

1977 (1977) 0791  
BM/93

# THERMAL DECOMPOSITION OF LIMESTONE

48

by  
A. K. Gupta & Mohan Rai  
Central Building Research Institute,  
Roorkee-247 672

## ABSTRACT

The movement of calcination front depends mainly upon the diffusion of carbon dioxide outwards through the oxide layer and the conduction of heat inwards through the oxide layer. It has been concluded by various investigators that the conduction of heat plays a more important role than the diffusion of carbon dioxide, while calcining a lump of limestone.

A heat balance equation relating the surface heat transfer coefficient with various other factors has been derived and its value is calculated by using the experimental data obtained by Azbe under the conditions for which the relation has been derived.

## INTRODUCTION:

Calcination of limestone seems to be the simplest of all chemical reactions. But the mechanism with which calcination front proceeds is still not known very well. Burning of limestone still remains an art in the absence of sufficient scientific relationships. The present work consists of mathematical equations derived for the calculation of the rate of heat transfer in a lump of limestone.

A lump of limestone, if dropped in a furnace, at a sufficiently high temperature, is likely to be surrounded by a heat envelope (Fig. 1). A temperature gradient between the envelope and the surface and between the surface and the centre of the lump develops, which governs the transfer of heat. Once the surface temperature is increased above the dissociation temperature, the surface layer gets dissociated and between the dissociated and undissociated limestone, an interface forms. The following four processes take place simultaneously at the interface:

- (i) Heat is transported from the heat envelope to the surface of the lump by convection and radiation.
- (ii) Conduction of the heat which is necessary to dissociate as well as to raise the temperature of the interface to the dissociation point.
- (iii) Dissociation of limestone at the interface takes place and carbon dioxide is liberated.
- (iv) Carbon dioxide is transported by diffusion from the interface to the surface of the lump.

It follows that either the heat conduction or the diffusion of carbon dioxide through the oxide layer is a rate controlling step. Furnas<sup>1</sup> in 1931 and Charles<sup>2</sup> in 1959 published their work supporting the view that it is heat conduction only which is a rate controlling step.

With continuous heating in a zone of increasing temperature, a growth of layer crystal at the expense of smaller ones takes place. As a result of this process

the pore dimension reduces. Any change in the pore dimension and number of pores can very well increase the diffusional resistance by several powers of ten.<sup>3</sup> Murray<sup>4</sup> and other investigators<sup>5</sup> noted the shrinkage of the oxide layer with time and temperature. As a result of shrinkage the volume of the oxide layer reduces, while that of the carbonate remains unaffected. Therefore the pore dimension reduces at the expense of the fine cracks formed in the oxide layer due to shrinkage. This fact is in coincidence with the findings of Fischer,<sup>6</sup> who observed that the porosity of the oxide layer is maximum in the temperature range of 1070-1180°C, and smaller outside this range.

Hence, it can be concluded that if we restrict the temperature in the kiln below 1180°C, the rate of

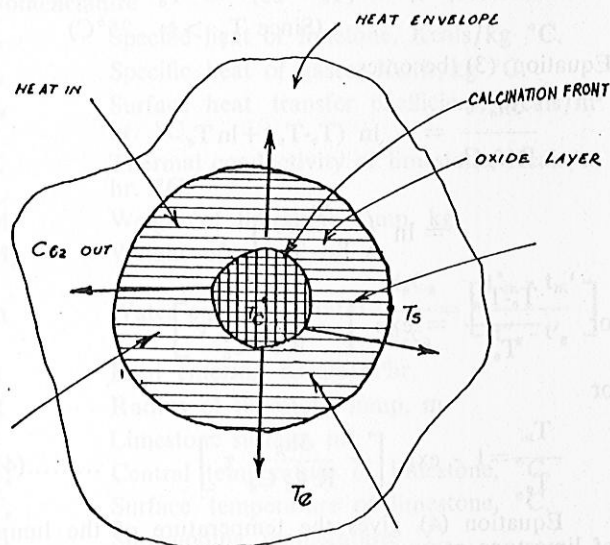


FIG.1 FIGURE SHOWING THE ADVANCEMENT OF CALCINATION FRONT.

calcination will depend only on the rate of heat transfer. Many investigators<sup>7-15</sup> have already tried to correlate their data and in the present work the authors have tried to correlate some of these experimental data.

**DERIVATION**

Consider a spherical lump of  $S$  m<sup>2</sup> surface area, surrounded by a heat envelope at a temperature  $T_0$  at any instant of time  $d\tau$ . Let  $T_m$  be the temperature of the lump of limestone at this instant. Assuming that the properties of limestone do not vary with time,

$$M_s C_s dT_m = h_s (T_0 - T_m) S d\tau \quad \dots\dots\dots (1)$$

Where  $h_s$  is the surface heat transfer coefficient. Rearranging and separating the variables

$$\begin{aligned} \frac{dT_m}{(T_0 - T_m)} &= \frac{h_s S}{M_s C_s} d\tau \\ &= \frac{3 h_s}{R \rho_s C_s} d\tau \quad \dots\dots\dots (2) \end{aligned}$$

Integrating equation (2) we get

$$\frac{3h_s}{R \rho_s C_s} \tau = - \ln (T_0 - T_m) + \ln \lambda \quad \dots\dots\dots (3)$$

$\lambda$  is a constant of integration.

Initial conditions are

$$\tau = 0; T_m = 25^\circ C$$

$$\text{Therefore, } \lambda = (T_0 - 25) = T_0 \quad \text{(Since } T_0 \gg 25^\circ C)$$

Equation (3) becomes,

$$\begin{aligned} \frac{3h_s \tau}{R \rho_s C_s} &= - \ln (T_0 - T_m) + \ln T_0 \\ &= \ln \left( \frac{T_0}{T_0 - T_m} \right) \end{aligned}$$

$$\text{or } \frac{T_0 - T_m}{T_0} = \exp \left[ - \frac{3h_s}{R \rho_s C_s} \tau \right]$$

or

$$\frac{T_m}{T_0} = 1 - \exp \left[ - \frac{3h_s}{R \rho_s C_s} \tau \right] \quad \dots\dots\dots (4)$$

Equation (4) gives the temperature of the lump of limestone at any instant. Now, if  $q$  be the amount of heat transferred to the lump, then

$$q = 2k \frac{(T_s - T_0)}{R} \quad \dots\dots\dots (5)$$

also,

$$\begin{aligned} q &= \frac{dT_m}{d\tau} \frac{M_s C_s}{S} \\ &= \frac{R \rho_s C_s}{3} \frac{dT_m}{d\tau} \quad \dots\dots\dots (6) \end{aligned}$$

Differentiating equation (4) and substituting the value of  $dT_m/d\tau$  in equation (6)

$$q = \frac{R \rho_s C_s}{3} \left[ (-1) \exp \left\{ \frac{-3h_s}{R \rho_s C_s} \tau \right\} \right] \left[ (-1) \frac{3h_s}{R \rho_s C_s} T_0 \right]$$

or,

$$q = h_s T_0 \left[ \exp \left\{ \frac{-3h_s}{R \rho_s C_s} \tau \right\} \right] \quad \dots\dots\dots (7)$$

Comparing equations (5) and (7) we have

$$T_s - T_0 = \frac{h_s R T_0}{2K} \left[ \exp \left\{ \frac{-3h_s}{R \rho_s C_s} \tau \right\} \right] \quad \dots\dots\dots (8)$$

$$\text{or } \ln \left[ \frac{T_s - T_0}{T_0} \right] = \ln \left[ \frac{h_s R}{2K} \right] - \frac{3h_s}{R \rho_s C_s} \tau \quad \dots\dots\dots (9)$$

Equation (9) is an equation of a straight line whose

slope is  $\frac{-3h_s}{R \rho_s C_s}$  and intercept is  $\ln \left( \frac{h_s R}{2K} \right)$ .

**DISCUSSION**

Azbe conducted experiments in an electric furnace on a 5.0 cms (2 inch) sphere of a high calcium limestone. The variation of furnace temperature, limestone surface temperature and central core temperature with time is shown in Fig. 2. The values of  $\ln \left( \frac{T_s T_0}{T_0} \right)$  for various

values of  $\tau$  have been calculated and plotted on a simple graph paper. The resultant straight line has a slope equal to -0.2 and intercept equal to -3.8 (Fig. 3).

Now, for example, if specific heat of limestone,<sup>16</sup>  $C_s = [0.25]$  KCals/kg °C.

Specific gravity of limestone,<sup>17</sup>  $\rho_s = 2700$  kg/m<sup>3</sup> and thermal conductivity of limestone,<sup>18</sup>  $k = 0.67$  KCals/m-hr °C then,  $h_s$  (experimental) = 1.145 KCals/m<sup>2</sup> hr. °C.

The value of heat transfer coefficient so obtained cannot be utilized directly for the calculation of kiln dimensions, since the effect of flow of gases across the limestone lump is not considered in the present study which in turn results in the increased value of 'h'. For the calculation of actual value of  $h_s$  with the help of experimental value of  $h_s$ , the following equation<sup>19</sup> may be used

$$\ln \left( \frac{T_s - T_0}{T_0} \right) = \ln \left[ \frac{h_s R}{2K} (1-m) \right] - \frac{3h_s}{R \rho_s c_s} (1-m) \tau \quad \dots\dots\dots (10)$$

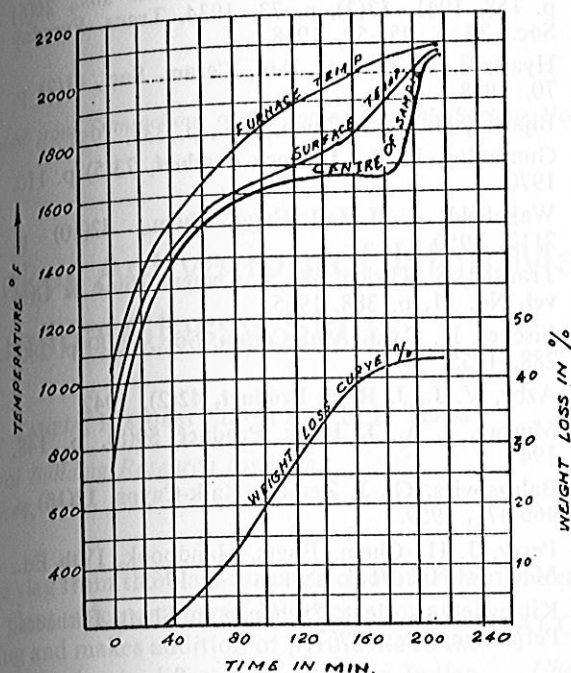


FIG. 2 TEMPERATURE HISTORY OF THE CALCINING OF A 2IN SPHERE OF HIGH CALCIUM LIME STONE .

where,  $m = \frac{M_s C_s}{M_g C_g}$  ..... (11)

In the above equation (10)  $T_o$  becomes the temperature of the gases entering the bed. The value of  $m$  which is less than unity is calculated by simple heat balance equation:

$M_s C_s \Delta t_m = M_g C_g \Delta t_g$  ..... (12)

or  $m = \frac{M_s C_s}{M_g C_g} = \frac{\Delta t_g}{\Delta t_m}$  ..... (13)

Comparing equations (9) and (10) it could be concluded that

$h_s |_{actual} = \frac{h_s |_{experimental}}{1-m}$  ... (14)

These equations are applicable in the period during which limestone is heated from normal atmospheric temperature to a temperature above the dissociation temperature. Hence, the value of 'h<sub>s</sub>' found out by the above method determines the dimensions of preheating zone and dissociation zone of the kiln. The value of  $m$  will be different in preheating and dissociation zone. The value of  $h_s$  in the cooling zone may however be calculated in a similar way.

**CONCLUSION**

The results of an experiment conducted in a similar manner may be used to determine the experimental value of the heat transfer coefficient with the help of

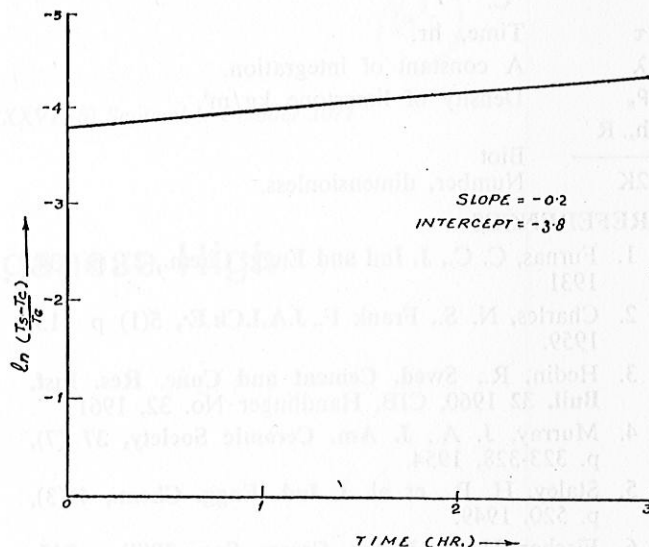


FIG. 3 FIGURE SHOWING VARIATION OF  $\ln \left( \frac{T_s - T_c}{T_e} \right)$  WITH TIME

equation (9). Then by fixing the temperatures of the ingoing and outgoing streams of gases and limestone, the more reliable value of  $h_s$  may be calculated with the help of equation (14). It is to be noted that the total surface of a crushed limestone is about 25 per cent higher than that of a spherical lump. Also, of the total surface only about 60 per cent surface is available for the heat transfer to take place. Therefore, the total surface to be considered while calculating the kiln dimensions in present case will be  $1.25 \times 0.6 \times 4\pi (2.5)^2$  or 58.88 sq. cm.

**Nomenclature**

- $c_s$  Specific heat of limetone, Kcals/kg °C.
- $c_g$  Specific heat of gases, Kcals/kg °C.
- $h_s$  Surface heat transfer coefficient, Kcals/m<sup>2</sup> hr. °C.
- $K$  Thermal conductivity of limestone, Kcals/m hr. °C.
- $M_s$  Weight of limestone lump, kg.
- $M_g$  Weight of gases, kg.
- $m$  Water equivalent ratio  $\frac{M_s C_s}{M_g C_g} = \left[ \frac{t''_m - t'_m}{t''_g - t'_g} \right]$
- $q$  Heat entering KCals/m<sup>3</sup>hr.
- $R$  Radius of limestone lump, m.
- $S$  Limestone surface, m<sup>2</sup>
- $T_o$  Central temperature of limestone, °C.
- $T_s$  Surface temperature of limestone, °C.
- $T_e$  Surrounding temperature, °C.
- $T_m$  Temperature of limestone at any instant, °C.
- $t'_g$  Temperature of gases leaving the bed, °C.
- $t''_g$  Temperature of gases entering the bed, °C.
- $t'_m$  Temperature of limestone entering the bed,

$t''_m$	Temperature of limestone leaving the bed, °C.
$\tau$	Time, hr.
$\lambda$	A constant of integration.
$\rho_s$	Density of limestone kg/m <sup>3</sup> .
$h_s, R$	Biot Number, dimensionless.
2K	

REFERENCES

1. Furnas, C. C., *J. Ind and Engg. Chem.*, **23**, p. 534, 1931
2. Charles, N. S., Frank F., *J.A.I.Ch.E.*, **5**(1) p 115, 1959.
3. Hedin, R., *Swed. Cement and Conc. Res. Inst. Bull.* **32** 1960, CIB, Handlinger No. 32, 1961.
4. Murray, J. A., *J. Am. Ceramic Society*, **37** (7), p. 323-328, 1954.
5. Staley, H. R., et al, *J. Ind. Engg. Chem.*, **41**(3), p. 520, 1949.
6. Fischer, H. C., *J. Am. Ceram. Soc.*, **38**(7) p. 245-251, 1955.
7. Britton, H.T.S., et al, *Faraday Soc. Trans.*, **48**, (1) p. 63-75, 1952.
8. Zedwadski, J., Bretsznajder, *Ceramic abs.*, **20**(6) p. 158, 1941, **13**(3), p. 73, 1934, *Trans. Faraday Soc.*, **34** p. 951-59, 1938.
9. Hyatt, E. P., et al, *J. Am. Ceram. Soc.*, **41**(2) p. 70, 1958.
10. Bijawat, H. C., *J. Chem. Ind.*, p. 331, 1957.
11. Gunsaulus, R. K., *J. Rock Product*, **73**(5) p. 110, 1970.
12. Wakefield, A., *J. Ind. Engg. Chem.*, **42**(10) p. 2117, 1950.
13. Translet, S., Ulrich, W., *J. Cement Lime & Gravel*, No. **11**, p. 388, 1965.
14. Fischer, H. C., *J. Am. Ceram. Soc.*, **38**(8) p. 280-288, 1955.
15. Azbe, V. J., *J. Rock Product*, **42**(2), 1942.
16. Murray, J. A., *J. Rock Product* **50**(8), p. 148, 1947.
17. Balazsovcics, G., *J. Zement Kalk-Cayps*, **12**(10) p. 466-471, 1959.
18. Perry, J. H., *Chem. Engrs. Handbook*, IVth Ed., McGraw Hill Book Co., p. 3-8, 1963.
19. Kitaev et al, *Heat Exchange in Shaft Furnaces*; Pergamon Press, 1967.