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Quality assessment of limestone deposit found in Demsa local government area of Adamawa state, Nigeria

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Research Paper

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Sourcing of raw materials from the abundant natural endowment of Nigeria, Adamawa state inclusive, for industrial use has not generated significant success due to lack of technical information on the integrity of these natural endowment. Limestone is one mineral with enormous diversity of uses. It is used in cement industries, ceramics, paper, glass, animal feed, textile, pharmaceuticals, cosmetic production, water treatment and agriculture. The X-ray fluorescence revealed the major elemental oxide of the limestone in the study area in the order $CaO>SiO_2>Al_2O_3>Fe_2O$>others, in four locations and the composition shows $CaCO_3$ content ranging from 73.79 ± 0.02% to 96.28 ± 0.02% with an average of 86.69 ± 0.10% calcite. While the order of $SiO_2>CaO>Al_2O_3>MgO>Fe_2O_3$>others, are in two locations with 29.64 ± 0.01 and 33.75±0.01% $CaCO_3$. The minor oxides are in quantities below 3% and LOI ranging from 10.00± 0.04% to 34.50 ± 0.2%. The limestone deposits in these locations are rich in calcite which can be useful in production of cement, in agriculture and in chemical/industrial uses.

Key words: X-Ray Fluorescence, composition, calcite, quality assessment, cement.

INTRODUCTION

Limestone is a sedimentary rock, composed largely of the minerals calcite and aragonite which are different forms of calcium carbonate and dolomite (Areola et al., 1999). It is often formed from concentration of broken pieces of seashell, and fragments of calcite minerals produced by corals and algae. Limestone can be precipitated either by action of organisms or directly as a result of inorganic processes (Carlson et al., 2008). The term limestone is usually used for rocks containing 50% or more calcium carbonate (Cox et al., 1974), but mineralogical limestone may be regarded as any rock which the carbonate minerals (calcite, $CaCO_3$ and dolomite, $CaMg(CO_3)_2$ exceed the non-carbonate minerals that is calcite and dolomite must be more than 50% in the rock sample (Duncan 1963, Neendorf et al. 2005).

Limestone is one rock with enormous diversity of uses such that it is used in more ways than any other (Kogel et al., 2006). It finds application in industries for cement production, metallurgy (iron and steel making), and manufacturing (glass food processing, paper making, leather, water purification, waste water treatment, flue gas desulphurization, adhesive, insulation and pH control), agriculture (fertilizers, fungicides, animal feed) and construction (mortar, cement, white wash, building stones purposes) Rao et al., (2011).

Limestone has been said to occur only in the sedimentary basins in Nigeria, and occurs mainly in the Benue trough (lower, middle and upper). The limestone deposits of the Benue trough appear to contain the largest and economically viable limestone resource in the country (Fatoye and Gideon 2013). Most of the limestones in Nigeria are of high quality, generally containing over 80% $CaCO_3$ (RMRDC, 2001). Opeloye and Dio (1999) also reported the occurrence of limestone deposits in Guyuk, Lamurde and Numan local government areas of Adamawa state, with assertion that they are of good quality. Deposits of this vital mineral resource have also been discovered in some parts of Demsa local government area of the state, however, little or none is documented on their quality in terms of calcite and dolomite contents.

This paper makes an attempt at elucidating X-ray fluorescence of the major elemental oxides of limestone in some parts of Adamawa state. This is the first mineral study, in the marked area and is aimed at providing additional findings on solid mineral potentials of Adamawa state and will form the rudiments for further studies of the sort in Adamawa state in Nigeria.

MATERIALS AND METHODS

Location

Demsa local government area is located between latitudes 9°12'N and 9°42'N of the Equator and between longitudes 11°38'E and 12°20'E of the Prime Meridian (Figure 1). It is situated at the confluence of the Yola and Gongola arms of the Benue trough which was subjected to several depositional cycles that resulted in the formation of the albian and cenomanian sedimentary rocks of varied compositions and ages (Bawden 1972; Kogbe 1981; Opeloye and Dio, 1999). Consequently, the area is characterised by sedimentary rock varieties which include calcareous sandstones, feldspathic sandstones, limestones and shales with sandstone intercalations as well as shelly limestones.

Sampling

Samples were collected from 6 places in Demsa local government area: Borrong, Demsa, Bange, Murgarang, Pudan and Kadumon settlements. The sampling points were spaced at about two meters (2m) apart for possible variations in their constituents. Samples were then randomly collected from ten points (10) in each sample site by chiselling. The chiselled samples were then mixed together to give a representative sample. About 500 g of the rock samples from each site was transferred into labelled polythene bags.

Sample Preparation

Sample preparation according to Alexander et al. (2011) was adopted. The collected rocks were dried in an oven at 31°C for 12 h to dry thoroughly. The dried samples were crushed and ground to powder using pestle and mortar. The samples were reduced in size after crushing, by coning and quartering as described by Okunola et al. (2008). This is to achieve a well homogenized original sample. After all the samples had been mixed thoroughly by coning, the mass was flattened and a circular layer of material was formed, this was quartered and alternate quarters were discarded. This process was repeated as often as desired until the required quantity suitable for analysis was obtained. The samples were then kept in air-tight polythene bags.

X-Ray fluorescence analysis

The samples were analysed for elemental oxides using XRF. Method adopted by the National Geological survey laboratory (NGSL) Kaduna and by Alexander, (2011), was followed: The powered samples were further reduced to less than 63 microns using a tema vibrating mill. Each sample was analyzed for major and minor elements expressed as oxide weight percent by preparing glass beads. These were prepared by first drying the sample powder in an oven at 110°C for 24 h to remove moisture in the rock powder. About 5.0 g of the dried rock powder was weighed in a silica crucible and then ignited in a furnace at 1000°C for 2 to 3 h for the calcinations of impurities in the rock powder. The samples were then removed from the furnace and allowed to cool to room at temperature in desiccators. Each ignited rock powder was then weighed again to determine the weight of calcinated impurities (H_2O and CO_2). One gram of the stored ignited rock powder was weighed with exactly 5 times of flux (X-ray flux-type 66:34%) 66% Lithium tetraborate and 34% Lithium metaborate) was added to lower the Vitrification temperature of the rock powder. The weighed mixture was mixed properly in a platinum dish and ignited in a pre-set furnace (Eggon 2 Automatic flux bead maker) at 1500°C for 10 min to form glass bead. Each glass bead was labelled and slotted into the computerized XRF (Epsilon 5 Panalytical model) Quantitative analyses of the samples were carried out using emission – Transmission (E-T) method for which a number of quantification methods have been developed and applied. Each sample (bead) was analyzed by XRF using an annular 25 mCi 109 Cd as the exciting source that emit Ag-K X-ray (22.1KeV) in which case, all elements

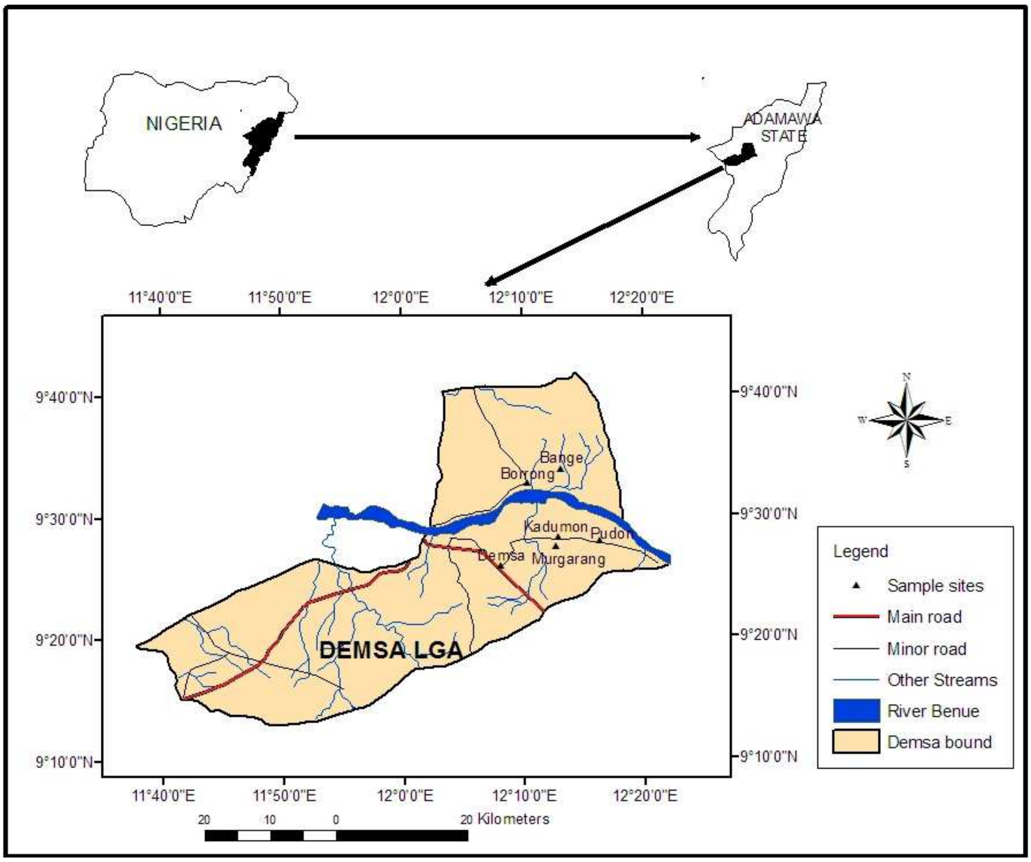

Figure 1. The Study Area.

with lower characteristics excitation energies were accessible for detection in the samples.

RESULTS AND DISCUSSION

Table 1 shows that the major component in the samples from Demsa, Borrong, Bange, Murgarang, Pudan and Kadumon is calcium carbonate. Demsa town has the highest percentage of CaO with 53.92±0.02%, while Pudan has the least with 16.60±0.03%. The least element in abundance was vanadium (V_2O_5) with 0.0001-0.0005%. Phosphorus (P_2O_5) was beyond the detection limit of the equipment < 0.00001% in all the sample areas except Demsa that has 2.30±0.01% concentration. Sulphur (S_8) was only detected in Murgarang and Demsa 0.02±0.01% and 0.05±0.01% respectively. Barium (BaO) is below 1% in all the areas while MgO content is higher in Pudan and Kadumon with 11.51±0.03% and 10.17±0.02% respectively. Murgarang has the highest concentration of Manganese (MnO) 2.82±0.01%, followed by Demsa with 2.06±0.01% and Borrong with 1.03±0.02%. Iron (Fe_2O_3) is highest in Pudan with 10.63±0.01% followed by Kadumon with 10.18±0.01% while Murgarang and Borrong have 4.53±0.01% and 4.45±0.01% respectively. The result shows that CaO is the most abundant in Borrong, Bange, Demsa and Murgarang followed by SiO_2,then Al_2O_3, Fe_2O_3 and others CaO>SiO_2>Al_2O_3>Fe_2O_3>others. while Pudan and Kadumon SiO_2 is the highest follow by others, in decreasing order thus:SiO_2>CaO>Al_2O_3>MgO>Fe_2O_3> others. It is worth noting that Pudan and Kadumon deposits showed lower values of CaO 16.60± 0.03% and18.90± 0.03% respectively and lower, Loss on ignition (LOI) , with elevated MgO content compared to similar rock deposits in Demsa, Borrong, Bange and Murgarang. These low and high values of CaO and MgO bear similar pattern to results obtained of metacarbonate rock (marble) in FCT (31.82% and 19.60%), Nsofang (35.79% and 16.70%) and Igbeti (28.94% and 20.70%) in respect of CaO and MgO, (Davou and Ashano, 2009; Bassey,2011; Emufuriata and Ekuajemi,1995). SiO_2, Fe_2O_3, Al_2O_3 and TiO_2 are also higher in these two locations than the other four areas. SiO_2 seems to be the dominant oxide in Pudan and Kadumon, Bange has a concentration of 2.95+0.01%, while the least

Table 1. X-Ray Fluorescence of Rock samples.

%Oxide content	Murgarang	Borrong	Bange	Pudan	Kadumon	Demsa
Al_2O_3	6.30±0.01	3.30±0.01	3.30±0.01	16.00±0.01	13.00±0.02	0.70±0.03
SiO_2	17.00±0.01	10.00±0.02	8.00±0.01	25.00±0.01	28.00±0.01	2.20±0.01
SO_3	0.02±0.01	<0.0001	<0.0001	<0.0001	<0.0001	0.05±0.01
P_2O_5	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	2.30±0.01
K_2O	2.02±0.03	1.30±0.01	0.956±0.001	2.70±0.02	3.23±0.03	0.36±0.01
Na_2O	0.21±0.01	0.14±0.03	<0.0001	0.10±0.01	0.75±0.02	<0.0001
CaO	41.32±0.02	48.86±0.01	50.09±0.02	16.60±0.03	18.90±0.03	53.92±0.02
MgO	1.02±0.01	0.78±0.02	0.41±0.03	11.51±0.03	10.17±0.02	0.21±0.01
TiO_2	1.84±0.01	0.71±0.01	0.84±0.01	5.09±0.01	4.17±0.02	0.25±0.01
MnO	2.82±0.01	1.03±0.02	0.083±0.02	0.35±0.02	0.45±0.03	2.06±0.01
Fe_2O_3	4.53±0.02	4.45±0.01	2.95±0.01	10.63±0.01	10.18±0.01	2.43±0.01
BaO	0.52±0.01	0.53±0.01	0.31±0.01	0.72±0.02	0.63±0.03	0.91±0.02
LoI	22.20±0.04	28.40±0.03	32.67±0.01	11.25±0.01	10.00±0.01	34.50±0.02
V_2O_5	0.0005±0.0001	0.0002±0.0001	0.0002±0.0001	0.0001±0.0001	0.0003±0.0001	0.0001±0.0001
$CaCO_3$	73.79 ±0.02	87.25 ±0.01	89.45 ±0.01	29.64 ± 0.01	33.75± 0.01	96.28 ± 0.03
$MgCO_3$	2.14 ± 0.01	1.64 ± 0.01	0.86 ± 0.01	24.17 ± 0.02	21.36 ± 0.02	0.44 ± 0.01
Total CO_3^{2-}	75.93 ± 0.01	88.89 ± 0.01	90.31 ± 0.02	53.81 ± 0.03	55.11± 0.03	96.72± 0.02
CaO/MgO	34.48	53.20 0.01	104.01	1.23	1.58	218.82

(±) values are the standard deviation of triplicate analysis.

concentration is found in Demsa with 2.43+0.01%. Na_2O was not detected in Bange because it was beyond the detection limit of the equipment, it was found to be less than 1% in all the other locations. K_2O occurs in higher quantity in Kadumon with 3.23±0.01%, followed by Pudan 2.70±0.03%, then Murgarang with 2.02±0.03%, Borrong 1.30±0.01%, Bange and Demsa with less than 1.% each. TiO_2 was found to be higher in Pudan and Kadumon with 5.09±0.01% and 4.67±0.01% respectively, followed by Murgarang with 1.84±0.01%, Demsa has the least concentration with 0.25±0.01% while Borrong and Bange have less than 1%.

Loss on ignition (LOI), ranges from 34.50±0.03% in Demsa with 10.00±0.01% in Kadumon, Bange with 32.67±0.01%, Borrong with 28.40±0.03% then Murgarang with a concentration of 22.20±0.04%. Pudan and Kadumon have lower values of 11.25±0.01 and 10.00±0.01% respectively. The calcium carbonate content ranges from 29.64% in Pudan being the least to 96.28% in Demsa. Borrong has 87.25%, Murgarang 73.79% Bange 89.45% and Kadumon with 33.75%. Total carbonate from Murgarang is 75.93%, Borrong 88.89%, Bange 90.31%, Pudan 53.81%, Kadumon 55.11% and Demsa with the highest value of 96.72%. CaO/MgO ratio shows that Demsa has the highest value with 218.82, followed by Bange 104.01, Borrong with 53.20, Murgarang 34.48 while Pudan and Kadumon with less than 2 that is 1.23 and 1.58 respectively. The higher the CaO/MgO ratio the better the grade of limestone (Bassey, 2011). This therefore shows that Demsa has the best grade followed by Bange, Borrong and Murgarang, while Pudan and Kadumon have low grade limestone.

According to Cox et al., (1974), the term limestone is normally used for rocks containing 50% or more of calcium carbonate. It therefore confirms that the rock deposits in Demsa, Murgarang, Borrong and Bange are limestone with calcium carbonate content of 96.28%, 73.79%, 87.25% and 89.45% respectively.

Pudan and Kadumon deposits did not show any calcite and their calcium oxide content were below 30% therefore not pure limestone based on Missouri, Department of Natural Resources (2011) classification of mineral and chemical composition of pure limestone. However their MgO content of 11.51% and 10.17% fall within the range 4 -17% of limestone referred to as dolomite (The Great Soviet Encyclopedia, 1970-1978). Demsa, Bange, Borrong and Murgarang deposits can be referred to as calcite limestone based on their $CaCO_3$ content. However mineralogy limestone may be regarded as calcite, magnesium calcite (dolomite) or an aggregate with varying proportions of each of these minerals (Neendorf et al., 2005). Duncan, (1963) also asserted that a limestone is any rock in which the carbonates ($CaCO_3$ and $CaMg(CO_3)_2$ minerals exceed the non- carbonate minerals i.e. calcite and dolomite must be more than 50% .Therefore Pudan and Kadumon deposits are also limestones, because their total carbonate contents are more than 50%. They are more of dolomite limestone than calcite limestone because their MgO content of 11.51 and 10.17% fall within the range 4-17% which characterizes dolomite limestone (The Great Soviet Encyclopedia, 1970-1978).

Based on the economic importance, the rock deposits of Demsa study area can be used for Portland cement with less than 3% MgO, 0.5% total alkalies and $CaCO_3$ ranging from 73.79-96.25%. Even as low as 69.75% $CaCO_3$ content had been used in Ash Groove cement company in Nebraska, U.S.A. (Wheeler, 1999). Also based on Duncan (1963) recommendation for rock deposit use in the production of lime, requiring phosphorus at trace level and acceptable lower grades of less than 98% $CaCO_3$, the rock deposits in this study area meet this requirement.

CaO the major constituent obtained in the study is good as alkali in the production of biodiesel (Kouzu et al., 2008). It is also used in petroleum as water detector paste, mixed with phenolphthalein. It has been used to regenerate sodium carbonate in chemical recovery at Kraft pulp mills and the Demsa sample area deposits can be used in textile dyeing because it meets the requirement of $CaCO_3$ with greater than 94% and Al_2O_3 plus Fe_2O_3 not more than 3% Duncan (1963). It also qualifies for use as flux in steel industry for its high $CaCO_3$ content and less than 5% SiO_2 with less than 0.1% sulphur content. While the deposits in Borrong, Bange and Demsa with total carbonates ($MgCO_3$ and $CaCO_3$) of above 85% can be used in agriculture. For use in flue gas desulphurization (FGD) the deposit in Demsa can be utilized with $CaCO_3$ grade of not less than 90% (NERC 1992). For use as lubricant, $CaCO_3$ with less than 92.60% is required Duncan (1963), then Demsa, Murgarang, Bange and Borrong fall in this category.

The deposits in the six locations are all good for concrete aggregate and road base (ASTM, 1976). Whereas the deposit in these locations may not find relevance in glass manufacture, refractories and chemical production, sugar refining and soda ash manufacture all because of the high purity demand of the $CaCO_3$ content which should not be below 98% (NERC, 1992), however it can be used in ceramics with more than 79% $CaCO_3$ and allowed percentages of Al_2O_3, SiO_2, and Fe_2O_3 (Lee, 2008).

Conclusions

The grade of limestone obtained in Demsa local government study area can be harnessed for Portland cement production since the percentage carbonate content varies from plant to plant (Duncan 1963). It can be used as dimension stones and for ceramic production, used in putty making, sealing, vinyl floor covering, carpet backing, adhesive and asphaltic products. The limestone from this study area meets the ISO standard for use as filler in paper, plastic and paper coating (Agnello, 2003).
The rocks from Pudan and Kadumon can find application in chemical industry as source of magnesium and in chrome-based product because of the elevated MgO content. They can be used in agriculture for magnesium deficiency compensation and in soil neutralization for farming purpose (Bassey, 2011).They can serve as good aggregate in cement (British Standard Institute, 1983).

The findings reveal the order thus CaO > SiO_2 > Al_2O_3 > Fe_2O > others, in four locations and the composition shows $CaCO_3$ content ranging from 73.79 ± 0.02% to 96.28 ± 0.02% with an average of 86.69 ± 0.10% calcite. Meanwhile the order of SiO_2 > CaO > Al_2O_3 > MgO > Fe_2O_3 > others, are in two locations with 29.64 ± 0.01 and 33.75±0.01% $CaCO_3$. The minor oxides are in quantities below 3% and LOI ranging from 10.00± 0.04% to 34.50 ± 0.2%.

RECOMMENDATION

It recommended that this type of researches be carried out in all parts of the state in order to let the indigenes be informed and enhanced to use their environment for their benefit.

AUTHORES` DECLARATION AND APPROVAL

We declare that this research is an original design by our research team published in Direct Research Journal of Chemistry and Material Science (DRCMS) and approved by us as not being considered elsewhere.

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