

CHEMICAL ANALYSIS OF SOME NIGERIAN GYPSUM AND LIMESTONE SAMPLES UTILIZED BY A LEADING CEMENT MANUFACTURING INDUSTRY.

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(Received 15 August 2003; Revision accepted 23 September, 2003)

ABSTRACT

X-ray fluorescence analyzer (XRF) was employed in the analysis of some local and imported stocks of gypsum and limestone utilized by a leading cement manufacturing industry in Nigeria. In addition, the recycled dust standard reference samples were also analyzed along with the raw materials in question. The gypsum samples were found to have purity varying between 86.3% and 96.17% for both local and imported stocks. The limestone stock had purity of 42.2% to 95.39%, and these samples were obtained locally within and outside the factory location. Impurities detected at a measurable level included Na, K, Al, Si, Mg and S, and these were calculated as their respective oxides. The production economy of the industry was appraised with respect to total dependence on locally produced gypsum.

KEYWORDS: Gypsum, Limestone, Analysis, Purity, Impurity

INTRODUCTION

The use of cement in building industry dated back to the Roman Era when they made concrete consisting of broken stone with burnt limestone as binding medium (Microsoft Encarta Encyclopaedia Deluxe, 2003, Kirk-Orthner Encyclopaedia, 1992). This form of construction material was called "*Opus Caementum*". Later on, a term '*Cementum*' was used to denote that admixture of lime, brick dust and volcanic tuff (Kirk-Orthner Encycl., 1992, Stocchi, 1990, Austen, 1984). The lime imparted 'hydraulic' properties to this mixture by making it to set and harden under moist condition (Microsoft Encarta Encycl. Deluxe, 2003, Stocchi, 1990). Evidences of cement usage can be found in various Roman Architectures like 'the Pantheon'; a circular temple in Rome built around 120 A. D. (Microsoft Encarta Encycl. Deluxe, 2003, Kirk-Orthner Encycl. 1992). The development of cement was a continuous process over the ages until the present 'State-of-art' product available today was accomplished. This was through various innovation, blending and modification of the component materials. There are many patents of Portland cement, a typical example being the German Standard DIN1164 which defined cement as a finely ground hydraulic binding medium for mortar and concrete. This patent prescribed the constituents as compound of CaO and Fe₂O₃ formed by sintering or fusion (Microsoft Encarta Encycl. Deluxe, 2003). These components are usually derived from limestone, clay and gypsum.

The limestone and gypsum are the materials of subjective interest in this report.

Limestone, chemically CaCO₃, occurs globally and its application in building industry is a subject of historical interest. Other forms of limestone include dolomite, calcite, marble and quartz depending on their levels of purity. Saint Augustine in his book titled '*The City of God*' alluded to the use of limestone and its product during the Roman Era (St. Augustine, 1984). In his writing he explained how CaO assumed the name quicklime. In Nigeria, the occurrence of this mineral is widespread, and it's principally used for cement manufacturing. Popular sources include Yandev, Kalambaima, Ukpilla, Mfamosin, Ewekoro, Shagamu, Igbetti, Nkalagu and Shokoshoko. Nduji and Opara (1985) carried out the chemical analysis of this mineral in some deposits.

Gypsum, CaSO₄.2H₂O, also occurs widely in the country, particularly close to limestone deposits. Notable mines include those located in Bajoga and Ashaka areas of Gombe State, Fika in Yobe State, Goronyo in Sokoto State and Yandev in Benue State. Uses include the manufacture of building and surgical Plaster of Paris, clinker in cement industry, tiles and ceramics. Ajayi et. al., (2003) characterized the Sokoto and Gombe gypsum samples with short-lived nuclides of neutron activation analysis. However, the chemical information obtained was scanty. Hence, the need to accomplish this with x-ray fluorescence analysis.

X-ray fluorescence spectroscopy is a versatile, sample-nondestructive, multi-element

technique. Reported applications include the analysis of food, mineral, environmental and geological samples (Klockenkamper et al., 1992, Frank and Preiss, 1983, Adesina et al., 2003). In this analysis, the local samples as well as imported samples were analyzed using x-ray fluorescence analyzer (QXXRF) of the West African Portland Cement Industry, Shagamu, Nigeria. Other samples examined included various stocks of limestone as well as cement dust of certified concentration as reference materials.

MATERIALS AND METHODS

Samples

The samples employed in this analysis include the recycled dust reference samples DRPA – DRPI, local and imported gypsum and local limestone LOC 1 – LOC 12. The recycled dust DRPA – DRPI as well as the limestone samples LOC 1 – LOC 10 were all obtained from WAPCO, Shagamu, while limestone LOC 11 and LOC 12 were from Mfamosin mines in Cross River State. The gypsum samples S, G and B were respectively obtained from Sokoto, Gombe and Bauchi States of Nigeria. Samples T and iC were imported gypsum respectively from Thailand and presumably England the Blue Circle partner of the company.

Sample preparation

The samples; limestone, gypsum and standard reference samples were milled into

powder using agate mortar. 25 mg each of the samples was weighed into a crucible dried and cooled in a desiccator. 20.0 mg each of the dried samples was weighed and mixed with 0.80 g stearic acid for pellet making. The mixed sample was then transferred into a pellet cup containing 10.0 g of stearic acid. The resulting product was pressed into pellet with a 12-ton load Graseby T40 hydraulic auto press. The resulting pellet was transferred to X-ray Analyzer Model QX XRF.

X-ray Analyzer

X-ray Analyzer Model type QX XRF was used for this analysis. This equipment made different calibrations for the different samples used, and it was equipped with a dedicated computer for data handling and operations. Calibration software Method 4 was used for the gypsum samples while calibration software Method 5 was employed for limestone analysis. The prepared pellets were transferred to the sample holder for x-ray bombardment. The resulting secondary x-ray signals were obtained and processed for analysis using the appropriate data handling software of the system. For accuracy check, the certified standard reference samples were analyzed along with the real samples.

RESULTS AND DISCUSSIONS

The results of the x-ray fluorescence analysis accomplished with the X-ray Analyzer

Table 1: Analysis of Recycled Dust Standard Reference Samples.

Parameter	DRPA	DRPB	DRPC	DRPD	DRPE	DRPF	DRPG	DRPH	DRPI
Na ₂ O (%)	0.02	0.03	0.03	0.02	0.01	0.02	0.01	0.01	0.01
MgO (%)	0.68	0.68	0.68	0.54	0.52	0.54	0.40	0.40	0.38
Al ₂ O ₃ (%)	2.30	2.35	2.30	1.15	1.15	1.20	0.85	0.85	0.85
SiO ₂ (%)	9.95	10.0	9.90	3.85	3.90	3.95	3.15	3.20	3.10
SO ₃ (%)	35.2	35.1	35.3	40.9	41.1	40.9	40.2	40.0	40.6
K ₂ O (%)	0.23	0.23	0.23	0.10	0.10	0.10	0.07	0.07	0.07
CaO (%)	31.2	31.1	31.1	31.3	31.3	31.3	32.9	32.9	32.7
Fe ₂ O ₃ (%)	1.4	1.4	1.4	0.6	0.6	0.7	0.4	0.4	0.4
Purity (%)	75.7	75.57	76.0	88.06	88.41	88.06	88.54	86.04	87.33

Table 2: Analysis of Gypsum samples.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	Purity
B	0.02	0.54	1.55	3.85	40.96	0.10	31.30	0.60	88.06
G	0.00	0.56	1.56	5.08	40.15	0.13	29.45	0.59	86.32
S	0.1	0.54	1.19	4.00	40.00	0.15	30.20	0.49	86.00
T	0.00	0.57	0.14	0.37	44.73	0.01	32.36	0.01	96.17
IG	0.01	0.60	0.81	2.68	38.66	0.40	33.61	0.30	83.12

Concentrations in percentage per weight (%).

Table 3: Analysis of some local limestone samples.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	Purity
LOC 1	-	0.46	0.69	3.15	-	0.10	51.02	1.23	91.20
LOC 2	-	0.50	0.78	9.44	-	0.05	47.91	0.96	85.55
LOC 3	-	-	0.61	5.38	-	-	53.42	1.02	95.39
LOC 4	-	1.47	1.30	6.21	-	-	50.93	1.02	90.94
LOC 5	-	0.74	0.74	6.24	-	0.05	50.04	1.17	89.36
LOC 6	-	0.74	0.93	9.26	-	0.06	47.17	1.11	84.20
LOC 7	-	0.74	0.76	6.40	-	0.08	49.81	1.34	88.95
LOC 8	0.01	0.51	0.93	4.94	0.03	0.10	50.64	1.48	90.43
LOC 9	0.01	0.51	0.95	4.25	0.03	0.10	50.42	2.23	90.04
LOC 10	0.01	0.50	0.96	4.40	0.02	0.12	50.50	2.20	90.18
LOC 11	0.01	0.51	0.53	1.54	0.04	0.15	53.27	0.51	95.13
LOC 12	0.01	0.51	8.57	17.21	0.04	2.07	23.63	1.23	42.20

Concentrations in percentage per weight (%)

QX XRF are shown in Tables 1 – 3. The results in Table 1 convey the concentrations of oxide contents of the Recycled Dusts Standard Reference samples. Table 2 shows the analysis of gypsum samples while Table 3 contains the oxide profiles of the limestone samples. The concentrations of the metals were expressed as their respective oxides as required for the consumption of the cement industry.

Table 1 contains the results of the analysis of the recycled dust standard samples. The metals detected were expressed as the percentage of their respective oxides. The percentage purity ranging from 75.57% to 88.54% was calculated for each of the nine samples; DRPA –DRPI. The most pure being DRPG with purity of 88.54%, to 75.57% recorded in DRPB. These samples consisted mainly of CaO and SO₃, and these happen to be the main constituents of gypsum. Nsi and Shallsuku (2002) examined the pollution emanating from cement dust in Benue State. The recycled dust was often used as substitute for gypsum in the raw material assemblage particularly when there was an embargo on the importation of this commodity. This is a laudable waste management regime devised by this company. This was so because of the prohibitive cost of transporting gypsum from the mine depots in the northern parts of the country.

Five gypsum samples B, G, S, T and IG were analyzed and their concentrations are as shown in Table 2. B, G, S, T and IG respectively stand for Bauchi, Gombe, Sokoto, Thailand and WAPCO imported gypsum. The elements detected and measured and calculated as their respective oxides included Na, Mg, Al, Si, S, K Ca and Fe. The CaO content ranged between 29.45% for Gombe and 33.61% for imported sample IG. The silica SiO₃ content amounted to between 0.37% for T to 5.08% for the Gombe sample. Sulphur trioxide SO₃, another major

constituent ranged between 38.66% (IG) and 44.73% (T). The calculated percentage purity of gypsum samples ranged between 83.12% and 96.17%. The purest sample is Thailand sample, with the IG, another imported stock having the least purity. The relatively purest sample T had 0.00% Na₂O, 0.57% MgO, 0.14% Al₂O₃, 0.37% SiO₂, 44.73% SO₃, 0.01% K₂O, 32.36% CaO and 0.01% Fe₂O₃. Relatively, this sample had the least concentration of impurities like SiO₂, MgO, Na₂O, Al₂O₃ and Fe₂O₃. The brownish, mud-impregnated Sokoto Sample S expectedly had high alumina, silica, ferric oxide and sodium oxide contents. Gombe sample G equally had high alumina, silica and ferric oxide contents and the lowest value of CaO. The Bauchi sample B had a high purity next only to the Thailand sample T with equally high ferric oxide, silica and alumina contents. The imported gypsum sample IG being consumed by WAPCO ironically had lowest purity index of 83.12%, but with moderate concentrations of impurities like Na₂O, MgO, Al₂O₃, SiO₂, K₂O and Fe₂O₃.

Ten limestone samples within the WAPCO vicinity and two from Mfamosin mine near Calabar, Cross River State were examined and their results are as shown in Table 3. These samples were respectively labeled LOC 1 to LOC 10 for the WAPCO mines and LOC 11 and LOC 12 for the Mfamosin stocks. Sodium oxide and sulphur dioxide were not detected in measurable quantities in Samples LOC 1 to LOC 8, while the other four samples contained traces (0.01 – 0.04%) of these impurities. The purity of the limestone ranged from 42.20% (LOC 12) and 95.39 for LOC 3. The major component of CaO determined ranged from 23.63% for LOC 12 and 53.27% for LOC 11. Magnesium oxide, MgO, another component of limestone occurred in all the samples with concentration ranging between 0.46% (LOC 1) and 1.47% recorded for LOC 4. Similarly, alumina, Al₂O₃, a major component of

clay and an important raw material for cement also occurred in measurable concentration ranging from 0.53% for LOC 11 and 1.3% (LOC 4). Similarly, relatively higher silica contents were recorded for these samples compared to what generally obtained for gypsum (Table 2). LOC 12 from Mfamosin mine uniquely had the lowest purity and the highest concentrations of impurities like silica, alumina, potassium and ferric oxides. Nduji and Opara (1985) had earlier analyzed a number of local limestone samples excluding the Shagamu's lime. The parameters analyzed included CaO, MgO, Fe₂O₃ and purity as CaCO₃. The values obtained in this analysis compared favourably with what Nduji and Opara (1985) recorded for limestone. In fact, Mfamosin sample LOC 11 had a purity of 95.13% relative to 90.69% previously recorded by Nduji and Opara (1985). These samples were found to be suitable for the intended purpose of cement manufacturing.

The problem of gypsum supply to the consuming cement industries nationwide was peculiarly paramount in the period between 1994 and 2000, when the importation of this raw material was banned. Some industries with gypsum mines close by were able to adapt their manufacturing technologies to the local supplies, while other without such supplies had pay more to transporting gypsum from mines located about

1500 to 2000 kilometers away. Notable sources of gypsum were in Bauchi, Gombe and Yobe States which were close to Ashaka Cement Industry, Ashaka in Gombe State, and Goronyo in Sokoto State which supplies to the Cement Industry of Northern Nigeria, Kalambaima, in Sokoto State. These two companies had little or no problem with regards to gypsum; they had to blend both local imported stocks in their manufacturing processes. West African Portland Cement Company, WAPCO, initially had to obtain their supplies from the gypsum mines in the north at the rate of nine thousand five hundred Naira (N9, 500.00) per tonne relative to two thousand Naira (2,000.00) per tonne for imported stock (IG). A partial solution to this was the recycling of cement dust at a relatively lower cost of eight thousand five hundred Naira (N8, 500.00) per tonne. This obviously would add to the production cost. The recycling of dust was a laudable project as it would reduce the amount of dust being dispersed to the environment.

CONCLUSION

The analysis of some Nigerian limestone and gypsum samples was accomplished with x-ray fluorescence spectroscopy. Analysis of both local and foreign gypsum samples showed that

they compared well and they were appreciable pure for the intended purpose of cement manufacturing. In addition, the local gypsum had purity comparable with samples imported from Thailand and Britain. The manufacturing industries with nearby gypsum mines should be encouraged to use the local sources rather than imported, while others not so favoured can blend both imported and local gypsum raw materials. The local limestone stocks with exception of one out of twelve examined had purity above 83.3%. Ten of these samples were obtained from Shagamu's mine and these had certified purity above 83.3%. The recycled cement dust was found to be relatively rich in gypsum which the cement industry under review was using to augment imported and local supplies. The recycling of cement dust may be beneficial on the long run both for the environment and manufacturing economics.

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