CHEMICAL ASSESSMENT AND INDUSTRIAL QUALITY OF GONGILA LIMESTONE, GONGOLA BASIN NIGERIA

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ABSTRACT: The limestone facies of the Gongila Formation constitute an important sedimentary unit in the Gongola Basin. At Ashaka Cement quarry, where the limestone is well exposed and being worked for cement manufacturing, logging and sampling of the limestone beds were carried out and samples selected for geochemical analysis. The chemical composition of ten limestone samples provides insight into the industrial quality of the limestone and environmental effects of some of the associated elements in the study area. Chemical analysis of the limestone shows high CaO (43.06%) content but low MgO (0.70 %) indicating that calcite is the principal carbonate mineral. The low MgO suggests lack of dolomitization process. The limestone saturation factor L.S.F, A.R and S.R values indicate a moderate purity limestone that is suitable for the manufacture of Portland cement. Fe_2O_3 with average of 2.01% indicates low oxidizing conditions and that the pH of the water was not favourable for formation of Iron III oxides. Low alumina (Al_2O_3 4.36%) probably reflects low energy environment. The concentration of level of some toxic Trace elements and heavy metals were evaluated and their mean values (ppm); Pb (4.92), Ti (0.94), Cu (8.41), Rb (36.03), Ni (6.70), As (5.87), Cd (0.1), Sn (1.23), and Zn (15.9) are considered not too high to cause health hazard in the environment.

INTRODUCTION

In the Upper Benue Trough, two sub-basins, the N/S trending Gongola and the E-W trending Yola Basins are distinctly delineated (Fig. 1). The earliest sediments consist of the Aptian-Albian Bima Sandstone which overlies the Precambrian-Lower Paleozoic basement complex. Gongila Formation is one of the many sedimentary carbonate bearing Formations in the Gongola Basin deposited during the Mid- Cretaceous worldwide transgression (Fig. 2). The Formation is well exposed in the limestone quarry of the Ashaka Cement Factory at Ashaka village in Gombe State, north eastern Nigeria (Obaje *et al*, 2000) and was described as Kanawa Member and interpreted as outer shelf marine sequences (Zaborski *et al.*, 1997). The Formation was first named by Carter *et al* (1963) to distinguish it from the almost similar Pindiga Formation on the ‘Zambuk Ridge’. The Formation is lithologically characterized by calcareous limestones intercalated with shales and minor sandstones.

Popoff *et al*., (1986), Zarboski *et al*., (1997), Obi (1998) and Obaje *et al.* (2000), Ojo and Akande, (2000, 2001) and Ojo, (2004) have variously carried out studies on aspects of the stratigraphy, origin, depositional environment and geological significance of the Gongila Formation. However, despite these studies, none has focused on the industrial quality and environmental evaluation of the trace and rare earth elements in this cement production area. Trace elements are elements whose concentrations are less than 0.1% in geological materials like soils, water, rocks and plants. Examples of such trace elements particularly the toxic ones are Cd, Hg, V, As and Pb. All trace elements are toxic if ingested or inhaled at sufficiently high levels for long enough periods of time (Appleton *et al.*, 1996). Their presence in geological materials above the background values could pose some threat to the well being of consumers (Adriano *et al.*, 2004).

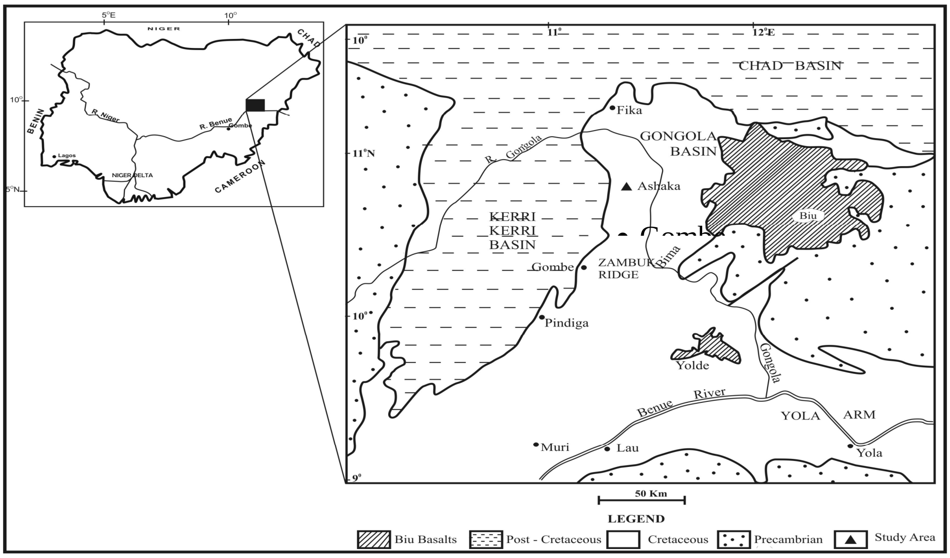

Fig. 1: The location map of Ashaka quarry with inset (Nigeria).

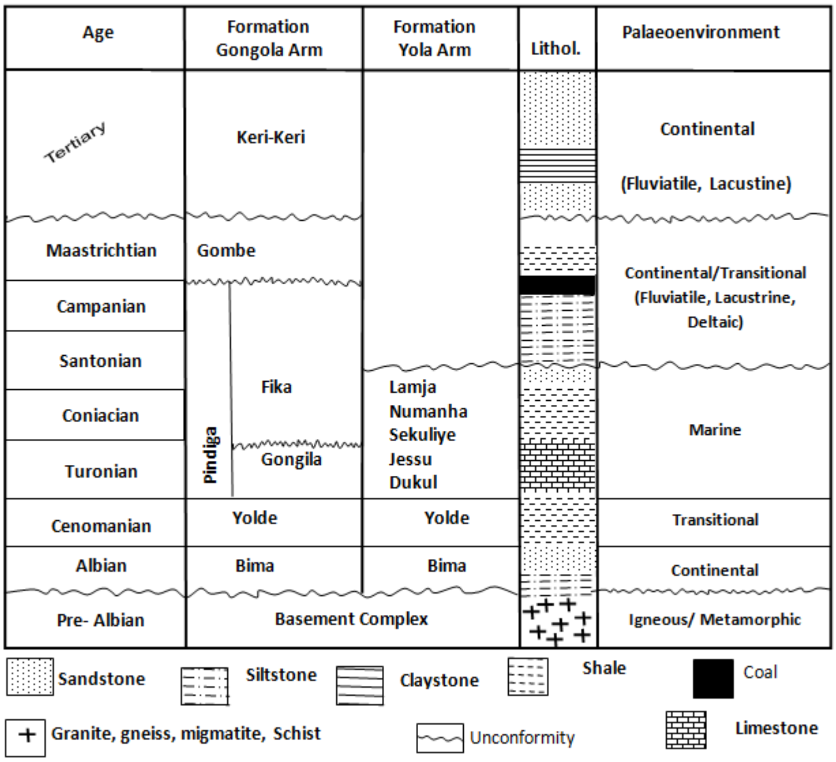

Fig. 2: Geological division of the Benue Trough in Nigeria. (Modified after Obaje and Abaa, 1996)

MATERIALS AND METHOD

The method involved detailed mapping of the Gongila Formation exposed at Ashaka Cement Quarry at Ashaka. The lithologies encountered at each location were properly identified, measured and documented. Fresh samples of each lithology were also collected, sealed in sample bags and labeled properly. Ten samples of the limestone were analysed using X-Ray Fluorescence (XRF) and standard Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) methods at Acme Laboratory Canada.

RESULTS AND DISCUSSION

Field Occurrence of the Limestone and Depositional Setting

In the entire quarry, the thickest section of the Gongila Formation is about 28.36 meters thick (Fig. 3). The basal part is represented by limestone-shale alternation beds of about 1.0m thick; the limestone is very rich in the broken shell of pelecypod and bivalve while the overlain reddish-dark shale of about 0.5m has bands of gypsum. The alternating limestone-shale bed is overlain by sequence of shelly, micritic and light grey stylotized, indurated limestone beds that are rich in ammonite and broken shells of pelecypods, high-spired gastropod and bivalves. This passes into the middle part of the section with more beds of shale than limestone. Unlike the lower part that has higher deposit of limestone, in this mid part, an average thickness of shale is 0.6m, while the limestone bed has an average thickness of 0.1m. There is gradual increase in the amounts of ammonite and shells of faunas upward the section. At the topmost part of the section is sandstone that overly shale. This sandstone is about 4.0m and its lower part is white-yellowish, parallel laminated, trough cross, fine-medium grained while the sandstone at the top is a brownish, coarser type. At the top of the, the sandstone is cut across by fault that is already filled with reddish brown materials. The limestone and shale interbeds are interpreted as deposits of marine transgression (Ojo, 2004) while the sandstone represents a regressive marine phase.

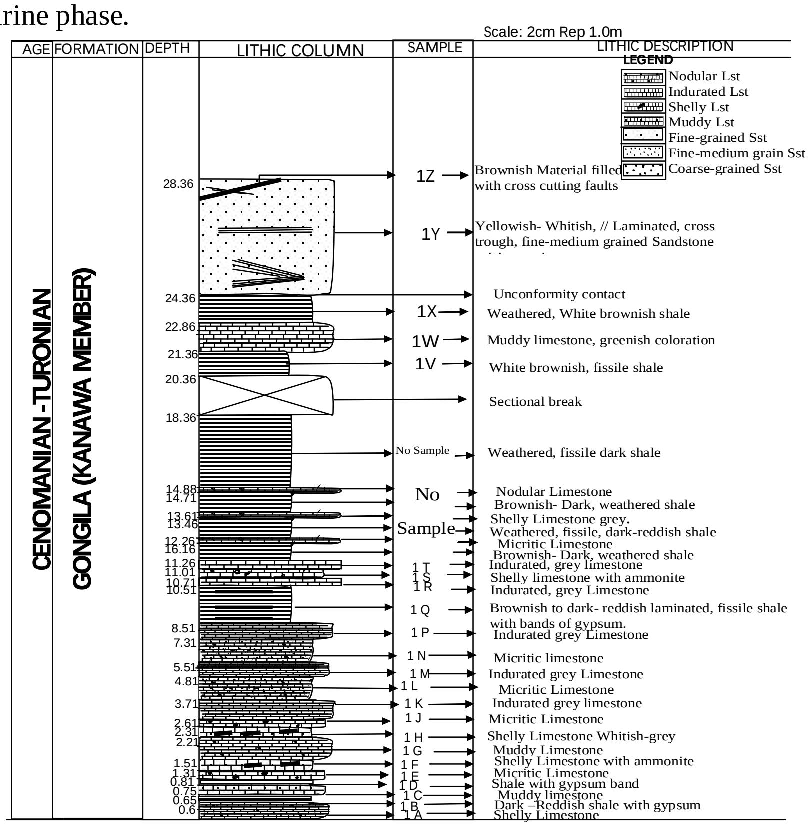

Fig. 3: Lithologic section of Gongila Formation exposed at the Ashaka Cement Quarry (ASKQ1). Elevation at bottom=290.3m, Long. =N$10^0 56^1 100^{11}$. Lat. =E$11^0 27^1 278^{11}$. Elevation at the top=303.6m.

Major Elements Distribution

Bulk chemical analyses of the major elements confirmed that the predominant mineral within the quarry is calcite. The geochemical assay of ten samples of limestone shows Calcium Oxide (CaO) contents ranging from 35.96% to 54.19% (averaging 43.06%) (Table 1).

Table 1: Major Oxide composition (%) of Gongila Formation Limestone at Ashaka

Sample No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO2	SiO_2/Al_2O_3
ASQ1C	12.8	4.29	1.58	43.0	0.78	0.18	0.65	0.08	0.2	2.98
ASQ1F	11.0	4.59	1.9	43.93	0.7	0.07	0.53	0.06	0.21	2.40
ASQ1H	18.8	6.03	2.66	37.64	0.66	0.05	1.19	0.11	0.3	3.12
ASQ1J	18.5	5.13	1.76	38.96	0.64	0.06	1.33	0.09	0.25	3.61
ASQ1M	1.2	0.43	0.8	54.19	0.39	<0.01	0.05	0.36	0.02	2.80
ASQ1N	13.4	5.41	2.02	41.53	0.6	0.05	0.6	0.1	0.27	2.48
ASQ1P	6.0	2.41	1.09	49.25	0.72	0.05	0.19	0.21	0.11	2.49
ASQ1S	14.6	5.69	3.15	36.58	0.77	0.07	0.65	0.13	0.33	2.57
ASQ1T	5.3	2.35	1.62	49.6	0.84	0.03	0.14	0.18	0.12	2.26
ASQ1W	18.1	7.3	3.52	35.96	0.92	0.07	0.6	0.17	0.37	2.48
Mean	11.97	4.36	2.01	43.06	0.70	0.06	0.59	0.15	0.22	2.72

The results show that calcium oxide (CaO) is the dominant constituent of the limestone which is due to the fact that the limestone is primarily calcite (Pettijohn, 1975) and this supports the suitability of limestone of this deposit for cement production. Magnesium Oxide (MgO) has value ranges from 0.39% to 0.92% (averaging 0.70%) and this lower value also supports/signifies purely calcite process. The percentage of Silicon (SiO_2) is fairly high as it is ranges from 1.20% to 18.80% (averaging 11.97%). This signifies that the presence of non-carbonate detritus such as silt or sand, siliceous spicules or chert is maximal in the overlying shale unit. It is also an indication that the lower sandstone of Bima Formation has pronounced effect on the limestone. Fe_2O_3 values are generally low ranges from 0.80% to 3.52% with an average of 2.01% and this suggests a low oxidizing effect in the depositional environment. The low values indicates that the depositional environment is a reducing type and suggest that the pH of the water as well as the redox potential of the environment do not favour the precipitation of Iron (III) to Iron (II) and that the oxides is thus leached away (Brand, 1983).

The ratio of the SiO_2 to Al_2O_3 which is used to determine the grains constituent is generally low with an average of 2.72%. This shows that the limestone is composed of little silt size grains. The low alumina contents are also an indication of a low energy environment. The appreciable mean values of SiO_2, Al_2O_3 and K_2O from the samples suggest the presence of detritial materials including silt size (grains) as impurities and indicate serious contamination by quartz and shaly materials (Greensmith, 1978).

The Al_2O_3, Fe_2O_3 and significant amount of SiO_2 can be interpreted as a reflection of the presence of some non-carbonate detritus which could have caused the contamination. However, the CaO and MgO contents are lower at the base than the top of the Formation and this is probably a reflection of the sandy nature of this part of the formation.

Another observation is that the elements CaO, SiO_2, Al_2O_3 and Fe_2O_3 are preferentially enriched. It is also revealed from the analyses that the samples with lower lime content have significantly higher proportions of SiO_2 compared to those of the higher lime content. The high silica content could be adduced probably to incorporation of highly siliceous shells, continental influx of silica as well as precipitation of SiO_2 from the solution. However, there is also a mark correlation between the silica and the lime conflict. While there is an increase in silica content, there is corresponding decreasing in the lime content. Hence samples with lower lime content have higher proportions of SiO_2 compared to those of higher lime content compared to these of higher lime content. The higher LOI is due to water and CO_2.

Industrial Quality

Limestone is an invaluable raw material in the chemical industries. Considering the three major chemical ratios which are the raw mix proportioning material to ensure that a satisfactory cement clinker of right composition is formed; Limestone Saturation Factor (LSF), Silica Ratio (SR), Alumina Ratio (AR), L.S.F is the most important, because it determines the CaO that can be combined in the mix. In the cement-making industries, limestone and shale are mixed in a proportion of 4:1 and fired in a rotary kiln to produce clinker, which is responsible for strength in cement. In this study, the L.S.F is 98.12; S.R is 1.88, while the A.R is 2.17 (Table 2). The L.S.F, A.R and S.R fall in the normal range of chemical ratio used in the industry for production of quality Portland cement. International Portland cement standards specify that the LSF should be between 0.66 and 1.02 for cement clinker. Also, S.R should be between 1.50 to 4.00 and 1.4 to 3.5 for A.R. (Scott, 1984; Ogbazue, 1992).

Limestone is a versatile raw material as it belongs to various groups on the basis of usage and value. The soft and coral-rich varieties can be used in construction industry as low grade aggregates. High purity limestone is used in the metal and foundry industry for oxygen steel making and as flux for reduction of iron ore. In the glass industry, a specification of $CaCO_3$ (98.5%), Fe < 0.035% and very low organic matter content < 0.1 % is required for the production of colorless glass while in the chemical industry, limestone (with 95% CaO, 1% SiO_2, MgO < 1.5% and LOI < 3% are used for production of lime for steel industry (Anderrson and Vernon, 1971). The chemical composition of a carbonate rock is an important determinant of its use in the industry. Limestone with 75% - 85% carbonate is suitable (or water lime production) while those that have 35% - 65% carbonate is good for the manufacture of Portland cement.

Table 2: Some industrial parameter of the Limestones at Ashaka

Sample No	Limestone Saturation Factor (L.S.F)	Silica Ratio (S.R)	Alumina-Iron Ratio (Al-Fe)
ASQ1C	102.34	2.18	2.72
ASQ1F	117.03	1.69	2.42
ASQ1H	60.78	2.09	2.37
ASQ1J	65.90	2.69	2.91
ASQ1M	1122.94	0.98	0.54
ASQ1N	91.63	1.80	2.68
ASQ1P	241.42	1.71	2.21
ASQ1S	73.96	1.65	1.81
ASQ1T	265.06	1.34	1.45
ASQ1W	58.25	1.67	2.07
Mean	219.93	1.78	2.12

Limestone is used in liming acid soil for improved crop production. A lower threshold value of 32.20% CaO is required for the process (Rayer, 1979). Each of the analysed samples of Ashaka limestone transcends the minimum 32.20% value, and crushed to less than 4.00mm particle size and calcined to form lime, it would be useful in stabilizing acid soil for improvement of crop production. Particle size of between 3.00 to 8.00mm could also be made into poultry grit.

Generally, lime is the cheapest form of alkalis in the chemical industry. Its production in the lime kiln generates large quantities of CO_2 gas that could be annexed and utilized for refrigeration, brewing and fire extinguishing. Other chemicals that could be produced from the limestone are bleaching powder, carbide, ethyne and sodium carbonate. The assay meets the standard for glass manufacturing. The grey-coloured shelly limestone can be polished and made into attractive decorative stones. Its occurrence as large blocks devoid of cracks and joints with consistent patterns of colorations endowed by the shell fragments explains the suitability.

Also, the chemical composition is unable to meet the required standard for flux in the modern basic oxygen steel making industry. The highest value of 48.78% CaO in Ashaka is much lower than the required 95%. Loss on ignition and silica content far outstrip the maximum 3% and 1% maximum value respectively specified by Anderson and Vernon (1971).

Trace Elements and Evironmental Implications

Heavy metals are the main source of trace element toxicity in the environment because most organisms are not adapted to dealing with them when they occur locally at concentrations higher than the normal levels that can be tolerated in the alimentary canal during the ingestion of food and water and inhalation of dusts (Sharma and Sharma, 1997*)*. According to Xiu (1996), only ten elements can be considered to be essential to the proper functioning of the human body, deficiency of any of these elements poses health problems, while an excess of other elements may lead to toxicity and associated health problem.

Some elements are harmful to health and environment, though some trace and rare earth elements like Zn are essential for good health and development, are also dangerous to health and the environment if their concentration exceeds some limit (Hambidge *et al*., 1987; Wang *et al*., 1996; Adejumo *et al*., 1994). Olaleye and Oluyemi (2010) pointed out that the extent of contamination depends on location distances from the cement factory as well as the wind direction. But it is known that the concentration of the elements in the air decreases with the increase in distance from the plant while the toxic elements are usually enriched. So, the particulate emission from any industry mining this limestone must be closely monitored by all, (Oladeji, 1992).

Many minor and trace elements in carbonate rocks are known to be dangerous to health and environment. Amongst these are found in the limestone of the area with their value ranges and their equivalent mean values as; Pb (1.0-8.0; Av = 4.92), Ti (0.1-0.6; Av = 0.17), Cu (1.4-24.7; Av = 8.41), Rb (4.5-62.7; Av = 36.03), Ni (0.1-15.8; Av = 6.04), As (3.0-13.2; Av = 5.87), Cd (1.0), Sn (1.0-2.0; Av = 1.2), Ta (0.1-0.4; Av = 0.32), Sr (242.4-693.7; Av = 400.46) and Zn (3.0-30.0; Av = 15.9) (Table 3). The values of Cu, Ni, Pb and Cd were compared with those obtained from limestones in some parts of the world (Table 4) and they meet the level that does not constitute health hazard.

Table 3: Trace and rare earth elements (ppm) of the limestone value at Ashaka

Sample No	Cu	Rb	Ni	As	Pb	Sn	Ta	Sr	Zn	Cd
ASQ1C	24.7	25.8	3.4	3.0	5.5	1.0	0.2	410.8	16.0	<0.1
ASQ1F	9.8	31.2	8.4	5.9	5.4	1.0	0.4	565.2	14.0	<0.1
ASQ1H	8.8	59.9	9.0	5.0	6.5	2.0	0.4	305.4	23.0	<0.1
ASQ1J	6.8	54.1	4.7	3.0	5.6	1.0	0.4	693.7	15.0	<0.1
ASQ1M	1.4	4.5	<0.1	3.7	1.0	<1.0	<0.1	242.4	3.0	<0.1
ASQ1N	7.9	35.3	4.7	4.9	4.0	1.0	0.4	387.7	15.0	<0.1
ASQ1P	3.9	19.2	1.0	5.3	4.0	<1.0	0.2	344.8	10.0	<0.1
ASQ1S	7.8	48.8	11.8	13.2	6.6	1.0	0.5	348.8	22.0	<0.1
ASQ1T	4.1	18.8	1.5	5.4	2.6	<1.0	0.2	362.3	11.0	<0.1
ASQ1W	8.9	62.7	15.8	9.3	8.0	2.0	0.4	343.5	30.0	<0.1
Mean	8.41	36.03	6.70	5.87	4.92	1.23	0.34	400.46	15.90	<0.1

Table 4: Comparison of the mean value (ppm) of heavy metals of the limestone at Ashaka with other parts of the world

Elements (Heavy metals)	This study (Gongila Sediments)	Merian (1984)	Hungary (Xiangdong and Thorton, 1993)	England (Xiangdong and Thorton, 1993)	Global Value Krauskpof (1967)
Cu	13.23	4.0	75.0	50.0	5.5-50.0
Ni	9.4	15.0	40.0	30.0	7.0-68.0
Pb	12.17	5.0	100.0	50.0	2.0-5.7
Zn	21.47	23.0	-	-	20.0-90.0
Cd	<0.1	0.17	1.0	1.0	0.028-0.3

CONCLUSION

The results show that calcium oxide (CaO) is the dominant constituent of the limestone which is due to the fact that the limestone is primarily calcite and this supports the suitability of limestone of this deposit for cement production. The analysis indicates suitability in the production of Portland cement, lime utilizations for agricultural purposes, fillers in the construction works, and as major raw materials in the chemical industries. However, the values are found to be unsuitable for all-important fluxing in basic oxygen steel making and glass production, which requires high chemical purity and high strength.

The heavy metals concentration in the limestones is within the tolerable limit and does not constitute health risk to environment. The dust emitted from the limestone processing into cement may however require some evaluation for these metals.

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