

The Kinetics of Calcination of High Calcium Limestone

P. C. Okonkwo*, S. S. Adefila **

Department of Chemical Engineering, Ahmadu Bello University, Zaria Nigeria;

ABSTRACT

The kinetics of calcination of a high calcium type of limestone was studied. Ukpilla limestone found in the central region of Nigeria was studied. The limestone composition shows that the limestone has 51.29% calcium oxide and 41.53% loss on ignition and magnesium oxide content of 2.23%. The following parameters were determined; diffusion coefficient of lime layer, and mass transfer coefficient, conductivity of lime layer and heat transfer coefficient, convective parameter and diffusive parameter for temperatures 900⁰C, 1000⁰C, 1060⁰C and 1080⁰C.

The reaction was found to be limited by mass and heat transfers across the lime layer of the calcining article, the optimal temperature of calcination was found to be 1060⁰C. Diffusivity and mass transfer coefficient decreases with increase in calcination temperature. The thermal conductivity increases with increase in temperature. The diffusive and convective parameter decreases with increase in temperature. The reactivity of lime calcined at different temperatures were determined. The reactivity of the lime increases with decrease in calcination temperature.

Keywords – Calcination, Kinetics, Mass transfer, Heat transfer, Ukpilla limestone

1.0 INTRODUCTION

Limestone is one of the most basic raw materials employed in the industry and has been compared to one leg of a six-legged stool around which modern industry revolves, the oilier legs being coal, petroleum, iron ore, sulphur and salt [1]. Lime (CaO) is one of the oldest chemicals known to man and the process of limes production is one of the oldest chemical industries [2]. Quicklime was produced in US as early as 1635 [3] in Rhode Island, Technical progress while non existing in centuries past has rapidly advanced the lime industry during the last fifty years in the area of process methods and design.

Limestone deposits are widely distributed in Nigeria [4], The limestones and limes from the various deposits differ in physico-chemical properties and can be classified according to their chemical composition, texture and geological formation. Limestone is generally classified into the following types:

- a) High calcium: The carbonate content is composed essentially of calcium carbonate with a magnesium carbonate content of no more than 5% (usually less)
- b) Magnesian: This contains magnesium carbonate to about 5 – 20%.
- c) Dolomitic: This contains over 20% MgCO₃ (magnesium carbonate), however the maximum MgCO₃ content will not exceed 45.6%, the exact amount contained in a true pure, equimolar dolomite with the balance calcium carbonate.

Furthermore the varying properties of the limestones have profound influence on the processing methods. It is thus necessary to obtain a comprehensive information such as physico-chemical properties of the limestones, the burning characteristics and kinetic parameters for the calcination of the limestones. These usually aid optimal design and operation at lime kilns.

In this work, the kinetic studies of the calcination of Ukpilla limestone (a local high calcium limestone resource) was studied. There is an estimated reserve of about 1x10⁸ tonnes of Ukpilla limestone [4]. This deposit can

support chemical lime and other lime products production facilities over a reasonable length of time,

2.0 Theory

At calcinations temperatures of about 900°C dissociation of limestone proceeds gradually from the outer surface of the stone particle inward like a growing shell [5] Simple conservation shows that the rate of the reaction is described by:-

$$\dot{n} = 4\pi r^2 \ell_{CO_2} \frac{dr}{dt} \quad (1)$$

where \dot{n} = the rate of decomposition of the limestone

r = radius of calcining particle

ℓ_{CO_2} = molar density of carbon dioxide g/cm³

which suggests that diffusion of CO₂ through the thin layer of active lime to the outer surface lays a major role in the rate determination. It has been shown conclusively by Hill [6] that the progress of the reaction is related to the loss in weight of the calcining limestone in the form

$$r^* = r/r_0 = (m^*)^{1/3} = (Mt/(M_0))^{1/3} \quad (2)$$

Where r^* = dimensionless radius

M_t = mass of calcining particle g

M_0 = initial mass of the limestone particle g

m^* = dimensionless radius

If the reaction rate is characteristically limited by chemical kinetics and the interface moves at constant speed, $(m^*)^{1/3}$ should vary linearly with time. But this is not so. This therefore suggests that transport phenomena play an important role. Investigations have show that combined effect of heat and mass transfer determine the rate of the reaction. This implies that the chemical step is sufficiently rapid for equilibrium to be maintained at the interface. The partial pressure of CO₂ in the gas phase at the reaction front (P_{CO_2})_R can therefore be predicted from the reaction temperature. Assuming the reaction is controlled by mass transfer alone, the CO₂ partial pressure at the reaction front is the decomposition equilibrium pressure (P_{CO_2})_{eq}. Baker [6] has investigated the equilibrium for calcination of limestone and found that the equilibrium constant K_p (atm.) is best given by.

$$\text{Log}_{10} K_p = \log_{10} [P_{CO_2}]_{eq} = \frac{8308}{T} + 7.079 \quad (3)$$

Where T = calcination temperature

P_{CO_2} = Partial pressure of CO₂ atm

Investigations by Hills [7] 1968 and Dennis [8] have indicated a maximum 11K temperature difference between the reaction interface and the surrounding temperature.

Murray, Fischer and Sabcen and Azbe [9] have shown that the lime layer is fine. The mechanism of CO₂ diffusion through it would therefore be Knudsen diffusion. The result obtained by Ar [10] and Moffat[11] is consonance with that of Hills. Okonkwo [12] established the that the decomposition of limestone is not limited by chemical reaction. Further investigations by Khraisa and Dugwell[13] have suggested shrinking core kinetics for limestone decomposition which is in agreement with other investigations. The rate at which CO is transferred from the reaction front to the bulk gas phase around the sample can be represented by:

$$\dot{n} = \frac{4 \pi r D \{ [PCO_2]_R - [PCO_2]_G \} r}{R'T \{ (1/r^*) - 1 + (D/k_g r_o) \}} \quad (4)$$

Where

D = diffusivity of lime layer cm² sec⁻¹

K_g = mass transfer coefficient

[PCO₂]_R = partial pressure of CO₂ at reaction front atm

[PCO₂]_G = partial pressure of CO₂ in the bulk gas

R' = universal gas constant in mechanical terms cm² atm.gmole⁻¹k⁻¹

Equation (4) can be rearranged in the form

$$\frac{[PCO_2]_R - [PCO_2]_G}{\dot{n}} = \frac{R'T}{4 \pi D r_o} [(1/m^*)^{1/3} - 1] + \frac{R'}{4 \pi k_g r_o^2} \quad (5)$$

a graph of

$(PCO_2)_R - (PCO_2)_G / \dot{n}$ against $[(1/m^*)^{1/3} - 1]$

should be a straight line. The diffusion and mass transfer coefficients can be obtained from the slope and intercept respectively.

The slope is equal to $R'T / 4\pi D r_o$

The intercept is equal to $R' T / 4k_g \pi r_o$

Hills 1968[7] and Dennis 1985[8] have shown with little error that the rate of heat transfer to the reaction interface is

given by

$$q = -Hn \quad (6)$$

and

$$q = \frac{4 \pi k (T_R - T) r_o}{((1/r^*) - 1 + (K/h r_o^2))} \quad (7)$$

Where

H = molar heat of decomposition of calcium carbonate cal.gmole⁻¹

q = rate of heat transfer to the reaction front J/s

k = thermal conductivity of lime layer cal. cm⁻¹sec⁻¹C⁻¹

T_R = temperature of reaction front K

T = temperature of calcination environment K

h = heat transfer coefficient across lime layer

These equations can be rearranged to give

$$\frac{T_R - T}{n} = \frac{H}{4\pi kr_o} ((1/m^*)^{1/3} - 1) + \frac{H}{4\pi hr_o} \quad (8)$$

a graph of $(T_R - T) / n$ against $(1/m^*)^{1/3} - 1$ is a straight line graph.

The slope is equal to $H / 4\pi kr_o$.

The intercept is equal to $H / 4\pi hr_o$.

The thermal conductivity and heat transfer coefficient were obtained from the slope and the intercept respectively.

The diffusive parameter is correlated as;

$$\frac{1}{\Gamma} = 1/D + \frac{[P_{CO_2}]_{eq} H^2}{R'R''T^3 k} \quad (9)$$

Where Γ = diffusive parameter

R'' = universal gas constant in heat units cal g-mole⁻¹k⁻¹

R' = universal gas constant in mechanical units cm³.atm gmole

The convective parameter is correlated as

$$\frac{1}{\Lambda} = 1/k_g + \frac{[P_{CO_2}]_{eq} H^2}{R'R''T^3 h} \quad (10)$$

Where Λ = convective parameter

The equilibrium relationship assuming $T_R - T$ is small is

$$PY_R = PY_e + a(T_R - T) \quad (11)$$

Where $a = dK_p/dt$

P = Total pressure of gases atm

Y_e = mole fraction of CO₂ at the interface at equilibrium

Hills(1968) used equations (4) and (7) and equation (11) with the continuity equation to obtain

$$3r_o^2 - 2r^*3 - \frac{2\Gamma(1-r^{*3})}{r_o\Lambda} = \frac{1-6VP(Y_e - Y_p)t}{R'Tr_o} \quad (12)$$

Where Y_p = mole fraction of CO₂ at the reaction interface

V = molar volume of calcium carbonate cm³/g

The time for complete calcinations is obtained when $r^* = 0$

$$t_c = [1 + 2\Gamma/r_o] / [6VP(Y_e - Y_p)/R'Tr_o^2] \quad (13)$$

Where t_c = time for complete calcination of the limestone particle s

Hills for pure calcium carbonate established that;

$$D=A+B(T-830^{\circ}\text{C}) \quad (14)$$

where

$$A = 0.083 + 0.002 \text{ cm}^2 \text{ Sec}^{-1}$$

$$B = 0.00021 \pm 0.00003 \text{ cm}^2 \text{ Sec}^{-1} \text{ C}^{-1}$$

3.0 Experimental

3.1 Calcination:

A laboratory muffle furnace of dimension 30cm by 20cm manufactured by Philip Harris UK was used. The furnace is electrically heated with temperature regulator thermostatically controlled. The temperatures used in the study are usually set and sized limestones are burned in very clean nickel crucibles. The weight of the samples are monitored over the periods of calcination. The weights are measured with electronic balance to ~ 0.01. This is by withdrawing the sample from the furnace at intervals and taking the weight. The measurement is done very fast. This is to ensure that the sample readily assumes the temperature of the furnace.

The opening of the furnace door at intervals ensures the sweeping of air through the furnace to keep the composition of the gas phase around the sample fairly constant during each run. The sensitivity of the experiment is improved using first degree least squares with five points smoothing technique. The rate of reaction was obtained by numerical differentiation of the sample weight using Lagrange's five point interpolation formula [14]. The sized samples are assumed to be spherical since all previous works have used spherical samples or samples are treated as if they are spherical.

3.2 Reactivity Test

Rise in temperature of the paste formed upon the addition of a definite quantity of distilled water to a definite weight of caustic lime is an accepted criterion for chemical "reactivity". The method as reported by MacIntire and Stansel [15] was used. Here a 7.5g (100mesh) charge was placed in a tall insulated glass cylinder and its temperature and that of the freshly boiled distilled water were recorded. Twenty millilitres of that water was added to the lime charge and the mixture was stirred constantly. Reading were made at intervals of 15 seconds until rise in temperature was maximal. Then the readings are taken at intervals of 30 seconds. This was determined for lime samples calcined at different temperatures.

4.0 Results and Discussion

4.1 Reaction Limiting Step

The plot of variation of $(1/M^{*1/3})$ at 900°C , 1060°C and 1080°C for Ukpilla limestone is shown in Figure 1. It exhibits characteristic S shaped curves. Hills 1968[7] observed the position of reaction interface by painting sections of partially calcined samples of calcium carbonate with an alcohol solution of thymophtalein (as dye), the interface was seen to remain spherical and sharply defined and the sample weight calculated from the position of the interface agreed with the measured weight within experimental error, thus agreeing with the

relation;

$$r/r_0 = (M^*)^{1/3} = (Mt/Mo)^{1/3}$$

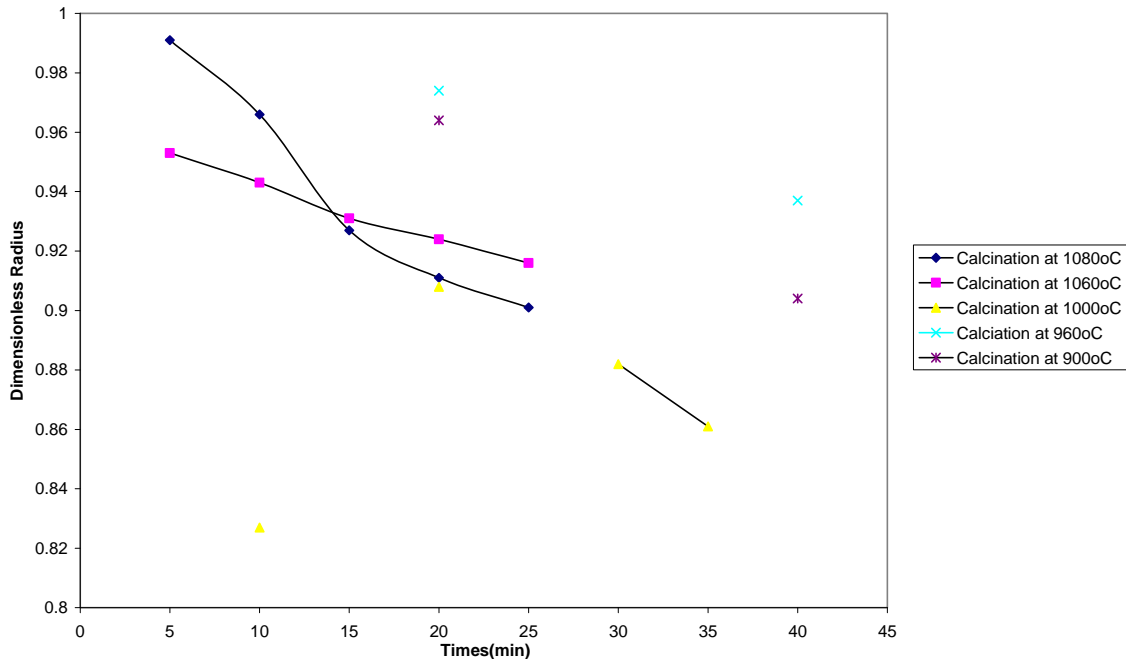


Figure 1 Variation of Dimensionless radius with Time

If the reaction is chemically controlled and the interface moves at a constant speed ($1/M^*^{1/3}$) should vary linearly with time, However the plot in figure 1 has a characteristic S shape suggesting that the reaction for particles in the range of 10mm size is controlled by mass and heat transfer phenomena. Similar range of particle of limestone were employed in this work thus the shape of the plot suggest heat and mass transfer controlled reaction. For Ukpilla limestone it was established that 1060°C is the optimum calcination temperature as shown in Figure 2 and that the progress of the reaction hence time for total calcination of a particle is dependent on the size of the particle as shown in Figure 3.

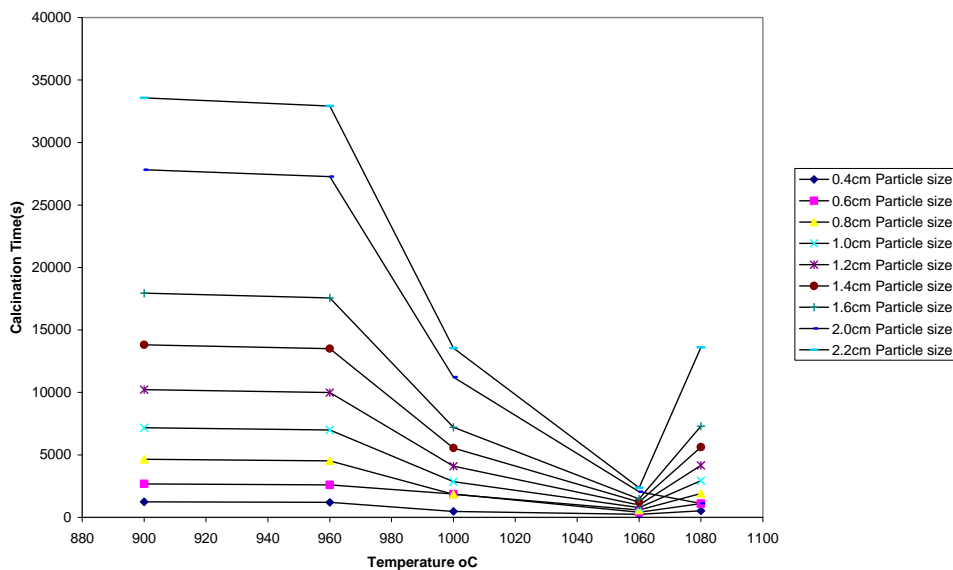


Figure 2 Variation of Calcination Time with Temperature for Ukpilla Limestone

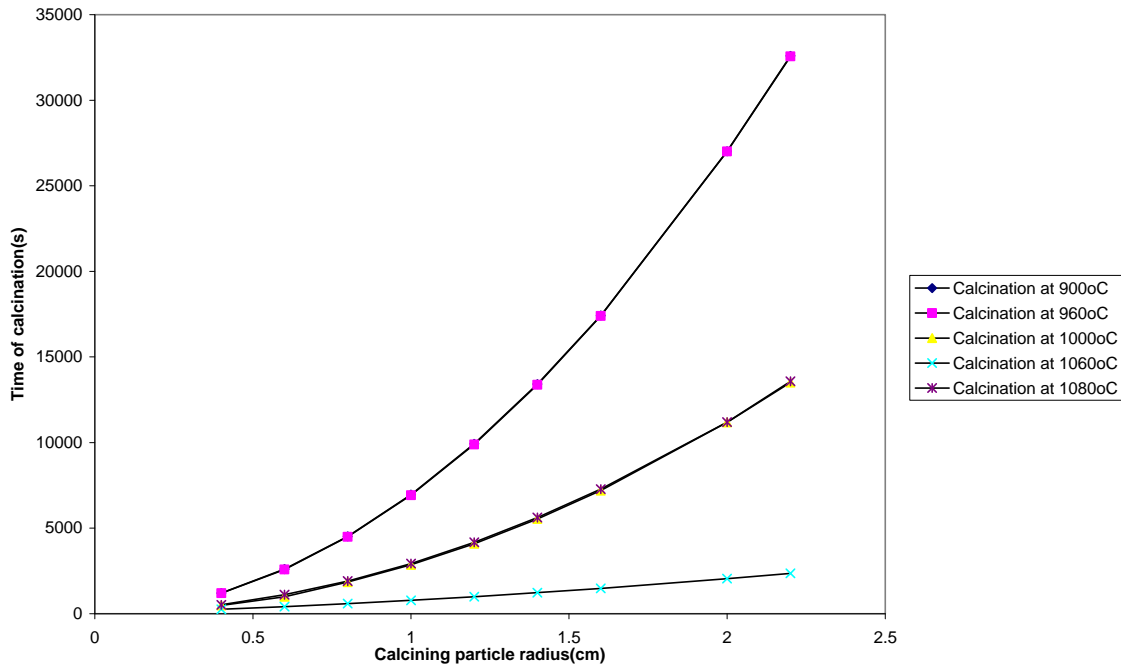


Figure 3 Variation of calcination time with particle radius at -345mmH20(Ukpilla Limestone)

4.2 Diffusivity and Mass Transfer Coefficient

The plot of $(P_R - P_G) / \dot{n}$ against $[(1/m^*)^{1/3} - 1]$ at 900°C, 960°C, 1000°C, 1060°C and 1080°C as shown in Figure 4 show a high degree of linearity of the plots further confirming that transport phenomena rather than chemical step control the calcination reaction. The Diffusivity and mass transfer coefficient were calculated from the slope and the intercept of the plots as shown in Tables 1 and 2, Least square method was used to obtain the best fit lines. The correlation coefficients are in the range of 0.95 – 0.97. The values of Diffusivity has been correlated in the form [7] as

$$D = A + B(T - 830^\circ\text{C})$$

where

$$A = 0.83 \pm 0.002 \text{ cm}^2 \text{ sec}^{-1}$$

$$B = 0.00021 \pm 0.00003 \text{ cm}^2 \text{ Sec}^{-1} \text{ C}^{-1}$$

The relatively high values of Diffusivity that were obtained can be due to the decrepitation behaviour of Ukpilla limestone. This leads to increase in the surface area of the calcining particles over the period of calcination and possible occurrence of bulk diffusion via the cracks of the calcining particle. But the literature values were based on Knudsen diffusion through the lime layer. There is a decrease in diffusivity with temperature increase, This can be attributed to hard burning of lime relative to that of lower temperature with the resultant decrease in fineness and porosity of the lime.

TABLE 1 Average Experimental Values of Transport Properties of Ukpilla Lime

PROPERTIES	900°C	960°C	1000°C	1060°C	1080°C
Diffusivity $\text{cm}^2 \text{sec}^{-1} \times 10^{-4}$	0.399	1.125	0.179	0.685	0.058
Mass transfer coefficient $\text{Msec}^{-1} \times 10^{-2}$	4.27	4.81	2.365	0.52	0.74
Thermal conductivity $\text{Jm}^{-1}\text{sec}^{-1}\text{c}^{-1}$	0.371	0.195	0.52	6.279	0.859
Heat Transfer coefficient $\text{Jm}^{-2}\text{sec}^{-1}\text{c}^{-1}$	8.2×10^2	9.2×10^3	9.1×10^3	6.69×10^2	8.3×10^3

TABLE 2 Determined Values of Diffusive and Convective Parameters for Ukpilla Lime

TEMPERATURE °C	DIFFUSIVE PARAMETER Γ	CONVECTIVE PARAMETER Λ
900	0.068	3.839
960	0.045	3.984
1000	0.057	2.035
1060	0.415	0.282
1080	0.031	0.503

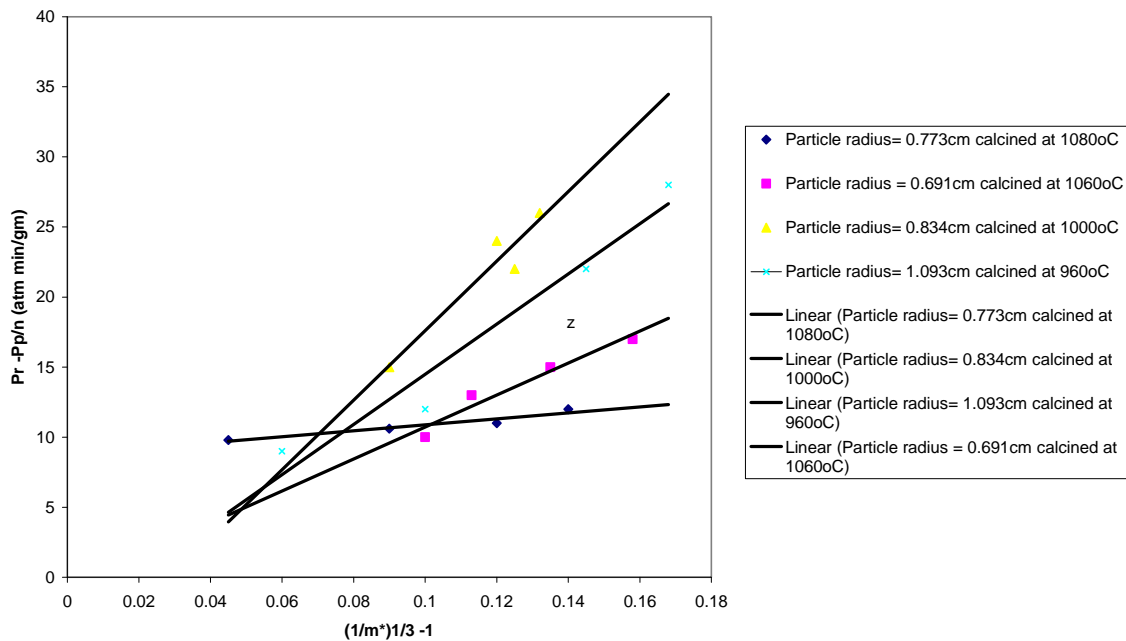


FIGURE 4 $Pr - Pp/n$ versus $(1/m^*)^{1/3} - 1$ FOR UKPILLA LIMESTONE

4.3 Thermal and Heat Transfer Coefficient.

The plot of $T_r - T/n$ versus $[(1/M^*)^{1/3} - 1]$ for a range of particle sizes at 900°C, 960°C, 1000°C, 1060°C and 1080°C were done as shown in Figure 5. Least square method was used to obtain the best fit lines. The correlation coefficients are in the range of 0.95 - 0.97. The thermal conductivity and heat transfer coefficient were calculated from the slope and intercept of the plots respectively. The values are shown in Tables 1 and 2. It was found out that the thermal conductivity increases with temperature. The sharp decrease of thermal conductivity value at 1080°C cannot never be immediately explained. The large scatter of heat transfer results is due to the fact that heat transfer rate largely dependent on factors outside the sample.

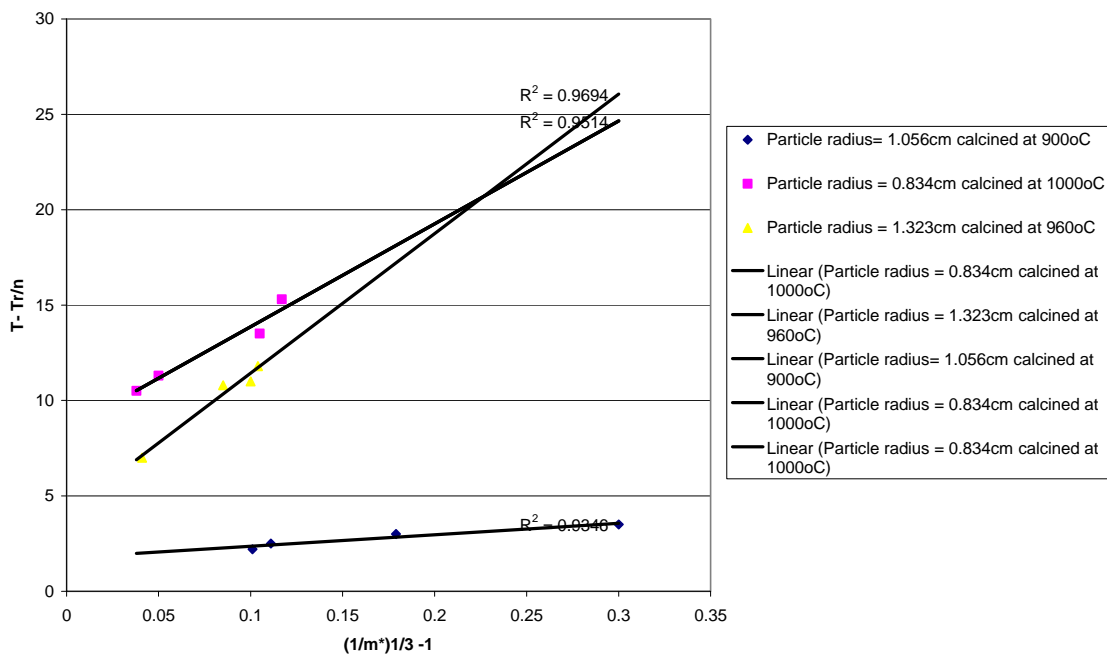


FIGURE 5 T- Tr/n versus (1/m*)^{1/3}-1 FOR UKPILLA LIMESTONE

4.4 Reactivity Test

The plot of the elevation of temperature versus time on addition of a definite quantity of water to definite amount of limes are shown in Figures 1 for Ukpilla lime . The high elevation of temperature at shorter times for limes produced at lower temperatures indicate high reactivities of these limes. At lower temperature of calcination the lime formed is of fine structure. If the limestone is calcined under severe calcining condition at high temperature, the stone shrinks by 20 – 50% of the original size. This shrinkage densifies the resultant lime narrowing and occluding its micropores and fissures so that the reactivity of lime is reduced (Boynton 1980)

[1]. The limes from Ukpilla limestone showed high reactivities within the range of temperature of study. This confirms that Ukpilla lime is of fine structure. The limes produced at 1060°C calcination temperature showed high reactivity for Ukpilla lime as shown in Figures 6 . This then suggests that at 1060°C calcination temperature reactive limes can be produced at high kiln throughputs.

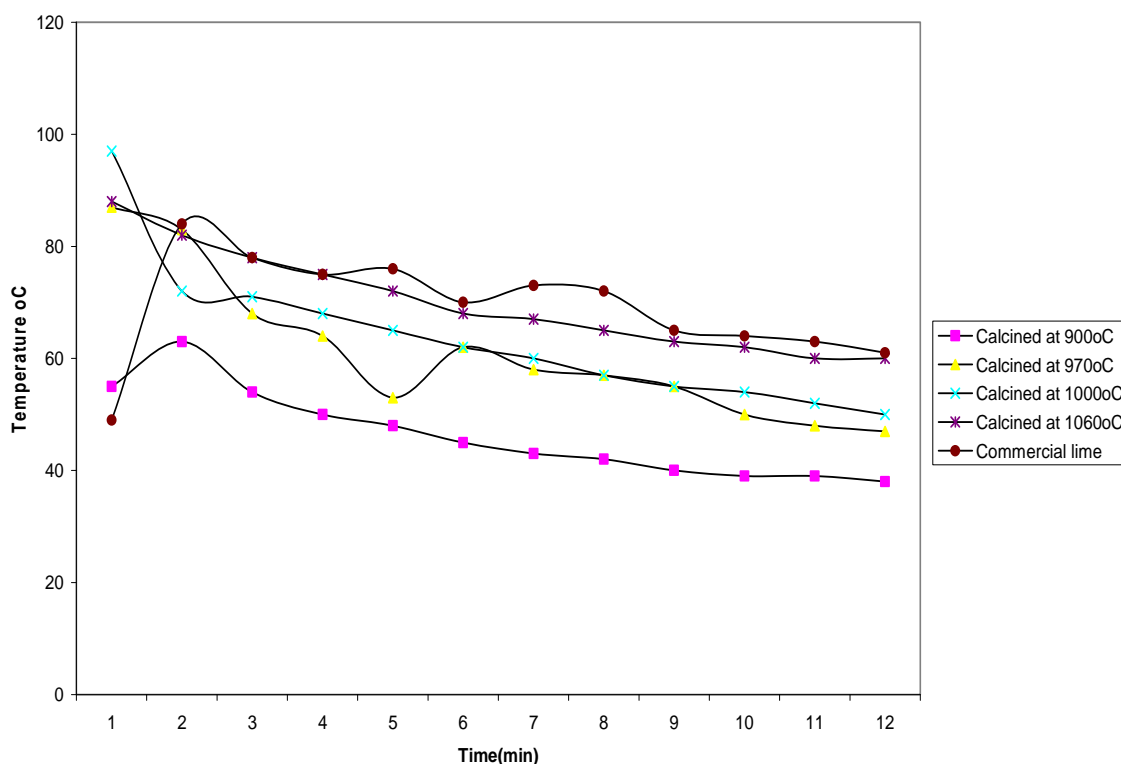


Figure 6 Hydration Reactivity of Ukpilla lime calcined at different Temperatures

5.0 Conclusion

The kinetic studies showed that at calcination temperature of 1060°C the lowest calcinations time was obtained. The trend of the values of the calcinations parameters obtained compare favourably with literature. 1060°C was found as the optimum calcination temperature. The incidence of decrepitation during burning is found to be prevalent with Ukpilla limestone. This is likely to cause clogging of the burning zone in vertical shaft equipment. The kinetic parameters obtained are very useful for the design of efficient kiln for the burning of the limestone. The parameters will also aid in operation of kilns employed for the burning of the limestone to achieve energy efficiency and high productivity of the kilns.

References

- [1] Boynton R.S Chemistry and Technology of Lime and Limestone. Wiley Interscience Pub London 1980
- [2] Mark F.H and Standen A. Encyclopedia of Chemical Technology Edited by Kirk Othmer Interscience Pub. Inc. New York 1975
- [3] Kirk Othmer Encyclopedia of Chemical Technology' 3rd Edition vol. 14 pg. 361. John Wiley and Sons 1981
- [4] Abdullahi A. Potentials of Solid Minerals Industry in Nigeria. Mufadenic Press Nigeria 1996
- [5] Bogwardt R. Calcination Kinetics and Surface Area of Dispersed Limestone Particle .The Chemical Engineering Journal Vol. 31, pp. 103-111 1985
- [6] Baker , E.H . Journal of Chemical Society 464 1962
- [7] Hills A.W.D Chemical Engineering Science Vol.23 pp. 297 1968
- [8] Dennis J.S PhD Dissertation University of Cambridge 1985
- [9] Murray, J.A, Fischer H.C and Sabeen D.V Proc. Am. Sc. Test. Mat 50 1950
- [10] Ar I. D " Calcination Kinetics of High Purity Limestone Particles" The Chemical Engineering Journal Vol. 83 Issue pp. 103 2000
- [11] Moffat W. and Walmsely " Understanding Lime Calcination Kinetics For Energy Cost Reduction .59th Appita Conference Auckland New Zealand 2006
- [12] Okonkwo P.C MSc Thesis Ahmadu Bello University Zaria Nigeria 1991
- [13] Khraisa Y, and Dugwell " Thermal Decomposition of Limestone in Thermogravimetric Analyzer" Chemical Engineering Research and Design vol.67 pp.48 1989
- [14] Hovanessian S.A " Computational Mathematics in Engineering" Lexington Books.1976
- [15] MacIntire W.H and Stansel T.B Ind. Eng. Chem. Vol.45 pp. 170 1953