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Chemical Analysis of Some Limestone Samples from the Middle Belt Zone, Nigeria and Their Possible Industrial Applications

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ABSTRACT

Chemical analysis of fifteen (15) limestone samples, 13 of which were locally sourced, was carried out using gravimetric as well as flame emission and uv- visible spectroscopic methods. The range of parameters determined in percentages were as follows; loss on drying (0.10 – 1.68), loss on ignition (40.97 – 47.24), insoluble matter (1.43 -2.73), SiO_2 (0.94 – 2.51), Fe_2O_3 (0.178 – 0.622), MnO_2 (0.00 – 0.34), Al_2O_3 (0.00 – 0.188), TiO_2 (0.00– 0.12), K_2O (0.049 – 0.270), Li_2O (0.047 – 0.159), Na_2O (0.012 – 0.296), $CaCO_3$ (82.24 – 96.68), CaO (46.08 – 54.85), MgO (0.44 – 10.92), CO_3^{2-} (59.62 – 62.18) and CO_2 (43.72 – 45.61) . From the Pearson correlations, some of the locally sourced samples could serve as possible replacements for reference samples A and B used in pigment/ink production. The results also indicated that most of the limestone samples were found to meet some industrial raw material specifications used in the cement, agriculture (liming of soil and fish ponds), ceramics, glass, silica bricks, pharmaceutical, coal dust fire dampener, paint, poultry and metallurgical purification processes in the steel industry and some other filler applications.

Keywords: Industrial, Ink, Limestone, Local Source, Spectroscopy.

INTRODUCTION

Limestones are known to include organic matter (Chambers Encyclopaedia, 1970), marl (Iyah, 2004), marble (Friedman, 2000) and chalk (Hamblin, 1992; Friedman, 2000). It may also include layers of clay or sand which form the attractive flow bandings and the colours found in decorative marbles (Snyder and Russel, 2005). Nigeria is the only country in Africa where substantial amounts of limestone have been found and a number of cement works have been set up based on this mineral (Leon, 1981).

Geochemical studies of the Ewekoro limestone revealed that it has about 50.96% CaO and less than 1% MgO. This confirmed mineralogical proportion of calcite. The average of 4.2% silica is an evidence of the presence of non-carbonate detritus while SO_3^{2-}, P_2O_5 and Na_2O occur only in trace amounts (Ojo *et al.*, 1996). Ohafia area in south eastern Nigeria is characterised by shale limestone snale sequence. The limestone units have relatively high CaO content (41-53%), with most of the samples having CaO values of over 45% and a few with less than 40% CaO (Ibe and Ogezi, 1997). A few samples have silica contents between 1 and 21% with alumina values of 0.5 – 3.0%, MgO values of less than 1% and TiO_2 values of less than 0.30%, SrO concentrations of between 200 and 1300 ppm and lime saturation factor values of between 40 and 82.3% (Ibe and Ogezi, 1997).

The marl mineral in Jigawa State occurs in association with clayed and silty sandstone. This has been found in various parts of the state particularly at Gumel, Mallam Madori, Auyo, and Hadejia among other places (Iyah, 2004). Associated with these occurrences are brownish nodules which comprise of 49.2% SiO_2, 43.12% Fe_2O_3, 7.50% Al_2O_3 and 0.08% TiO_2. The results of the chemical analysis of the marl nodules in percentage are; CaO (27.00-34.18), MgO (0.26 – 0.65), $CaCO_3$ (48.20-62.01), $MgCO_3$ (0.54 – 1.36) and acid insolubles (38.40 – 50.37) (Iyah, 2004).

Results of the geochemical analysis of some marble deposits in Nigeria show variations which essentially relate to differences in the mineralogy of the rocks. Although the total carbonate contents are similar and ranged from 95.03 – 99.39%, there are significant differences in their Ca^{2+}/Mg^{2+} ratios. The Igbetti marble contains more $MgCO_3$ (37.8 - 45.6%) but lower $CaCO_3$ (44.26% - 67.26%) than the Jakura and Ososo marbles. In the Igbeti marble, the average Ca^{2+}/Mg^{2+} ratio is 1.66 which is much lower than the Ca^{2+}/Mg^{2+} ratios of 36.33 and 204.89 in Ososo and Jakura marbles respectively (Emofurieta and Ekuajemi, 1995).

The usual compositional disparities between the samples imposed corresponding differences in their industrial and economic utilization. For such reasons, this research work aim to assess the composition and possibly characterize the limestone samples obtained from Tawada Ink (Nigeria) Limited, assess their suitability for security ink production and ascertain their qualities and potentials for other industrial purposes.

MATERIALS AND METHODS

Thirteen limestone samples, labelled C to O were collected from various locations in the middle belt zone of Nigeria, comprising of Kogi, Edo and Benue States and FCT. The samples were sourced through Tawada Ink (Nigeria) Limited, a subsidiary of the Nigerian Security Printing and Minting Company, Abuja and all believed to be from the same geological area. In addition two reference samples labelled A and B were also provided by Tawada Ink (Nigeria) Limited for comparison. Each sample was broken into chips, pulverized into powder using a disc- mill.

A known weight of each sample was subjected to the determination of loss on drying at 110^{o}C for 1 hour to determine the adsorbed moisture. They were also subjected to a temperature of 1000^{o}C for 4 hours to determine loss on ignition which gives a rough proportion of the carbonate contents in the test samples (Vogel, 1978).

Gravimetric methods were used for the determinations of the proportions of insoluble matter, pure silica, combined oxides, calcium and magnesium oxides in the test samples as described by Jeffery et al. (1997).

Flame emission spectrometric method was used for the determination of the composition of sodium, potassium and lithium. A known weight of the limestone samples were digested with HNO_3-$HClO_4$-(1+5) HCl acid mixture according to the method described by Kawasaki and Arai (1996). A Jenway Clinical Flame Photometer (model PSC-7) was used to measure the emission intensities of the test samples at 766.5, 589 and 670.8nm for K, Na and Li, respectively in comparison with standard solutions (Jeffery *et al*., 1997).

A Camspec UV- visible spectrophotometer, model M201 was used for the determination of aluminium, iron, manganese and titanium at 535, 480, 545 and 410nm respectively. In the determinations; thiocyanate method for iron, periodate method for manganese, eriochrome method for aluminium and peroxide method for titanium were used as described by Jeffery *et al*. (1997). The absorbance of test sample solutions were compared to those of standard solutions similarly prepared.

The reaction of carbonate samples with excess hydrochloric acid to produce carbon dioxide was utilized to ascertain the carbonate level of the limestone samples. Careful measurement of the volume of carbon dioxide produced was used to calculate the percentage carbon dioxide and carbonate contents of all the individual samples. Gas law calculations including correction for water vapour, gas solubility and Dalton's law of partial pressure were all used to determine the correct volume of carbon dioxide evolved from each sample at laboratory conditions (Kurt *et al*., 1981). The efficiency of this method was tested with Analar grade calcium carbonate (Ex-May and Baker, Nig. Limited).

RESULTS AND DISCUSSION

Limestone is chiefly made up of $CaCO_3$. Its percentage in samples analysed was found to range from 82.24 ± 0.65 to 96.67±0.28 with a percentage mean value of 93.01 ±4.47. The reference samples A and B were found to have the least $CaCO_3$ content (82.24±0.6520 and 83.50±0.0449) when compared to 13 local samples (Fig. 1). The $CaCO_3$ content in all samples was found to positively correlate to CaO content which was also least in the reference samples A and B (Fig. 2). Since the percentage $CaCO_3$ was found to be low in reference samples A and B when compared to other 13 samples, it will be expected that other carbonate minerals might be present (in addition to other reasons).

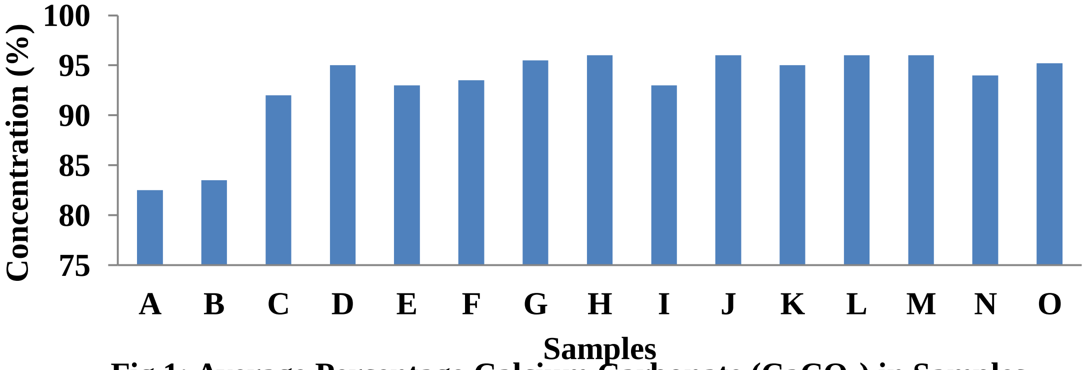

Fig 1: Average Percentage Calcium Carbonate ($CaCO_3$) in Samples

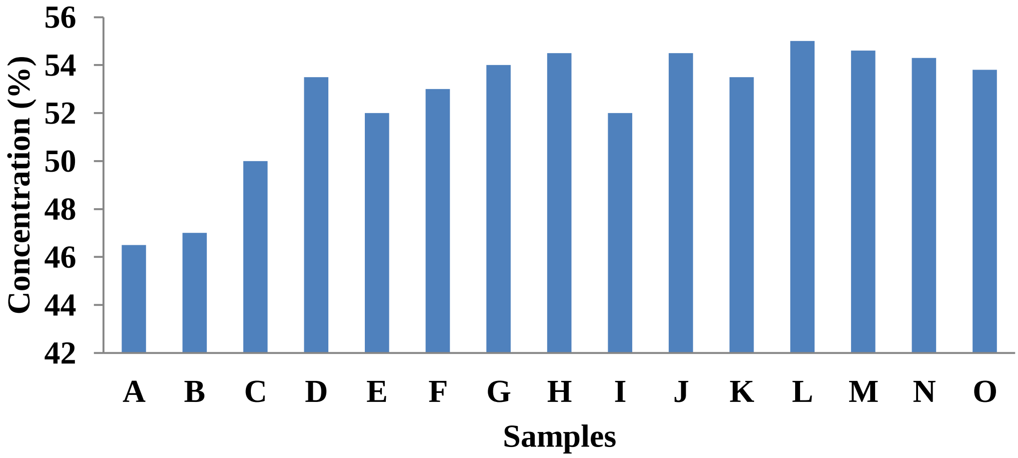

Fig 2: Average Percentage Calcium Oxide (CaO) in Samples

From the results of analysis, the percentage of MgO in all samples is lower than in the reference samples A and B (Fig. 3). These could be attributed to the large proportion of $MgCO_3$ present in the reference samples A and B. It is therefore expected that the samples could possess some dolomitic properties (Brady and Well, 1999).

Percentage carbonate in these limestone samples was roughly determined during loss on ignition (LOI) analysis, but that was not enough to provide the actual carbonate/carbon dioxide content values of these samples since alkali carbonates do not decompose on heating (Stewart, 2001). As such, a different method described by Kurt *et al*. (1981) was employed to determine the actual percentage of carbonate/carbon dioxide composition in the samples. Most of the samples have their percentage carbonate/carbon dioxide content higher than those of reference samples A and B (Fig. 4).

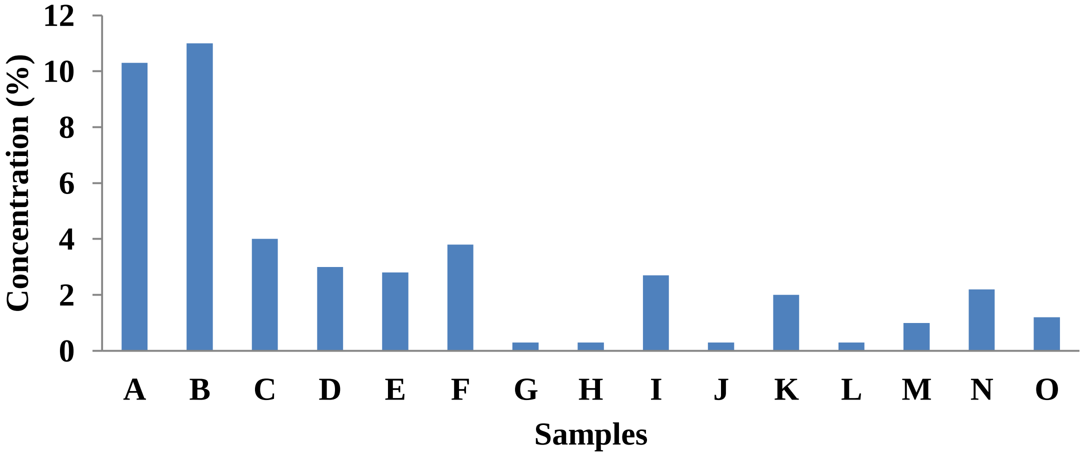

Fig 3: Average Percentage Magnesium Oxide (MgO) in Samples

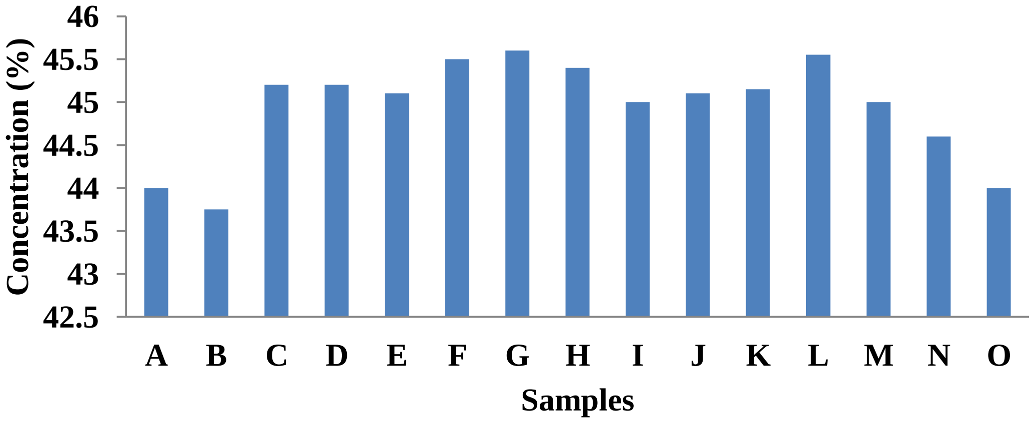

Fig 4: Average Percentage Carbon Dioxide (CO_2) in Samples

Other determinations carried out include; insoluble matter, pure silica, iron as Fe_2O_3, manganese as MnO_2, aluminium as Al_2O_3, potassium as K_2O, lithium as Li_2O, sodium as Na_2O and titanium in form of TiO_2. With exception of insoluble matter and pure silica, all other percentage compositions were found to be less than 1.0 % (Figs. 5 – 10).

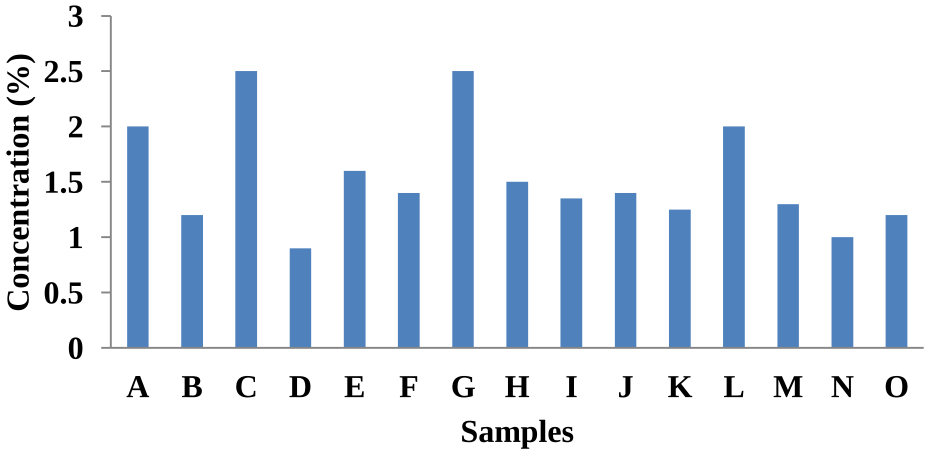

Fig 5: Average Percentage Silica (SiO_2) in Samples

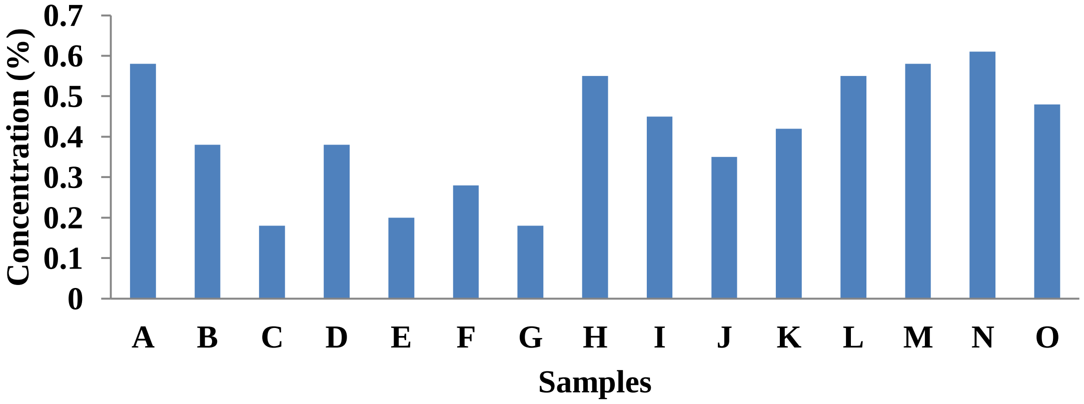

Fig 6: Average Percentage Iron Oxide (Fe_2O_3) in Samples

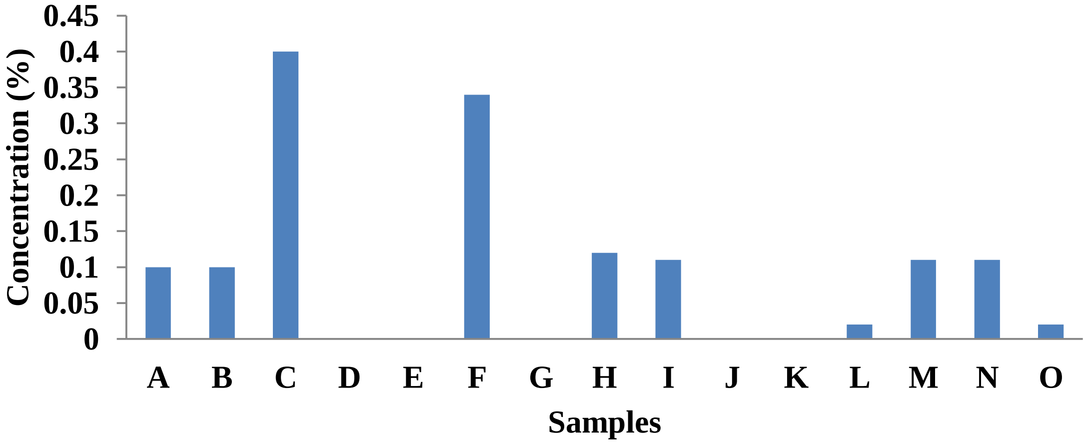

Fig 7: Average Percentage Manganese Oxide (MnO_2) in Samples

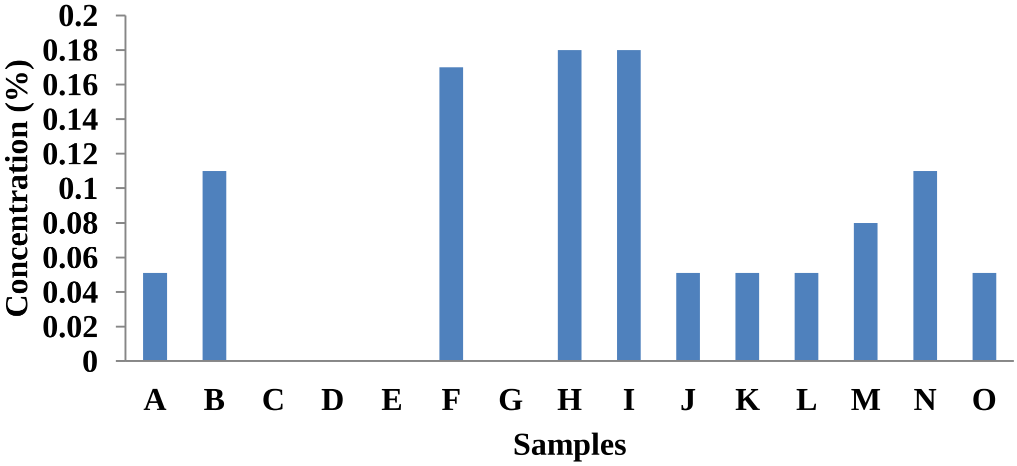

Fig 8: Average Percentage Aluminium Oxide (Al_2O_3) in Samples

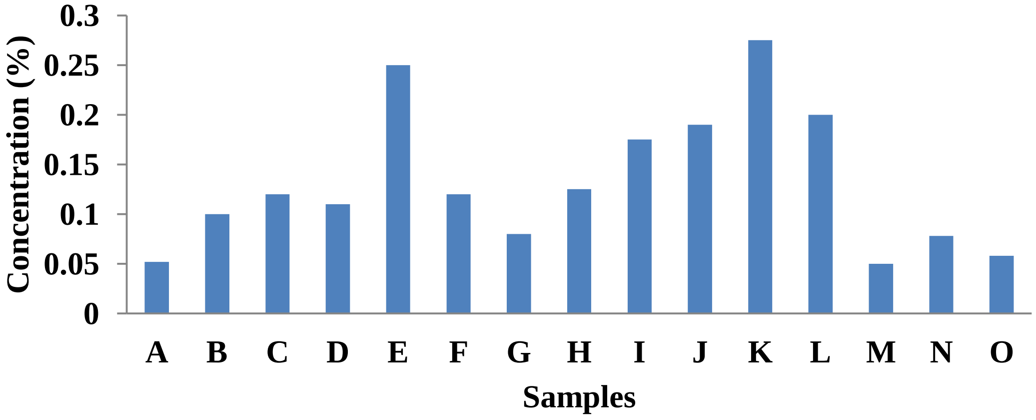

Fig 9: Average Percentage Potassium Oxide (K_2O) in Samples

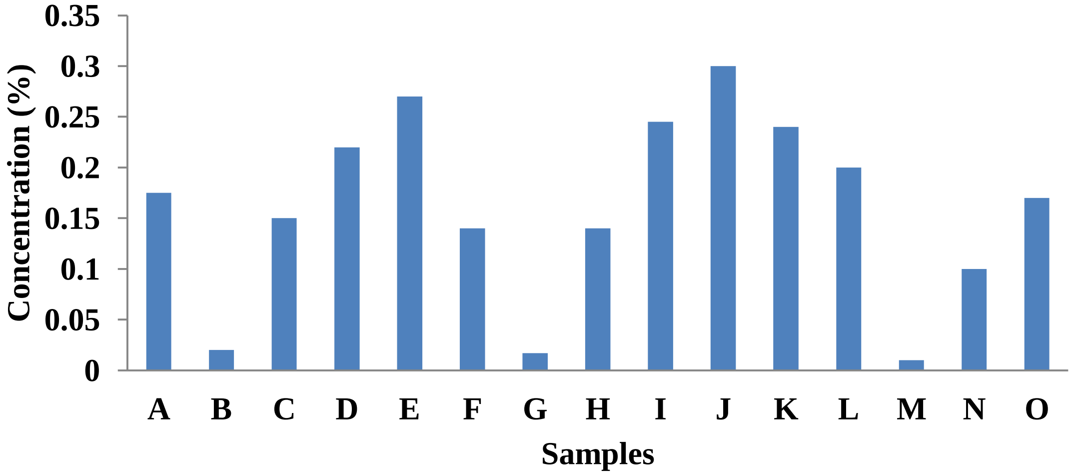

Fig 10: Average Percentage Sodium Oxide (Na_2O) in Samples

Even though these samples were all sourced from middle belt of Nigeria, variations still existed between them because of the complex composition of the solutions from which they must have crystallized as there is ample opportunity, during their growth for the composition of mineral crystals to vary (Chambers Encyclopaedia, 1981). It has been noted that compositional variation occurs not only between crystals of a given mineral from different localities and between different crystals of the same mineral from one locality but also within a single crystal variations are evident (Maes and Cremers, 1977). Such variations in composition are generally known as ionic substitution which are made possible by replacement in a given crystal structure of one ion or ionic group for another of similar size (Chambers Encyclopaedia, 1981).

It has been established by Pearson Product Moment Correlation method of analysis that there is no significant difference between reference samples and the 13 local samples because the correlation coefficients between samples was insignificant at 0.01 level (2-tailed) and ranged from 0.952-1.000.

Some of the samples do not meet the requirements/ specifications for ink and pigment production. 13 of the 15 samples have $CaCO_3$ contents within the specified range of less than 96. 63% (Harben, 1995). SiO_2, Fe_2O_3 and Al_2O_3 contents of all the samples were within the specification of >0.37%. Moisture content of only 4 samples were found to be slightly lower than the specification of > 0.20% for ink production. Also the $MgCO_3$ contents of 5 samples were found to be lower than the specification (Harben, 1995). Therefore 8 of the local samples were found to meet all the chemical specifications for ink/pigment production and thus can serve as potential replacements to reference samples A and B (Table 1). Besides ink production, these limestone samples could serve in other industrial applications. The samples have been found to meet the industrial raw material specifications for the production of glass based on their CaO, MgO, acid insolubles, Fe_2O_3, Al_2O_3, SiO_2 and moisture contents (Table 1) (Harben, 1995). In drug manufacturing, the specifications for limestone use are; 98.8% $CaCO_3$ max, 2.0% loss on drying, 0.2% acid insolubles, 0.0005% fluoride, 3ppm arsenic, 3ppm lead, 0.05% magnesium and alkali salts. The only probable obstacle to the application of the samples in pharmaceutical product formation is pyrites if present, which was not analysed. This could cause some problems to the body if used in oral drugs since H_2S is liberated upon addition of acid. Other than this, most of the samples analysed met the pharmaceutical requirements reported by Harben (1995).

The chemical composition of most of the samples meet the specifications of high $CaCO_3$, less than 1% SiO_2 and negligible S and P contents, therefore could be used for steel smelting (Harben, 1995). Furthermore, all the samples could be used as aggregates in concrete, coal dust fire dampener, acid rain neutralization and cement production, (Table 1) (Harben, 1995). It was also found by compositional comparison that the limestone samples could serve as replacements to the highly calcitic Ososo and Jakura marbles which constitute suitable raw materials in the cement, agriculture (liming of soil and fish ponds), ceramics, glass, silica bricks, pharmaceutical, paint, poultry and metallurgical purifications processes in the steel industry. This is based on their $CaCO_3$, CO_2, MgO, CaO, MnO_2, Al_2O_3, SiO_2 and Fe_2O_3 contents (Emofurieta and Ekuajemi, 1995).

Table 1: Average Chemical Composition of the Samples and Industrial Specifications

% Elements	**Test Samples (Average)**	**Test Samples (Range)**	***Ososo**	***Jakura**	****Pigment**	****Flat Glass**	****Container Glass**
SiO_2	0.53	0.10-1.68	1.18	0.44	0.37	Nil	Nil
Fe_2O_3	0.041	0.18-0.62	0.07	0.04	0.09	0.075	0.1
Al_2O_3	0.07	0.00-0.19	0.1	0.07	0.28	0.35	0.35 ± 0.05
MnO_2	0.07	0.00-0.34	0.003	0.002	Nil	Nil	Nil
CaO	52.17	46.08-54.85	53.64	55.33	Nil	54.85	54.85
MgO	1.77	0.44-10.92	1.75	0.32	1.16	0.8	0.80 ± 0.3
Na_2O	0.19	0.01-0.30	0.02	0.03	Nil	Nil	Nil
K_2O	0.13	0.05-0.27	0.01	0.001	Nil	Nil	Nil
CO_2	44.97	43.72-45.61	43.26	43.5	Nil	Nil	Nil
$CaCO_3$	93.01	84.24-96.68	95.72	98.76	96.63	Nil	Nil
Acid Insolubles	1.86	1.43-2.73	Nil	Nil	Nil	0.6	0.6
TiO_2	0.01	0.00-0.12	Nil	Nil	Nil	Nil	Nil
Loss on Drying	0.61	0.10-1.08	Nil	Nil	0.2	0.005	Nil
Ca^{2+}/Mg^{2+}	29.47	Nil	36.33	204.89	Nil	Nil	Nil

* Emefurieta and Ekuajemi (1995)

** Harben (1995)

CONCLUSION

From the results of chemical analysis, correlation coefficients, and comparison with industrial specifications, it is clear that some of the samples studied could serve as potential substitutes to the 2 reference samples used in pigment and ink production. The limestone samples were found to meet some industrial raw material specifications used in the cement, agriculture (liming of soil and fish ponds), ceramics, glass, silica bricks, pharmaceutical, coal dust fire dampener, paint, poultry and metallurgical purifications processes in the steel industry. Further studies on the limestone samples sourced within Nigeria should also be focused on meeting the specifications for pharmaceutical use and sugar refining.

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