

GLOBAL JOURNAL OF GEOLOGICAL SCIENCES VOL. 7 NO. 2 2009: 171 - 180
COPYRIGHT© BACHUDO SCIENCE CO. LTD PRINTED IN NIGERIA. ISSN 1596 – 6798

AN ASSESSMENT OF THE CALCINATION CHARACTERISTICS OF THE MFAMOSING LIMESTONE FOR QUALITY COMMERCIAL LIME PRODUCTION.

major carbonate body and is up to 450m thick. The basal lithofacies of the Mfamosing limestone is the stromatolitic boundstone which is up to 3m thick in places. The thickest lithofacies in the lower part of the carbonate bodies comprises a dolomitic sandy limestone. The middle lithofacies is mostly a fossiliferous algal boundstone with rhodoliths and lenses of oolitic

wackestone and packstone and is well displayed in the quarry (Fig. 2).

A chalkified limestone is at the top of the middle part. The upper part of Mfamosing limestone is a definitive oolitic packstone and grainstone microfacies though in places this top unit is an admixture of siliciclastics and carbonates with silt and fine sand lithologies.



Figure 1: Location of Limestone, Marble and Dolomite deposits in Nigeria (after Ofulume, 2008)

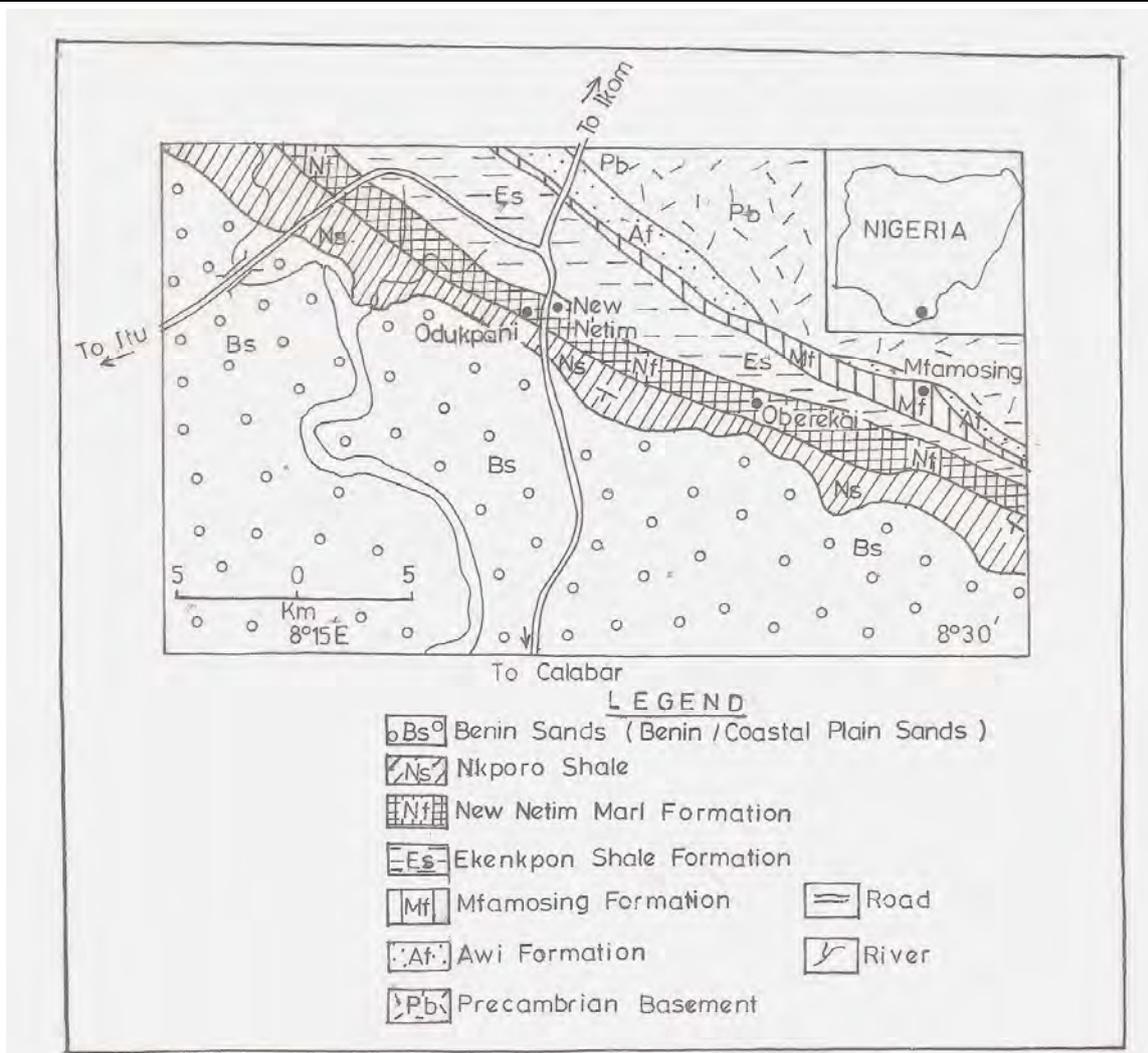


Figure 2: Sketch geological map of Mfamosing area, NE Calabar showing distribution of major lithologic units (after Ekwueme, et al 1995)

The Mfamosing limestone was deposited in a lagoonal setting on the landward side where it merged with a siliciclastic hinterland (Petters and Reijers, 1987). Diagenesis influenced the sediments right from the moment of deposition (micritization) and late diagenetic process created (micro)stylolites which are locally abundantly present. Prolonged denudation on the Flank uplifted near the tectonically active Cameroon Volcanic axis led to the extensive weathering and the formation of tropical karst scenery of the Mfamosing limestone (Petters and Reijers, 1987).

SUITABILITY OF LIMESTONE FOR LIME MANUFACTURE

Suitability of a limestone for lime manufacture depends on the quality of the raw stone and on the calcination or burning process.

Factors such as chemical purity, crystal structure and density affect quality of the raw stone. On the other, physical size of limestone, CO₂ concentration in the kiln, temperature/retention time in kiln, and type of kiln are critical factors in the calcination process. These factors are considered below:

QUALITY OF RAW STONE

Chemical Purity

High premium is placed on the chemical purity of the raw stone (limestone) because the purity of the lime is dictated by purity of the limestone and by the calcination process. The limestone should have high and uniform calcium carbonate content. A general requirement for commercial lime production is a rock with a minimum of 95% CaCO₃ (Power, 1985) however British Standards Institute

BIS (IS:10345:1982) prescribed 52% CaO minimum (ie 92.8 CaCO₃%) for use for lime manufacturing for fluxing in steelmaking. The chemical purity of the limestone has been determined (Table 1) using XRF by Sofresid Laboratory, France. X-ray diffraction (XRD) analyses (Fig 3) of the limestone have enabled detailed mineralogical identification of the impurities present. These impurities include dolomite, pyrrhotite, fluorapatite, quartz, plagioclase etc (Fig 3). When appreciable amounts of these impurities are present in any limestone they constitute serious impediment to a wide spectrum application of the limestone and lime prepared from it. Consequently cement manufacture becomes their ultimate application.

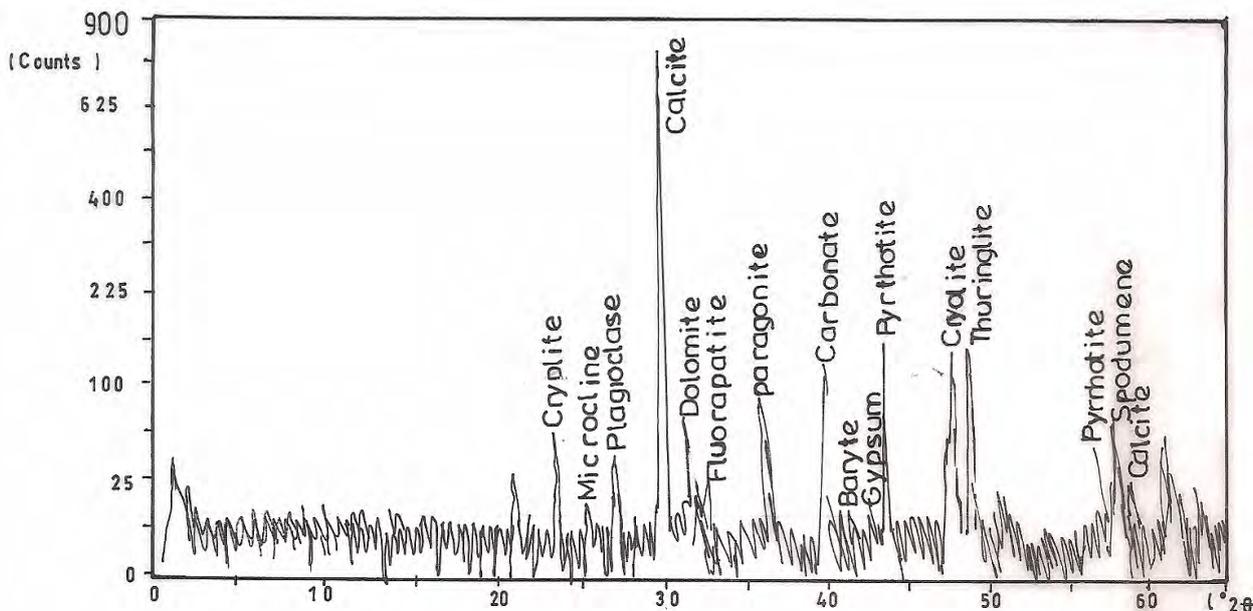


Fig.3 XRD Trace of Mfamosing LIMESTONE.

Lime producers are constantly striving to obtain the purest stone deposits since the purest stone usually provides the best quality lime. Impurities dilute the quality of the lime and adversely affect reactivity.

Also absorption of impurities from fuel occurs on the most reactive portion of the lime particles - its surface. Hard-burned lime of sluggish reactivity does not possess as strong an affinity for the acid oxide impurities as soft-burned. If silica in the ash is in contact at high temperature with a lump of lime whose surface is partially hard - and soft-burned the most reactive CaO molecules react with the SiO₂ first, the hard-burned CaO molecules react more slowly (Boynton, 1980). With integral impurities in the stone at low temperature (899-927°C) relatively little silica and other impurities combine with the lime. But as the temperature increases, the uncombined acid oxide impurities are increasingly absorbed, forming various complex calcium compounds such as mono calcium and di calcium silicates, calcium aluminates, di calcium ferrite.

A slagging effect occurs that tends to occlude the pores in the quicklime and mute its reactivity. This means that when the lime is slaked, water encounters more difficulty in penetrating to interior of the lime because of its clogged pores, thereby retarding hydration. As a result lime abnormally high in impurities may react like a hard burned or recarbonated lime with water, even though over burning did not occur.

Crystal Structure of Stone

The physical characteristics of the various limestones determine the quality of the lime product. The physical attributes are shown in Plate 1. The Mfamosing limestone is fine grained. The texture of the limestone is a factor in successful calcination of the stone into lumps of lime. The coarse grained limestones are prone to fracturing and crumbling into fines when heated. They can be disintegrated to dust by the heat of

the calcination process. This situation is dreaded by lime manufacturers because the product is rendered unsaleable for many uses. On the other hand, the fine grained limestone can easily be calcined to produce lumps of lime because the crystals resist the temperature stresses.

Another factor that contributes to resistance of the expansion stress is the presence of network of minute fissures separating the small crystals. These fissures behave like expansion joints as the heat causes the crystals to dilate thus maintaining integrity of the matrix.

Density of Limestone

The density and crystal structure of limestone are related.

The shape of crystal determines the void spaces in the limestone sample and hence the density. Larger void will allow easy passage for CO₂ gases during calcination but it also results in a reduction of volume during calcination. Some limestone tend to fall apart during calcination process due to its crystal structure. They possess high crystallinity and seriously complicate the calcination process.

CALCINATION

The limestone samples were prepared as lumps by trimming them to size (about 2cm diameter). These lumps were placed inside crucibles and then shock calcined using a laboratory muffle furnace. This implies that they were introduced into the furnace only when the furnace had attained and stabilized at the desired calcination temperatures of 950°C, 1000°C, 1050°C and 1100°C.

Physical Size of Limestone/Type of Kiln

Generally larger stone sizes are more difficult to calcine uniformly and require more time. This is because

dissociation always penetrates gradually from the surface to the interior of stone. To expel the CO₂ from such large stones high temperatures are necessary to generate sufficient CO₂ pressure in the interior of the crystal lattice for the escape of the gas. Frequently these high temperatures over_burn the surface layer of the stone causing excessive shrinkage which narrows and closes the fissures.

The size of stone used depends on whether the kiln is a vertical or horizontal rotary. Vertical kilns usually use limestone sizes between 13-20cm while horizontal kilns use 4-5cm (1½-2") size.

The smaller sizes tend to calcine faster at a lower temperature than the larger fraction since the CO₂ gas has a shorter escape distance in the smaller size samples. Consequently Boynton (1980) prescribed that the ideal stone to calcine for optimum quality, uniformity and thermal efficiency would be of small size (1.25cm) and be of uniform size and shape. Although the energy efficiency of kilns is very important in choosing a system, the initial decision must depend on the properties of the raw material and how well the kiln can handle it, plus the desired quality of the end product.

CO₂ Concentration in Kiln

As CO₂ is released from limestone during calcination, concentration of CO₂ in the kiln atmosphere is increased. For proper calcination the CO₂ must be vented on a continuous basis. If CO₂ is not vented a concentration of high CO₂ and high calcination temperature will re_carbonate the lime on the surface of the pebbles and convert CaO back to CaCO₃.

Temperature and Retention Time in the Kiln.

Since the temperature and time can easily be controlled, they were thus varied so as to determine best calcination parameters for the limestone by testing the quality of the lime product using such technological tests as loss on ignition of lime, decrepitation, mechanical strength, and reactivity and by inference porosity and surface area of the lime.

Loss on ignition of lime

This is the loss on ignition of lime and should not be confused with weight loss or loss on ignition of limestone. After calcining at the appropriate temperature the lime was allowed to cool in a dessicator and thereafter about 2g weighed accurately again to four places of decimal, placed in a crucible and then calcined further at 1100°C for 60 minutes. It was cooled to room temperature in a desiccator and then weighed again. The difference in weight was expressed as a percentage of the original weight to give the loss on ignition of lime at the particular calcined temperature. Table 2 shows the values obtained and the corresponding calcination temperature.

Decrepitation

After calcination at the prescribed temperature and duration the lumps of lime were allowed to cool to room temperature in a desiccator. They were then poured into 1.18mm sieve and shaken gently. The quantity of minus 1.18mm sieve material generated was measured and expressed as percentage of the original

weight and then reported as percentage decrepitation. Table 3 presents the values obtained.

Mechanical Strength

Screen analysis was carried out on the calcined stone. After shock-calcining the samples at the appropriate temperature the lime products were subsequently weighed and poured unto a set of sieves of aperture sizes 13.20mm, 9.50mm, 4.75mm, 2.36mm, 1.18mm and 0.60mm and then given extended shaking with the hand for about 10 minutes. Screening the stones for 10 minutes gives some indication of the tendency of the stone to decrepitate in the kiln. Results are shown in Table 4.

Reactivity (Slaking Test)

It is primarily for comparing the reactivity of quick lime, and especially for monitoring the burning conditions in a small lime kiln. The maximum temperature reached through the exothermic reaction of quick lime with water is a good indicator of the quality of the lime at least in terms of the available CaO (Ruskulis, 1997). American Society for Testing of Materials (ASTM) stipulated the guidelines for measurement of reactivity of lime. It specified the use of 100gm of lime in 400ml of distilled water at 25°C.

The apparatus used was not automated but instead consisted of Thermos flask, thermometer reading up to at least 100°C, stop clock, a scale, a pestle, and mortar for crushing the quick lime and a rod as stirrer (Ruskulis, 1997). The sample was prepared to pass 2.36mm sieve as quickly as possible and then left in a dessicator to cool to room temperature before the slaking test. 100gm of lime was added to 400ml of distilled water at 25°C in the Thermos flask and the cover replaced quickly without delay. The rod was employed in stirring it continuously and reading of temperature was taken at 30 seconds interval. Readings were recorded until less than 0.5°C temperature change was noted in each of three consecutive readings. The total active slaking time would then be the time at which the first of three consecutive reading was taken. The initial temperature was subtracted from the final temperature to obtain the total temperature rise. Also the initial temperature was subtracted from the temperature at 2 minutes to obtain temperature rise in 2 minutes (Table 5). Suitable curves showing temperature rise as the ordinate and time as the abscissa were then plotted (Fig. 4). The results were reported as temperature rise in degree after 2 minutes.

Type of Fuel

Most calcining is done by the use of oil, coal or natural gas for fuel. Both oil and gas contain sulphur compounds which vary from 0.5 to 3%. Sulphur will combine with CaO at proper temperature and produce calcium sulfide or calcium sulphate. This generally happens on the surface of CaO pebbles and renders them non-porous thus not suitable for slaking. Natural gas is the cleanest fuel and is mostly used in vertical kiln (Hassibi, 2002).

DISCUSSIONS

Loss on ignition (LOI) of lime refers to the loss of carbon dioxide and combined water when sample is heated at 1100°C. Principally, the CO₂ arises from incomplete decomposition of limestone. It also occurs as a result of atmospheric carbon dioxide absorption subsequent to manufacture and also in some kilns which are usually badly operated through recombination of freshly made lime with kiln gas. Combined water arises from absorption of moisture from atmosphere in the cooling zone of the kiln and during handling and stocking after lime leaves the kiln.

Loss on ignition is done to determine if calcination was complete (Boynton, 1980). In the BOF (Basic Oxygen Furnace) levels of LOI is generally less than 3% (Anderson and Vernon, 1971). If higher it is considered to have significant effect in reducing potential for scrap melting and may lead to uncontrolled foaming and slopping. The LOI was 1.19% at calcination temperature of 1050C and the highest value of 1.6% was obtained for 1000°C/60minutes calcine (Table 2). It

has been noted that some microscopic physical changes occur in some calcitic lime at 800°C, below dissociation point.

Generally, this heat causes expansion in the crystal matrix of the limestone. In the highly crystalline limestone the heat produces stresses in the individual crystals causing them to fracture. The degree of decrepitation of these crystals maximizes with crystals of the largest linear dimension. In contrast crystals of fine grained stone generally resisted the temperature stresses without cracking. The highest decrepitation of 0.87% was obtained for the 1050°C/90minutes calcine. These values are considered quite minimal compared with 14.64% decrepitation that has been reported for Jakura marble that decrepitated (Ofulume 2008). Decrepitation drops when the stone has become dead burned.

The Mfamosing lime being fine grained does not decrepitate and does not generate fines either in the kiln or during mechanical handling as evidenced by the quantity of less than 0.60mm sieve material.

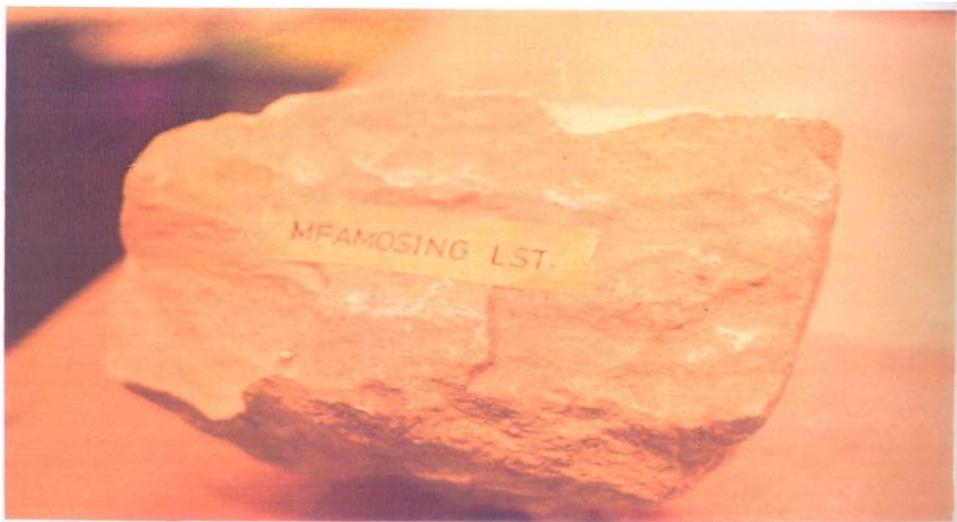


Plate 1: Mfamosing Limestone Sample: White, Fine Grained

Reactivity as measured by the slaking test is a function of porosity, chemical purity, surface area as well as temperature and duration of burning of the stone. The three properties reactivity with water, porosity and surface area are more or less inter-related. High degree of activity is usually associated with a highly porous lime which also has a high surface area. The higher the values of these parameters at the same temperature, the higher is the reactivity of the lime.

The 950°C/90minutes and 1000°C/60minutes calcine did not show appreciable reactivity. The 1000°C/90 minutes and 1050°C/90 minutes calcines as well as 950°C/120 minutes calcines recorded 43°C, 51°C and 46°C reactivity

TABLE 1. CHEMICAL COMPOSITION OF THE MFAMOSING LIMESTONE (AFTER OFULUME, 2008).

%	MF 1	MF2	MF 3	MF 5	MF 6	MF 8	MF 9	MF10	MF11	MF13	MF14	MF15	MF16	MF17	MF18	MF19	<u>MF20</u>
SiO ₂	0.49	0.73	1.81	1.09	0.27	1.19	0.15	0.23	2.39	0.03	0.23	0.28	0.46	2.97	2.28	0.21	0.47
TiO ₂	0.03	0.01	0.01	0.02	0.00	0.02	0.01	0.01	0.03	0.01	0.005	0.007	0.01	0.02	0.02	0.003	0.014
Al ₂ O ₃	0.29	0.37	0.31	0.38	0.13	0.46	0.14	0.17	0.62	0.16	0.15	0.18	0.20	0.55	0.49	0.16	0.21
Fe ₂ O ₃	0.09	0.09	0.03	0.04	0.01	0.10	0.04	0.02	0.12	0.002	0.002	0.02	0.04	0.07	0.14	0.003	0.01
MnO	0.10	0.08	0.06	0.06	0.06	0.10	0.07	0.05	0.11	0.07	0.07	0.05	0.08	0.05	0.08	0.66	0.07
Mgo	2.34	0.71	1.01	0.63	0.21	2.49	0.02	0.39	1.59	0.92	0.62	0.39	1.14	0.45	0.88	0.40	0.69
CaO	52.07	54.78	52.81	54.37	55.22	51.28	55.58	55.16	52.55	54.61	55.10	55.90	55.38	53.34	52.56	55.35	54.82
P ₂ O ₅	0.03	0.03	0.04	0.01	0.01	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.02
SO ₃	0.18	0.23	0.12	0.23	0.07	0.25	0.07	0.01	0.29	0.44	0.11	0.07	0.15	0.23	0.35	0.07	0.10
L01	43.9	43.41	42.83	43.65	43.87	43.9	43.54	43.55	42.48	43.84	43.71	43.75	43.85	42.65	42.40	43.80	43.70
Total	99.42	100.35	99.03	100.46	92.64	98.81	99.94	99.62	100.19	100.37	100.01	100.66	100.33	100.36	99.60	100.08	100.08
CaCO ₃	92.98	97.82	94.30	97.08	98.61	91.57	99.25	98.50	93.3	97.52	98.38	99.82	98.89	95.25	93.85	98.83	97.89

Average CaCO₃% 96.69%

CaCO₃ % range = 91.57 – 99.82%. Source: (Ofulume,2008)

This limestone is the purest in Nigeria.

TABLE 2: LOSS ON IGNITION OF LIME (LOI) TEST RESULT

Calcination Parameter	LOI %			
	Sample 1	Sample 2	Sample 3	average
950 ^o C/90min calcine	1.52	1.53	1.53	1.53
1000 ^o C/90min calcine	1.22	1.20	1.21	1.21
1050 ^o C/90min calcine	1.19	1.17	1.20	1.19
1100 ^o C/90min calcine	0.37	0.38	0.38	0.38
950 ^o C/120min calcine	1.02	1.05	1.03	1.03
1000 ^o C/60min calcine	1.62	1.64	1.61	1.62

TABLE 3: DECREPITATION TEST RESULT

Calcination Parameters	Decrepitation %			
	Sample 1	Sample 2	Sample 3	Average
950 ^o C/90min	0.84	0.82	0.81	0.82
1000 ^o C/90min	0.83	0.85	0.85	0.84
1050 ^o C/90min	0.87	0.86	0.87	0.87
1100 ^o C/90min	0.77	0.79	0.81	0.79
950 ^o C/120min	0.75	0.76	0.77	0.76
1000 ^o C/60min	0.80	0.79	0.82	0.80

TABLE 4: SCREENING TEST (MECHANICAL STRENGTH) RESULT

Aperture	1000 ^o C/90min calcine	1050C/90min calcine	1100 ^o C/90min calcine
13.20mm	90.93	90.98	90.96
9.50mm	18.92	18.87	18.89
4.75mm	6.33	6.29	6.37
2.36mm	5.65	5.74	5.68
1.18mm	1.28	1.26	1.24
0.60mm	0.41	0.38	0.36

TABLE 5: REACTIVITY WITH WATER (SLAKING TEST) RESULT

Calcination parameter	Temperature rise after 2 min.
950 ^o C/90min calcine	13 ^o C
1000 ^o C/90min	43 ^o C
1050 ^o C/90min	51 ^o C
1100 ^o C/90min	33 ^o C
950 ^o C/120min	46 ^o C
1000 ^o C/60min	26 ^o C

Table 6: Chemical composition of Shapfell, and Mfamosing limestones.

Components	1	2
	Shapfell	Mfamosing
CaO	54.72	54.15
MgO	0.35	0.45
SiO ₂	0.71	0.89
Al ₂ O ₃	0.52	0.28
Fe ₂ O ₃	0.34	0.05
SO ₃	0.025	0.13
LOI	43.07	43.82
CaCO ₃ %	97.71	96.69

1. Carboniferous limestone at Shapfell
Source: Downie et al (1982)
2. Mfamosing Limestone, SE. Nigeria
Source: Ofulume, (2008)

Table 7: British Standard Institute (BSI) Specification of limestone for use in the preparation of bleaching powder, caustic soda, calcium carbide and sugar.

	BLEACHING POWDER	CAUSTIC SODA	CALCIUM CARBIDE	SUGAR
LOI	46.0	46.0	46.0	44
SiO ₂ (max.)	0.75	-	1.0	2.0
Fe ₂ O ₃ (max.)	0.15	-	0.25	-
CaO (min.)	54.0	53.0	54.0	50.0
MgO (max.)	2.0	1.0	0.80	1.0
Mn ₂ O ₃	0.06	-	-	-
CO ₂ (min.)	42.0	42.0	42.0	41.0
S (max.)			0.10	-
P (max.)			0.10	-
Al ₂ O ₃			0.50	1.50

respectively (Table 5) As for the 1100^oC/90min calcine there was a drastic drop in reactivity to 33^oC. What can be inferred from these values is that the porosity and surface area of the lime were increasing with rise in temperature until at 1100^oC when the lime's porosity and surface area decreased sharply because the lime was getting dead burned and denser and therefore shrinking in size. This is interpreted as onset of sintering.

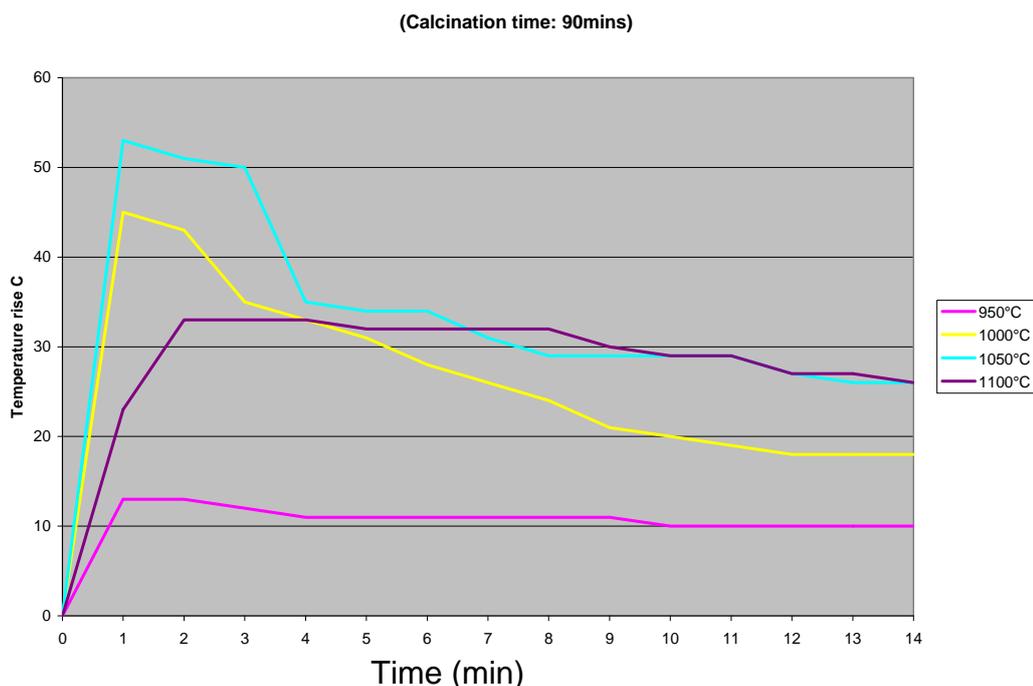
American Society for Testing of Materials (ASTM) has defined a highly reactive lime as one that shows a temperature rise of 40^oC or more in less than 3 minutes and taking 10 minutes or less to complete reaction.

On the basis of this definition therefore the lime made from Mfamosing limestone is a highly reactive lime and calcining the limestone at 1050^oC for 90 minutes is the best calcination parameter (Ofulumbe 2008). In accordance with (Boynton 1980, O' Driscoll 1988) that categorized diverse limestone types based on their calcination behaviour: 1. Those that fracture and decrepitated readily during preheating and at low

calcination temperatures. 2. Those that yield a porous reactive lime under most calcination conditions and are difficult to over burn. 3. Those that yield a dense unreactive lime of low porosity even under the mildest calcining conditions. 4, Those that yield a porous reactive lime under mild temperature conditions and a dense less porous lime under harder burning conditions; the Mfamosing limestone belongs to the fourth group - those that yield a porous, reactive lime under mild temperature condition and a dense, less porous lime under harder and higher burning condition.

The Mfamosing limestone compares well with pure quality limestone at Shapfell, UK (Table 6) utilized for metallurgical purposes because of its low silica. Shapfell limestone is actually the source of Basic Oxygen Steelmaking (BOS) lime in the United Kingdom (Downie, et al.,1982).

The Mfamosing limestone also falls in line with the British Standard Institute (BSI) specification for limestone for chemical manufacture and sugar refining (Table 7).



Activity defined by temperature rise (°C) after 2minutes.

Figure 4: Reactivity Graph of Mfamosing lime.

CONCLUSION

The Mfamosing limestone is chemically and technologically excellent for commercial lime manufacturing.

The best calcination parameters are temperature of 1050°C and retention time of 90 minutes. This produces a soft burned, porous, highly reactive (51°C rise in less than 2 minutes on slaking) and compact lime very much desired by lime producers.

The lime produced from Mfamosing limestone will have a very broad spectrum of applications that span chemical, metallurgical, constructional, environmental, agricultural, food and food by-products as well as sugar and petroleum industries applications.

REFERENCES

- Akpan, E.B., 1985. Ichnology of the Cenomanian – Turonian rocks of the Calabar Flank, S.E. Nigeria Geol. Mijnb., 64, 365-372.
- Akpan, E. B., 1990. Trace fossils and the depositional environments of the Mfamosing limestone, Calabar Flank, SE Nigeria. (Ed) Ofoegbu, C.O. The Benue trough: Structure and Evolution. Friedr. Vieweg and Sohn. Braunschweig/Wiesbaden.
- Anderson, L.C. and Vernon, J., 1971. Quality and production of lime for basic oxygen steel making. The quarry managers journal. Institute of Quarrying transaction pp 169-175.
- BIS (IS:10345: 1982) British Standard Institute specification for limestone for fluxing in steel plants.
- Boynton, R. S., 1980. Chemistry and Technology of lime and limestone – Wiley Inter Science p 482.
- Downie, D. G., Walden, T. and John, F., 1982. Modern Lime-burning Plant at Shapfell. Quarry management and products. March 1982 p. 163 - 173
- Ekwueme, B. N., 1985. The Chemical composition and industrial quality of limestone and marls on the Calabar Flanks S.E Nigeria. J.Mining and Geol. vol. 22 1-2 P. 51-56.
- Ekwueme, B. N., Petters, S. W., Nyong, E. E. and Essien, N. U.. 1995. Geologic field guide of the Calabar Flank.
- Fayose, E. A., 1978. Depositional Environments of carbonates of Calabar Flank, Southeastern Nigeria. J.Mining and Geol. Vol.15 p.1-13.
- Hassibi, M., 2002. Factors affecting the quality of quicklime (CaO) from mining to manufacturing to usage. Retrieved from www.chemcoequipment.com/qualityofquicklime.
- Nair, K. M and Ramanathan, R. M., 1981. Sedimentology, Stratigraphy and Paleogeographic Significance of lower Cretaceous Gboko Limestone, Nigeria. Journal of Mining and Geology vol. 21 nos 1&2 p.203-210
- Nyong, E.E. and Ramanathan, R. M., 1988. Geologic history and Cretaceous Stratigraphy of the Calabar Flank S.E. Nigeria .J. African earth Sc.
- O'Driscoll, M.,1988. Burnt lime/dolime. Seeking market green. Industrial Minerals. May 1988 p. 62-78.
- Ofulume, A. B., 1993. An assessment of suitability of the Jakura marble for use as a flux in steelmaking. Jour. Mining and Geol Vol. 29 (1):1-8.
- Ofulume, A. B., 2008. The Geology, Geochemistry and Economic Potentials of Nigeria Limestone and Marble Resources. Unpublished. Ph.D Thesis, Abubakar Tafawa Balewa University Bauchi. P.142.
- Petters, S. W. and Reijers, T. J. A., 1987. Cretaceous carbonates on the Calabar Flank. (Ed) Matheis and Schandelmeier. Current Research in African Earth Sciences. Bakama Rotterdam.
- Petters, S. W., 1981. Caves and tower karsts near Calabar Nigeria. Nigerian Field 46:9-20.
- Petters, S. W., 1982. Central West African Cretaceous – Tertiary benthic foraminifera and stratigraphy. Paleontographic Abst A 197: 1-04.
- Power, T., 1985. Limestone specification - limiting constraints on the market. Industrial Minerals, October pp 65-84.
- Ramanathan, R.M and Fayose, E. A., 1990. Cretaceous transgression and Regression in Calabar Flank, SE Nigeria. In: C.O. Ofoegbu(Ed) The Benue Trough: Structure and Evolution, Friedr.Vieweg of Sohn 59-75.
- Reyment, R. A., 1965. Aspects of geology of Nigeria. Ibadan University Press 145 p
- Ruskulis, O., 1997. Methods for testing lime in the field. Retrieved from <http://www.itdg.org./docs/technicalinformationsevice/testinglime>.
- Scott, P. W., 1983. Industrial Rocks and Minerals: Exploration and evaluation. Jour Min. & Geol Vol 21 (1 & 2) P. 1-12