Geochemical Quality Assessment of Limestone of the Kanawa Member of Pindiga Formation exposed at Ashaka Quarry, Gongola Basin, NE Nigeria

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Abstract

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The limestone of the Kanawa Member of Pindiga Formation from the Gongola Basin within the Upper Cretaceous Series form part of the limestone deposit of Ashaka Quarry which is characterized by occurrence of several sedimentary successions. The study is based on the geochemical composition of 8 samples obtained from the mining site. Geochemical analysis shows that calcium oxide (CaO) has the highest concentration with an average value of 78.67%, followed by silica which has10.40%, the least is Na₂O which relatively has 0.0%. MgO has low values indicating that the calcite is principally the dominant carbonate. Limestone Saturation Factor (L.S.F), Alumina Ratio (A.R), and Silica Ratio (SR) values are relatively suitable for the manufacture of Portland cement. Fe_2O_3 which has an average value of 3.23% indicates low oxidizing conditions and that pH of the water was not favourable for formation of Iron (III) oxide. Low alumina (Al₂O₃) probably reflects low energy environment. It can be concluded that, the limestone samples collected and analyzed geochemical investigation are suitable to good for Portland cement manufacturing.

Keywords: Geochemical Quality, Limestone, Kanawa Member, Ashaka Quarry and Gongola Basin

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I. Introduction

Limestones are one of the most important of all the sedimentary rocks. Limestones are composed mostly of the calcite {(CaCO₃), Nouraddine Bouazza *et al.*, 2016}. They may also contain some other carbonate minerals and several non- carbonate impurities. Limestones are the raw materials widely used, although the limestone is the first raw materials for cement making industry where chemical properties are important. Portland cement is produced by calcining finely ground raw meal consisting of a mixture of about 75% limestone and 25% clay, at about 1450° C in a rotary kiln to form a calcium silicate clinker which is then ground and mixed with a small amount of gypsum which acts as a setting retardant. The compositional chemistry of cement depends largely on geochemistry of its raw materials i.e. limestone. Approximately 75% of the cement raw materials consist of lime (CaO) – bearing material (Lea, 1970). The Nigerian cement industry is a major player in the development of the country because growing needs for cementing products for the construction of buildings and communication infrastructures are considerable. Limestone investigation was conceded out of purpose, its chemical composition to determine its quality for the manufacture of cement. Portland cement clinker is a hydraulic mineral which must be composed of at least two- thirds by mass of calcium silicate [(CaO)₃. SiO₂], [(CaO)₂. SiO₂], containing the remaining part iron oxide (Fe₂O₃), aluminium oxide (Al₂O₃) and other oxides.

The mass ratio $(CaO)/(SiO_2)$ should not be less than two according to (Nouraddine Bouazza *et al.*, 2016). Magnesium oxide (MgO) must not exceed 5% by mass. Evaluation of limestone deposits for cement manufacturing involves study of geological setting and determination of the physical, mechanical, mineralogical and chemical properties of the stone.

Geology

The study area is a limestone quarry of the cement plant in Ashaka, Gongola Basin in Gombe State and belongs to the Kanawa Member of Pindiga Formation, located within the "Dumbulwa Bage High" of Zaborski *et al.*, (1997). Regionally, the geology of the study area falls within the Benue Trough which is linear stretch of sedimentary basin trending **NE-SE** direction. It stretches from Niger-Delta around Onitsha through Makurdi following the course River Benue up to Gombe and Yola areas (Kogbe, 1976). The trough is flank to the west

and east by basement complex bounded on the SW and SE respectively by the Benue and Calabar flank. In the north, it is separated from Chad Basin by Zambuk ridge.



Figure 1: Geological map of Nigeria showing the location of the study area (After Obaje *et al.*, 1999)

The Upper Benue Trough which is the North eastern "Y" shaped part of the basin, is subdivided into three groups, the Yola Garau branch trending **WNW-ESE**, the Gongola branch and Muri Lamurde domain trending N55⁰E, the Middle Benue Trough and found in the SW. The Benue Trough is occupied by the Upper Cretaceous sediments of 600m thick; the sediments range from Albian to Maastrichtian. The sediments are folded predominantly **NE-SW** axis and faults also exist. The origin and tectonic history of the trough is associated with breakup of Africa and America plates and the formations of south Atlantic (Benkhelil, 1989; Freeth, 1990). The Upper Benue Trough comprises the area extending from Bashar- Mutum Biyu line in the south to as far as the "Dumbulwa Bage High" of Zaborski *et al.* (1997) in the north. The "Dumbulwa Bage High" is an anticlinal structure that separates the Gongola Basin from the Bornu Basin. An early study of the Upper Benue Trough and the southern Chad Basin was carried out by numerous researchers such as (Falconer, 1911; Jones, 1932; Raeburn and Jones, 1934; and Barber *et al.*, 1954). Carter *et al.* (1963) undertook a regional study covered by Geological Survey of Nigeria 1:250,000 Series Map Sheets 25 (Potiskum), 36 (Gombe) and 47 (Lau), and provided the basis for all later works. The Upper Benue Trough has become known and has been remapped by several researchers (e.g. Aliix, 1983; Benkhelil, 1985, 1986, 1988; Popoff, 1988; Guiraud, 1989, 1991, 1993 and Zaborski *et al.*, 1997) and documented its structural framework.

The Cretaceous succession in the Upper Benue Trough comprises of Early Cretaceous succession. Late Cretaceous thermo- tectonic sag condition prevailed, while sedimentation processes was strongly influenced by transgressive- regression phase. The Upper Cretaceous may be divisible into discrete pre- Santonian and Campano- Maastrichtian parts; the Latter was deposited during a renewed phase of rifting (Zaborski *et al.*, 1997). The Upper Benue Trough includes an E-W trending Yola arm and an N- S trending Gongola Basin. The continental Bima Group comprises of the oldest sediments in the Upper Benue Trough which directly overlie the crystalline basement rocks. Principally, the reference section is to the south in Lamurde Anticline, where

Carter *et al.* (1963) and Allix (1983) gave the description of the sequences exposed and recognized a three subdivision. Further description of the Bima Group was also presented by Popoff *et al.* (1986), but comprehensive description of the Bima Group was done by Guiraud (1990a; and 1990b) into three as:

---- the "Upper Bima Sandstone" ("B³"), fairly arenaceous relatively mature, fine to coarse- grained sandstone with planar, convolute, and overturned cross- beds.

---- the "Middle Bima Sandstone" ("B²"), widely distributed, trough and tabular cross- bedding characterizes the sandstones, while clays and palaeosols also occur in the loos of individual cycles with overall thickness in some beds from 100m to 500m (Zaborski, 1998).

---- the "Lower Bima Sandstone" ("B¹"), highly variable with an overall thickness of 0 to over 1500m, lacustrine deposits with interbedded clays, fine- grained sandstones and calcareous sandstones. The name "Yolde Formation" was first proposed by Carter *et al.* (1963) for "transition beds" recognized earlier by Falconer (1911) between the Bima Group and Pindiga Formation. A type section was recognized in the Yolde Stream, western part of Yola arm. Zaborski *et al.* (1998) reported that the Yolde Formation gives rise to a subdued topography often with a sparse vegetation cover. The formation has feldspathic sandstones mostly coarse- grained and cross- bedded and grey mudstones. Bioturbations (Planolites) is common towards the top while groove marks are present on some beds (Zaborski *et al.*, 1997). The Pindiga Formation makes up the greater part of the Upper Cretaceous deposits in the Upper Benue Trough. Carter *et al.* (1963) referred age-equivalent beds in Gongola Basin to the "Gongila Formation" which is made up of a lower limestone- shale member and an upper sandstone- shale member, and to the "Fika Shales" for the overlying argillaceous beds. Zaborski *et al.* (1997) have characteristically described the Pindiga Formation to be best understood as consisting five members;

----- above, Fika Member, being the equivalent of the "Fika Shales" of Carter *et al.* (1963) and upper, shaly part of the Pindiga Formation.

----- the Dumbulwa Member, being probable equivalent of the upper, sandstone- shale member of the "Gongila Formation" of Carter *et al.* (1963).

----- the Deba Fulani Member, a previously unrecognized unit.

----- the Gulani Member, being the "Gulani Sandstone" of Carter et al. (1963).

----- below, the Kanawa Member, being the "Kanawa Formation" of Thompson (1958) and the lower, shalelimestone members of the "Pindiga Formation" and "Gongila Formation" of Carter *et al.* (1963). The Gombe Sandstone is restricted to the western part of the Gongola Basin. It weathers to produce a ferruginous capping. There is a marked angular unconformity between the Gombe and the Kerri- Kerri Formation. Passing upward, the sandstone beds become more persistent and make up the greater part of what is here termed the "bedded facies". Post- Cretaceous rocks of the Gongola Basin are concealed to the west by the Kerri- Kerri Formation and to the extreme east by the Biu Plateau Basalts (Zaborski *et al.*, 1997). It consists of coarse grained arkosic sands and grits with interbeds of sandy gravel, minor clays, silts and fine- grained members also occur (Thompson, 1958).

The Upper Benue Trough includes an E-W trending Yola arm and N-S trending Gongola arm. A series of N-S to NNE-SSW trending faults controls the trends of the Gongola Basin (Zaborski *et al.*, 1997).





Figure 2: Lithostratigraphic subdivision of the Gongola Basin (After Zaborski et al., 1997)

II. Materials and Methods

Geochemical Analysis

About eight (8) limestone samples were collected at different stratigraphic locations along the sampled successions of the Kanawa Member (Fig. 1). The samples collected during the field work were taken to laboratory for analysis. Geochemical analysis of major oxides was carried out using X- ray fluorescence (XRF) at the Centre for dry Land Agriculture, Bayero University, Kano. The analytical procedure was adopted from...

III. Results and Discussions

Table 1 shows the concentration of some selected major oxides analysis of limestone of the Kanawa Member of Pindiga Formation collected from Ashaka Quarry site for quality assessment. Figures 3 and 4 are distribution of major oxides showing peaks of concentrations, calcium oxide has the overall higher peaks as always been the case, this evident because it is always the dominant element for most limestones composition.

Г	Table 1: Co	oncentrat	tion of m	ajor oxides	s of limesto	one {all ox	ides are in	percentag	e (%)}

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Sample N0.	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	Na ₂ O	MnO	TiO ₂	K ₂ O	SO ₃
L_1S_2	2.77	0.98	1.07	93.82	0.0	0.0	0.51	0.06	0.24	0.17
L_2S_2	12.61	4.99	3.84	73.87	0.8	0.0	0.27	0.57	1.66	0.86
L_3S_2	11.58	3.85	2.47	78.62	0.8	0.0	0.60	0.44	0.60	0.76
L_4S_2	16.01	5.60	4.07	69.63	0.9	0.0	0.25	0.58	1.63	0.85
L_5S_2	12.78	5.22	4.02	73.10	0.8	0.0	0.25	0.56	1.68	1.06
L_6S_2	13.42	5.29	4.24	71.90	0.9	0.0	0.25	0.61	1.83	1.00
L_7S_2	6.67	2.61	2.26	86.52	0.0	0.0	0.44	0.25	0.57	0.39
L_8S_2	7.43	3.56	3.93	81.97	0.7	0.0	0.53	0.28	0.43	0.96

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Average 10.40 4.01 3.23 78.67 0.61 0.0 0.38 0.41	1.08	0.75

The facies is massive gray and crystalline in appearance. It is characterized by different chemical composition in (Table 1). SiO₂ range from 2.77 to 16.01% with an average of 10.40%, Al₂O₃ range from 0.98 to 5.60% with an average of 4.01%, Fe₂O₃ range from 1.07 to 4.24% with an average 3.23%, CaO range from 69.63 to 93.82% with an of 78.67%, MgO range from 0.0 to 0.9% with an average of 0.61%, Na₂O has 0.0% in all the analyzed samples, MnO range from 0.25 to 0.53% with an average of 0.38%, TiO₂ range from 0.06 to 0.61% with an of 0.41%, K₂O range from 0.24 to 1.83% with an average of 1.08% and SO₃ range from 0.17 to 1.06% with an average of 0.75%.



Fig. 3. Plot of concentration of major oxides



Fig. 4. Plot of average concentration of major oxides

Quality of Limestone of Ashaka Quarry for cement Production

From the chemical composition of limestone in the study area (Table 1), it is evident that for the production of Portland cement, some quantity of clay, sand and iron must be added to compensate for the percentage of silica, alumina, and iron oxides for suitable limestones. According Nouraddine Bouazza *et al.*, (2016) the content of volatile components (K_2O , Na_2O and SO_3) is low in all samples that will not have a meaningful effect on the final quality of the cement produced or on the manufacturing process.

Samples L_1S_2 , L_6S_2 and L_8S_2 have the highest concentration of CaO which makes it of great quality (Fig. 3 and 4). Great content of alumina and silica makes it more important for making high strength Portland cement and

can result in the reduction of clay. The overall results showed that CaO is the dominant constituent of the limestone which is due to the fact that is primarily calcite (Pettijohn, 1975) and this support the suitability of limestone for cement production.

MgO has low values which signify purely calcite process. Silica has the highest concentration of noncarbonate detritus as silt, sand and siliceous spicules or chert is maximal. It is an indicator that the Dumbulwa Member of same formation has proximal effect on the limestone. Fe_2O_3 are generally low which suggest a low oxidizing agent effect on the depositional environments and suggest that the pH of the water as well as redox potential of the environment do not favour the precipitation of iron (III) or iron (V) and that the oxides thus leached away (Brand, 1983; Adepoju *et al.*, 2012).

It is also observed that some samples with low lime content relatively have high silica and other variables higher in composition. Al_2O_3 , Fe_2O_3 and significant amount of SiO₂ are dominant amongst the oxides which can be a reflection of the presence of some non- carbonate detritus which can cause contamination. Such values in some facies have been reported by earlier by (Adepoju *et al.*, 2012). Oxides such as CaO, SiO₂, Al_2O_3 , K_2O and Fe_2O_3 are preferentially enriched (Fig. 3 and 4). High silica content could be probably due to incorporation of highly siliceous shells, continental influx of silica as well as precipitation of SiO₂ from solution.

Production Quality of Ashaka Quarry Limestone

Limestone is an indispensable raw material in the manufacturing industries. Three major factors of chemical ratios should be taken into consideration for cement clinker of appropriate composition; Limestone Saturation Factor (LSF), Silica Ratio (SR) and Alumina Ration (AR). Adepoju *et al.* (2012) stated that the LSF is the most important because it determines the CaO that can be combined in the mix. Limestone and shale are mixed in the ration 4:1 and fired in a rotary kiln to produce clinker, which is responsible for strength in cement. Limestone with 75%- 85% carbonate is suitable, while those that have 35%- 65% carbonate is good for manufacture of Portland cement. Therefore, the geochemical data obtained for limestone of the study area can be said to be of suitable to good quality for the production of cement.

IV. Conclusion

The investigation carried out showed that calcium oxide (CaO) is the dominant element in the analyzed oxides of the limestone facies which is believed to be the primary major constituent and supports the suitability of limestone for cement production. The non- carbonate actors which present in considerable amount also plays certain roles in the production of cement. The analysis finally reveals that the limestone of the Ashaka Quarry is relatively of high grade for the manufacture of cement.

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