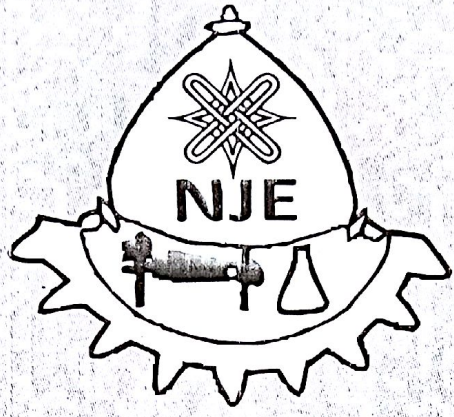


30

ISSN: 0794 - 4756



NIGERIAN JOURNAL OF ENGINEERING

Vol. 21 No. 2, March, 2015



1. ANALYSIS OF CLIMATE VARIABILITY AND ITS IMPACT ON CROP YIELD IN ZARIA 1 - 11
A. Adamu, D. B. Adie and C. A. Okuofu
2. VALIDATION OF PLANTING PERFORMANCE OF A MECHANICAL PLANTER ROBOT 12 - 23
K. Ahmad, M. B. Muazu and D. D. Dajab
3. STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN CHLORIDE ENVIRONMENT 24 - 28
I. I. Ahmed, A. G. F. Alabi, J. K. Odusote, N. I. Aremu, J. A. Adebisi, T. Yahaya, S. I. Talabi, R. A. Yahya and S. B. Lyon
- ✓ 4. CALCINATION KINETICS OF OKPELLA LIMESTONE FROM THERMOGRAVIMETRIC DATA FOR LIME PRODUCTION 29 - 38
M. N. Bello, J. O. Okafor and A. Mukhtar ✓
5. STUDY OF E-WASTE GENERATION AND MANAGEMENT IN HOUSEHOLDS WITHIN KADUNA METROPOLIS 39 - 47
F. B. Ibrahim, D. B. Adie, A. Giwa and C. A. Okuofu
6. PROMOTING TRANSESTERIFICATION OF COTTON SEED OIL (CSO) BY USE OF CO-SOLVENT 48 - 53
F. Iwalaiye, B. O. Aderemi, M. S. Galadima and C. S. Ajinomoh
7. MODELLING OF FLOW OVER OBLIQUE COMPOUND CRESTED WEIRS 54 - 59
M. M. Muhammad, A. Ismail, J. A. Otun and D. B. Adie
8. APPROPRIATE WATER PUMPING SCHEDULE AND THE DETERMINATION OF THE REQUIRED STORAGE CAPACITY 60 - 65
I. M. Sanni, D. B. Adie, A. Ismail and M. O. Nwude
9. EFFECTS OF THERMAL TREATMENT ON THE HARDNESS OF ANTIMONY-MODIFIED AL-SI-MG ALLOY 66 - 70
G. O. Adeboye, M. Abdulwahab, F. Asuke and S. A. Yaro
10. EFFECTS OF ACID TYPES ON THE RECYCLING OF USED LUBRICATING OIL 71 - 80
B. Suleiman, A. S. Abdulkareem, E. A. Afolabi and E. O. Oluwaseyi
11. THERMO-ECONOMIC ANALYSIS OF THIDC-PSA SYSTEM FOR BIOETHANOL REFINING 81 - 91
B. Suleiman, A. S. Olawale and S. M. Waziri
12. EFFECT OF SILICA SOURCE ON THE FORMATION OF NANOSIZED ZEOLITE Y VIA SEEDING METHOD 92 - 97
S. Yunusa, S. A. Abdulkarim, G. B. Solomon, F. I. John and D. Mohammed
13. CLASSIFICATION AND CHARACTERIZATION OF BULARAFA DIATOMITE USING AIR CYCLONE 98 - 102
M. Abubakar, A. S. Ahmed, I. A. Mohammed-Dabo, S. G. Bawa and F. Mohammed



CALCINATION KINETICS OF OKPELLA LIMESTONE FROM THERMOGRAVIMETRIC DATA FOR LIME PRODUCTION

M. N. Bello, J. O. Okafor and A. Mukhtar

Federal University of Technology, P. M. B. 65 Minna, Niger State, Nigeria.
Author for correspondence, bellomuhhammad5@gmail.com, Tel: +234(0)7034676334

ABSTRACT

Thermal decomposition kinetics of Okpella limestone was investigated by using TGA data. Determination of kinetic parameters for different particle sizes of 120 μ , 600 μ and 2000 μ as well as the plots of $\ln(y)$ against $1/T$ show linear relationships for both first and second order kinetics with coefficients of regression as 0.994, 0.987 and 0.947 for first order and 0.997, 0.997 and 0.983 for second order kinetics respectively. Activation energies and frequency factors which are temperature dependent were obtained from the plots of $\ln(y)$ against $1/T$ for both first and second order kinetics. However, the linear relationship in the graphs confirmed that heat transfer is the rate controlling mechanism in the calcination of limestone. Similarly, for all particle size fractions at 20°C/min heating rate, the basic endothermic peaks were observed. The conversion fraction was calculated as the ratio of mass loss at a given temperature to a total mass at the end of the process. For the kinetic analysis of non-isothermal thermogravimetric data, the reaction order was determined and the value that gave the best fit to the plot of $\ln(-\ln(1-\alpha))/T^2$ against $1/T$ by iteration.

INTRODUCTION

Limestone is important in the economic development in 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 for construction industry (Wheeler, 1999). Limestone deposits are also primary raw materials for some manufacturing industries such as sugar, fertilizer and ceramics (Neville, 1992). It is also used in the manufacture of Pig iron and glass (Kirk, 1982), Chemicals, (Agnello, 2003), Fillers and extenders (Ofulume, 1988).

Limestone or calcium carbonate ($CaCO_3$) is an abundant natural resources and a low cost material (US\$10-20 per metric ton) for producing lime (Smith, 2001). On heating, limestone decomposes and releases its CO_2 content a process referred to as the calcination of limestone. The product of limestone calcination is mainly quicklime. However, depending on the relative humidity of the atmosphere and the temperature of the calcination gas, the produced lime can react with water to form hydrated lime $Ca(OH)_2$.

Limestone is one of the most basic raw materials employed in most industries and has been

compared to one of a six legged stool on which modern industry revolves (Boynton, 1980) and others being coal, petroleum, iron-ore, sulphur and salt.

As a natural occurring mineral, limestone exists nearly all over the world and its chemical composition varies greatly from region to region as well as between different deposits in the same region. Thus, the end product from each deposit differs. For a stone to be classified as a limestone suitable for lime processing, it should contain a minimum of 50% calcium carbonate (Hassibi, 2002).

Limestone is generally classified in to high based calcium carbonate containing only about 5% of $MgCO_3$, magnesia based carbonate, having 5-20% $MgCO_3$ content and dolomitic based carbonate with:

$MgCO_3$ Content greater than 20% but less than 45.6% (Richard, 2010).

On the other hand, limestone can be obtained from a huge variety of sources and various limestone differ considerably in their chemical composition and physical structure. The chemical reactivity of different limestone shows a large variation as a

result of their differences in crystalline structure and also because of the nature of impurities such as silicon, iron, magnesium, sodium, and potassium (Borgwardt and Harvey, 1972).

The mechanisms and the rate expressions for calcination reactions were analyzed extensively by many researchers and several models such as shrinking core model, homogeneous reaction model and structural models which include grain models proposed for gas-solid reactions were tested. A kinetic study of limestone calcination process is very important as it is used in the design and optimization of equipment (kiln) used for calcination. It also enables the determination of suitable operating conditions for the calcination processes.

Kinetic study of different limestone have been investigated by some researchers for example, Dogu and Ar,(2001), Borgwardt (1985), Feng and

Lombardo (2002) but up-to-date there has been any reported work for the calcination kinetics using thermogravimetric data of Okpe limestone. For this reason, a fundamental investigation of this research is necessary with view to generate a reliable data for energy saving product quality lime kiln design, optimization and modeling as well as to provide basis for comparison with other limestone, especially now that the country is at the threshold of industrial development.

On the other hand, TGA replaces traditional analytical technique that require vacuum oven, muffle furnaces or micro wave ovens. It offers enhanced capabilities such as high accuracy, high throughput weight measurement and simultaneous control system temperature improving overall instrument reliability, functionality and robustness. (Skoog *et.al.*, 200

KINETIC ANALYSIS

Coats-Redfern Method

Calcination reaction of limestone can be described as thermal decomposition of solid material. stoichiometry of the reaction is as shown below:



The rate of calcination of a solid material ($CaCO_3$) can be expressed as:

$$\frac{dX}{dt} = k(1 - X)^n \tag{2}$$

Where X = conversion fraction

t= time (s)

k= rate constant (s^{-1}) for first order and ($\frac{m^3}{mol.s}$) for second order reaction.

n= reaction order.

If the heating rate of calcination process is expressed as $q = \frac{dT}{dt}$ and rate constant $k = Ae^{\frac{-Ea}{RT}}$

i.e. $q = \frac{dT}{dt}$

$qdt = dT$

Therefore, $dt = \frac{dT}{q}$ (3)

Also, $k = Ae^{\frac{-Ea}{RT}}$ (4)

Substituting (3) and (4) in to (2) gives,

$\frac{dX}{dT} q = k = Ae^{\frac{-Ea}{RT}} (1 - X)^n$ (5)

Multiplying through by $\frac{1}{q}$

$\frac{1}{q} \frac{dX}{dT} q = Ae^{\frac{-Ea}{RT}} (1 - X)^n \frac{1}{q}$

$\frac{dX}{dT} = \frac{A}{q} (1 - X)^n e^{\frac{-Ea}{RT}}$ (6)

Dividing Equation (6) by $(1 - X)^n$ results to,

$$\frac{dX}{dT} + (1-X)^n = \frac{A}{q} (1-X)^n e^{-\frac{E_a}{RT}} + (1-X)^n \quad (7)$$

If Equation (7) is multiplied by dT, we have,

$$\frac{dX}{dT} \frac{1}{(1-X)^n} dT = \frac{A}{q} e^{-\frac{E_a}{RT}} dT + (1-X)^n dT$$

Therefore,

$$\frac{dX}{(1-X)^n} = e^{-\frac{E_a}{RT}} dT \quad (8)$$

On integration of Equation (8),

$$\int_0^X (1-X)^n dx = \frac{A}{q} \int_0^T e^{-\frac{E_a}{RT}} dT$$

$$\frac{1-(1-X)^{-n+1}}{-n+1} = \frac{A}{q} \int_0^T e^{-\frac{E_a}{RT}} dT \quad (9)$$

The right hand of Equation (9) has no exact integral, but can be modified if the right hand side of the equation is expanded in to asymptotic series and the higher order terms ignored.

$$\frac{1-(1-X)^{-n+1}}{T^2(1-n)} = \frac{AR}{qE_a} \left(1 - \frac{2RT}{E_a}\right) e^{-\frac{E_a}{RT}} dT \quad (10)$$

(For n ≠ 1)

Where $\frac{AR}{qE_a}$ is constant for any definite value of n and of heating rate. Assuming that $\frac{2RT}{E_a} \ll 1$,

Equation (10) reduces to:

$$\frac{1-(1-X)^{-n+1}}{T^2(1-n)} = \frac{AR}{qE_a} e^{-\frac{E_a}{RT}} dT \quad (11)$$

(For n ≠ 1)

However, for n = 1, Equation (11) results to Equation (12) with the same assumptions:

$$\frac{-\ln(1-X)}{T^2} = \frac{AR}{qE_a} e^{-\frac{E_a}{RT}} dT \quad (12)$$

If the following functions are defined:

$$f(x) = \frac{1-(1-x)^{-n+1}}{(1-n)} \quad (\text{for } n \neq 1) \quad (13)$$

$$f(x) = -\ln(1-X) \quad (\text{for } n = 1) \quad (14)$$

Therefore, the following general equation can now be written as:

$$\ln \left(\frac{f(x)}{T^2} \right) = \ln \left(\frac{AR}{qE_a} \right) - \frac{E_a}{RT} \quad (15)$$

A plot of $\ln \left(\frac{f(x)}{T^2} \right)$ vs $\frac{1}{T}$ gives a straight line of slope $-\frac{E_a}{R}$. The frequency factor can be calculated from the intercept of this straight line.

EXPERIMENTAL

The limestone sample used in this research work was obtained from Okpella limestone deposit in Edo State, Nigeria. Chemical analysis of the ore were done with X-ray diffraction (XRD), X-ray fractionator (XRF), and Scanning Electron Microscopy (SEM). As observed from Table 1, Figures 1 and 2, the ore consists mainly of $CaCO_3$. The ore was crushed and sieved to give 120 μ , 600 μ and 2000 μ size fractions for TGA data analysis. The calcination experiments were carried out in the temperature range of 278 to 900°C. Decomposition of limestone was investigated using LINSEIS STA PT 1600 TGA system. For TGA analysis, a given amount of sample was

placed in a platinum crucible and the limestone sample was observed at 20°C/min heating rate in an N_2 gas flow.

Scanning Electron Microscopy (SEM) provides information about mineral morphology, crystal features and chemical composition. In this study, a JEOL JSM-5600/2008 Scanning Electron Microscope was used. The analysis was carried out using full back scattered detection. Operating conditions were 15kV accelerating voltage and 30 seconds counting times.

XRD measurements were performed using Shimadzu XRD600/2008 power X-ray

diffractometer with Ni filtered Cu- K_{α} radiation. The sample were scanned over 3-63 2θ interval at a scanning speed of $1.2^{\circ}/min$. However, quantitative estimates of the mineral phases were

derived from the X-ray power diffractometer data using the intensity of a certain reflection, the density and the mass absorption coefficient for Cu- K_{α} radiation for the mineral present.

RESULTS AND DISCUSSION

Thermal decomposition of limestone took place in the following form:



Table 4.1: Elemental composition of Okpella limestone using XRF after calcination

Element	Okpella Limestone (%)
Al ₂ O ₃	0.1342
B ₂ O ₃	0.0074
CaO	94.0275
CdO	0.0057
Co ₂ O ₃	0.0009
Cr ₂ O ₃	0.0003
CuO	0.0002
Fe ₂ O ₃	0.01723
K ₂ O	0.0082
MgO	2.5833
MoO ₂	0.0004
NiO	0.0006
SiO ₂	3.2134
TiO ₂	0.0005
V ₂ O ₅	0.0001
ZnO	0.0001
Total	100

The XRF analysis of Okpella limestone revealed that the sample is enriched in calcium, magnesium and silicon as the major elements forming the mineral. According to Table 1, it was shown that calcium oxide was the most predominant mineral phase composed of about 94.03% with respect to other components present in the sample. Magnesium and Silicon showed the peaks of 2.58% and 3.21% respectively. Other components ranged below 1% representing typical contents of minor importance.



Figure 1a: SEM image of Okpella limestone before calcination.



Figure 1b: SEM image of Okpella limestone after calcination.

Figure 1a shows the image of Okpella limestone before calcination, the image revealed a number of spots that correspond to the crystal features of the limestone under investigation. Each spot represents different confidence of the element present. Figure 1b also shows the SEM image of calcined Okpella limestone which shows the presence of prismatic limestone of micro calcite type as reported in the work of Scoffin (1987). The SEM image also showed that the micro calcite limestone is porous. However, the SEM image in Figure 1a has no pores as compared to the image in Figure 1b. Thus, thermal treatment has significantly contributed in creating these pores conferring on calcined products large surface areas.

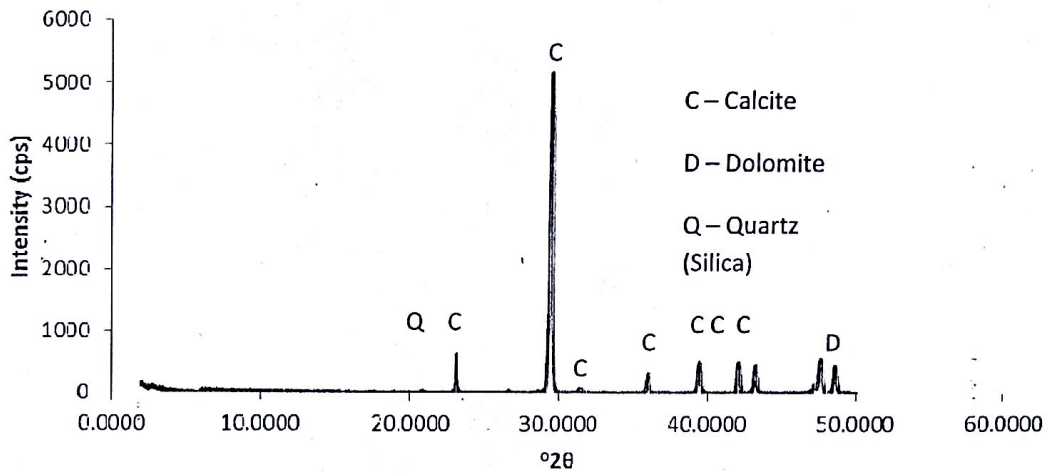


Figure 2: XRD Pattern of Okpella Limestone before calcination.

The XRD pattern of Okpella limestone was carried out using X-ray diffractometer as shown in Figure 2. The XRD pattern obtained were compared with ICDD data (International Centre for Diffraction Data) to determine the mineral phases present in Okpella limestone sample. The matching of XRD pattern with ICDD data showed that calcites were obtained at d-spacing of 29.46°, 20.97°, 36.03°, 43.23°, 47.59°

and 48.59° respectively, while quartz and dolomite were obtained at d-spacing of 23.1° and 42.1° respectively. This implies that calcite was the most predominant mineral phase present in Okpella limestone, followed by quartz and dolomite. This followed the same pattern with the XRD data obtained by Anbalagan *et.al.*, (2009) when limestone from India was used.

After calcination, the XRD pattern was carried out again as shown on Figure 3.

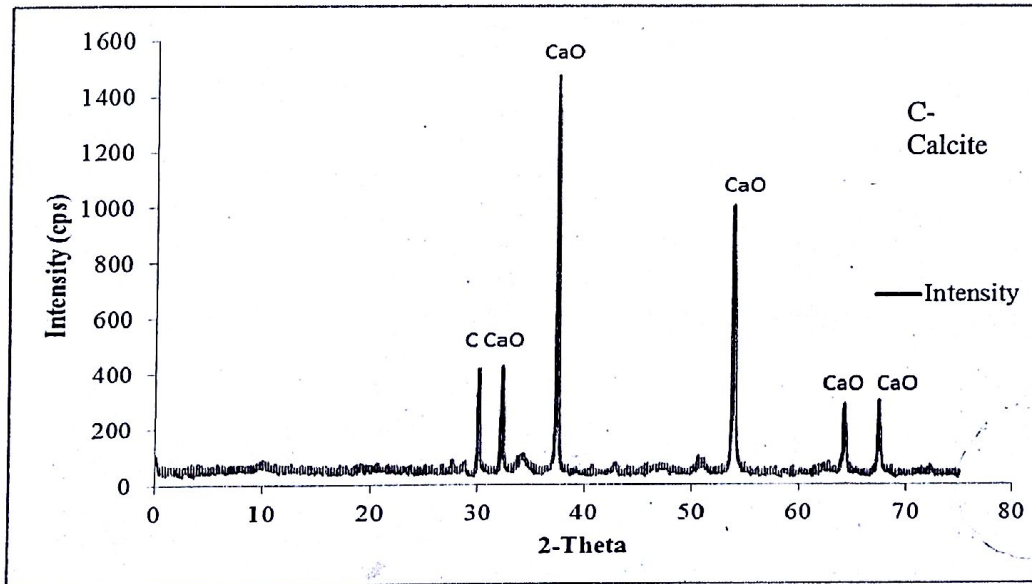


Figure 3: XRD pattern of calcined Okpella limestone.

The XRD diffractogram of calcined Okpella limestone was equally carried out as earlier described and the result shown in Figure 3. The diffractogram shown in Figure 3 were also matched with ICDD data to determine the mineral phases present in the calcined Okpella limestone. The peak matching with ICDD data showed that calcite was the mineral phase identified at d-spacing of 29.46°. Lime (CaO) was also identified at d-spacing of 32.22°, 37.38°, 53.89°, 64°.19°, and 67.44° respectively. It can be inferred that CaO is the predominant mineral phase identified in the calcined Okpella limestone. Therefore, thermal

decomposition of limestone according to Okonkwo (2002) is imperative in the production of quicklime. It is important to note that the peaks become more pronounced after calcination process, for example, the calcite intensity before calcination was a little above 500cps but rose above 1400cps after calcination. Therefore, Okpella limestone is a good and veritable source of lime production in Nigeria.

Kinetic analysis of Okpella limestone for different particle size of 120µ, 600µ and 2000µ for first and second order kinetic models are presented below:

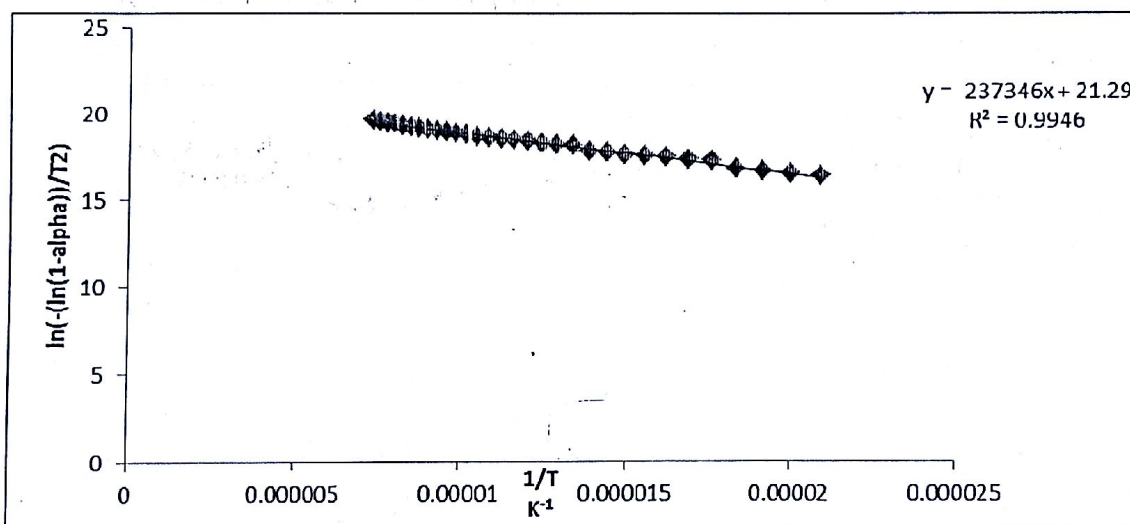


Figure 4: A graph of $\ln(-\ln(1 - \alpha)^n/T^2)$ against $1/T$ 120µ particle size for a first order kinetics.

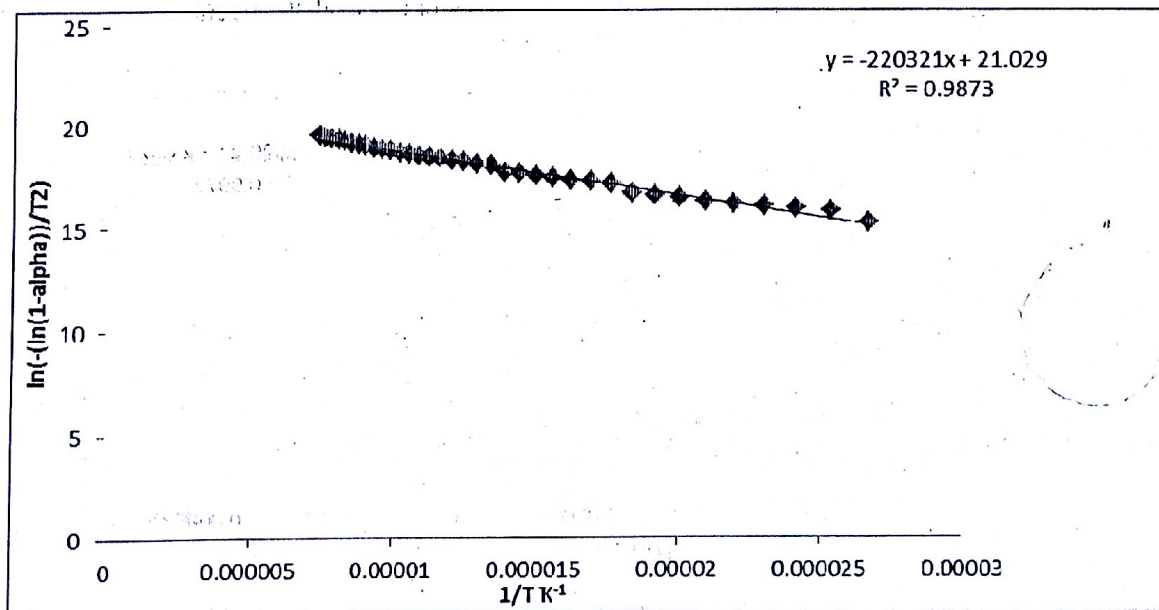


Figure 5: A graph of $\ln(-\ln(1 - \alpha)^n/T^2)$ against $1/T$ 600µ particle size for a first order kinetics.

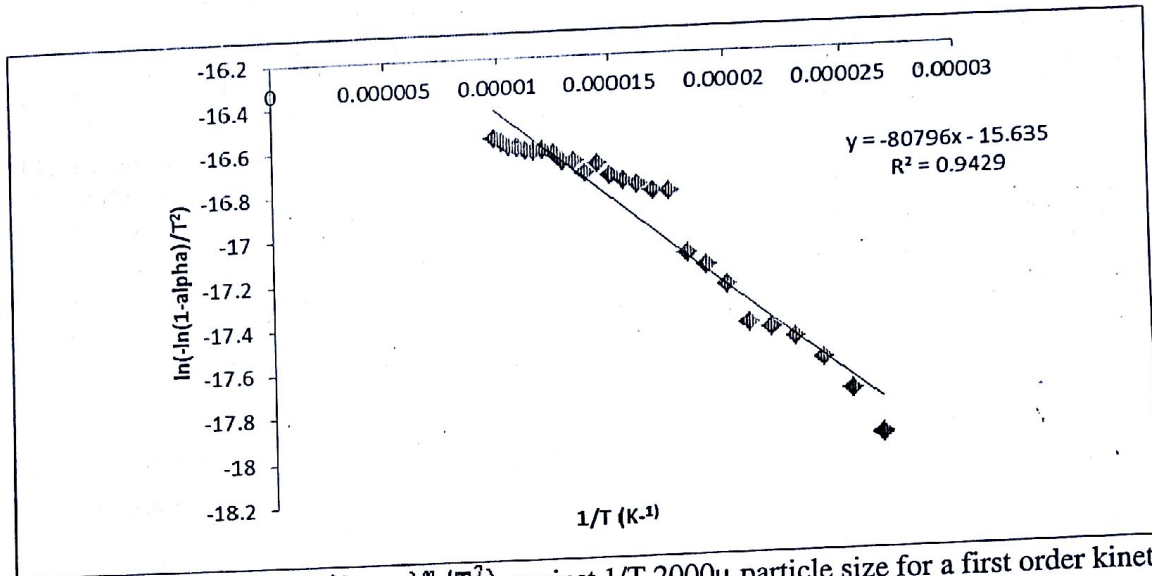


Figure 6: A graph of $\ln(-\ln(1-\alpha)^n/T^2)$ against $1/T$ 2000 μ particle size for a first order kinetics.

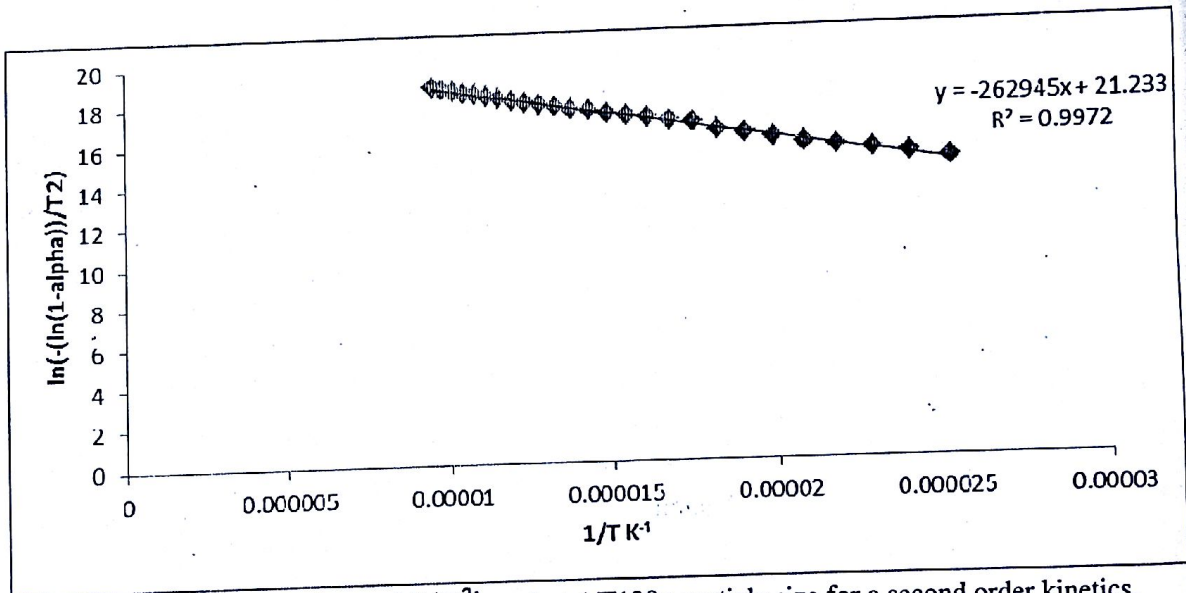


Figure 7: A graph of $\ln(-\ln(1-\alpha)^n/T^2)$ against $1/T$ 120 μ particle size for a second order kinetics.

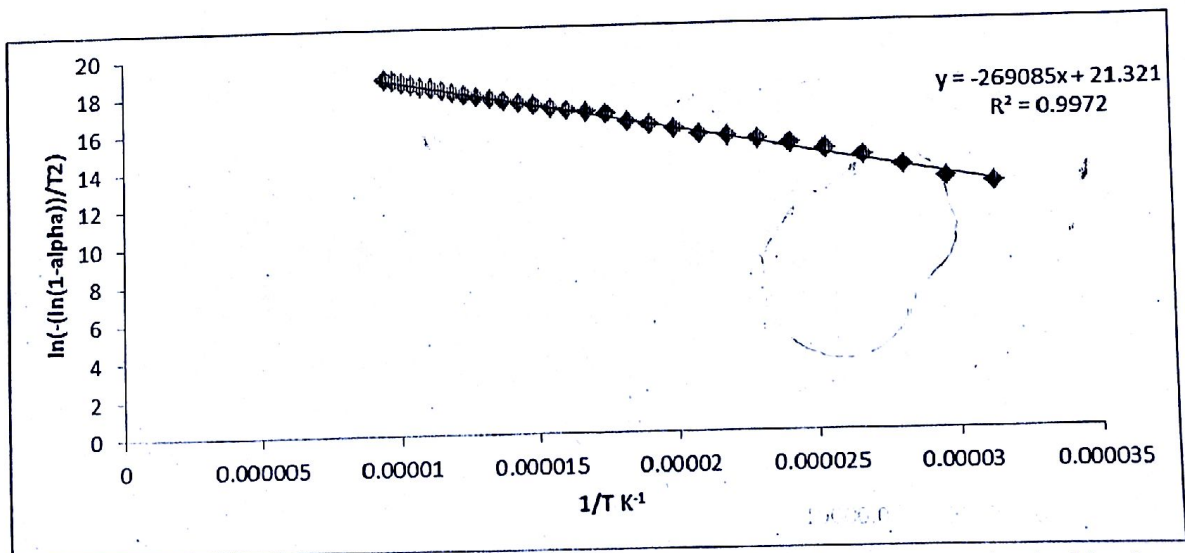


Figure 8: A graph of $\ln(-\ln(1-\alpha)^n/T^2)$ against $1/T$ 600 μ particle size for a second order kinetics.

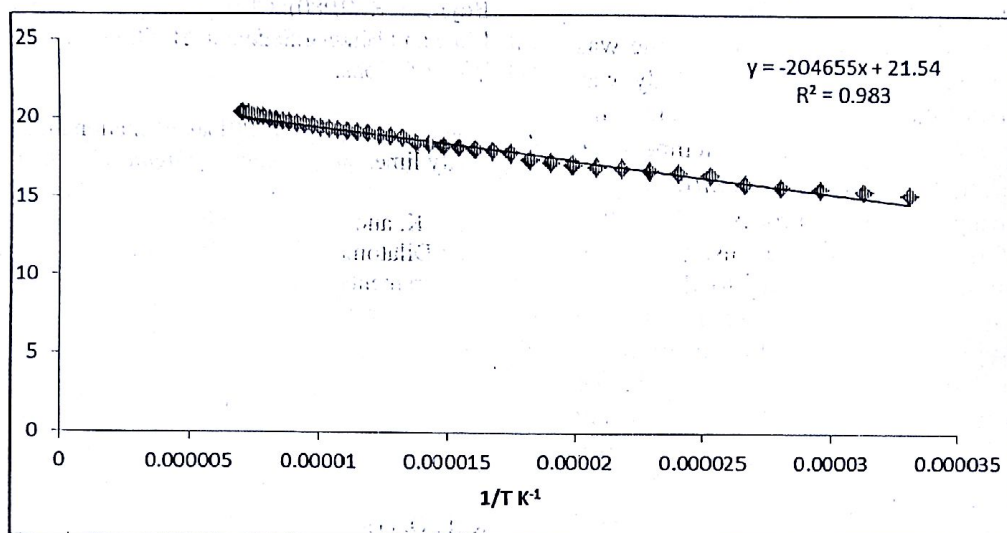


Figure 9: A graph of $\ln(-\ln(1-\alpha)/T^2)$ against $1/T$ 2000 μ particle size for a second order kinetics.

Figure 4 shows the plot of $\ln(-\ln(1-\alpha)/T^2)$ against $1/T$ for 120 μ particle size first order kinetics which shows a linear relationship with regression coefficient (R^2) of 0.994. Similar plots of $\ln(-\ln(1-\alpha)/T^2)$ against $1/T$ in Figure 5 to Figure 9 for 120 μ , 600 μ and 2000 μ particle sizes revealed regression coefficient (R^2) of 0.994, 0.987 and 0.947 for first order as well as 0.997, 0.997 and 0.983 for second order. Activation energy and frequency factor which are temperature dependent

were deduced from the slopes and intercepts of these plots with values of 1.97×10^5 kJ/mol, 2.23×10^5 kJ/mol, 2.19×10^5 kJ/mol, and 9.04×10^{14} , 1.04×10^{14} , and 9.39×10^{14} respectively. However, the linear relationship in the graphs confirmed that heat transfer is the rate controlling mechanism in the calcination of limestone and that there was significant mass loss with increase in temperature.

Table 2: Kinetic analysis for samples at various particle sizes using first order mechanism.

S/No	Particle size(μ)	E_A (kJ/mol)	A	R^2
1	120	1.97×10^5	9.04×10^{14}	0.994
2	600	1.83×10^5	6.45×10^{14}	0.987
3	2000	1.08×10^5	0.7922	0.947

Table 3: Kinetic analysis for samples at various particle sizes using second order mechanism.

S/No	Particle size(μ)	E_A (kJ/mol)	A	R^2
1	120	2.23×10^5	1.04×10^{14}	0.997
2	600	2.19×10^5	9.39×10^{14}	0.997
3	2000	1.70×10^5	1.01×10^5	0.983

CONCLUSION

Thermal decomposition of Okpella limestone was investigated by using TGA data. The study was used to verify the effects of particle size 120μ , 600μ and 2000μ at calcination temperature of 900°C and heating rate $20^{\circ}\text{C}/\text{min}$ on the reactivity of calcination process. To this effect, Coats-Redfern method was used and the results were examined. According to the Coats-Redfern method, the process fitted best in a second order kinetics model with regression coefficients between 0.983 and 0.997. The mass loss in the thermal decomposition increases with increasing temperature and decreasing particle size. Although significant change in mass loss was not observed at the starting temperatures. Significant changes occurred between 388.57 and 513.57°C . Based on the kinetic analysis, it was observed that calcination process was dependent on reaction temperature, heating rate and particle size. It also observed that the values of activation energies for both models i.e first and second orders generally decreased with decreasing particle size which can be attributed to the increasing intra particle resistance to the escape of CO_2 . The XRD pattern showed that calcite was the predominant mineral phase present in Okpella limestone, followed by quartz and dolomite. The XRF analysis also proved that the sample is enriched in calcium, magnesium and silicon as the major element forming the mineral, while SEM images showed the presence of prismatic limestone of micro calcite. Therefore, utilization of Okpella limestone from Edo State Nigeria has great potentials due to its availability and high percentage of CaO needed in many industrial applications.

REFERENCES

- Agnello, V.M. (2003). A review of dolomite and limestone industry in South Africa Report R(43) 2-10.
- Anabalagan, G. and Gunasekaran, (2009). Thermal decomposition of natural dolomite Material Science, 1 - 3.
- Borgwardt, R.H. (1985). Calcination kinetics and surface area of dispersed limestone particles, *AIChE J.*, (31), 103-111.
- Borgwardt R.H., Harvey, D.R. (1972). Properties of carbonate rocks related to SO_2 reactivity, *Environ. Sci. Technol.* (6), 213-222.
- Boynton, R. S. (1980). Chemistry and Technology of Lime and Limestone. Second Edition New York John Wiley & Sons.
- Dogu, G. and Ar, I. (2001). Calcination kinetics of high purity limestone. *The Chem. Engineering J.* 3(2), 84-91.
- Feng, K. and Lombardo, S. (2002). Kinetic Analysis from Dilatometry and mass Spectrometry measurements of the decomposition and sintering of calcium carbonate. *J. Ceramic Process. Res.* 3(3), 108.
- Hassibi, M. (2002). Factors affecting quality of quicklime (CaO) from mining or manufacturing usage.
- Kirk, O. (1982). Encyclopedia of chemical technology, 4th edition, (12), McGraw Hill Book Company, New York.
- Neville, A.M. (1992). Lime and other alternative cements. Hill Book Company, New York 4th edition, 120-121.
- Ofulume, A.B. (1988). The Jakura filler/extender in paints, paper and plastic industries. *Journal of mining and geology* 22(2) 187-191.
- Okeke, O.C. (1991). Role of mineral raw material in the development of indigenous building materials industry in Nigeria. *Journal of mining and geology.* 22(2) 127-133.
- Richard, A.C. (2010). Investigating the use of Concentrated Solar Energy to Thermally Decompose Limestone. A Ph.D thesis submitted to the School of Mechanical and Chemical Engineering, University of Adelaide, Australia. 22.
- Scoffin, T. P. (1987). An introduction to Carbonate Sediments and Rocks, Blackie 45.
- Skoog, D. A., Holler, F. J. and Nieman, T. A. (2000). Principles of instrumental Analysis, Philadelphia. Saunder College Publisher, 134 - 137.
- Smith, D. (2001). SO_2 Controls: Cost of Scrubbers Down to \$100/kW. Power Engineering. Web. (accessed April, 2012).
- Wheeler, B.D. (1999). Analysis of limestone and dolomites by X-Ray Fluorescence Spectrophotometer. *The Rekaigu Journal* 10(1), 16-20.