Thermochimica Acta, 213 (1993) 223–240
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of limestone in a large scale thermogravimetric analyzer

Jia-Twu Lee[a], Timothy C. Keener[a], Mark Knoderer[a] and
Soon-Jai Khang[b]

[a] *Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0171 (USA)*
[b] *Chemical Engineering Department, University of Cincinnati, Cincinnati, OH 45221 (USA)*

(Received 11 December 1991)

Abstract

The decomposition of calcium carbonate spheres has been investigated using limestone particles of sizes 7, 5 and 2 mm in a large scale thermogravimetric analyzer under near isothermal conditions. Experiments were conducted in atmospheres of pure N_2, and 7%, 14% and 21% CO_2–N mixtures. Data are interpreted in terms of apparent activation energy E and frequency factor A assuming a first-order reaction and Arrhenius temperature dependence of the rate constant. Microscopic analysis has shown that the decomposition reaction takes place at the boundary between the undecomposed carbonate and the layer of porous lime formed outside. This boundary moves towards the center of the particle but remains spherical in shape.

LIST OF SYMBOLS

A	Arrhenius pre-exponential factor, g cm^{-2} s^{-1}
E	Activation energy, kcal mol^{-1}
K	reaction rate constant, min^{-1}
k	reaction rate coefficient, g cm^{-2} s^{-1}
α	fraction of conversion
ρ_s	particle density, g cm^{-3}
M_{CaO}	molecular weight of CaO
M_{CaCO_3}	molecular weight of $CaCO_3$
P_{CO_2}	partial pressure of carbon dioxide, atm
P_{eq}	equilibrium pressure of carbon dioxide, atm
R	gas constant
r_s	radius of unreacted core, cm
R	linear regression correlation coefficient
T	temperature, K
t	time, s
τ	time for complete decomposition, s

Correspondence to: T.C. Keener, Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0171, USA.

INTRODUCTION

The thermal decomposition of calcium carbonate is an industrially important reaction which has many interesting features. Although the calcination of $CaCO_3$ has been studied by many investigators, there is considerable inconsistency in the data concerning reaction kinetics and thermodynamics.

Calcination is an equilibrium reaction. In principle, $CaCO_3$ will decompose to lime if the ambient partial pressure of CO_2 is below the equilibrium value of the partial pressure at a given temperature. Conversely, any lime formed will be transformed back to carbonate if the partial pressure of CO_2 exceeds this equilibrium value. The rate of the decomposition reaction will thus be governed by the partial pressure of CO_2, the reaction temperature and the particle size. At 700°C and atmospheric pressure the rate of the reaction becomes exceedingly slow, even in the absence of CO_2. The chemical reactivity is known to vary between sources, not only because of the differences in crystalline structure but also depending on the nature of the impurities, such as silicon, iron, magnesium, manganese, sodium and potassium.

PREVIOUS WORK

Several investigations have been undertaken to determine the mechanism and kinetics of this reaction. Hills [1], from studies with dense particles of calcium carbonate, reported that the reaction is controlled by the heat transfer rate to, and the rate of mass transfer of carbon dioxide from, the sharply defined reaction interface. He proposed three models based on the shrinking core concept to explain his experimental results. Kupper and Tiggesbaumker [2] claimed that the carbonate is transformed to an activated state prior to decomposition, whereas Hyatt et al. [3] suggested that active lime is initially formed upon decomposition. This active lime is more susceptible to the reverse reaction than the normal crystalline form, to which it eventually changes.

Asaki et al. [4] have developed a mathematical model for the calcination of fluidized $CaCO_3$ particles in air. Their model considers that the calcination reaction occurs at the interface between a shrinking core of undecomposed $CaCO_3$ and an outer shell made of decomposed lime, and assumes that the outer diameter of the particle remains unchanged. The classical overall reaction rate equation incorporates terms for (1) the chemical reaction at the interface, (2) the diffusion of CO_2 gas produced through the lime shell, and (3) the diffusion of CO_2 gas through the gas film formed at the particle surface. In addition, the overall rate depends on the rate of heat transfer, the rates of mass transfer and combinations thereof, depending upon the particular circumstances under which the calcination proceeds. In their own fluidized bed experiments, Asaki et al.

[4] reported control by heat transfer from the reactor wall to the particle surface for 150–250 μm diameter particles, and control by both the chemical rate and the heat transfer rate for 0.6–1 mm diameter particles. Hills [1] reported control by heat and mass transfer in their experiments with 10 mm diameter spheres, and Ingraham and Marier [5] reported control by diffusion of CO_2 through the lime shell for their work with pelletized 455 mg samples. In contrast, Borgwardt [6] reported chemical control for the calcination of fine limestone particles (10–90 μm).

The activation energy of the calcination reaction has been reported to be between 37 and 60 kcal mol^{-1}, with values predominantly close to 50 kcal mol^{-1}, compared with the theoretical value of 39–41 kcal mol^{-1} at equilibrium. The uncertainty derives from the inherent complexity of the calcination process which, assuming a shrinking core model, involves a seven step mechanism. Heat must be transferred (1) to the the particle outer surface, then (2) conducted through the calcinated outer shell to the internal reaction interface, where (3) a chemical reaction occurs; the CO_2 evolved must either (4) react at the interface, or (5) diffuse from the interface to the outer surface; it then (6) diffuses away from the surface to the surrounding atmosphere, and (7) CO_2 from the surrounding atmosphere also diffuses to the reaction interface.

The observed rate of calcination may be governed by any one or any combination of these steps.

In large scale TGA experiments, transfer to the reaction interface is dependent upon the sample size, the heating rate, and the thermal conductivity and flow rate of the sweep gas. The sweep gas flow rate also affects the degree of dilution of evolved CO_2 at the particle surface.

The complexity of the calcination process, and the dependence on the experimental technique employed, have led to the wide range of values quoted for the reaction rates; for example, results have been between 0.3 and 1.2 times the apparent activation energy (between 33 000 and 80 000 kcal mol^{-1}) and having a frequency factor of between 3000 and 8000 g cm^{-2} s^{-1}. The design and operation of commercial precalciners are critically dependent upon a knowledge of the calcination rate of the feed material, since profitable operation will require achievement of a specified minimum degree of conversion. Traditional reliance on the TGA of limestone sources to predict their performance in precalciners clearly involves a degree of uncertainty. The authors are currently engaged in large scale TGA experiments in which an isothermal condition can be reached within 5 s; this is done with a view toward improving the reliability of the prediction procedure.

EXPERIMENTAL SETUP

The reactor used in the thermal decomposition studies was constructed as shown in Fig. 1. This reactor allowed for the determination of weight

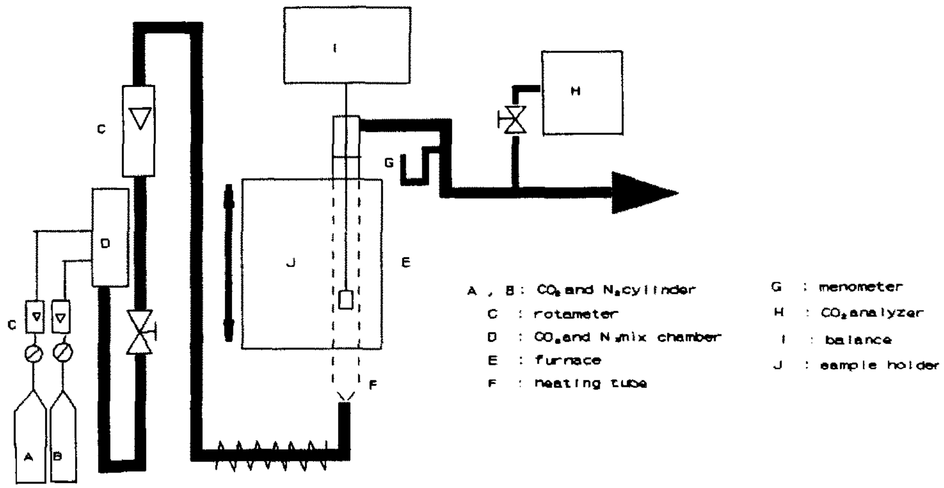

Fig. 1. Schematic arrangement of furnace and equipment.

TABLE 1

Some experimental work on calcination reaction

Type of reactor	Experimental conditions	Material	Size	Reference
TGA	500–900°C 1.5–8 $cm^3 s^{-1}$	Calcite and aragonite (Spain)	3.05–0.84 mm 4–78 mg	A. Romero Salvador [7]
TGA	650–900°C 60 $cm^3 min^{-1}$	Gauldon limestone	90 μm, 2–10 mg	Y.H. Khraisha [8]
TGA	620–800°C	Calcite single crystals	7 mm diameter, 1–2 mm thick	T. Darroudl [9]
TGA	640–900°C	Calcite single crystals	$1.0 \times 0.5 \times 0.15$ cm^3	E.K. Powell [10]
Isothermal differential	516–1000°C, nitrogen	Fredonia limestone and Georgia marble	1–90 μm	R.H. Borgwardt [6]
Isothermal	650–900°C	Calcite single crystals	$1.0 \times 0.5 \times 0.15$ cm^3	E.K. Powell [11]
Isothermal suspension	800–900°C	Gauldon limestone	60–90 μm	Y.H. Khraisha [8]
Isothermal large scale TGA	650–900°C 400 $cm^3 min^{-1}$, nitrogen, CO_2	Marble limestone	2, 5, 7 mm diameter, 100–600 mg	J.T. Lee [12]

loss (i.e. degree of decomposition) with respect to time for isothermal decomposition conditions. The reactor had the advantage of allowing the quick (within 5 s) immersion of the sample into the heated ceramic tube by means of a movable furnace section. A Fisher digital balance was used to measure weight loss. The temperature was recorded as a function of time. A platinum line (0.2 mm) was used as a sample holder.

Table 1 contains data obtained from experiments conducted in an atmosphere of pure N_2 and in a gas mixture (CO_2 21%, N_2 79%) which is representative of possible conditions in a commercial precalciner. Some data from experiments conducted in pure CO_2 have also been included. A standard gas flow rate of 400 $cm^3\ min^{-1}$ was used in all experiments.

Samples from the thermal decomposition were obtained for various degrees of decomposition (i.e. 20%, 40%, 60% and 80%) as a function of temperature and size. Some samples were cleaved, stained and examined by optical microscopy in order to verify the existence of a distinct product layer.

The large scale TGA data were analyzed assuming an Arrhenius temperature dependence for the rate constant, giving an apparent activation energy E and frequency factor A. The reaction order of unity was chosen as appropriate for the small particle size used; this has been found to fit the data satisfactorily.

RESULTS AND DISCUSSION

Thermal decomposition of marble limestone is a complicated process, involving both physical and chemical mechanisms. The morphology and chemical properties of the solid structure change during thermal decomposition. Many studies indicate that the area where most of the thermal decomposition occurs has a surface skin which exhibits properties that differ from those of the bulk material. For example, in $CaCO_3$, as thermal decomposition proceeds, CO_2 must migrate through this surface skin before entering the environment.

Morphology

Sample before thermal decomposition

Marble limestone was used in this research because of its high purity (96–100%) and natural abundance. A ball mill attritor produced particle sizes of 2, 5 and 7 mm. These sizes were chosen because they are representative of the sizes used in fluidized bed combustors. One limestone sample was observed; the average size of the particles was about 7 mm in diameter. The fine pores which formed averaged around 4–7 μm in diameter; the pore size was found to depend upon the length of the formation period. If the formation period was long and the environ-

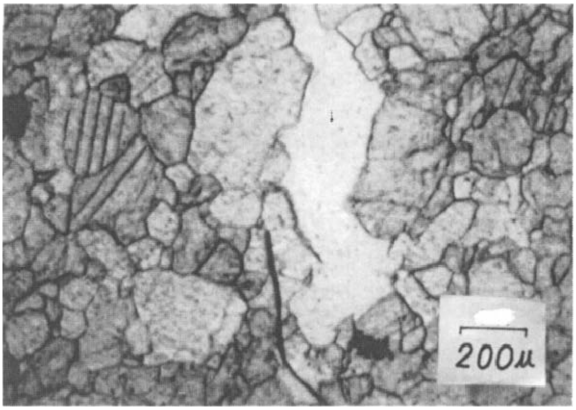

Fig. 2. Thin section showing appearance of typical marble and scattered mesoporosity (in black). Original magnification 40×.

Fig. 3. Thin section showing appearance of typical marble and scattered mesoporosity (in black). Original magnification 200×.

mental pressure was high, the basic unit pore size was small. The porosity in limestones may be due to depositional processes, or to dissolution related to diagenesis, or both. The normal case is a loss of the majority of the primary porosity because of cementation and compaction some time after deposition [13]. In modern carbonate sediments the average porosity is 60–70%, whereas ancient limestones usually have porosities of less than 2% [13]. Typical samples are shown in Figs. 2 and 3. Figure 3 shows that the average pore size for primary porosity is about 5–6 μm.

Sample after thermal decomposition

A total of five samples were observed under thermal decomposition. The exterior color of all of the samples changed from white to gray during the process. All of the thermal decomposition samples were fractured and examined with an optical microscope (see Fig. 4). On every fractured

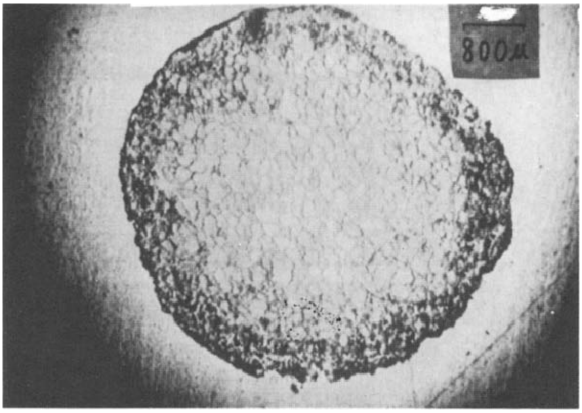

Fig. 4. Thin section showing appearance of typical $CaCO_3$ and reaction layer CaO. Original magnification 10×.

sample surface, a blackish gray kernel was observed. We believe that the blackish gray color of the outer layer is caused by the thermal decomposition of $CaCO_3$. The thickness of the surface layer increased in proportion to the duration of thermal decomposition. If the temperature was increased, the thickness of the surface layer increased. This result was as expected, as the reaction layer is composed of CaO.

After thermal decomposition had occurred for a period of time, most of the unreacted kernels were still spherical in shape; the exceptions were those samples which decomposed at higher temperatures or with longer durations. Distortions from sphericity are caused by impurities in the compound and high temperatures. At times, narrow white bands appeared in the dark gray layer. A small thermal gravimetric analyzer was also used to identify the reaction layer by weight change. Figure 5 demonstrates that the decomposition reaction took place at a definite boundary between the undecomposed carbonate and the layer of porous

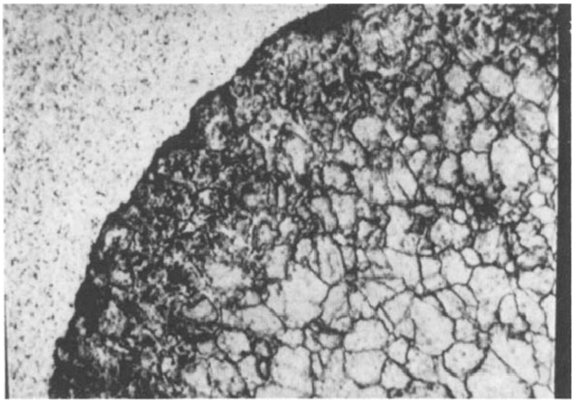

Fig. 5. Thin section showing appearance of typical $CaCO_3$ and reaction layer CaO. Original magnification 40×.

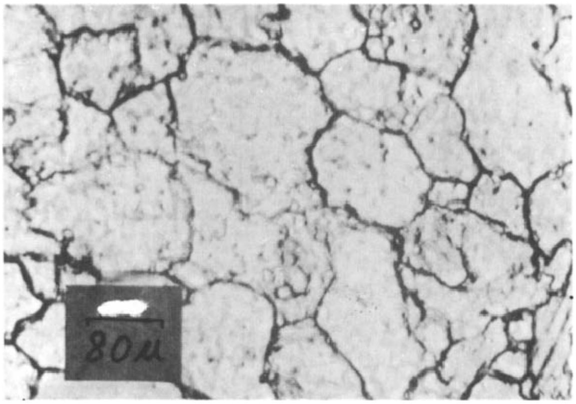

Fig. 6. Thin section showing appearance of typical $CaCO_3$ and secondary porosity. Original magnification 100×.

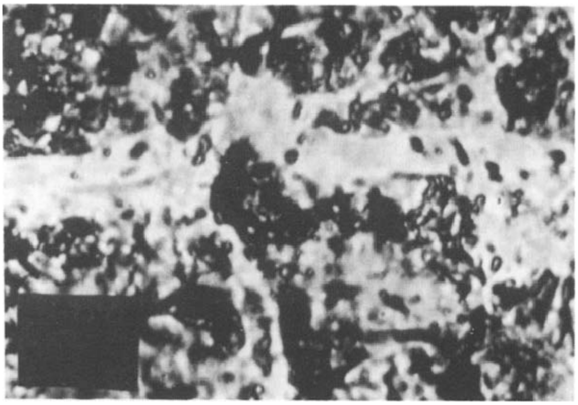

Fig. 7. Thin section showing appearance of typical $CaCO_3$ and secondary porosity. Original magnification 100×.

lime formed outside it. This boundary moves towards the center of the particle but remains spherical. Figure 6 shows that in the unreacted core the primary pores are enlarged. This is secondary porosity. Figure 7 shows large pores in a typical reaction layer.

Thermal decomposition analysis

Effect of particle size

The effect of particle size on thermal decomposition was investigated by testing a run of marble samples at 700, 800 and 900°C. Three ranges of particle sizes (2, 5 and 7 mm) were tested, and the results are given in Figs. 8, 9 and 10. According to the decomposition mechanism in which the decomposition of a solid takes place at an interface advancing inwards from the outside of each particle (as discussed earlier), small particles will decompose more quickly than large particles. In the case of large

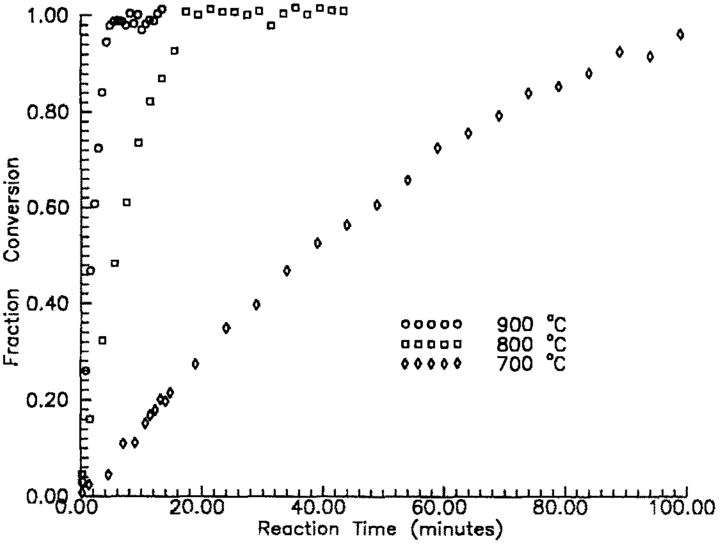

Fig. 8. Fraction conversion vs. reaction for 2 mm particles.

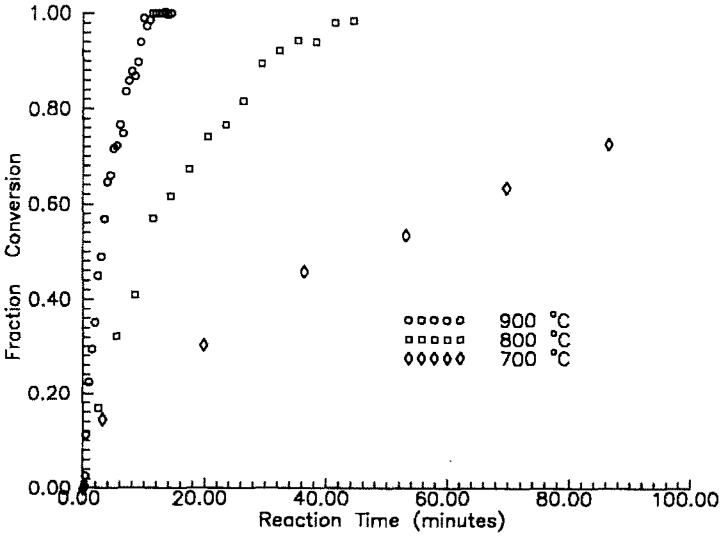

Fig. 9. Fraction conversion vs. reaction time for 5 mm particles.

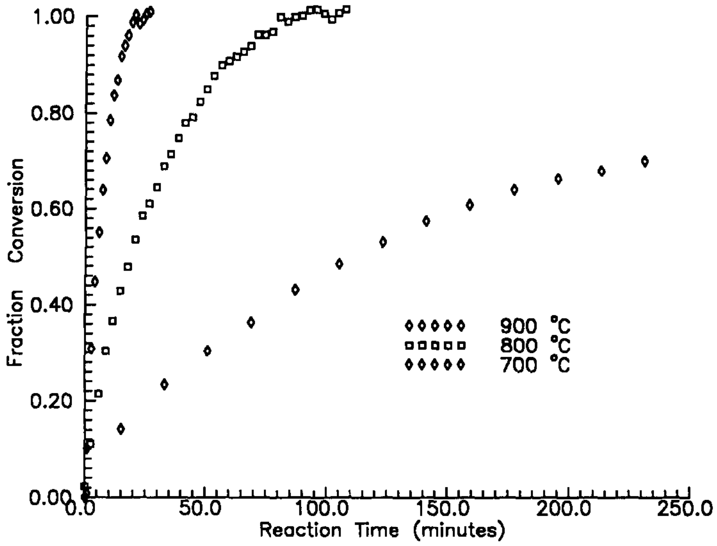

Fig. 10. Fraction conversion vs. reaction time for 7 mm particles.

particles, the product layer formed will begin to sinter during prolonged calcination times, which results in a decrease in the porosity of the product layer. In this case the resistance to CO_2 diffusion away from the reaction zone will be increased; consequently the formation of a new surface area is slowed by this process. Therefore, the surface area produced by the decomposition of small particles will be greater than that from the decomposition of larger particles.

Effect of temperature

The thermal decomposition of $CaCO_3$ at the test condition (i.e. temperatures of 700, 800 and 900°C, calcined in nitrogen) shows large differences in the decomposition rate, as illustrated in Figs. 11, 12 and 13. Greater resistance occurs in the larger particles. A comparison of the curves for 2, 5 and 7 mm particle sizes shows that, under similar conditions, the decomposition rate obtained for 7 mm particles is much smaller than that obtained for 2 mm particles. This probably arises because 2 mm particles decompose more rapidly than 7 mm particles (Fig. 13) and, as a result, have a longer time in which to sinter. The measurement of weight loss (%) versus time at 700°C indicates that the 7 mm particles obtained a weight loss of 95% within 8 h, but the 2 mm particles obtained a weight loss of 95% in only 2 h.

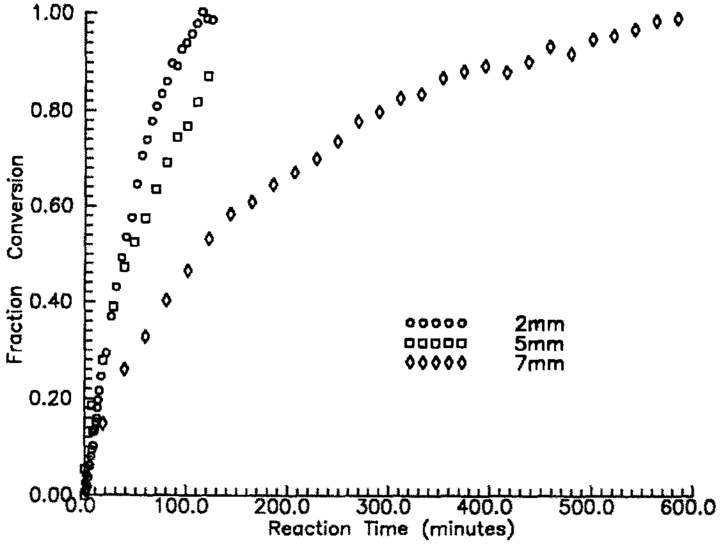

Fig. 11. Fraction conversion vs. reaction time at 700°C.

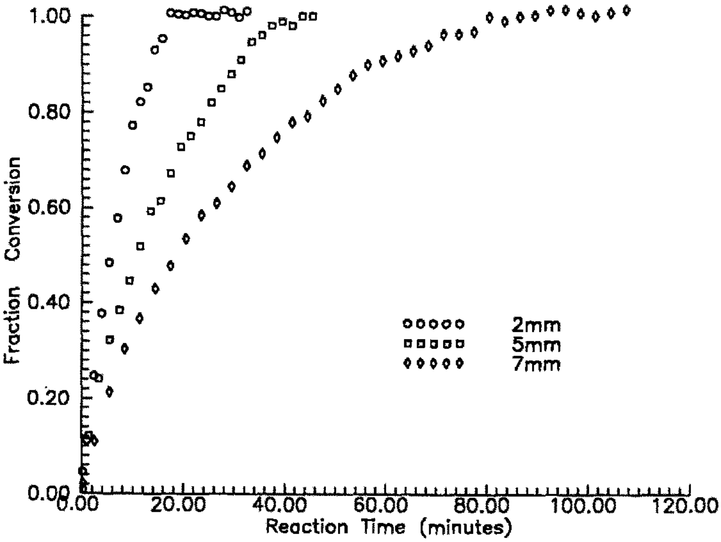

Fig. 12. Fraction conversion vs. reaction time at 800°C.

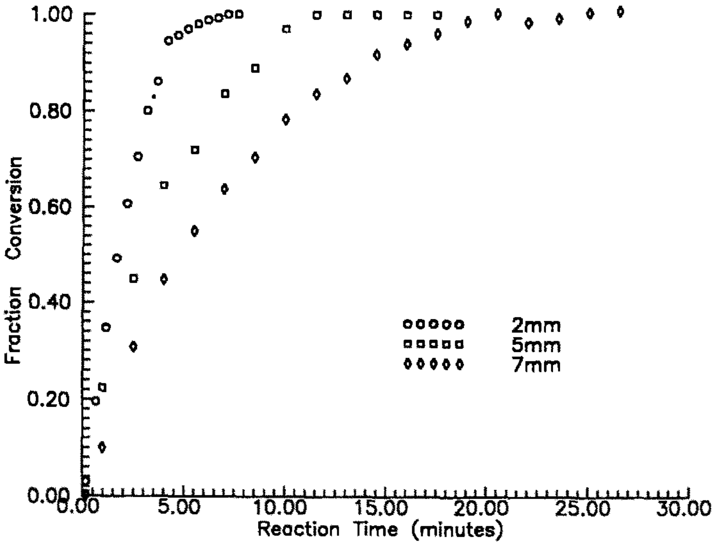

Fig. 13. Fraction conversion vs. reaction time at 900°C.

Effect of carbon dioxide

Isothermal calcination in carbon dioxide/nitrogen mixtures was studied in order to test the extent to which the ambient partial pressure of carbon dioxide suppresses the reaction. The literature contains several works which assumed that the reaction rate is suppressed by the factor $(1 - P_{CO_2}/P_{eq})$. The experimental results are shown in Fig. 14. The reaction rate is lower than that for particles of similar diameter in a pure nitrogen atmosphere.

Isothermal calcination in nitrogen

Isothermal measurements of the rate of limestone calcination were obtained from large samples in a TGA. In the shrinking core model of a spherical particle

$$\frac{d\alpha}{dt} = K(1 - \alpha)^{2/3} \tag{1}$$

This equation was used to calculate the rate constant. Integration gives

$$F(\alpha) = 3[1 - (1 - \alpha)^{1/3}] = Kt \tag{2}$$

By plotting $F(\alpha)$ against time, the rate constant is evaluated as the slope of the least squares line. The isothermal calcination of 2, 5 and 7 mm marble limestone particles (see Tables 2, 3 and 4) yielded a rate constant in the range of 10^{-1}–10^{-3} min^{-1}.

The isothermal parameters A and E provide a simple means of estimating the rate of reaction at any given temperature. The values of the rate coefficients extracted from Tables 2, 3 and 4 are plotted in Fig. 19.

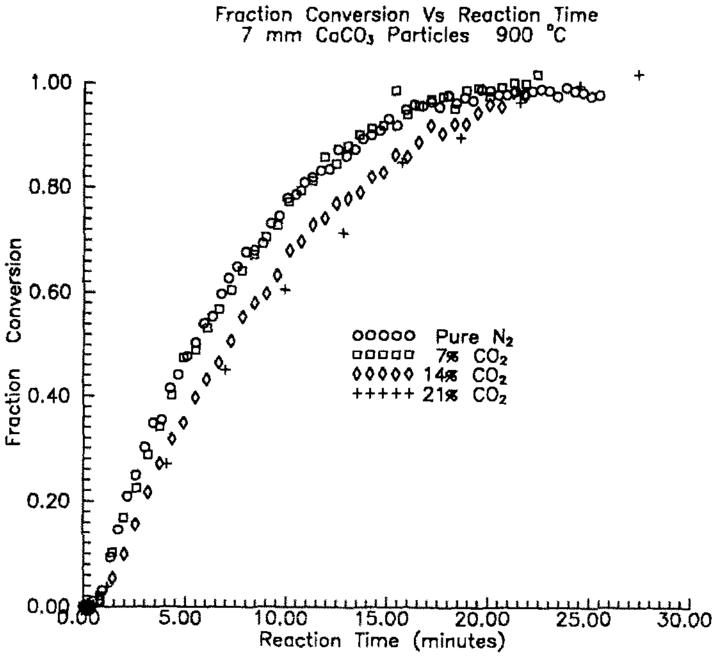

Fig. 14. Fraction conversion vs. reaction time for different CO_2 mixtures.

TABLE 2

Reaction constant for 7 mm diameter

Temp. (K)	K (min^{-1})	Constant	R^2	Std. error
700	0.0011	0.0348	0.962	0.012
800	0.0088	0.0344	0.992	0.019
900	0.0504	−0.032	0.990	0.022

TABLE 3

Reaction constant for 5 mm diameter

Temp. (K)	K (min^{-1})	Constant	R^2	Std. error
700	0.0026	0.0509	0.956	0.022
800	0.0161	0.027769	0.959	0.040
900	0.0658	−0.00037	0.973	0.038

TABLE 4

Reaction constant for 2 mm diameter

Temp. (K)	K (min^{-1})	Constant	R^2	Std. error
700	0.0061	−0.012	0.995	0.015
800	0.0400	−0.014	0.993	0.011
900	0.1301	−0.054	0.980	−0.05

TABLE 5

Sample	E (kcal mol^{-1})	A (g cm^{-1} s^{-1})	R^2	Std. error
2 mm	−36791	2229	0.9898	0.12
5 mm	−36444	1796	0.9910	0.13
7 mm	−39213	5288	0.9250	0.389

Using $F(\alpha)$ versus t (as in Fig. 18) for K and assuming an Arrhenius form

$$K = A\,\mathrm{e}^{-E/RT} \tag{3}$$

The regression line through these points gives $R^2 = 0.9898$. The Arrhenius form therefore appears quite reasonable. The experimental values of the activation energy E and the pre-exponential factor A are shown in Table 5.

The activation energies determined by various investigators vary from a low of about 35 kcal mol^{-1}, as determined by Britton et al. [14], to a high of 230 kcal mol^{-1}. The majority of the reported values lie in the range 37–55 kcal mol^{-1} [1, 3, 5, 15]. This result supports the above assumption that the decomposition reaction is kinetically controlled in this temperature range. By comparing the different temperatures in Figs. 8, 9 and 10, it is found that the slope is steeper for higher temperatures. The reason is that at higher temperatures particles have larger pores. The larger pores increase the rate of the diffusion process.

Finally, eqn. (4) may be used to compute the time τ for 100% decomposition ($X \rightarrow 1.0$) of a $CaCO_3$ particle of radius r_s. This time is given by

$$\tau = \frac{\rho_{\mathrm{CaO}} M_{\mathrm{CaO}} r_s}{k M_{\mathrm{CaCO_3}}} \tag{4}$$

This result was verified by calculating values of τ by use of the experimental data. Values in Figs. 15, 16 and 17 have been computed according to eqn. (4), with the value of rate constant k determined from the activation energy E and the pre-exponential factor A. The experimental values of τ were established by conducting a regression analysis on the $[1-(1-\alpha)^{(1/3)}]$ vs. t/τ ratio. The results of this analysis are shown in Fig. 20, where eqn. (2) and the indicated values of τ are compared with the data for three representative particle size–temperature sets. The τ values are compared with those computed from eqn. (4) in Fig. 20, yielding a value of $R^2 = 0.95$. Equation (4) therefore appears adequate for estimating decomposition times.

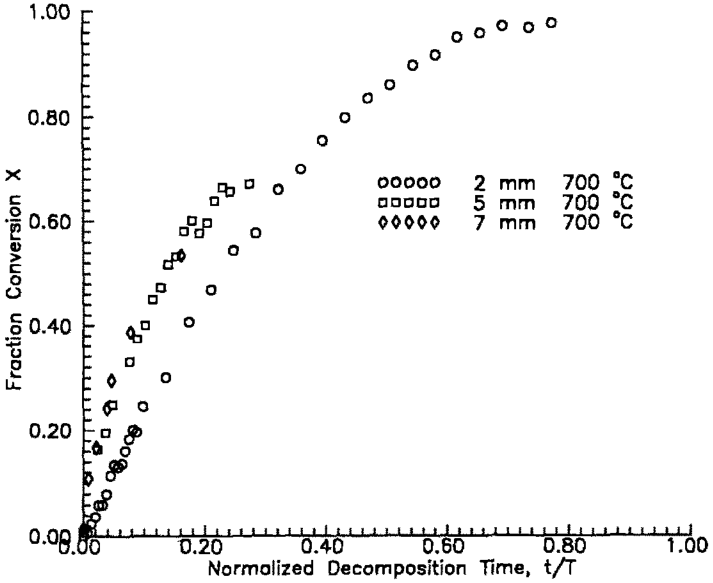

Fig. 15 Progress of reaction of a single spherical particle measured in terms of time for complete conversion at 700°C.

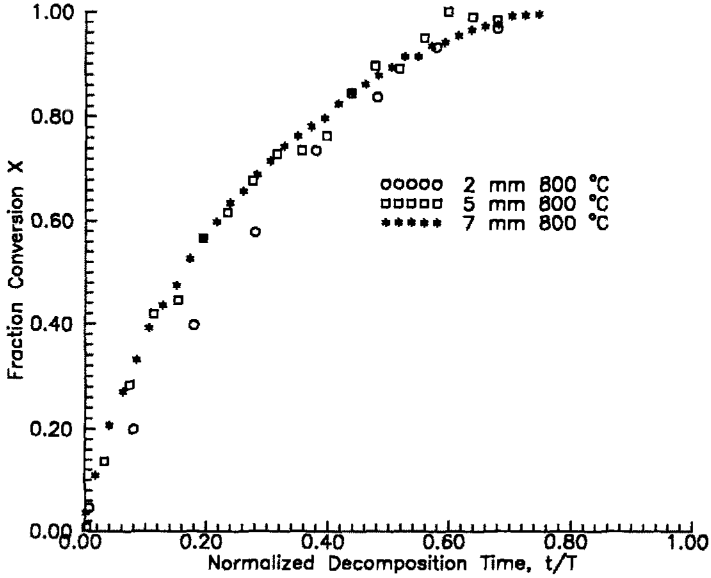

Fig. 16. Progress of reaction of a single spherical particle measured in terms of time for complete conversion at 800°C.

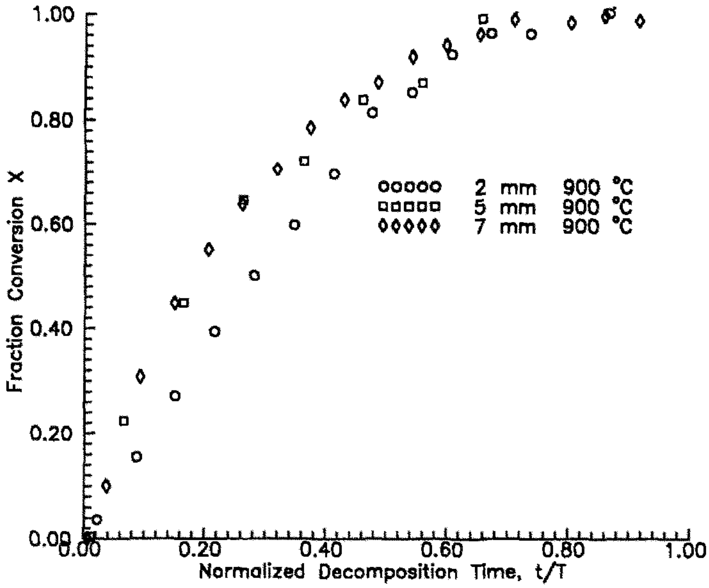

Fig. 17. Progress of reaction of a single spherical particle measured in terms of time for complete conversion at 900°C.

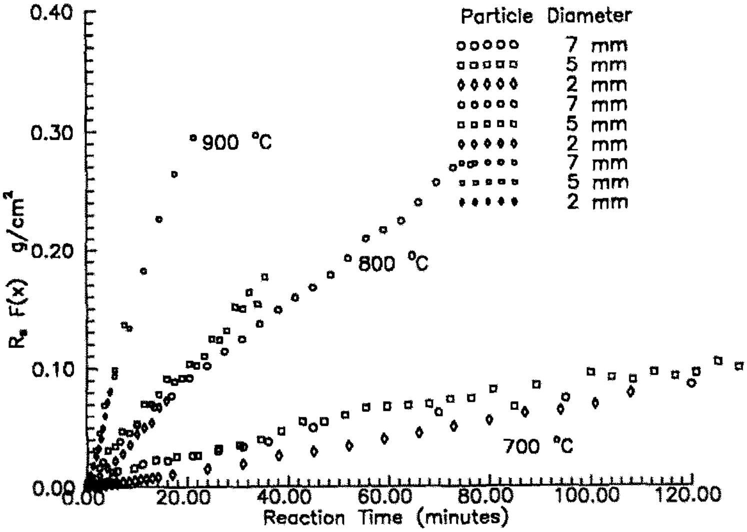

Fig. 18. Test of the reaction controlled, shrinking core model for decomposition of calcium carbonate.

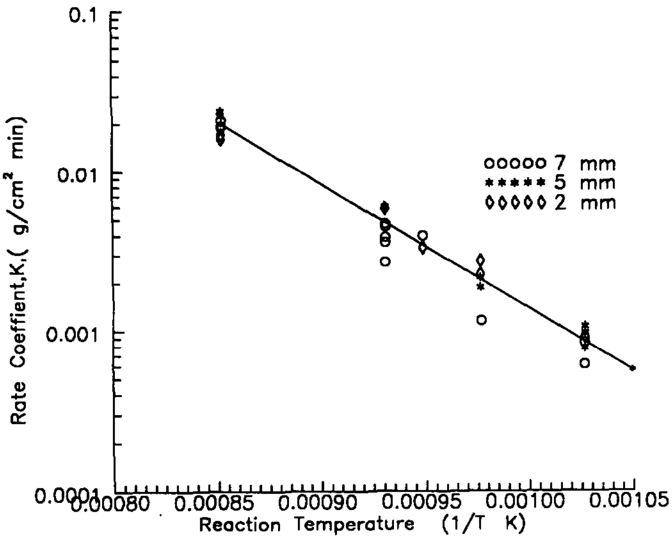

Fig. 19. Arrhenius plot for the decomposition reaction.

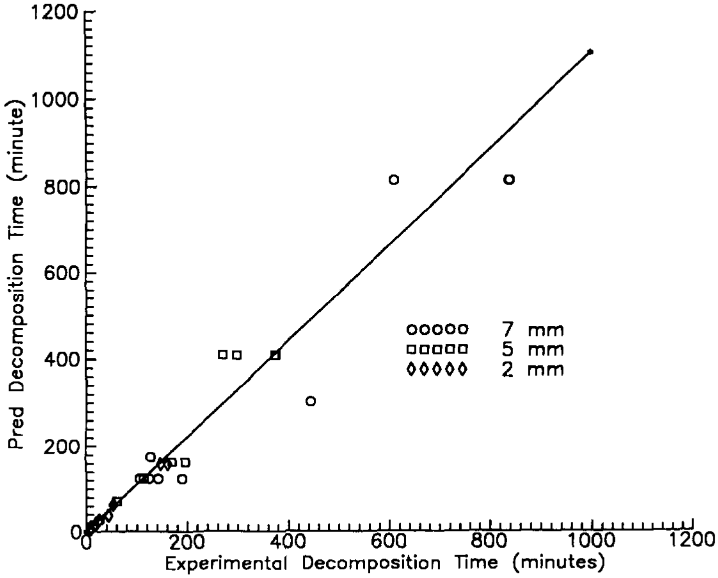

Fig. 20. Comparison of the experimentally determined decomposition times with predicted values.

CONCLUSION

Marble limestone (Will Co., IL) has been calcined in a large sample TGA apparatus under atmospheres of pure N_2 and 7%, 14% and 21% CO_2–N_2 mixtures. The kinetic parameters measured are in the region reported in the literature for similar conditions in terms of magnitude and dependence on concentration of CO_2, sample size and temperature.

In general, good agreement has been observed between measured and calculated values of E and A. At the completion of the reaction, gradual slopes were obtained for the large scale TGA curves, which indicates lower values of E when CO_2 is present. In the gas mixture there is a clear reduction in E and A with increasing sample size.

The values of E and A for pure N_2 are in the range reported in the literature for similar TGA experiments: the simplest interpretation of this linear relationship is provided by the Arrhenius equation for the rate constant k. Thus, evaluation of the slope of the line permits calculation of a single temperature which is representative of the reaction conditions. Values of 900, 800 and 700°C for N_2 and 900°C for CO_2 have been derived. The variation of the rate constant with temperature is shown in Tables 2, 3 and 4 for pure N_2 and the mixtures. The effect on the temperature is again seen to be more marked when CO_2 is present.

ACKNOWLEDGEMENTS

This work was supported by the Ohio Coal Development Office. The experiment was conducted in the Civil and Environmental Engineering Department of the University of Cincinnati.

REFERENCES

1 A.W.D. Hills, Chem. Eng. Sci., 23 (1968) 297.
2 D. Kupper and P. Tiggesbaumker, Zem.-Kalk-Gips, 5 (1983) 275.
3 P. Hyatt, B. Culter and F. Wadsworth, J. Am. Ceram. Soc., 41 (1958) 70.
4 Z. Asaki, Y. Fukunaka, T. Nagase and Y. Kondo, Metall. Trans., 5 (1974) 381.
5 T.R. Ingraham and P. Marier, Can. J. Chem. Eng., (August) (1963) 170.
6 R.H. Borgwardt, AIChE J., 31 (1985) 103.
7 A. Romero Salvador, Thermochim. Acta, 143 (1989) 339.
8 Y.H. Khraisha and D.R. Dugwell, Chem. Eng. Res. Des., 67 (1989) 48.
9 T. Darroudl and A.W. Searcy, J. Phys. Chem., 85 (1981) 3971.
10 E.K. Powell and A.W. Searcy, Metall. Trans. B, 7B (1980) 427.
11 E.K. Powell and A.W. Searcy, Commun. Am. Ceram. Soc., (March) (1982) C-42.
12 J.-T. Lee, Ph.D. Dissertation, University of Cincinnati, 1991.
13 D.W. Rich, Ph.D. Dissertation, University of Illinois, 1980.
14 H.T.S. Britton, S.J. Gregg and G.W. Winsor, Trans. Faraday Soc., 48 (1952) 63.
15 A.E. Potter, Ceram. Bull., 9 (1969) 855.