THE MOVING BOAT TECHNIQUE AND PRACTICAL STUDIES ON THE DECOMPOSITION OF CARBONATES. PART 1. COMPARATIVE ASSESSMENT OF THE DECOMPOSITION RATES OF LIMESTONE AND DOLOMITE SAMPLES

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ABSTRACT

The decomposition behaviour of four limestone samples and three dolomite samples has been studied by several methods. These include isothermal decomposition experiments, thermogravimetry (non-isothermal) and a new technique termed the moving bed technique (MBT) which allows rising temperature studies on relatively larger samples. It is shown that the new technique described in the text affords a convenient and effective approach in differentiating decomposition rates and, therefore, a reliable approach in comparative studies.

INTRODUCTION

The subject of proper assessment of the decomposition behaviour of limestone and dolomite samples is of much importance in several industries, yet proper assessment is beset with several problems. The decomposition behaviour and temperature changes in a carbonate sample are interrelated. A decomposition reaction which is endothermic tends to arrest the temperature rise, the lowered temperature slowing down the reaction rate. It is also known that for bulky, compact samples the reaction may even be controlled by transfer of heat to the cooler interior. Obviously the importance of the thermal aspects will depend on the size and nature of the sample.

When several carbonate samples are considered, no valid comparison of decomposition behaviour is possible without a reference to the heating characteristics. A direct comparison becomes possible if the variation of temperature with time is identical for all samples under test. Khan et al. [1] have shown that, for a given particle size, calcite decomposes at a lower rate compared to limestone in spite of the fact that calcite heats up more rapidly when equal weights of samples are introduced into a furnace set at a predetermined temperature. In this case, therefore, one can definitely say that the rate of decomposition of calcite would be even lower if temperatures are comparable. It is possible to ensure a uniform heating schedule in TG

where the sample size is necessarily small. The restriction on the sample weight, particularly for simultaneous TG and DTA, however, involves the uncertainties of heterogeneity in test samples and sampling error. There is, therefore, need of a method which can use relatively larger samples and, at the same time, ensure uniform heating schedules.

The present paper presents decomposition data of seven limestone and dolomite samples used in a steel plant in India. The data have been obtained using the following techniques on samples of fixed particle size.

(a) Measurement of rate of temperature rise when different samples of a fixed weight are suddenly introduced into a furnace maintained at a predetermined temperature.

(b) Measurement of weight loss at fixed time intervals when samples of a fixed weight are suddenly introduced into a furnace maintained at a predetermined temperature.

(c) Simultaneous DTA, TG and DTG.

(d) The moving boat technique.

As has been discussed earlier, neither (a) nor (b) may allow direct comparison of dissociation behaviour. If there is no sampling error then results of (c) serve as a reliable guide. It is shown that the new technique (d) perhaps yields the most reliable data. The principles and scope of this technique have been published elsewhere [2]. Here, we give only a brief outline.

MOVING BOAT TECHNIQUE (MBT)

Figure 1 outlines an arrangement which can be used to impose a well-defined heating programme on relatively larger samples. The set-up employs a furnace at a constant temperature and a moving boat in which is placed a series of crucibles containing the reaction mixture (~ 1 g). The leading edge
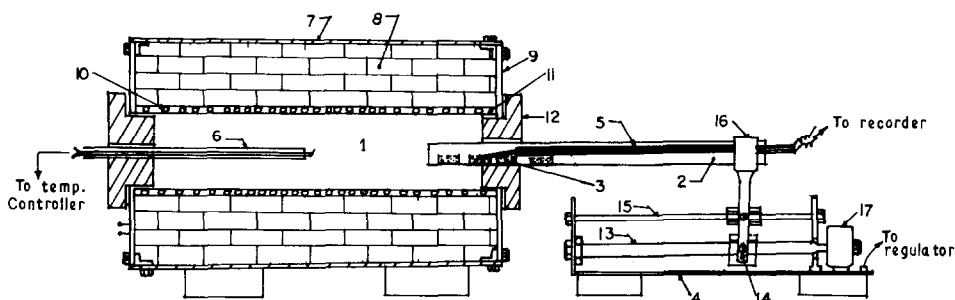

Fig. 1. Schematic diagram of the moving boat set-up. (1) Furnace, (2) stainless-steel channel; (3) carbonate sample, (4) moving arrangement, (5) chromel/alumel, (6) Pt/Pt-13% Rh thermocouple, (7) furnace shell, (8) fire clay bricks, (9) sindonia board, (10) heating coil, (11) sileminite tube, (12) furnace refractory plug, (13) lead screw, (14) nut, (15) supporting shaft, (16) clamp, (17) stepping motor.

of the boat initially rests at the furnace mouth. It is then introduced into the furnace at a constant speed using a special pushing device. As soon as the entire boat goes into the furnace it is quickly withdrawn and the reaction mass in crucibles allowed to cool quickly.

Under this arrangement the crucible at the leading edge spends maximum time inside the furnace, the succeeding crucibles spending progressively lesser times, although all crucibles are individually heated in the same manner. The reaction time, of course, differs from a maximum for the crucible at the leading edge to a minimum for one at the trailing edge. The length axis of the moving boat represents time, which is determined from the total length of the boat, the total travel time and the location of the crucible. The variation of temperature with time, which is identical for all crucibles, is determined by having a thermocouple embedded in a crucible near the leading edge.

It should be noted that this technique leaves, in the crucibles, a record of the physical state of the system at various periods during rising temperature conditions. Non-isothermal kinetic data are obtained by weighing the crucibles or chemically analysing the contents or measuring some property related to the degree of reaction. The contents of the series of crucibles as such describe the progress of reaction in a plug flow type reactor. This technique has been used to simulate the reduction of Fe_2O_3 by solid carbon in a horizontal kiln [3].

The nature of the temperature–time curve, which describes the heating schedule, depends on the steady-state temperature profile of the furnace, the speed at which crucibles move and the thermal properties of the sample. Accordingly, the heating programme can be changed by altering the boat speed and the temperature of the furnace hot zone. This has been discussed in Part 2 of this communication [4].

EXPERIMENTAL

Raw materials

The samples of limestone and dolomite used in the present work were collected from Durgapur Steel Plant, India. Table 1 gives the sources (all Indian) and available composition. Lump samples were ground and size fraction $-90 + 45$ μm collected for experiments. All samples were dried at 120°C for 24 h and kept in desiccators prior to use. Sample numbers indicated in Table 1 will be used throughout this communication.

Experimental techniques

Measurement of heating characteristics
This was carried out by placing a given weight of sample (~ 0.5 g) for

TABLE 1

Composition of various samples

Sample no.	Material	Source (all in India)	Composition (%)					
			CaO	SiO$_2$	Al$_2$O$_3$	FeO	MgO	LOI
1	Limestone	Birmitra pur (Orissa)	45.34	8.62	2.49	1.13	4.95	38.32
2	Limestone	Nandini (M.P.)	41.67	5.68	3.2	NA	7.14	NA
3	Limestone	Chopan (U.P.)	42.5	11.24	2.05	1.07	4.63	NA
4	Limestone	Satna (M.P.)	49.60	2.96	NA	NA	NA	NA
5	Dolomite	Chopan	NA	–	7.5	–	19	–
6	Dolomite	Birmitra- pur (Orissa)	NA	3.86	1.32	NA	20.5	NA
7	Dolomite	North Bengal	NA	2.23	NA	NA	21.0	NA

NA, not available.

different periods in the hot zone of a furnace maintained at a fixed temperature. The heating time required to attain the furnace temperature was measured by thermocouples embedded in the sample mass.

Isothermal decomposition experiments

These were carried out by placing a given weight of sample (~ 0.5 g) for different periods in the hot zone of a furnace maintained at a fixed temperature. The samples were weighed after removal from the furnace. The degree of reaction was obtained as the ratio of measured weight loss to the maximum possible weight loss observed when decomposed for 6 h at 1000°C which ensured complete decomposition in all cases.

Thermal analysis

Simultaneous DTA, TG and DTG were carried out using a Stanton-Redcroft thermal analyser (model STA-781). Standard conditions maintained were as follows:

Particle size $-90 +45$ μm
Heating rate   15°C min^{-1}
Sample weight ~ 29 mg
Nature of packing   five taps on the crucible
Gas atmosphere   as generated by the sample undergoing decomposition

Moving boat technique (MBT)

The MBT employed a horizontal furnace with a central tube of length 62

cm and internal diameter 38 cm. A narrow stainless-steel channel (70 × 2 × 1.5 cm) was used as the boat. The moving mechanism employed a lead screw principle as illustrated. A threaded shaft (39 × 1.5 cm diameter, 1.7 mm pitch) was coupled to a reversing stepping motor of rating 3 kg cm torque, 1.25 A and 220 V, AC line voltage. The transverse motion generated by a nut and plate attachment was used to push the boat into the furnace.

RESULTS AND DISCUSSION

Figure 2 shows the pattern of temperature variation during heating of the samples when they were suddenly put into the hot zone. It is found that nearly 5 min elapsed before the samples came to thermal equilibrium with the furnace. For an isothermal run lasting 2 h or more, therefore, one can ignore this heating up period. Excepting in one case, the temperature variation was almost identical, presumably because the sample was rather small.

Figures 3 and 4 show isothermal decomposition data for 721 and 860°C (±4°C), respectively. Data were also collected for 791°C where the nature of curves was intermediate. It is seen that while decomposition data for dolomite show inflections at lower temperatures these inflections tend to disappear at higher furnace temperatures because of overlapping of the dissociation reactions for $MgCO_3$ and $CaCO_3$. The data approximately fit the kinetic equation for phase boundary controlled reactions, namely

$$1 - (1 - \alpha)^{1/3} = kt \tag{1}$$

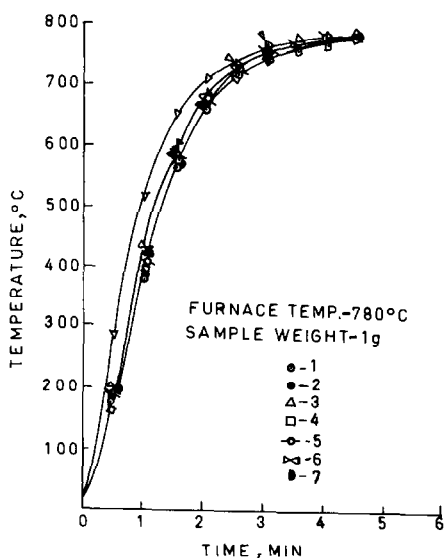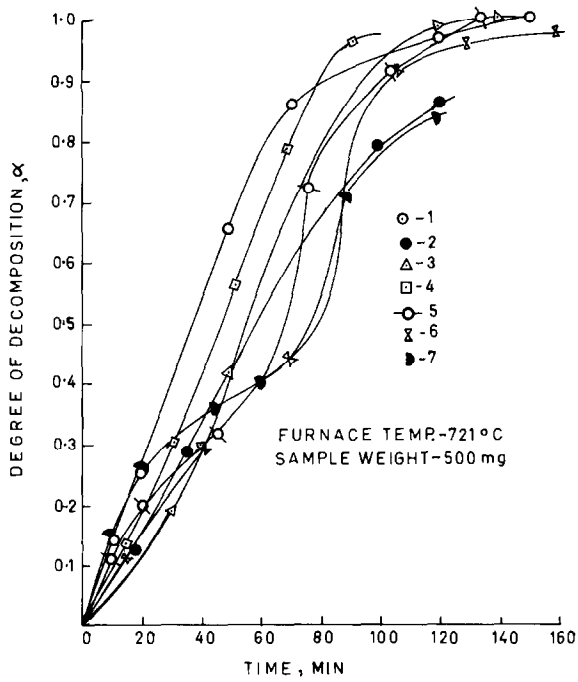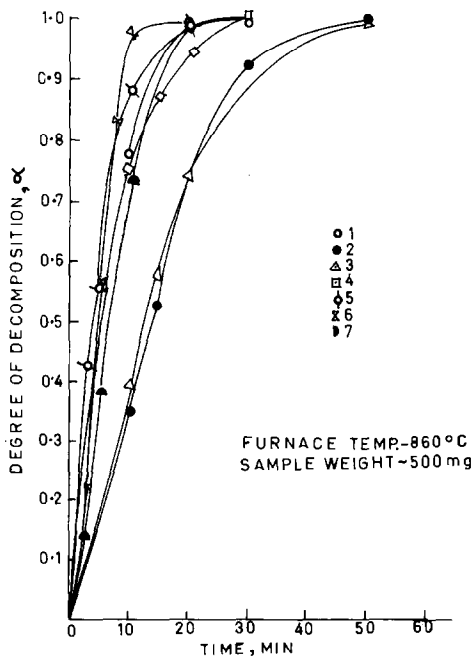Fig. 2. Temperature–time plots for various samples during the heating period.

Fig. 3. $\alpha-t$ plots for isothermal decomposition at 721°C.

Fig. 4. $\alpha-t$ plots for isothermal decomposition at 860°C.
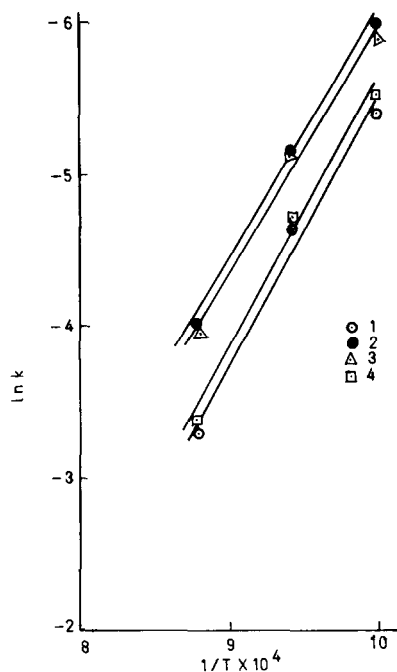
Fig. 5. Plots of ln k versus reciprocal temperature for isothermal decomposition data.

where α is the degree of conversion and t is time. The slopes of the linear plots of the left-hand side of eqn. (1) versus t give values of the rate constant, k. Figure 5 shows the Arrhenius plots for four limestone samples. These plots, of which three are nearly parallel, yield an activation energy value of around 40 kJ mol^{-1} (33 kcal mol^{-1}).

It is seen that the dissociation behaviour of different samples can be compared in terms of the α–t plots. We may arrange them in decreasing order of ease of decomposition as follows:

Limestone: 1, 4, 3, 2
Dolomite: 5, 6, 7

The order is based on α values at fixed values of t. Thus at a given instant, sample 1 shows a higher degree of decomposition compared to samples 4, 3 and 2.

Figure 6 shows the DTA plots for the various samples. These plots clearly show the double peak for dolomite samples and single peak for limestone and, therefore, are useful in indicating the presence of the mineral phases. However, the peak temperature may not serve as an index for comparison of the decomposition behaviour. This is done better with the help of the TG plots shown in Fig. 7. These plots identify, for example, sample 1 as the best in terms of ease of decomposition, which is in agreement with results discussed earlier.
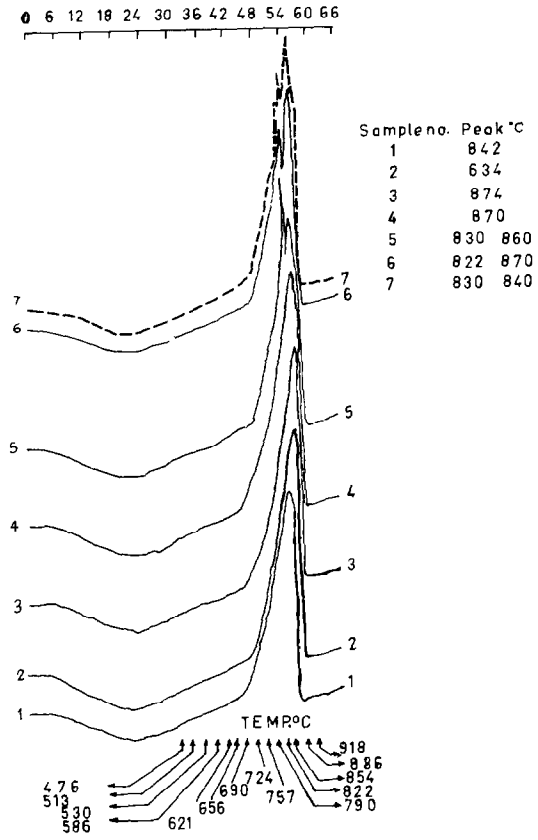
0 6 12 18 24 30 36 42 48 54 60 66

Sample no.	Peak °C	
1	842	
2	634	
3	874	
4	870	
5	830	860
6	822	870
7	830	840

TEMP °C

918
886
854
822
790

476
513
530
586 621 656 690 724 757

Fig. 6. DTA plots for different samples.

RATE OF HEATING-15°C/min
PARTICLE SIZE -90 to +45 μm
WT. OF SAMPLE -29.5 mg
ATMOSPHERE -STATIC AIR/CO$_2$

DEGREE OF DECOMPOSITION, α

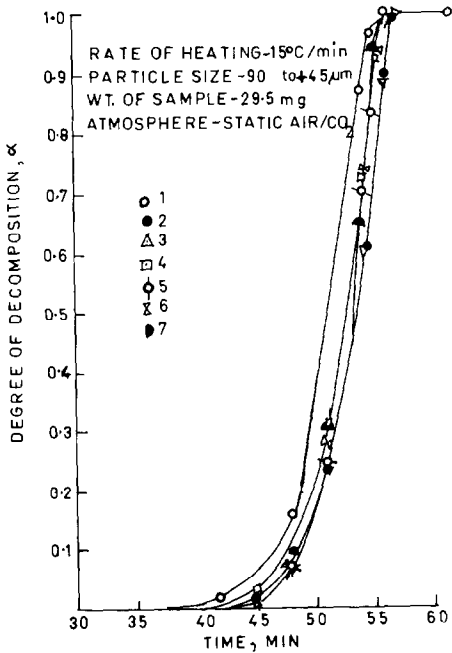○ 1
● 2
△ 3
◻ 4
⬦ 5
✗ 6
◗ 7

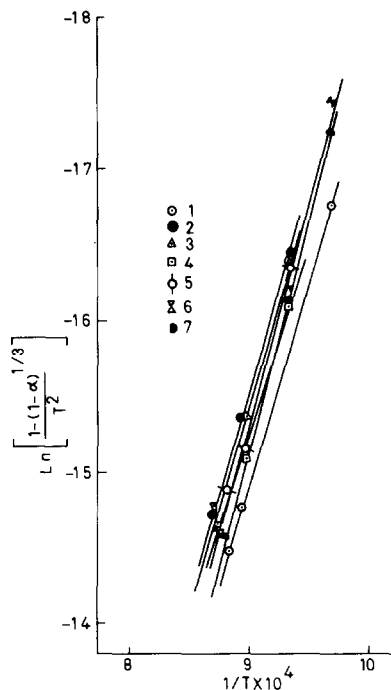TIME, MIN

Fig. 7. TG plots for different samples.

Fig. 8. Coats and Redfern plots for TG data.

There are several ways of analysing the TG data for evaluation of the non-isothermal apparent activation energy value (E). Figure 8 shows the Coats and Redfern plot [5] for the data shown in Fig. 7. The slopes of the linear plots yield a value for E which, in this case, ranges between 220 and 253 kJ mol^{-1} (51–59 kcal mol^{-1}). Linear plots are also obtained by plotting ln[1 − (1 − α)$^{1/3}$] against reciprocal temperature as suggested in the literature by Dixit and Ray [6]. In this case E values are slightly greater and range between 223 and 271 kJ mol^{-1} (52–63 kcal mol^{-1}). Linear plots were also obtained using Dollimore's approach [7], i.e., by plotting ln[dα/dT/f(α)] against reciprocal temperature. These plots yield E values in the range 250–288 kJ mol^{-1} (58–66 kcal mol^{-1}). It is seen that there are minor differences between the E values, and they depend on the calculation procedure. The temperature dependence of reaction rate is similar for all samples and, therefore, the E value cannot be used in distinguishing the decomposition behaviour of one sample from another.

The moving boat experiments were carried out using, in the crucibles lined up in the boat, samples of ~ 1 g. For a fixed furnace temperature profile and boat speed, different limestone and dolomite samples were all found to be heated in the same manner. Figure 9 presents the α–t plots for different samples for a set of fixed experimental conditions. The measured variation of temperature with time is also shown. These plots were obtained
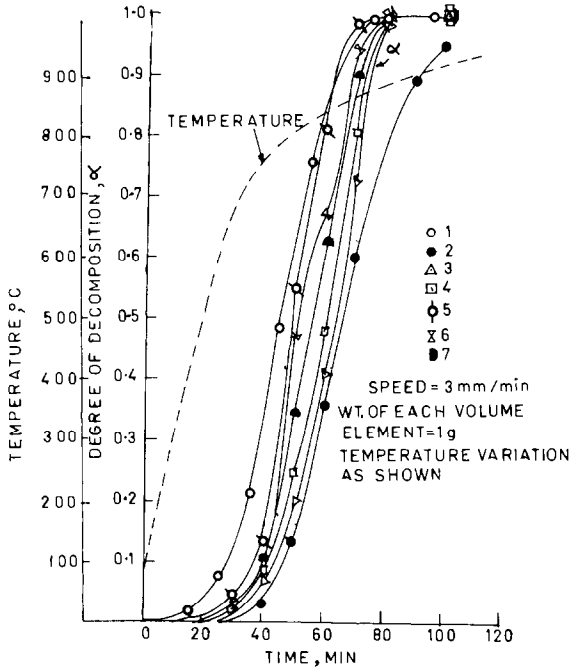
Fig. 9. $\alpha - t$ plots generated by the moving boat technique.

from eight different runs, one for each sample. It is, however, possible to generate all these data from a single run if the moving boat is wide enough to take several rows of samples. Plots given in Fig. 9 show that the MBT affords a convenient and effective method for establishing the difference in decomposition behaviour since the $\alpha - t$ plots are well separated. Samples may be arranged in decreasing order of the ease of decomposition as follows:

Limestone: 1, 4, 3, 2
Dolomite: 5, 6, 7

The orders are identical with those established through isothermal decomposition experiments discussed earlier.

In the moving boat experiments under discussion the heating rate was not constant throughout, as was the case for the TG studies. However, the temperature varied approximately linearly in the initial stages as shown in Fig. 9. It is interesting to compare the TG data with data generated by MBT under approximately similar heating rates. Such a comparison for three samples is shown in Fig. 10. It is seen that the relative positions of the $\alpha - t$ plots are similar in each case but the general orientations are different. With the MBT, the decomposition reaction appears to be initiated earlier and
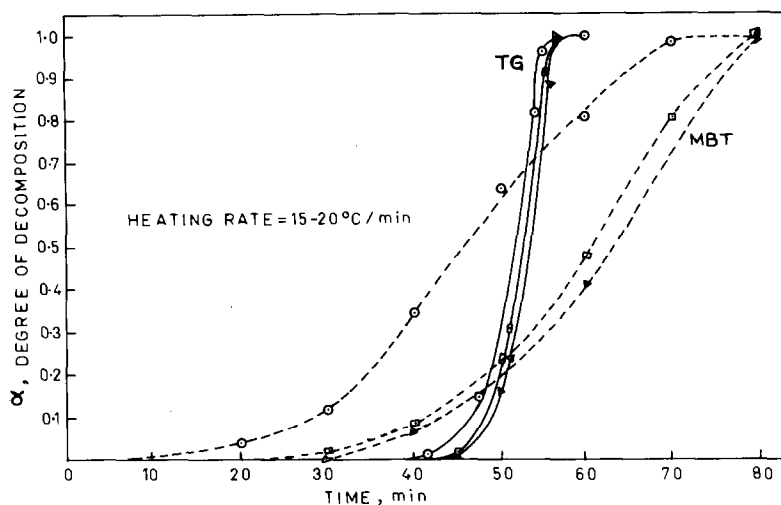
Fig. 10. Comparison of TG and MBT data.

then prolonged over a longer period, the effect of rising temperatures being, therefore, less marked. The MBT data can be analysed to obtain E values. Calculations reported elsewhere [8] show that E is much smaller in this case. For limestone the range is $77-142$ kJ mol^{-1} $(18-33$ kcal mol$^{-1})$. The difference in the apparent value presumably arises from the difference in sample size and heat and mass transfer effects prevalent in larger samples.

CONCLUSION

It is shown that while one can study the decomposition of carbonates using TG or isothermal decomposition experiments, a comparative assessment of decomposition characteristics is more conveniently done using a new technique called the moving boat technique. In this technique one can study decomposition of relatively larger samples under rising temperature conditions, and $\alpha-t$ plots for several samples can be generated simultaneously from a single run.

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