CHARACTERIZATION AND DETERMINATION OF THE INDUSTRIAL POTENTIAL OF OSARA DOLOMITE DEPOSIT

NNUKA, E. E. AND OLAREWAJU, F.
Department of Mechanical Engineering
University of Agriculture, Makurdi.

ABSTRACT

Osara dolomite deposit has been studied in this research work to investigate the chemical composition, sintering point, cold crushing strength, differential thermal analysis (D. T. A.), bulk density, porosity, specific gravity, water absorption, abrasion resistance and thermal shock resistance. Chemical composition was determined using the wet analysis technique, sintering point was determined by the heating and piercing method, cold crushing strength was measured using a mechanical strength testing machine. D. T. A. was analysed on the equipment model 404-5 while bulk density, porosity, specific gravity and water absorption were determined by the immersion technique. Abrasion and thermal shock resistance were determined using the Moh's hardness testing kit and the heating and cooling techniques respectively.

It was established that osara dolomite belongs to the low flux group of dolomite refractory and that the composition is essentially 34 per cent lime (CaO), 16 per cent periclase (MgO) and 46 per cent volatile material. The sintering point is 1500°C. D. T. A. shows that osara dolomite contains magnesite ($MgCO_3$) and calcite ($CaCO_3$), that the endothermic reactions take place at 780°C and 880°C respectively and correspond to the liberation of carbon dioxide gas during the decomposition of the two minerals and the formation of periclase and lime respectively. The established characteristics confirm the sample as dolomite. Comparism of the characteristics of osara dolomite to those of major deposits in England shows that it constitutes a good refractory material. The firing colour and the setting temperature indicate its suitability in white ware and porcelain manufacture. The chemical properties indicate its potential in chemical, fertilizer, paint, cement, oil and other industries. It is, therefore, recommended that osara dolomite be utilized in the enumerated industries and as a refractory material for lining the walls of basic iron and steel furnaces.

INTRODUCTION

The current economic reality in Nigeria has forced local entrepreneurs to look inward, for the sourcing of their industrial inputs. Consequently large reserves of suitable industrial raw materials have been located in various parts of the country [1]. Dqlomite has been discovered in Burum near Abuja and Osara near Lokoja in Kogi State[2]. Dolomite and magnesite ores have also been located in Mfamisin quarry in Akamkpa L. G. A. in Cross River State[3].

The potential of dolomite as an industrial mineral is great. It is a class of limestone[4], characterised by Dolomieu[5] in 1799 and shown by Retgers to be composed of $CaCO_3.MgCO_3$. Pure dolomite has a specific gravity of 2.85 and is whitish in colour. It has been reported[6] that dolomite refractories are basic in character and are used in the production of basic ferro alloys in the metallurgical industry. Effective utilization of the mineral demands accurate knowledge of its characteristics especially the chemical composition which is the major determinant of the areas of application. It is therefore necessary to characterise Osara dolomite deposit with a view to recommending areas of its utilization to needy indsutries.

The uses of dolomite are various. It serves as an excellent replacement of limestone as a concrete aggregate, road metal, rail road ballast, poultry grit, filler, whitening, soil conditioner, acid neutralizer and as raw material in glass making[6]. Like dimension stone limestone, dimension stone dolomite may be used for building purposes. It also finds application in the production of magnesium metal and magnesium carbonate[7] which is one of the most commercially important magnesium compounds. Large quantities of magnesium carbonate find applications in the manufacture of basic refractory bricks and as lining for open hearth furnace. It is also used extensively in the manufacture of heat insulating compositions, in the paint and printing ink industries.

Technically pure grades are utilized in the manufacture of fire-proofing, fire-extinguishing, flooring and

polishing compositions, as a filler for paper, plastics, paints, varnishes, and rubber. The carbonate can be utilized in the production of magnesium metal and oxychloride cements. In the pharmaceutical industry, it finds application as an antacid and a bulking compound in powder formulations. It also serves as an anticaking agent in table-salt. The pure carbonate has been shown[7] to be the preferred starting material for the manufacture of other pure magnesium compounds.

Other areas of utilization of dolomite include the agglomeration process for the physical beneficiation of iron ores. Dolomite fines or limestone are added to the sintered feed to produce a self-fluxing sinter[8]. It has also been shown[9] to be used in the blast furnace process as flux to maintain the proper ratio of basic constituents (CaO and MgO), to acid constituents (SiO_2 and Al_2O_3), and as a source of CaO and MgO, for glass production. In well drilling operations, dolomite finds application as a weighting material in drilling fluids[10] while in white way bodies it is used as a source of magnesium and calcium oxides[11]. In the far future the industrial mineral may solve the crises created by the exhaustion of oil reserves for the chemical industries because a reaction of limestone or dolomite with hydrogen under high preasure and temperature produces hydrocarbons with simultaneous liberation of CaO (quick lime) or $CaO(OH)_2$ (slaked lime).

At present, the bulk of the dolomite utilised in Nigerian industries is imported from far away Europe and America. The cost of importation is huge and has streamlined the number of industries engaged in utilization of the mineral, especially the small scale ceramic industries.

During the last few years, the consumption of refractories by the Nigerian high temperature industry ranged between 38,000 and 120,000 tons per year [12]. The refractory need of the metallurgical industry alone has been estimated at 110,000 tons per year, when the plants are operating at full capacity [12,13]. As at 1990 the cost stood at 114 million naira. A closer look at the growth rate for refractory demand in Nigeria between 1975 and 1987 shows that at an estimated 10 per cent growth rate, refractory consumption in Nigeria will stand at over 300,000 tons per year by the year 2,000AD[13]. Significant reduction will certainly be achieved in both the quantity and cost of refractories imported into the country through the development and utilization of local deposits.

This research is an effort, therefore, in characterising the Osara dolomite deposit and alerting potential users of areas of its utilization. It is intended that utilization of the raw material deposit will assist in conserving scarce foreign reserves, stimulate industial growth and create job opportunities for young unemployed Nigerians. This paper presents and discusses the results of the chemical and techological tests conducted on Osara dolomite. It also recommends the application of the mineral in the metallurgical, ceramic and other industries.

MATERIALS AND EXPERIMENTAL METHODS

The basic material used in this work is dolomite rock collected from Osara forest, near Lokoja, in South Western Nigeria. The geological map of the zone showing the site where the samples were collected is presented on figure 1. The data presented in this research work are the mean and range of values for the samples collected at random at three sites within Osara forest. Preliminary study including the digital thermal analysis (D. T. A.) showed that the rock is dolomite and in large enough reserve for exploitation. Initial weighting of the dolomite was conducted using digital meter. The weighed quantity was then crushed using a jaw crusher and the various proportions needed for the different analysis were measured out.

DETERMINATION OF CHEMICAL COMPOSITION:

The analysis was conducted to express the chemical composition of the dolomite sample in terms of the individual oxides. The classical chemical analysis (wet analysis) technique[7] was used in this investigation.

DETERMINATION OF SPECIFIC GRAVITY:

The true specific gravity of a substance is the ratio of its weight to that of an equal volume of water. To determine the specific gravity, a convenient size piece cut from a 5cm x 5cm cylindrical specimen was weighed and the weight recorded. A clean beaker was filled with water to a level to completely submerge the test piece. The level reading was taken as the initial volume (V_1). A piece of thread was tied to the test piece, and was used to lower the test piece into the beaker of water. The new volume was taken as the final volume (V_2).

The difference in the final volume and that of the initial volume gave the volume of the test piece. The specific gravity was then calculated from the formula given below:-

$$\text{Specific gravity } (g/cm^3) = \frac{\text{Weight of test piece}}{\text{Volume of test piece}}$$

DETERMINATION OF BULK DENSITY AND POROSITY:

The porosity and bulk density measurements were carried out on convenient sized piece cut from a 5cm x 5cm cylindrical test piece. The specimens were dried at 110°C for 3 hours, cooled in a dessicator, and weighed to the nearest 0.01g (weight D).

The specimens were in turn placed in a 250ml beaker in a vacuum dessicator fitted with a mercury pressure guage and a tap funnel. The dessicator was evacuated until a reduced pressure of 711mn of mercury was indicated; water was then allowed to run at 30ml per minute, from the tap funnel into the beaker containing the test piece, until the test piece was completely immersed. The specimen was allowed to soak for 5 minutes, with agitation from time to time to assist release of trapped air bubbles.

The vacuum was later broken and the beaker and test piece withdrawn. The specimen was weighed suspended in water. This gave the weight suspended (S). The beaker was removed from the balance and the test piece from the beaker. Surplus water was removed from the test piece by dabbing it with a damp cloth. The soaked piece was weighed (weight soaked 'W').

From these three weighings, the porosity and bulk density were calculated as follows:

$$\text{Apparent porosity (\%)} = \frac{W - D}{W - S} \times 100.$$

$$\text{Bulk density (g/cm}^3\text{)} = \frac{D}{W - S} \times$$

is the density of water = (1g/cm^3)

DETERMINATION OF WATER ABSORPTION:

A convenient size piece cut from the 5cm x 5cm cylinder specimen was weighed, and the value w, was recorded. The test piece was placed in a vacuum dessicator and the dessicator, filled with distilled water - about 2mm above sample. The dessicator was then connected to a water source (tap) and was allowed to run for 3 hours. The sample was later removed from the dessicator and surplus water was removed from the test piece by dabbing it with a damp cloth. The soaked piece was then weighed and the value W_2 was recorded.

The water absorbed was then calculated using the following formula:

$$\text{Water absorbed(\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

DETERMINATION OF SINTERING TEMPERATURE:

A laboratory combustion boat was filled with powered sample of dolomite. The boat was then placed in a high temperature furnace set at 1000°C, and increased at the rate of 5°C per minute. After heating for 20 mintues, the boat was removed and the sample pierced with a pointed object and returned to the furnace for further heating. This process was repeated (removal and piercing intermittently) until the pin could no longer penetrate the sample. The temperature at which sintering occured was then recorded.

DETERMINATION OF THERMAL SHOCK RESISTANCE (SPALLING RESISTANCE):

The American Foundary Society (A.F.S.) standard cylindrical specimens of 5cm x 5cm were for the determination of spalling resistance. The specimens were placed in a cold furnace and heated to 1400°C over a three hour period. They were retained at this temperature for thirty minutes and then withdrawn and placed on a refractory brick floor. After ten minutes cooling, they were returned to the furnace which had been maintained at 1400°C and soaked for a further ten minutes.

The cycle of cooling and heating for ten minutes intervals was continued until deep cracks were noticed on the surface of the test pieces. The number of cycles before deep crack was noticed was then recorded.

DETERMINATION OF COLD COMPRESSIVE STRENGTH:

A weighed quantity of ground dolomite sample was mixed with 5% sodium silicate binder. 170 grammes of mixture was placed in a sample mould, and rammed three times with a weight of 120kg. The rammed sample which measured 5cm x 5cm and cylindrical in shape was then removed from the mould and dried in an oven at a temperature of 110°C. It was allowed to cool in air before the cold crushing strength was determined and recorded using a mechanical strength testing machine.

The actual cold compression strength (CCS) was calculated as follows:

$$\text{C.C.S.} = \frac{\text{Crushing force (kN)}}{\text{Surface area (m}^2\text{)}}$$

DETERMINATION OF HARDNESS:

Hardness test was carried out on a solid rock sample using the Moh's hardness testing kit. The test piece was scratched by a series of standard minerals which increased progressively in hardness. The hardness value of the sample was recorded as that of the first mineral which produced a postitive scratch when viewed under a lane.

DIFFERENTIAL THERMAL ANALYSIS (D.T.A.):

D.T.A. was conducted to determine the endothermic characteristics during heating and cooling when the dolomite specimen and an equal amount of burnt kaolin (reference material) were used.

Equipment model 404-5 was used for this analysis. The sample and reference material cups were filled, and their different heating elements were put on. The equipment was operated as contained in the operating manual.

The heating rate was 10°C per minute, up to a temperature of 1400°C in air. The recorded chart was later cut out from the cabinet and the temperatures marked out.

EXPERIMENTAL RESULTS AND DISCUSSION

Results of the chemical composition of the investigated dolomite along with the chemical composition of some major deposites used in England are presented in Table 1.

Table 1: Chemical Composition of Osara Dolomite Deposit (determined) As Compared to the Composition of Some Major Deposits Used in England[14]

Oxide	Chemical Composition in %						
	Osara		Durham	Yorkshire	Derbyshire	North Wales	South Wales
	Range of Values	Mean Value					
CaO	34.2 - 34.6	34.4	32.0	29.5	30.3	31.7	30.2
MgO	15.2 - 16.8	16.4	19.7	21.0	19.8	19.0	19.5
FeO	-		-	0.4	-	0.1	-
Fe_2O_3	0.5 - 6.2	0.6	0.04	0.4	0.6	0.2	1.0
SiO_2	3.0 - 3.6	3.4	0.30	0.2	0.3	1.2	1.1
Al_2O_3	0.1 - 0.3	0.2	0.05	1.4	1.0	0.8	1.2
L. O. I. (mainly CO_2)	44.8	45.0	46.8	46.1	47.1	46.5	46.8

Table 2 presents the results of the physical analyses conducted on Osara dolomite

Table 2: Physical Properties of Osara dolomite (determined)

S/NO	PROPERTIES	MEAN VALUES	RANGE OF VALUES
1	Bulk density, g/cm^3	3.0	2.4 - 3.6
2	Porosity, %	1.6	1.6 - 2.0
3	Specific gravity g/cm^3	2.9	2.8 - 3.4
4	Water absorption %	0.5	0.3 - 0.8
5	Sintering temperature ^{0}C	1500	1500
6	Thermal shook resistance, cycles	5	5
7	Cold compression strength, kg/cm^3	456	450 - 460
8	Hardness, value on Moh's Scale	4	4

DISCUSSION

The suitability of Osara dolomite for the manufacture of basic refractory linings can be assessed on the basis of comparison of its chemical and physical properties with those of standard dolomite bricks used in metallurgical industries around the world.

The chemical compostion of Osara dolomite shows it to be within the range of raw dolomite popularly used in making basic refractory linings, in England[14], the dolomite falls within the range of low flux refractories, because of the relatively low percentage composition of fluxing oxides such as Alumina (Al_2O_3) and iron oxide (Fe_2O_3). The properties of Osara dolomite are similar and comparable to the properties of dolomite used in making tar bonded dolomite in Europe [5] and a range of products in England (Table 1).

The high alumina - silica ratio (Al_2O_3/SiO_2), is a strong indication that a high refractoriness - under-load can be achieved. The low silica content also suggests a high melting point. The ability of a material to sinter can be enhanced either by fine grinding or by the additon of fluxing oxides. This explains why a low sintering temperature was observed. The dolomite contains low amount of fluxing oxides. The low sintering point may be attributed to fineness of the dolomite. Fine grinding results to a higher degree of compactness of number of contact surfaces within the mass. Fine particles also increase the hydration rate of the dolomite.

The presence of alumina and iron oxide leads to the initial formation of a liquid phase which produces a suitable bond for the refractory material. This increases the mechanical strength of the refractory bricks. The percentage of iron oxide (Fe_2O_3) is not high, so the value of the dolomite rock as a refractory material is not unduly influenced.

The low amount of fluxing oxides, the very low porosity and high bulk density of Osara dolomite are strong indications to very good resistance to basic slag attack. The cold crushing strength and the hardness are pointers to good abrasion resistance of a refractory brick. Osara dolomite is of cold crushing strength and hardness comparable to those of other dolomites in use around the world[3] especially in England[14]

When the dolomite sample was calcined at a temperature of 1300^{0}C and left to cool, for sometime, the material started to crack as a result of hydration of free lime in the calcined sample. This explains the low thermal shock resistance, and the inability to determine the cold crushing strength at elevated temperature.

The calcined dolomite was tested for slaking, and it absorbed an equal weight of water added to it, resulting to an exothermic reaction. The sample become whiter and solidified. This process explains the conversion of free lime to slaked lime (Hydrated lime), which suggests a high CaO/MgO ratio. The high CaO/MgO ratio will tend to lower the melting point of

the dolomite. It also points to the fact that Osara dolomite is a good source for hydrated lime, lime, calcium carbonate and calcium.

A very serious constraint to this research is the non-availability of equipment to conduct the pyrometric cone equivalent test and the refractoriness - underload. The importance of these two tests cannot be under-estimated. However, the sintering point test is a very strong indicator of the value of these parameters. The sintering point of Osara dolomite was found to be 1500°C. True sintering however, which is manifest by the compact is usually acknowledged to start at the Tamman temperature[14], which is about 0.55 - 0.60 that of the melting point of the component. In view of this, it would be no exaggeration to estimate that Osara dolomite which sintered only at 1500°C has a pyrometric cone equivalent equal to Seger cone 42 which has a corresponding temperature of 2000°C.

It is known that basic materials, which are rich in magnesia have large expansion coefficient at high temperature, and tend to deteriorate seriously when subjected to cyclic thermal conditions.

Dolomite bricks have a comparatively large thermal expansion, but because the conductivity is also high at low temperature, they have moderately good resistance to thermal shock. The thermal shock resistance of Osara dolomite is in class with those of other dolomites used around the world[15].

Analysis of the D. T. A. curve shows that the peaks are at 780°C and 880°C respectively. They represent the characteristic endothermic reaction temperatures, in other words the temperature for liberation of carbon dioxide during the conversion of magnesium carbonate ($MgCO_3$) and calcite ($CaCO_3$) in dolomite to magnesia (MgO) and lime CaO) respectively.

The thermal effects assist in distinguishing the various minerals in the dolomite sample. It is known that the following peaks occur in the D.T.A. diagrams for dolomite mineral[15].

(a) 600 - 790°C - Endothermal peak for liberation of carbon dioxide from magnesium carbonate contained in dolomite.

(b) 800 - 920°C - Endothermal peak for the liberation of carbon dioxide from calcite contained in dolomite.

The correlation of the characteristics enumerated above with the D.T.A. curves is demonstrated in figure 2. The size relationship of the peaks holds for most dolomites.

An endothermic process observed in the investigated sample, as compared with the inert kaolin (reference material), indicate that there is heat absorption. The endothermic reaction is characterised by a negative thermal voltage in the differential circuit. The thermal differential therefore is less than zero ($\Delta T<0$).

It follows that the material investigated is doubtlessly dolomite. It is therefore, authenticated that Osara dolomite is potentially applicable, as a refractory material in metallurgical, cement and glass industries. It is also a rich source, for the production of lime, hydrated lime, calcium metal, and magnesium metal, as well as a potential raw material for our chemical and agricultural industries.

CONCLUSION

Osara dolomite has been characterized and its suitability as an industrial raw material has been discussed in view of its Chemical and Pysical Properties, found to be a good substitute for imported dolomite used in our metallurgical, ceramic, paper, paint, chemical, agricultural and many other industries. Proper control in the making of tar-bonded Osara dolomite bricks or stabilised Osara dolomite bricks, will bring the era of importing dolomite bricks to an end.

RECOMMENDATION

It is hereby recommended that:

(1) Further work be carried out to determine other important properties like refractoriness - under- load, and slag resistance;

(2) Means of enriching the magnesium content of Osara dolomite with a view to extracting magnesium metal for other applications, be examined in spite of the capital intensive technology involved;

(3) Osara dolomite be used in the production of dolomite refractory bricks and as raw material for the fertilizer, oil, agricultural, paint, ceramic, chemical and paper industries among others.

ACKNOWLEDGEMENT

The following are highly acknowledged for their immense contributions towards the success of this investigation; Dr. D. O. N. Obikwelu, Mr. Austin Eigbe, Mr. Yusuf M. A. and Mr. Steven all of Delta Steel Company Aladja; Mr. Segun Adewumi and the Management of the Federal Institute of Industrial Research Oshodi, the Head of Department, Mining, Kogi State Polytechnic, Osara Campus.

REFERENCES

1. **E. E. Nnuka and F. A. Okunoye** (1991): Industrial Potential of Ukpor Clay. Proceedings of the 1991 Annual Conference of N. M. S. pp 34.

2. **Orumwense Faraday, F. Osasere and Nwajagu C. O.** (1992): The status of the Refractory Industry in Nigeria. Proceeding of the 1992 Annual Conference of N. M. S. pp 29.

3. **S. O. Ubokwe** (1992): Refractory Materials for Electric Arc Furnace. Proceedings of the 1999 Annual Conference of N. M. S. pp 9.

4. **George S. Brady, and Henry R. Clauser** (1986): Material Handbook. 12th Edition, McGraw-Hill, Inc.

5. **J. H. Chester** (1983): Refractory - Production and Properties - 2nd Edition. The Metal Society London.

6. Encyclopedia of Material and Technology. Volume II. Non-metallic Minerals and Rocks, 1st Edition. J. H. Debussy and Longman Press pp. 87.

7. **Snell - Ettre:** Encyclopedia of Industrial Chemical Analysis. Volume 15. 1st Edition (1981).

8. **Snell - Ettre:** Encyclopedia of Industrial Chemical Analysis. Volume 13. 1st Edition (1981) pp 739.

9. **Snell - Ettre:** Encyclopedia of Industrial Chemical Analysis. Volume 11. 1st Edition (1980) pp 815.

10. **Kirk - Othmer:** Encyclopedia of Chemical Technology. Volume 17. 2nd Edition, John Wiley and Sons, Inc. (1968). pp 148.

11. **Snell - Ettre:** Encyclopedia of Industrial Chemical Analysis, Volume 5. 1st Edition (1979) pp 246.

12. **Milos Kuzvart** (1984): Industrial Minerals and Rocks. Helena Zarubova Press.

13. **Ajuwa I. Christopher and E. P. Oaikhinan** (1990): Developing a Domestic Refractory Industry in Nigeria. A Publication in the American Ceramic Society Bulletin. Volume 69, No 4, pp 656 - 657.

14. **Grimshaw R. W.** (1980): The Chemistry and Physics of Clay, 4th Edition, Halsted Press.

15. **J. O. Nwosu, A. G. Sanni, and A. O. Adeleke** (1992): An Assessment of the Suitability of the Osara Dolomite for BOF Refractory Lining at the Ajaokuta Steel Complex. Proceeding of the (1992) Annual Conference of N. M. S. pp. 96.

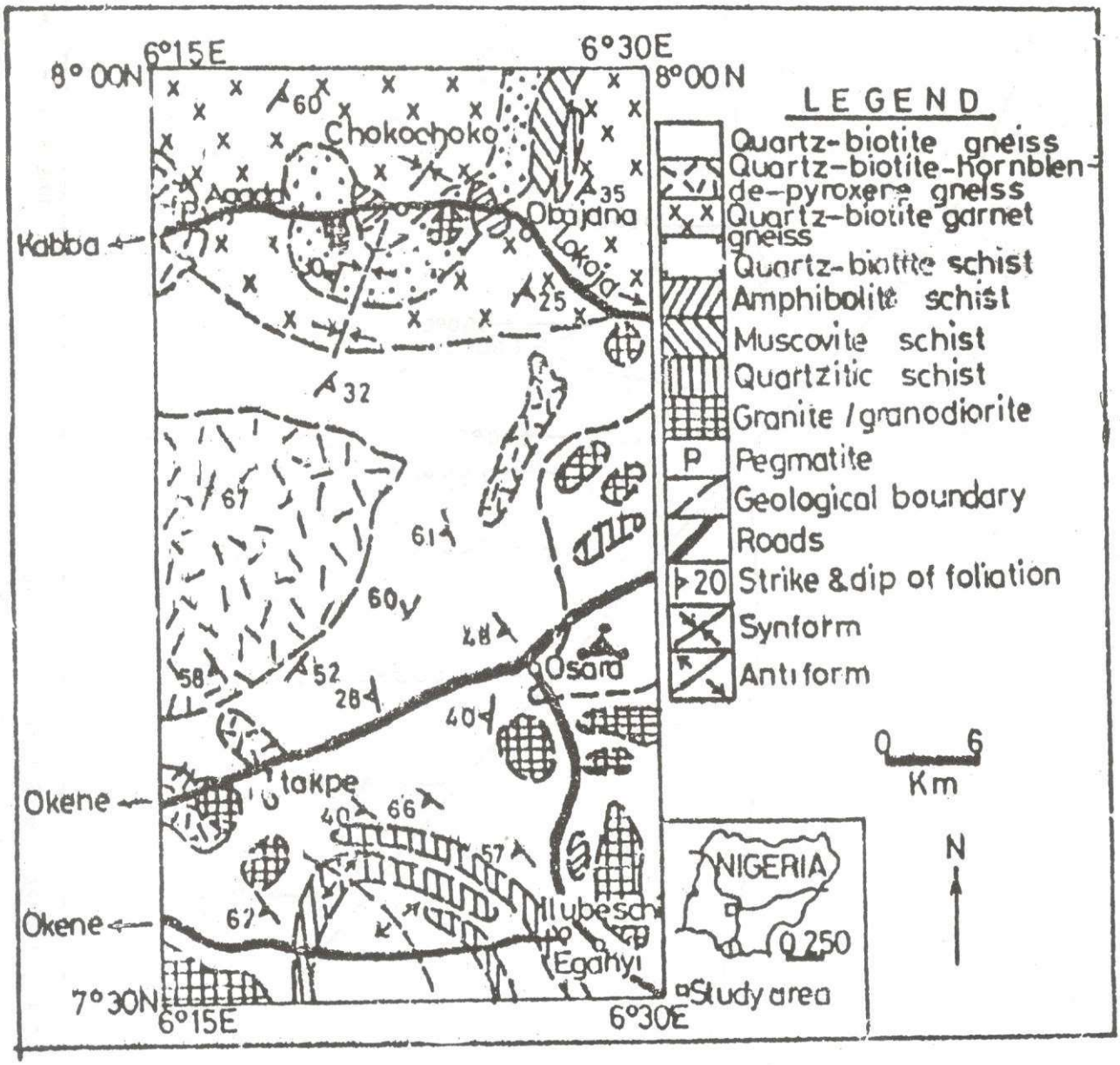


Fig. 1 Geological map of Okene - Lokoja Area, South-Western, Nigeria showing Osara (Δ)

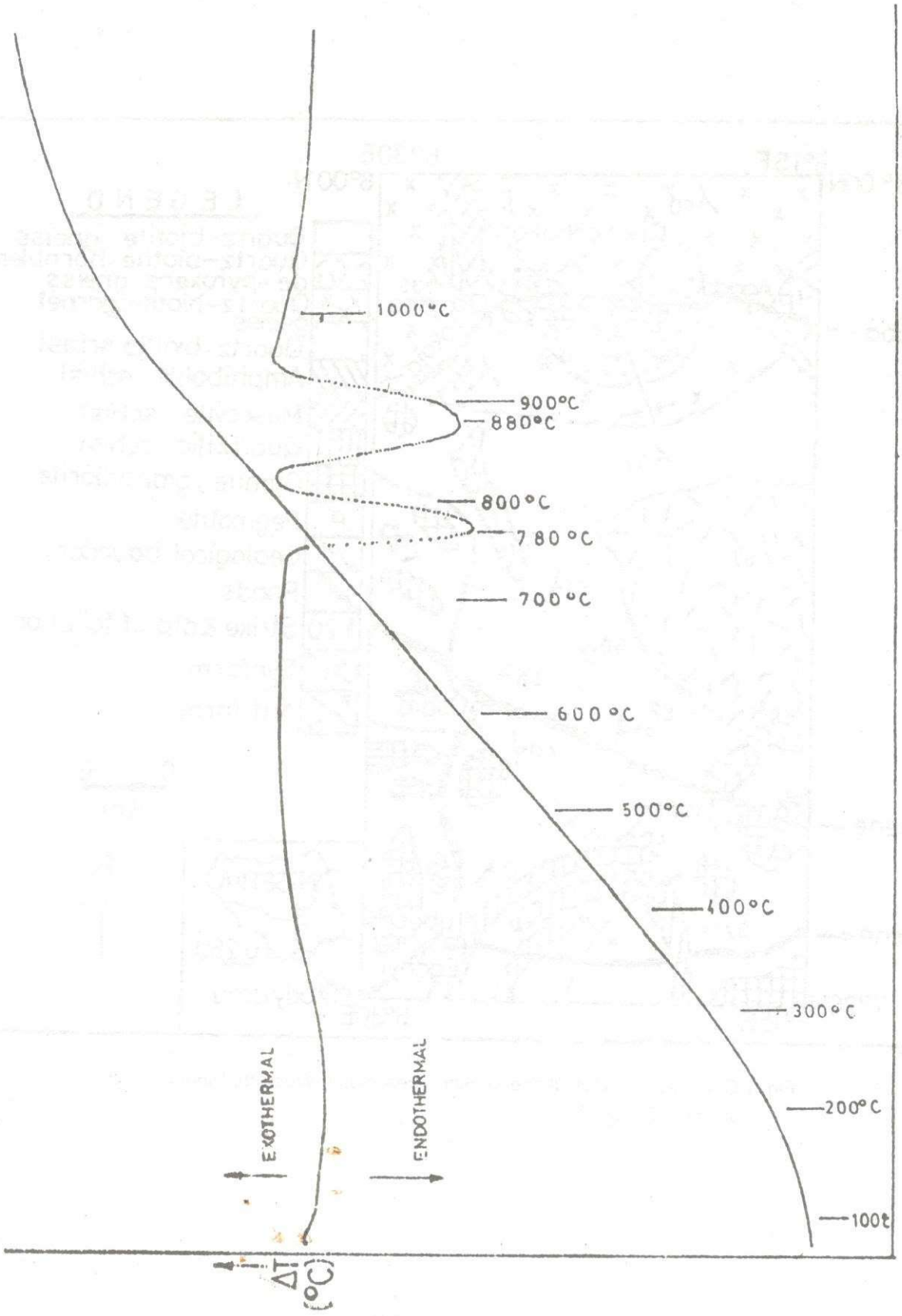


Fig. 2 DIFFERENTIAL THERMAL ANALYSTS (D. T. A.) CURVE