
COMPARATIVE ASSESSMENT OF LIMESTONE RESOURCES OF GUYUK AND ASHAKA AREAS FOR INDUSTRIAL UTILIZATION

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ABSTRACT

Limestone samples from Guyuk and Ashaka areas were investigated for their suitability for cement production and other industrial purposes using X-Ray fluorescence spectrophotometer (XRF). The chemical compositions of the deposits from Guyuk and Ashaka areas were determined and compared. Twenty four limestone samples were collected from different localities of these areas for chemical analysis. Results of these areas were compared to each other for their industrial utilization. The chemical composition of limestone deposits of these two areas indicate that the deposits could be used for production of cement, refining of sugar, animal feeds, paper, ceramic and chemical industries. The calcium carbonate (CaCO₃) content was found to be in the range of 76.64-89.12, 77.76-89.98%, lime (CaO) 42.94-49.94, 42.80-50.40% and average percentage composition of SiO₂, 9.55, 11.07%, Al₂O₃, 2.96, 2.09%, Fe₂O₃, 3.37, 2.27%, MgO, 0.59, 0.70%, SO₃, 0.09, 0.29%, K₂O, 0.25, 0.34%, Na₂O, 0.06, 0.18%, mgCO₃, 1.23, 1.83%, Total carbonate, 83.46, 84.19 and L.O.1 37.49, 37.47% in Guyuk and Ashaka Areas respectively. Sample preparation for this analysis has been performed by grinding and pelletizing or fusion with stearic acid. The chemical analysis was carried out by X-Ray fluorescence spectrometer (XRF) at Ashaka cement industry PLC. Gombe State, Nigeria.

Keywords: Limestone, Cement, x-ray Fluorescence Spectrophotometer, Sedimentary rock.

INTRODUCTION

Limestone is a sedimentary rock which is chiefly composed of calcium carbonate. It is formed by the compaction of corals, plant or animal remains through the action of rivers, sea, wind and glaciers (Areola, et al, 1999). It is also formed by direct crystallization of carbonates with some impurities such as clay, sandstones and shale (Greensmith, 1979).

Limestone is important in the economic development of a country like Nigeria. It is the most widely utilized non-metallic raw material in Nigeria (Okeke, 1991). The largest use of limestone is in the manufacture of cement used in the construction industry (Wheeler, 1999). Limestone deposits are also primary raw materials for some manufacturing industries such as sugar, fertilizer and ceramics (Neville, 1992). Pig. Iron and glass (Kirk, 1982), chemicals (Agnello, 2003), fillers and extenders (Ofulume, 1988).

In Nigeria limestone occurrences are widespread. It is found in the north east and north west region where they serve as source of raw materials for Sokoto and Ashaka cement factories: Large deposits are also found in the middle belt and the south where again, they serve as source of raw materials for about ten cement factories (Nigeria Ministry of Solid Mineral Development, 2000).

Occurrence of interbedded limestone of the limestone shale series exposed at the base slope of longuda plateau has been reported (Opeloye, 1999), in the vicinity of Dukul, Falu, Sekuliye, and Kurniyi of Guyuk Local Government Area. Previous studies have indicated that extensive deposits of raw materials such as limestone shale, gypsum and clay exist which has not been utilized as raw material for any manufacturing process (Opeloye and Dio,1999). . These limestone are mainly composed of calcite, dolomite and subordinate amount of quartz,illites and koalinite(Areola et al,1999 ,Duda,1975)

A number of representative limestone samples were collected from these two areas Guyuk Adamawa state and Ashaka in Bajoga Local Government Area, Gombe State for evaluation by X-ray fluorescence Spectrometer to study their suitability for utilization in cements, sugar, glass, ceramics and chemical industries.

MATERIALS AND METHOD

SAMPLING

The method described by Grosby and Patel (1995) was adopted for sampling. Twelve samples of limestone each were collected from Guyuk and Ashaka Areas at intervals. Sampling points were space about one hundred (100m) meters apart for possible variations in their constituents. Small pieces of limestone were chiseled and hammered out which formed gross samples representative of the bulk materials. About fifty grams (50g) per sample were obtained in the two locations, which gave a total of twenty four (4) gross samples.

SAMPLE TREATMENT

The methods described by Pasypaiko and Vasina (1984), was adopted for the treatment of the samples. The samples collected were ground to pass through a + 150um Mesh sieve. The gross samples were mixed, coned and quartered to get representative portion from bulk material and were analyzed by instrumental methods (Artho and Kelly, 1998, Jenkins and Synder, 1976)

ANALYSIS USING X-RAY FLUORESECNCE SPECTROMETER

The X-ray fluorescence (XRF) spectrometry used is the high-resolution energy dispersive X-ray fluorescence (EDXRF) LAB X3500 model at Ashaka Cement Factory. The energy dispersive X-ray fluorescence system is made up of an excitation source, sample chamber, silicon (lithium) drifted detector, signal processing and recording system (Preamplifier), multi-channel analyzer (MCA) and Video Display Unit (VDU). A schematic diagram of EDXRF instrumental system is shown on (Figure 1).

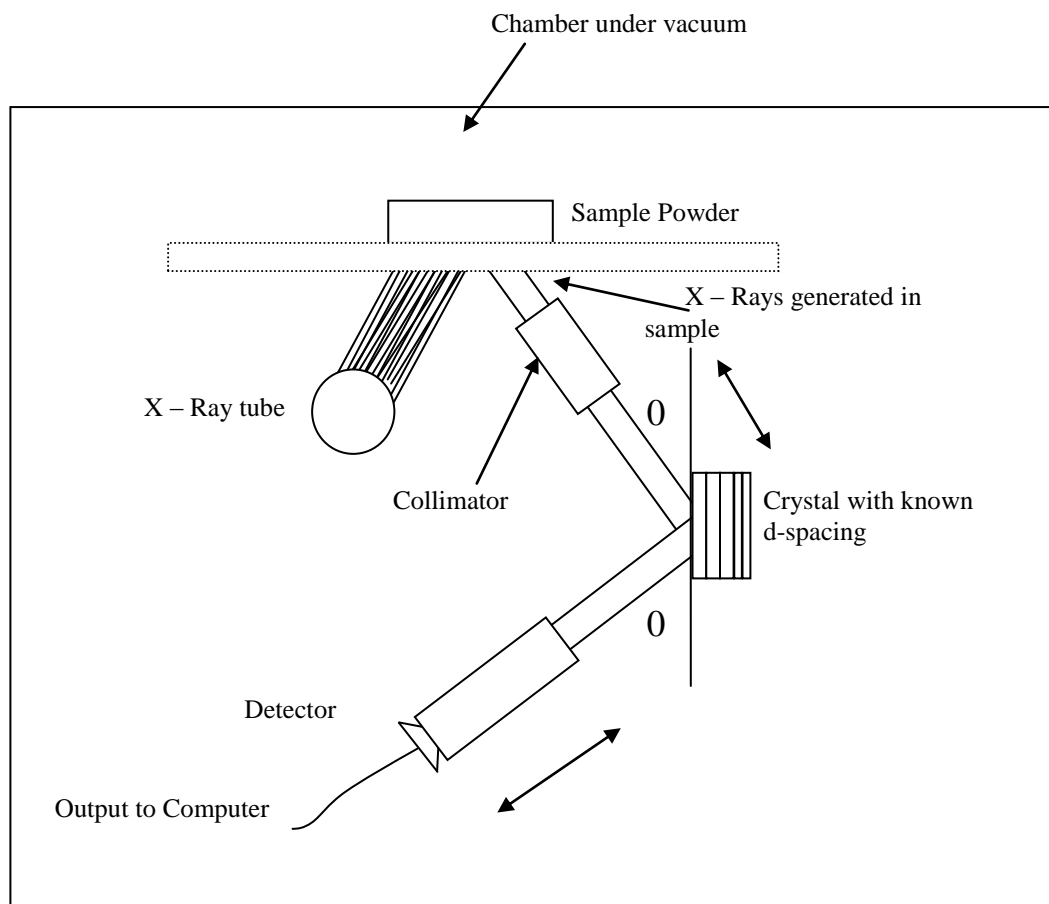


Figure1: A Schematic diagram of an Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry (Nelson, 2006).

DETERMINATION OF COMPONENTS

The procedure adopted was that described by Jenkins and Snyder,(1976)There were two steps involved; sample treatment and determination of the components using X-ray Fluorescence Spectrophotometer.

20g of the sample was weighed and 0.4g of stearic acid powder which acted as a binding acid or buffer so as not to allow the sample to disperse or scatter. The sample was transferred into a grinding mill barrette where it was ground enough into a fine powder.

The aluminum cup of the X-ray machine was half filled with a stearic acid powder as a backing material in order to avoid mineralogical and particle size effect. The aluminum cup was filled to capacity with the sample and the excess was struck off with a spatula in order to level the aluminum cup content.

The aluminum cup with the sample was then placed into a hydraulic pump vibrating compression machine at 200 KN for 10 seconds. The aluminum cup and the sample were pelletized, suitable for introduction into the XRF spectrometer. The process was repeated for all the samples studied.

Prior to the X-ray analyses, a standard sample (BCI, 1979) was used to calibrate the instrument. To start the analysis the aluminum cup with the samples was placed into the sample chambers and covered. Quantitative analysis was then selected from the spectrometer main menu, using the cursor. The programme desired was typed on PC screen and sample identity. The results were displayed on the PC screen and were printed out by the printer in percentage oxides of the elements.

RESULTS AND DISCUSION

The results of analysis for the chemical composition of limestone in Guyuk and Ashaka Areas are contained in table 1 and 2.

Table 1: chemical Composition of Limestone of Guyuk Area, Concentration (Wt % by X R F)

Sample No.	G-1	G-2	G-3	G-4	G-5	G-6	G-7	G-8	G-9	G-10	G -11	G-12	Range	Average
SiO ₂	12.56	11.74	9.38	9.75	7.20	9.27	9.97	7.95	7.47	7.71	10.25	11.40	7.20 - 12.56	9.55
Al ₂ O ₃	4.13	2.70	2.61	2.91	2.51	3.70	2.44	2.17	2.02	2.59	3.88	3.82	2.02 - 4.13	2.96
Fe ₂ O ₃	3.78	4.85	2.56	3.52	3.34	4.21	4.27	3.46	2.54	2.14	2.65	3.15	2.14 – 4.85	3.37
CaO	43.04	42.94	47.35	45.67	46.04	45.71	45.21	46.96	48.53	49.94	45.41	45.08	42.94 – 49.94	45.99
MgO	0.60	0.55	0.52	0.85	0.61	0.58	0.63	0.61	0.57	0.56	0.59	0.63	0.52 – 0.63	0.59
SO ₃	0.29	0.11	0.13	0.12	0.07	0.08	0.08	0.04	0.07	0.04	0.05	0.05	0.04 – 0.29	0.09
K ₂ O	0.36	0.31	0.28	0.25	0.19	0.32	0.15	0.13	0.23	0.17	0.29	0.27	0.13 – 0.36	0.25
Na ₂ O	0.05	0.04	0.05	0.06	0.08	0.05	0.06	0.05	0.05	0.06	0.07	0.07	0.04 - 0.07	0.06
CaCO ₃	76.83	76.64	84.51	81.52	82.17	83.37	80.70	83.80	86.62	89.12	81.04	80.45	76.64 - 89.12	82.23
MgCO ₃	1.26	1.16	1.09	1.22	1.27	1.22	1.33	1.29	1.19	1.18	1.23	1.31	1.09 -1.33	1.23
Total carbonate (CO ₃)	78.09	77.80	85.60	82.74	83.44	84.59	82.03	85.09	87.81	90.30	82.28	81.77	77.80 – 90.30	83.46
Moisture content	0.05	0.13	0.15	0.12	0.07	0.11	0.12	0.10	0.14	0.06	0.07	0.06	0.5 – 0.15	0.10
Loss on ignition (LOI)	35.17	34.78	38.20	37.00	37.24	37.95	36.61	37.91	39.07	41.27	36.97	37.74	34.78 – 41.27	37.49

Table 2: Chemical Composition of Limestone of Ashaka Area, Concentration (Wt % by X R F)

Sample No.	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	Range	Average
SiO ₂	13.73	12.29	13.11	8.10	8.94	11.74	14.06	13.26	14.86	8.84	7.31	6.60	6.60 – 14.86	11.07
Al ₂ O ₃	1.57	2.53	3.38	1.98	2.96	1.66	3.30	3.76	1.09	1.35	0.83	0.65	0.65 -3.76	2.09
Fe ₂ O ₃	1.63	2.41	5.40	2.58	2.98	1.60	3.17	4.97	0.86	0.85	0.47	0.35	0.35 -4.97	2.27
CaO	44.63	46.82	42.80	45.60	46.73	46.96	43.14	43.69	44.28	48.28	46.23	50.40	42.80 -50.40	45.79
MgO	0.44	0.56	0.87	0.90	0.73	0.44	0.89	0.83	0.76	0.90	0.47	0.66	0.44 -0.90	0.70
SO ₃	0.59	0.60	0.29	0.30	0.29	0.36	0.22	0.16	0.44	0.28	0.20	0.12	0.02 -0.60	0.29
K ₂ O	0.06	0.70	0.09	0.80	0.60	0.27	0.23	0.08	0.04	0.50	0.70	0.05	0.04 -0.70	0.34
Na ₂ O	0.15	0.60	0.08	0.50	0.40	0.08	0.65	0.04	0.59	0.03	0.06	0.07	0.03 – 0.59	0.18
CaCO ₃	78.95	80.12	77.76	83.93	84.66	29.18	81.24	79.28	82.18	86.43	83.40	89-.98	77.76 -89.98	82.35
MgCO ₃	2.13	1.88	2.01	1.91	2.03	2.29	1.07	1.24	1.82	1.09	2.08	1.19	1.07 -2.99	1.83
Total carbonate (CO ₃)	82.08	82.00	79.77	85.84	86.69	82.17	82.31	81.02	84.00	87.52	85.48	91.17	79.77 – 91.17	84.18
Moisture content	0.13	0.11	0.13	0.12	0.10	0.14	0.12	0.07	0.10	0.07	0.12	0.13	0.07 -0.14	0.11
Loss on ignition (LOI)	35.32	36.19	34.54	38.10	37.79	36.51	38.36	36.16	36.14	38.97	40.80	40.86	34.54 – 40.86	37.47

Limestone has a wide range of uses which are discussed in accordance with results obtained from these two areas, Guyuk and Ashaka Areas.

For these area chemical composition of the limestone are very consistent (Table1) and (Table2), indicating that these samples are very suitable for manufacture of cement. Guyuk limestone (Table 1) fully corresponds with the standard feed (SRF/1/1972), Ashaka cement plc and American Society For Testing and Materials (ASTM), specifications that is limestone suitable for cement production should have an average composition of lime (CaO) 43.12% magnesium oxide (MgO) 0.70%, Alumina (Al₂O₃) 3.43%, Iron oxide (Fe₂O₃) 2.66%, Silica (SiO₂) 13.26% and loss on ignition (L.O . I), 35.6% (BCI,1979,Conshohocken,1995). Lime content (CaO) in Guyuk area varies from 42.94-49.94% and Ashaka area 42.80 -50.40%. Results of the analysis of limestone of these areas indicated that they are suitable for cement production. Calcium carbonate content varies from 76.64-89.12% in Guyuk Area and 77.26-89.98% in Ashaka Area. (Table 1 and 2) .Generally, Ashaka limestone has high grade calcium carbonate (CaCO₃) content than Guyuk limestone. However, both are suitable for the manufacture of cement (Table 1 and 2). The results of the analysis indicated that the limestone can be used for sugar refining having magnesia content not more than 3% to precipitate colloidal impurities from juice.

Magnesium oxide (MgO) content of Guyuk and Ashaka Areas varies from 0.52-0.63% and 0.44-0.90% respectively (Table1 and 2).

Limestone with high calcium oxide (CaO) content, with less than 2% MgO is used for paper manufacturing (Agnello, 2003). Results of the analysis of both Guyuk area and Ashaka area are able to meet the requirement for this purpose.

The metallurgical industries used limestone as a flux in the production of pig-iron and non-ferrous metals, limestone used for the purpose must be for superior grade with SiO₂ and Al₂O₃ content less than 2% as rule as well as low sulphur and phosphorus content. These lime stones are recommended for these purposes (Neville, 1992).

Alumina (Al₂ O₃) in a combined state is an important constituent of cement in which it behaves as an acid (Lea and Desch,1976) . Alumina (Al₂O₃) content of Guyuk and Ashaka Area varies from 2.02-4.13% and 0.65-3.76% respectively. The limestone having higher silica (SiO₂) and (Fe₂O₃), which varies from 7.20-12.50% in Guyuk and 6.60-14.86% in Ashaka Areas, are not suitable for glass manufacture. The limestone may be used for ceramics as having more than 79% CaCO₃ with allowed percentages of Alkalis silica (Al₂O₃,SiO₂) and Fe₂O₃(Lee,2008). Alkalis are objectionable in cement as they enter in reaction with certain types of aggregates to produce products which expands and gives rise to cracking in concretes and mortar(Kurdowski,1974) . Alkalis present in the sample are lower than the objectionable levels for the use in cement industries.

CONCLUSION

The results of the investigation indicated that Guyuk limestone compares very well with Ashaka limestone for quality and industrial utilization. It shows that suitable quality and quantity of limestone exist in Guyuk for industrial uses.

Allowed percentage of SiO₂, Na₂O, K₂O, MgO, So₃ are found in the sample analyzed. Moderate percentage of Fe₂O₃ and Al₂O₃ in most of the sample permits its use in cement works and other industrial purposes.

The limestone deposit in Guyuk is suitable and in commercial quantity but is yet to be utilized. It can be used for cement production and other industrial purposes.

However, further study is recommended in Guyuk area to determine the economic feasibility and viability of these deposits for different industrial purposes to attract investors in this area.

This study is only a preliminary effort to spotlight the possible industrial uses of the resources available in this area.

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