocks include biotite schist, mica schist, quartz schist, quartz - muscovite schist, biotite - hornblende schist, marble, feldspathic quartzite, quartzitic schist, quartzite, gneissic granite and minor acid intrusive rocks including pegmatite and quartz veins. The remaining part of the area is overlain unconformably by gently dipping Cretaceous and Tertiary sediments belonging to the Anambra sedimentary basin. The sediments occur as outliers to the basement complex rocks in some places, and overly the basement complex rocks to the east. Recent alluvium forming a continuous strip up to 200m wide occurs along the bank of the River Niger (Fig. 2).

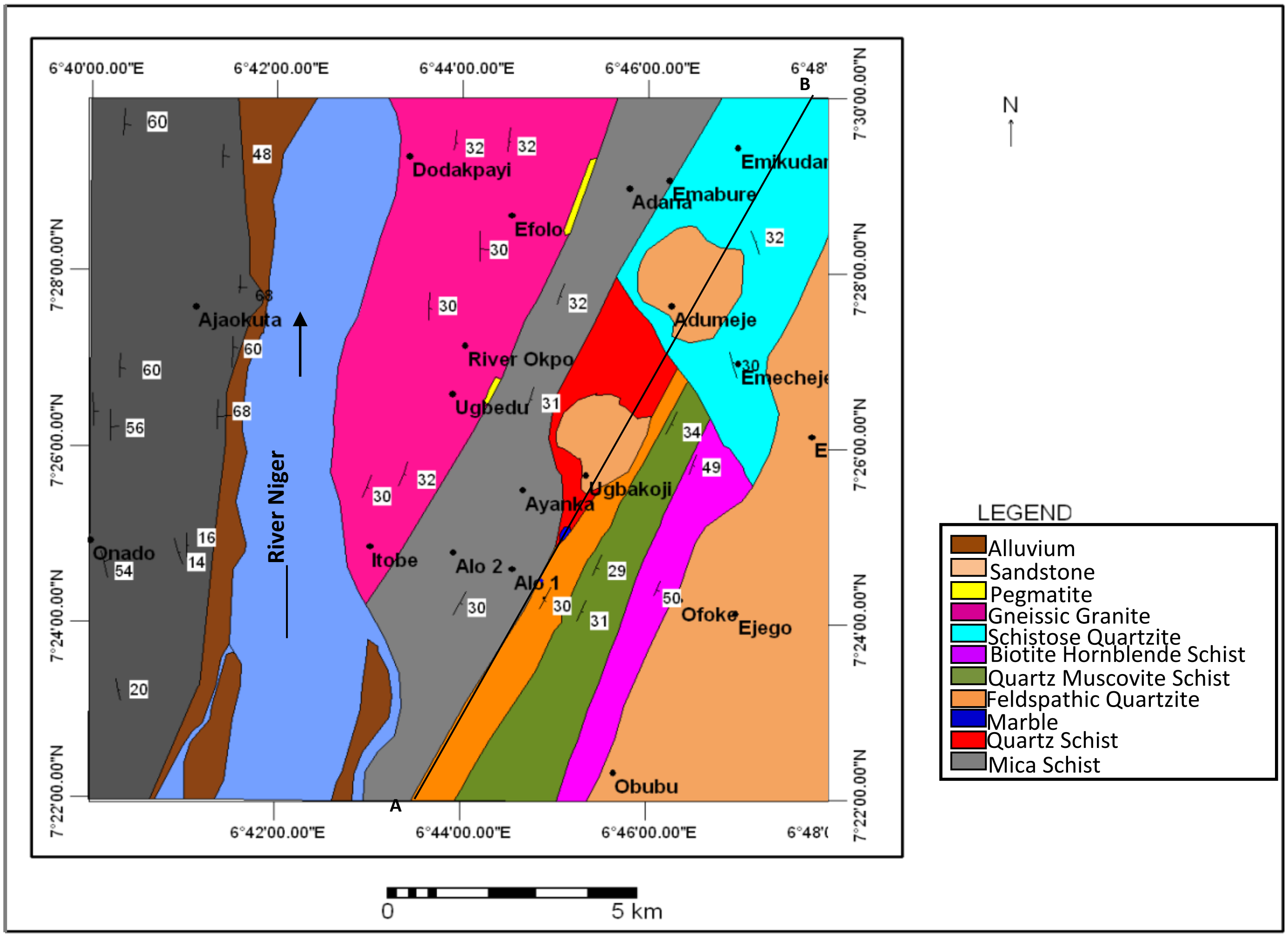


**Fig. 2 : Geological Map of the Itobe Marble Area**

The basement rocks maintain a consistent NE-SW strike direction, parallel to the strike of major lineament structures in the study area, and generally dip east with variable angles of dip. Two outcrops of the marble (described as mass I and mass II) have been recognized in the area. Mass I, covering a surface area of < 1.5m$^2$, is fine-grained, light grey and outcrops at the road cut about 150m to Alo I village along the Ayingba-Itobe road (Plate 1). Mass II, which is dark grey and medium grained, is a more massive unit, and outcrops on the Ayanka hill from an elevation of 132m to 138m (Plate 2). The Itobe marble body occurs within a host rock of mica/quartz schist and quartzite.

## III. METHODOLOGY OF STUDY

Chemical analyses of the marble samples include: (i) the X-Ray Fluorescence (XRF) Spectrometric analysis of whole rock samples to determine the major elements composition of the marble and (ii) PH test to determine the concentration of hydrogen ions in a weighted sample of the marble powder dissolved in distilled water.

Major element oxides determined include $SiO_2$, CaO, MgO, $Al_2O_3$, $Na_2O$, $K_2O$, $SO_3$ and total Fe as $Fe_2O_3$. Loss on ignition (L.O.I) of the marble samples was determined gravimetrically.

PH test was done using a PH meter. Forty (40) samples of mass II and ten (10) samples of mass I of the Itobe marble were subjected to X-Ray fluorescence (XRF) spectrometry while ten

(10) samples each of both masses I and II were subjected to the PH test.

**Procedure for XRF Spectrometry**

The marble samples for the XRF analysis were prepared by subjecting a wet portion of the rock samples (weighing about 5kg) to wet grinding on a silicon carbide disk mill to remove saw mark and unwanted materials. The samples were ultrasonically washed in distilled water and then methanol for 10 minutes and dried at 110 °C for at least 2 hours. Larger pieces were reduced to < 1cm in diameter in a Spex shatter box using a tungsten carbide grinding vessel for 1 - 2 minutes depending on the size of the sample. The powder was transferred to a clean paper and then to a sample vial and labeled.

Borate glass discs were prepared for the X-ray analysis by mixing 2g of ignited sample powder and 4g lithium tetra- borate ($Li_2B_4O_7$). The mixture in a platinum crucible, were melted together in an induction melting oven for some minutes. The melt obtained was turned into a disc mould and allowed to consolidate into a glass disc. Whole rock analysis for major elements Al, Na, K, Ca, Mg, total Fe ($Fe^{2+}$, $Fe^{3+}$), and S were made on the lithium borate discs using an ORTEC 6111 energy dispersive X-Ray Fluorescence spectrometer. A 30 Mci. 241 Am. Isotropic X-ray sources served as an excitation source. The spectral were collected for 30 minutes each and evaluated using AXIL computer program.

Instrument settings were at count of 800-1000 for standards and 100 seconds for major elements. The accuracy of analysis ranges from ± 1.0 to ± 3%.

**Procedure for PH Test**

A mass of about 150g was weighed into a beaker. About 25ml of distilled water was poured into the beaker containing the sample and the mixture was stirred vigorously and allowed to settle for about 30seconds. A Pen - type PH meter was inserted into the solution and readings were taken at the stabilized reading of the PH meter.

## IV. RESULT AND DISCUSSION

The mean and ranges of the major element oxides and the calculated values of $CaCO_3$, MgCO3, determined from the XRF analysis, and the PH values obtained from the PH test of the Itobe marble are presented in tables 1 and 2. The industrial application of the Itobe marble body based on the chemical data obtained from the analyses of the raw marble and the Industrial Specification of India, ISI (Bhargava, 1987) is presented below.

**Table 1: The Mean and Ranges of the Wt % of the Major Element Oxides and the Calculated Values of $CaCO_3$, $MgCO_3$ of the Itobe Marbles**

| | Mass I | | Mass II | |
|---|---|---|---|---|
| **Major element Oxides (%)** | **Mean N = 10** | **Range** | **Mean N = 40** | **Range** |
| $SiO_2$ | 3.78 | 6.13 – 2.47 | 6.39 | 14.87 – 1.60 |
| $Al_2O_3$ | 0.27 | 0.48 – 0.19 | 0.52 | 1.61 – 0.10 |
| $Fe_2O_3$ | 0.58 | 1.40 – 0.16 | 0.44 | 0.96 – 0.14 |
| MgO | 10.4 | 22.54 – 0.23 | 0.74 | 3.39 – 0.09 |
| CaO | 45.9 | 52.47 – 39.16 | 50.14 | 53.69 – 44.41 |
| $K_2O$ | 0.06 | 0.06 - 0.04 | 0.13 | 0.39 – 0.03 |
| $Na_2O$ | 0.06 | 0.11 – 0.10 | 0.03 | 0.25 – 0.01 |
| $SO_3$ | 0.02 | 0.04 - 0.01 | 0.07 | 0.55 – 0.11 |
| $CaCO_3$ | 81.61 | 93.40 – 69.71 | 89.26 | 95.57 – 79.05 |
| $MgCO_3$ | 21.20 | 47.11 - 0.48 | 1.38 | 7.09 – 0.19 |
| L.O.I | 38.15 | 42.89 – 31.70 | 41.27 | 43.39 – 38.75 |

**Table 2: PH values for Itobe Marble**

| Sample No | Mass I | Mass II |
|---|---|---|
| | | |
| 1 | 9.83 | 9.45 |
| 2 | 9.57 | 9.46 |
| 3 | 9.50 | 9.47 |
| 4 | 9.47 | 9.41 |
| 5 | 9.76 | 9.49 |
| 6 | 9.65 | 9.38 |
| 7 | 10.48 | 9.59 |
| 8 | 9.47 | 9.42 |
| 9 | 10.21 | 9.42 |
| 10. | 9.50 | 9.39 |
| **Mean** | **9.74** | **9.45** |

## Cement use

The range of CaO and $CaCO_3$ expected in marble used for the manufacture of cement are 46.65-52.46% and 83.50-93.90% respectively. The upper tolerable limit for MgO required for the manufacture of cement is 2% (Blue Circle Industries Ltd., 1978). Higher MgO values result in the formation of Periclase in the clinker which combines with water to form $Mg(OH)_2$. The consequential volume contrast between the initial MgO and $Mg(OH)_2$ causes structural inequilibrium which results in expansion often experienced with low quality cement.

To produce a satisfactory cement clinker, a raw meal of the correct chemical composition is required. Three chemical ratios: Silica Ratio (S.R), Alumina Ratio (A.R) and Lime Saturation Factor (L.S.F) are used to monitor the composition of the raw meal and the clinker. They are calculated using the contents of the oxides CaO, $SiO_2$, $Al_2O_3$ and $Fe_2O_3$. The standard (S.R.), (A.R.) and (L.S.F.) of a typical cement kiln feed are given as:

$$S.R = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

$$A.R = \frac{Al_2O_3}{Fe_2O_3}$$

$$L.S.F = \frac{100\,(CaO)}{2.8\,(SiO_2\%) + 1.2\,(Al_2O_3\%) + 0.65\,(Fe_2O_3\%)}$$

The recommended S.R, A.R and L.S.F ranges in limestone used in cement production are (1.9 - 3.2), (1.5 – 2.5) and (241 – 417) respectively.

Based on the above specifications, only Mass II of the Itobe marble meets the requirement for the manufacture of cement as it contains MgO < 2%. The S.R value (6.7) of Itobe marble does not fall within the recommended range of S.R (1.9 – 3.2) in marble used in cement production.

The alkalis (Na and K) can substitute for calcium and can lead to setting of cement in air if stored in humid conditions. The alkalis also react with active silica in some aggregates and cause disintegration of some concretes (Talbot, 1982). Therefore total alkalis must be sufficiently low in limestone used for cement manufacture. The total alkali ($Na_2O$ + $K_2O$) content of the Itobe marble is low (< 0.2 %). This value is sufficiently low as compared to the upper tolerable limit of 0.35% and falls within the recommended values for cement production.

Sulphur and phosphorus, regarded as most undesirable impurities in the manufacture of cement when present in more than 1% (Talbot, 1982) slows down the setting of Portland cement. The sulphur (III) oxide ($SO_3$) value in the Itobe marble is very low (< 0.1%) and this value is sufficiently low when compared to the upper tolerable limit of 1% recommended for cement production. Phosphorus was not detected in the Itobe marbles.

## Chemical use

This includes the manufacture of sodium alkalis, calcium carbide, bleaching powder and pesticide. One of the largest uses of raw marble and their lime products is in the manufacture of sodium alkalis i.e. sodium carbonate, bicarbonate and hydroxide by Solvay (or ammonia soda) process. The basic requirement is a total carbonate ($CaCO_3$, $MgCO_3$) content > 70% or lime /dololime (CaO, CaMgO) content > 80%. These specifications are met by masses I and II of the Itobe marble.

 

In the manufacture of calcium carbide, an important source of acetylene, quicklime (CaO) is mixed with coke and heated in an electric furnace to 2000 $^0$C. Molten carbide is removed from the furnace and crushed upon solidifying. It is then ground for use. For the manufacture of calcium carbide, the chemical specifications are: High calcium lime (CaO > 90%), $SiO_2$ < 3%, low Phosphorous (< 0.02%), MgO < 0.5%.

Based on these specifications, the two masses of the Itobe marble do not meet the requirements for the manufacture of calcium carbide as they both have CaO < 90% and MgO > 0.5%. For the manufacture of bleaching powder, the specification is lime (CaO) > 95%, total $Fe_2O_3$ + $Al_2O_3$+ $MnO_2$ < 2%, MgO < 2%, $SiO_2$ < 1.5%. Silica impedes solution and settling of bleaching. Based on these specifications, both mass I and mass II of the marbles are unsuitable for the manufacture of bleaching powder as they both contain CaO < 95%, $SiO_2$ > 1.5%.

In pesticide production (calcium arsenate), arsenic acid is reacted with a milk of lime forming calcium arsenate. Lime of CaO > 65% is required. Based on these specifications, both masses of the Itobe marble are not suitable for the manufacture of pesticide as they contain CaO < 65%.

**Glass Use**

The glass industry requires high calcium marble ($CaCO_3$ > 94.5%). For colorless glass, marble should contain > 98.5% $CaCO_3$; $Fe_2O_3$ should not be more than 0.04% and $SiO_2$ should be < 2.5%.

Based on the above specification, the two masses of the Itobe marble are not suitable for the manufacture of glass as they contain < 90% $CaCO_3$, > 0.2% $Fe_2O_3$ and > 2.5% $SiO_2$.

**Sugar Use**

In the sugar industry, lime is used for clarification of juice from cane. Milk of lime 1% in volume of cane juice added to pre heated juice. Marble to be used in sugar industry must be high in active lime (> 80% CaO), must be low in silica < 2%, MgO content should be < 1%. The presence of iron must be negligible or absent as iron tends to color the finished product. Based on the above specifications, the two masses of the Itobe marble do not meet the specifications for the production of sugar as they contain > 2% $SiO_2$, < 80% CaO.

**Metallurgical Use**

There are numerous applications of raw marble and their lime products in the metallurgical industry. However, the largest specific application is for fluxing steel. Eighty – five percent of total lime produced worldwide is used as steel flux (O'Drascoll, 1988). In steel manufacture, marble is used first to lower the temperature of melting and second to form calcium silicate by combining with silica of the iron which comes out as a slag. Another metallurgical application of lime is as refractory lime (dead burned dolomite). It is used for lining open heath.

The specifications for metallurgical lime include CaO > 65%, $SiO_2$, 1-1.5%, $SO_3$, 0.5-1%.

The specification for the use of lime as refractory lime is similar to those of fluxes except that the silica requirement is less stringent (2 - 4%).

Based on the above specifications, the two masses of the Itobe marbles are unsuitable for use as steel flux as the $SiO_2$ content in them is higher than the recommended upper tolerable limit of 1.5%. However, mass I of the Itobe marbles meet the specification for use as refractory lime as its silica content (3.14%) falls within the accepted range of 2-4% required for refractory lime.

**Environmental Use**

Raw marble and their lime products have found wide applications for environmental purposes (Boynton, 1980). These include water and sewage treatment.

For water treatment purposes, lime is very important, especially in water softening and PH adjustment. It also prevents the dissolution of undesirable materials from the piping system. In this case, lime removes the temporary bicarbonate hardness. In water purification, lime is added to water in retention tanks for 24 - 48 hours. High PH (about 11+) produced by lime kills most types of bacteria (Boynton, 1980). The major requirements of lime for water softening and purification include $CaCO_3$ > 80%, CaO > 65%, PH > 10%, MgO < 2%, $SiO_2$ < 0.01%. Based on these specifications, masses I and II are not suitable for water softening and purification as they contain CaO < 65% and $SiO_2$ > 0.01%. Marble is also used in water treatment as filtering gravel in which case $CaCO_3$ > 95%, CaO > 53.2% and $SiO_2$ < 1%. The Itobe marbles do not meet the requirement for filtering gravel as they contain CaO < 53% and $SiO_2$ > 1%.

In sewage treatment lime is useful in neutralization of acid water, silica and phosphate removal from sewage effluents. The specifications are similar to that for water softening and purification. Hence masses I and II of the Itobe marbles do not meet the specification for the treatment of sewage.

**Agricultural Use**

Soil liming is one of the oldest uses of raw or calcine marble (Ojo et al, 1998). The marble or lime function as a neutralizer of acid soils and plant nutrient enhancer. The requirements are PH > 8 with low grittiness. Marble is also used as grit in the manufacture of poultry feed. For this purpose, the degree of purity of marble is insignificant but alumina ($Al_2O_3$) content must be very low. Based on these specifications, masses I and II of the Itobe marble are suitable for use in soil liming and as grit in the manufacture of poultry feed as they contain PH > 8 and very low alumina content (< 1%), and low grittiness.

**Filler/Extender Use**

Marble is useful as fillers/extenders in the manufacture of paint, rubber, plastics, pulp and paper, animal feed, tooth paste and pharmaceuticals. The general specification for this is CaO > 52%, $Al_2O_3$ < 0.2%, $Fe_2O_3$ < 0.2%, MgO and $SiO_2$ must be low (< 3%), $SO_3$ < 0.2%, $P_2O_5$ < 0.15%). Based on this specification, the Itobe marbles are unsuitable for use as fillers/extenders as they contain < 52% CaO, > 0.2% $Al_2O_3$, > 0.2% $Fe_2O_3$ and > 3% $SiO_2$.

## V. CONCLUSION

On the basis of the chemical data obtained from the analysis of the Itobe marble and the Industrial Specification of India, mass II of the Itobe marble is suitable for the production of cement although it may need to be blended with shale and laterite to adjust the Silica Ratio (S.R) to meet up with the requirement of a typical cement kiln feed. Both masses I and II of the marble are suitable for the manufacture of sodium alkalis and as grit for the manufacture of poultry feed. Mass II is suitable for pesticide production. Mass I because of its relatively high MgO content is suitable for use as flux in the manufacture of steel and as refractory lime in the metallurgical industry.

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