INVESTIGATION OF THE PROPERTIES OF LOCALLY AVAILABLE DOLOMITE FOR REFRACTORY APPLICATIONS.

H.I. Moorkah and M.S. Abolarin
Dept of Mechanical Engineering, Federal University of Technology, PM.B. 65, *Minna, Nigeria*

ABSTRACT
A study to investigate the properties of the locally available dolomite for refractory applications has been carried out. Dolomite samples from four dolomite mining locations at Ikpeshi, Ugya, Osara and Kwakuti in Nigeria were used for this investigation. The internationally accepted methods for testing refractories were adopted and their properties compare favourably with most of those of standard dolomite currently in use in Europe, Asia and United Kingdom. These results make the Nigerian dolomite suitable for use as a basic refractory material especially in the machine tools and steel making industry.

Key words*: Refractories; refractoriness; permeability; mouldability index; flowability*

1.0 INTRODUCTION

Refractories are necessary in the metallurgical, cement, glass, and machine tools industries where kilns and furnaces are used for value addition process to materials. Dolomite refractories are currently in use in some foreign countries such as China, France, England India etc. Dolomite refractories have wide applications in the steel industry where it is used in open hearth, basic oxygen converters and other steel refining systems.

The shifts in metallurgical process and the aggravation of operating conditions by the use of oxygen have also caused changes in the qualities to be satisfied by refractories. The development of refractory products and of the lining technology has had to be adapted to these changed requirements [1].

Dolomite with an estimated reserve deposit of 24 million tonnes is found in Kogi, FCT, Niger, Oyo, Kaduna, Kwara and Edo states. At the moment, mining is pronounced in four states; Edo, Kogi, Nassarawa, and Niger states [2].

According to Chatillon, et. al. [3], the interest in dolomite as a refractory is hinged on the fact that the composition of dolomite makes it desirable for its use as a basic refractory. Dolomite is environmentally friendly and can be used for the production of pure and extra low carbon steels. Dolomite that is ceramically bonded exhibit high hot erosion resistance. Good quality dolomite, with low silica content is thermodynamically stable and has a significantly high heat sink characteristics. These qualities make dolomite refractory preferable to silica, alumina and even magnesite chrome refractories.

In Nigeria, at present there is a paradigm shift from large dependence on importation to local production of items with comparative advantage. Refractories are not isolated from these items. The recent drive by the federal government to resuscitate and jumpstart the iron and steel industry is another impetus for an investigation of this nature. At the Ajaokuta steel complex, the basic oxygen furnace and other furnaces in the plant will surely need dolomite as part of its refractory requirement.

Dolomite mineral is a double carbonate of calcium and magnesium having the formula $CaMg(CO_3)_2$[4]. It is slightly hard, transparent, and forms rhombohedron as its typical crystal habit. Dolomite used for refractory purpose should be hard and compact with uniform texture containing very low percentages of iron, silica, alumina etc. This is because these impurities adversely affect the refractoriness of dolomite refractories [5].

Under actual conditions of operation, refractories are subjected to mechanical loads. For this reason, refractory materials are assessed by their ability to withstand loads at high temperatures [6]. Each refractory composition has optimal conditions of heating and roasting which should be adhered to in order to prevent cracking, glass phase formations etc [7].

The chemical composition of refractories depends on the composition of the starting materials. The composition of refractories determines their activity in steel making slags. Refractories composed mainly of silica (an acid oxide) should not be in contact with basic slags' while those prepared from basic oxides (MgO, CaO) should be protected from contact with acid slags; otherwise, their particles in the lining will be slagged vigorously, resulting in quick failure of the lining [6].

The stability of refractories determines not only their consumption, but also the productivity of steel making. The refractory material for steel making should have low porosity i.e high density so as to avoid the erosion by the moving metal and slag [7].

The increasing demand for cleaner steel cannot be fulfilled in ladles lined with conventional silica containing refractories such as sand, fire clay, zircon or high alumina. It is therefore necessary to use basic linings. It is generally considered that the total impurity level of high performance dolomite products should not exceed 3%. Above this level the low melting point phases such as browmillerite and dicalcium ferrite have a detrimental effect on the refractoriness and corrosion resistance of fired dolomite products [3].

The physical properties of refractory bricks is a function of the physical properties of the original raw material and to a greater extent, those of the clinker. For steel refractory these physical properties include volume change, abrasion, compression, spalling properties which are indicated in their bulk densities, specific gravities, porosities, swelling index, linear shrinkage and crystallite sizes [8]. There is little or no study on the physical properties of refractory dolomite found in Nigeria. This paper is a research effort made at studying these properties and assessing their suitability for refractory applications.

2.0 MATERIALS AND METHODS

2.1 Materials

Quartering and cone method was used in sampling specimens for the experiments. The raw dolomite was quarried, crushed, partially washed and then introduced as lumps into a kiln for burning. During the burning process otherwise known as calcinations, the carbonates decompose between 780 and 1600^{0}C and are transformed into lime (calcium oxide) and periclase (magnesium oxide) while carbon dioxide ($C0_2$) is given off [3] as indicated in equation (2.1).

$$\mathrm{CaCO_3} MgCo_3 \rightarrow CaO + MgO + 2CO_2 \qquad 2.1$$

The calcined or burned dolomite lumps are crushed, milled and finally graded into fractions. After milling, the dolomite was thoroughly mixed to obtain a homogeneous mix. A binder (honey) 5% wt and 4% water is added during the mixing. The binder is added in order to impart green strength and also act as a plastifier and hydration protection After mixing, the batch is taken to a hydraulic press of about 100MN/m^2 where the mixed dolomite is introduced into the mould and shaped at high pressure. Thereafter, the shaped dolomite is oven dried at 110°C for 12 hours. After oven drying, the bricks were taken to a furnace of heat capacity of l500 - 1800^{0}C where the bricks were sintered. It is preferable to sinter at a high temperature. At the end of firing, the bricks are allowed to cool down within the furnaces and later, they are brought out to cool down before checking and measuring the characteristics under study. Most of the tests carried out involved cutting a section of the sintered dolomite refractory brick with a cut off wheel as specified by the refractory testing standards.

2.2 Methods

2.2.1 Chemical Analysis of Dolomite

Flame spectroscopy was utilized in the determination of the chemical composition. It involves obtaining a sample in an appropriate solution, evaporating same into atomic vapour and passing it through the equipment and detecting the wavelengths in the screen of the detector.

2.2.2 Loss on Ignition (L.O.I)

About 100g of dolomite was subjected to heating in a muffle furnace and later cooled in a desiccator and weighed. Thereafter, the L.O.I was calculated using the formula

Loss on ignition (LOT)

$$\frac{M_{2-}M_3}{M_{2-}M_1} \times 100\% \qquad 2.2$$

Where

M_1 = Mass of dried porcelain crucible

M_2 = Mass of sample of dolomite and porcelain crucible

M_3 = Mass of heated dolomite and porcelain crucible

2.3.0 Measurement of Physical Properties

The following were the methods adopted in the measurement of the physical properties.

2.3.1 Determination of Moisture content, Mouldability index and Flowability

The dolomite, water and binder mix was directly used for determining these properties without subjecting the test specimens to heating process. The mix is introduced into the moisture meter (carbide compartment) and there is a spontaneous reaction which gives off vapour. The vapour given off is directly proportional to the moisture content.

About 50g of the mix was also put into the mouldability and flowability equipment which has a cylindrical sieve that is rotated. During the rotation, the mix that passes through the sieve is collected and weighed. The weight is then divided by 2 to get the mouldability index while the percentages of the mix moulded and dropped dolomite mix is an indicator of the dolomite's flowability.

2.3.2 Swelling index

This quality indicates the ability of the material to rise in volume when exposed to moisture. The test procedure involves putting 2.5g of powdery dolomite and measuring the level in the test tube. Thereafter, add 20cc of water and allow for 24 hours. Drain the water from the Dolomite in the test tube by decanting and weigh the dolomite again. Swelling index is a measure of the ratio of weight of the hydrated dolomite to the dry one.

2.3.3 Permeability test

This is a test that determines the passage of a fluid (air, gas, molten or liquid) through the dolomite material. The dolomite particles bound together by honey and water is pressed into a cylindrical cup with a ramming rod under the pressure of a hydraulic press. The dolomite is thereafter placed in a permeability testing equipment which holds the cylindrical sample of 50x50for about 15 minutes. The permeability measurement is read off at the measurement device mounted on the equipment. This test can be done both dry or green depending on what factors are being considered.

In the absence of an automated measuring device, the permeability coefficient can be derived from the formula as presented in equation 2.3 by Degawa, et. al.[9].

Permeability Coefficient,

$$P_m = \frac{Vh}{APt} \qquad 2.3$$

Where V = Vol. of air
H=height
A = surface area
P = Pressure difference
t=time

2.3.3 Dry Compressive Strength and Dry Shear Strength

The dry compressive and dry shear strengths of dolomite were determined by using the Universal testing Machine. Specimens of size 050 x 50mm were sintered at 1600°C. The test specimens were inserted into the compression and shear heads. The readings at which the specimens failed were recorded as the dry compressive strength and dry shear strength respectively. Dry compressive and shear strength tests are important because refractory linings undergo different stresses from the materials being worked upon in the furnace. So there is need to test and find out whether the material can withstand such loads without failure during use.

2.3.5 Linear Shrinkage

Thermal effects have great influence on the dimension of refractories. It affects the dimensional stability, porosity and density of a refractory material. To test for linear change a specimen of 5cm x 5cm x 12.5cm size is cut using a cut-off wheel from a given refractory shape.

Volume of the specimen is determined and placed in a kiln having an oxidizing atmosphere such that the flame does not impinge on the specimen directly from the burner. The largest face of the refractory specimen should rest 011 a supporting refractory brick drawn from the same lot of refractories that are under test or which has equal refractoriness. Calcined kyanite of minus 85 micron (I.S. sieve) was placed between the test specimen and the supporting refractory brick. The specimens were kept 4cm apart from each other or from the kiln wall.

After holding the test specimens at the maximum desired temperature of 1600°C for the stipulated period of 2 hours, it was cooled to room temperature for over 10 hours in the closed kiln itself. The test specimen is then removed from the kiln, cleaned its surface of every blister and the length and volume measured again.

Linear change %

$$= \frac{\text{Final length} - \text{original length}}{\text{original .length}} \qquad 2$$

2.3.6 Porosity

Apparent porosity is very important in refractories as it affects other propernes, It may be determined by Boiling Point method or Evacuation method. The boiling point method was used for this investigation.

Test specimens measuring 6.5cm x 6.5cm x 4cm were cut from the already sintered refractory brick by a cut off wheel from within the centre of the refractory brick. All the particles adhering to the surface of the cut specimens were cleaned off. The specimens were oven-dried at 110°C to a constant weight (D). and then suspended in distilled water such that the specimens do not touch the bottom or sides of the container. The specimens were boiled for 2 hours while suspended in water, cooled to room temperature, the weights measured, then removed from the water, and the extra water on the surface of the specimens wiped off. The specimens were then weighed in air (W). Under this method, the apparent porosity was calculated using this formula [4].

$$P = VI/V x\, 100 \qquad 2.5$$

where

VI = Actual volume of open pores of specimen (CC) (W -D)cc

V = External volume of the specimen (cc) (W - S)cc

2.3.7 Bulk Density

Bulk density can be defined as the weight per unit volume of the refractory including the volume of open pore space. In essence the property helps to ascertain the strength of the refractory to compacting pressure and thus the volume stability of the refractory.

The test specimen is cut from the core of the sintered dolomite refraction. Wipe off all the adhering particles and dusts and weigh on a balance (WA). Pour approximately 1 000g of clear mercury into a 100 ml beaker and place on the balance pan centrally under the saddle. Allow the pointer to touch the surface of the mercury by adjusting with the handwheel. Set the balance to zero and raise the saddle and place the specimen on the surface of the mercury using crucible tongs.

Immerse the specimen on the saddle allowing the pointer to touch the surface of the mercury. Read the balance and term the weight, WB.

The bulk density is calculated from the expression

$$\text{Bulk Density} = \frac{\text{WA}\times\text{d}}{\text{WB}} \qquad 2.6$$

Where d = density of mercury

3.0 RESULTS AND DISCUSSION

The experiments and all the approaches at arriving at the objectives of this research yielded results, which are presented in tables and discussed in this section.

3.1 Chemical Composition of Dolomite

The chemical composition of the locally found dolomite under investigation is shown in Table 3.1. Calcium oxide (CaO) and Magnesium oxide (MgO) are the two major components of the dolomite refractory. For dolomite to be useful as a refractory it must have a reasonable percentage of Magnesium Oxide (MgO). This distinguishes dolomite from Limestone. Limestone is richly made of calcium oxide (CaO) and very small percentage of MgO.[9].

From the table, three deposits out of the four deposits under study have MgO content of 20.79%, 21.61% and 2l.89% while the dolomite at Ugya measures an MgO content of 20.49%. Hence most of the dolomite found in Nigeria can be used for refractory purpose judging by their chemical composition. During the chemical analysis, it was found out that the samples have some percentages of SiO_2, $A1_2O_3$, Fe_2O_3, Na_2O, K_2O and MnO_2 as expressed on Table 3.1. According to [3], high preponderance of SiO_2 have some deleterious effects on the refractoriness of refractories. SiO_2 in small quantity is also known to be a good source of tricalcium silicate which is regarded as the most stabilized form of dolomite refractory. The low content of SiO_2 and Fe_2O_3 in some of the dolomite especially the Osara and Ikpeshi deposit makes for their classification as low fluxing oxides. Low fluxing oxides possess a high crushing strength, high slag resistance and a much higher melting point (9). This makes these grades of dolomite desirable for refractory use and comparable with dolomite refractory in use in China, England, India and France.

3.2 Permeability

Permeability of the dolomite samples is given in Table 3.2. The permeability ranges between 35.3 71.6 npm for the samples under study. The Kwakuti deposit have a better permeability than the rest. It is directly related to the apparent porosity. The more the permeability, the more the porosity of the refractory.

3.3 Flowability

Flowability results of the dolomite samples are good (Table 3.2).The least flowability of a refractory should not be less than 25%. In the presence of the binder, the flowability of dolomite is good enough. This makes the dolomite grains to become more cohesive and impute strength before crystal to crystal binding.

3.4 Mouldability index

The dolomite samples have acceptable mouldability index in the presence of a binder (Table 3.2). So it becomes imperative that for sintered dolomite bricks, there is need for a binder and hydraulic press to help form and compact the material into acceptable shapes and forms.

3.5 Moisture Content (%

The moisture content (M.C) of the dolomite samples is as given in Table 3.2 Average values of Osara and Ugya were 4.46% and 5.18% respectively. The Ikpeshi followed with 5.24% while Kwakuti measured the highest moisture content of 5.54%. The dolomite refractory is good considering the water/binder mixture that went with the dolomite samples.

3.6. Swelling Index

The Swelling indexes of the samples are shown in Table 3.2. The Osara sample measured 0.81 while Ikpeshi averaged 1.62. The Ugya and Kwakuti samples had average values of 1.97 and 2.0 respectively. Most of the dolomite samples have acceptable swelling index

3.7 Bulk Density

Results for the Bulk density of dolomite is shown in Table 3.3. As the sintering temperature increased the bulk density also went up. It is assumed that the pores in the bricks closed up as the grains of the CaO and MgO formed crystallites. A Bulk density between 2.76 2.89 (glcm^3) recorded by the samples are realistic and can enhance good properties such as abrasion resistance, slag resistance, M.O.R etc.

3.8 Dry Compressive Strength

The result of the compressive strength test is as presented on Table 3.3.The dolomite deposit at Kwakuti showed a lower dry compressive strength of 48.7 MN/m^2 while the Osara dolomite maintained a dry compressive strength of 52.40MN/m^2 at sintering temperature of 1600°C.

The dry compressive strength at this sintering temperature are reasonably alright to withstand all compressive stresses on the refractory walls.

The dry compressive strength at 1600°C is higher than the corresponding dry shear strength at the same temperature. This is due mainly to the fact that dolomite refractory have the same characteristics with concretes which have better compressive strength than tensile or shear strengths [10]

3.9 Apparent Porosity

The apparent porosities of the various dolomite deposits decreased with increase in temperature. At 1700^{o}C, the average increase in apparent porosity were within the range of 23.26 23.62%. Osara dolomite maintained the least porosity of 23.26% while the Ugya dolomite recorded 23.62%. All the samples can be used for refractory purpose especially, in steel making furnaces and converters etc.

3.10 Linear Shrinkage

The results of the linear shrinkage of the dolomite samples are as given in Table 3.3. The dolomite samples shrank by 2.38 2.87%. The Osara sample proved a better stability than the others with a linear shrinkage of 2.38% while the dolomite at Ugya shrank by about 2.87%. As a basic refractory, the shrinkage is within the accepted value of ≤ 3.5% [5]. This level of shrinkage suggests that this refractory can beusedin BOFs

3.11 Dry Shear Strength (MN / m^2)

The dry shear strength of the dolomite specimens are as contained in Table 3.3. At 1600^{o}C, the shear strength of samples were between 37.20 38.00 MN/m^2. This level of shear strength is good enough for resisting the forces that is expected on the refractory/furnace structure. Shear stress on the walls of the refractory lining results from rubbing and impingement by the molten metal and charges in the furnace.

4.0 CONCLUSION

After a close study of the results of the experiments, the following conclusions are hereby made:

(a) Chemical analysis revealed that majority of the Nigerian dolomite have chemical composition comparable to dolomite currently in use in furnaces in China, England, France and India. They possess good contents of CaO and MgO and can therefore be used for refractory applications.

(b) The range of permeability was from 35.3 to 71.4 npm and this is within the acceptable range for basic refractories (between 20 to 100). Also, the swelling index hovers between 0.81 and 2.0 which is good enough as this will help counter hydration and spalling tendencies which is one of the limitations of most refractories.

(c) The linear shrinkage which is between 2.38% and 2.87% is considered adequate since the deviation from the standard is very minimal.

(d) The apparent porosities at 1700°C are also acceptable (23.26-23.62%)

(e) The shear/compressive strength are impressive and can resist all forms of impact and abrasion from the charge and the molten metal. At 1600°C the compressive strength range between 48.70 52.40 MN/m^2. This is really high while the shear strength hovers between 37.20 and 38.50 MN/m^2.

Table 3.1 chemical composition of raw dolomite (%).

DESCRIPTION BY LOCATION	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MnO_2	L.O.I	Lime magnesia Modulus
Osara Kogi State)	30.59	21.61	0.45	0.19	0.34	0.12	-	0.04	46.72	1.41
Ikpeshi, Edo State	29.47	21.89	0.43	0.15	0.21	0.37	-	0.42	46.26	1.35
Ugya, Nasarawa State	32.89	20.49	13.10	0.27	0.52	0.16	-	0.21	33.11	1.60
Kwakuti, Niger State	29.47	20.79	9.67	1.64	0.51	0.35	0.63	0.12	36.82	1.42
France	30.50	21	0.20	0.04	0.23	-	-	0.08	47.0	1.45
England	30.7	21.97	0.22	0.06	0.3	-	-	0.06	47.52	1.40
China	31.0	21.52	0.44	0.05	0.25	-	-	-	46.20	1.44
India	30.0	21.40	0.30	0.03	0.25	-	-	0.41	46.00	1.38

Table 3.2 Properties of dolomite.

Specimen of dolomite	Permeability (npm) at 1600^0C	Moisture content %	Mouldability index	Flowability %	Swelling index
OSARA	35.3	4.46	24.16	45	0.81
IKPESHI	40.2	5.24	24.00	24.25	1.62
UGYA	71.6	5.18	28.44	24.8	2.0
KWAKUTI	71.4	5.54	29.21	25	1.97
Intl. Std.	30.20	4.5	25	25-30	1.7

Table 3.3 Properties of dolomite refractory.

Specimen of dolomite	Dry compressive strength at 1600^0C (MN/m^2)	Dry shear strength 1600^0C (MN/m^2)	Linear shrinkage (%)	Apparent Porosity (%)	Bulk density (g/cm^3)
OSARA	52.40	38.50	2.38	23.3	2.84
IKPESHI	49.60	37.20	2.77	23.54	2.89
UGYA	48.90	38.00	2.83	23.62	2.87
KWAKUTI	48.70	38.00	2.87	23.58	2.87
Intl. Std	48.00	40	3.5	23	3.0

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