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THERMAL DECOMPOSITION OF DOLOMITE IN AN ATMOSPHERE OF CARBON DIOXIDE
The effect of procedural variables in thermal analysis

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Abstract

The effects of procedural variables on dolomite decomposition in carbon dioxide were investigated. The partial pressure of carbon dioxide causes dolomite decomposition to split into a two-stage process. It was observed that the first stage of dolomite decomposition is progressively displaced to higher temperatures with an increase in heating rate. However, the second stage is not affected significantly by changes in the heating rate. These studies also indicate that decrepitation analysis on dolomite in CO_2 provides better information as compared to experiments in other atmospheres. The flow rate of the purge gas does not influence the thermal behavior of dolomite.

Keywords: decrepitation, dolomite, procedural variables, thermal analysis

Introduction

Limestone exists in two distinct forms calcite and dolomite. Dolomite [$CaMg(CO_3)_2$] is a naturally occurring double salt of calcium and magnesium carbonate. Dolomite finds wide application both industrially and pharmaceutically. Dolomite is used as a calcium and magnesium supplement in the pharmaceutical industry. The $MgCO_3$ part of the dolomitic structure functions as a source of Mg to microorganisms and is therefore used as an additive for fertilizers. For the same reason it is also used as an additive in fodder and food. Industrially, dolomite is widely used in the mineral wool, ceramic, insulation, construction, glass, polishing powder, glaze and chemical industries [1]. The process and degree of dolomitisation are important in petroleum geology [1]. Dolomite is also of mineralogical significance. Thus, dolomite finds wide application and the thermal decomposition of dolomite has been the subject of study by many authors [2–8].

The thermal decomposition of dolomite is strongly dependent on the partial pressure of carbon dioxide. At low partial pressures of CO_2 (below 200 Torr inside

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and/or around the sample), dolomite decomposes via a single step mechanism represented by [2]

$$CaMg(CO_3)_2 \rightarrow CaO+MgO+2CO_2 \quad (1)$$

At higher partial pressures the decomposition occurs via a two-stage mechanism, which is depicted as follows [3]:

$$CaMg(CO_3)_2 \rightarrow CaCO_3+MgO+CO_2 \quad (2)$$

$$CaCO_3 \rightarrow CaO+CO_2 \quad (3)$$

These two stages appear as two separate endothermic peaks on the DTA and DTG plots. The effect of partial pressure of carbon dioxide has been studied in detail by McIntosh, Sharp and Wilburn [3]. They explain that in an atmosphere of carbon dioxide dolomite decomposes via a 2-stage mechanism, wherein the second peak is progressively displaced to higher temperatures as the partial pressure of carbon dioxide is increased. However, the first stage shows an anomalous behavior. As the partial pressure of carbon dioxide is increased, the first peak is initially displaced to lower temperatures. However, with a further increase in partial pressure this peak is displaced to higher temperatures. Change in the shape of thermal analysis curves due to alterations in the partial pressure of the CO_2 is an excellent example of how procedural variables can influence the thermal behavior of a substance.

Procedural variables can have a marked impact on the shape of TG, DTG and DTA plots. The influence of these variables can be quantified by performing kinetic analysis on the TG data. These variables may alter the kinetic mechanism as well as the kinetic parameters for the observed reaction. Such calculations are to be reported in a subsequent paper. The aim of this work is to study the impact of instrumental factors on the shape of the thermal analysis curves using dolomite as an example.

The procedural variables studied include: sample preparation, heating rate and flow rate of the purge gas. The method of sample preparation influences the particle size of the solid. If the sample is finely divided it has a higher surface area and greater reactivity. This high reactivity of the sample can lead to a lowering of the decomposition temperature. In the case of dolomite, particle size affects the decrepitation behavior. The relationship between particle size and decrepitation has been explained on the basis of water molecules trapped within the crystal lattice of dolomite. Another important program variable in thermal analysis is the heating rate. Using a theoretical model [9] it can be shown that both the peak temperature and height for the typical DTG curve increases with a corresponding increase in the heating rate.

The aim of using the purge gas in thermal analysis is to ensure that

- There is no reaction between the product gas and the gaseous environment,
- The product gas is removed as fast as possible from the decomposing sample.

The effect of the flow rate of the purge gas on the TG, DTG and DTA curves can be best studied by direct experiment.

Thus, the shape of the DTA, TG and DTG curves can be influenced greatly by experimental variables. Therefore, while comparing data for the same substance un-

der different experimental conditions the effect of these conditions should be kept in mind.

Experimental

Materials

The material studied was James River White Rock Dolomite. This sample was ground for 3 h using a ceramic ball mill equipped with a General Electric AC motor. The following set of U.S. standard sieves was used for size classification, namely the 20, 40, 60, 80 100, 120, 140, 170, 200, 230, 250, 300 and 325 mesh US Standard Sieves. The samples retained on each sieve represent a range of particle sizes. Table 1 gives the average particle size for samples retained on each mesh. The average particle size was calculated by finding an average of the sum of the opening size of the sieve on which the sample is retained and the opening size of the sieve above. Table 1 also provides information related to aperture dimensions and permissible variations of aperture dimensions for US standard sieves. A Rotap Sieve Shaker was used to hasten the size classification process. The period of operation for this equipment was one half-hour.

Table 1 Aperture dimensions and permissible variations of aperture dimensions for US standard sieves

Mesh No.	Sieve opening/	Average particle size/	Permissible variation in average opening from the standard sieve designation/	Maximum opening size for not more than 5% of openings/	Maximum individual opening/
			μm		
20	850	≥850	±35	925	970
40	425	637.5	±19	471	502
60	250	337.5	±12	283	306
80	180	215	±9	207	227
100	150	165	±8	174	192
120	125	137.5	±7	147	163
140	106	115.5	±6	126	141
170	90	98	±5	108	122
200	75	82.5	±5	91	103
230	63	69	±4	77	89
250	58	60.5	±4	72	83
300	48	53	±4	60	70
325	45	46.5	±3	57	66

Equipment

The SDT 2960 simultaneous TG-DTA (thermogravimetric analysis and differential thermal analysis) from TA Instruments, with Universal Analysis for Windows 95/NT Ver. 2.3 C, was used to examine the thermal decomposition of dolomite. Platinum pans were used to hold milligram quantities of material under study. An empty crucible was used as a reference. The purge gas used in all the thermal analysis experiments was carbon dioxide. Compressed carbon dioxide was supplied by AG gas. An electronic flowmeter from J & W Scientific, model ADM 1000, was used to regulate the flow of purge gas through the sample. The scanning electron microscope (SEM) studies were performed on the JOEL JSM-6100 microscope, wherein the surface of the sample was coated with a thin, electric gold conductive film, the excitation voltage used was 2 kV and the magnification used was 100×.

Procedure

The first step was to obtain SEMs for two representative samples to ensure that the sieving process was efficient enough to bring about size classification. For this purpose sample having grain size 100 and 200 mesh were used. The procedural variables studied include grain size, heating rate and flow rate. Dolomite is known to decrepitate and its decrepitation behavior is affected by grain size. For the decrepitation study, flow rate of the purge gas was maintained at 50 mL min^{-1} and the samples were heated at the rate of 10°C min^{-1}. Samples having grain size 20, 40, 60, 80, 100, 120, 140 and 170 mesh were analyzed. To quantify the degree of decrepitation the following approach was used. It was noted that decrepitation occurs in the temperature range of 500–700°C. Decrepitation leads to mini-explosions within the sample and this results in minute quantities of the sample being expelled out of the crucible. This process is recorded as a series of small peaks on the DTG baseline. The region exhibiting these minor peaks for each of the samples is marked and the temperature corresponding to this region is noted. Mass loss due to decrepitation is not obscured by mass loss due to sample decomposition in a carbon dioxide atmosphere (see Results and discussion). Thus, from the TG plots (not shown here) the mass loss occurring in the decrepitation temperature zone can be easily found out for each sample. The ratio of the mass loss due to decrepitation and the original mass is computed. This ratio is expressed as a percentage and is labeled % decrepitation. Finally, % decrepitation is plotted *vs*. grain size to correlate grain size with decrepitation behavior. To study the effect of heating rate and flow rate, dolomite sample having grain size of 200 mesh was used. The three different heating rates studied were 5, 10 and 20°C min^{-1}. For the heating rate studies the flow rate of the purge gas was maintained at 50 mL min^{-1}. For the flow rate study the heating rate was kept constant at 10°C min^{-1} and the three different flow rates were 25, 50 and 100 mL min^{-1}.

Fig. 1 SEM of ball milled dolomite, sieve size 100 mesh, using a magnification of 100× and an excitation voltage of 2 kV

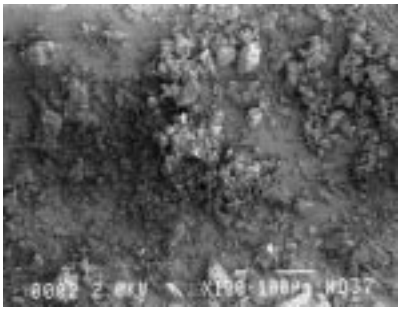

Fig. 2 SEM of ball milled dolomite, sieve size 200 mesh, using a magnification of 100× and an excitation voltage of 2 kV

Results and discussion

The SEMs for the two samples having grain sizes 100 and 200 mesh (Figs 1–2) indicate that the size classification was achieved and this validates the method for size classification. Thus, the sieved samples are suitable for carrying out further studies. Dolomite is known to decrepitate and to study the exact relationship between grain size and decrepitation a detailed study was carried out. For the decrepitating samples, carbon dioxide gas is the purge gas of choice. It has been observed that decrepitation of dolomite usually occurs in the region of 500–700°C. In atmospheres of air and nitrogen, decomposition and decrepitation overlap and it is difficult to correlate the degree of decrepitation with grain size. In a carbon dioxide atmosphere, the partial pressure not only causes the dolomite decomposition to split into two peaks but also leads to an increase in the decomposition temperature. This increase in decomposition temperature segregates the decrepitation and decomposition stages. This facilitates the task of finding a correlation between grain size and decrepitation.

The decrepitation study (Figs 3–5) indicates that maximum decrepitation occurs at intermediate particle sizes. Considerable degree of decrepitation is observed for samples having a mesh size in the range of 60–120. The coarse and fine particle samples show little or no decrepitation. These results match with the work done by

McCauley and Johnson [5]. The current belief is that decrepitation results from the pressure build up of the water within the lattice. A mini-explosion results when this

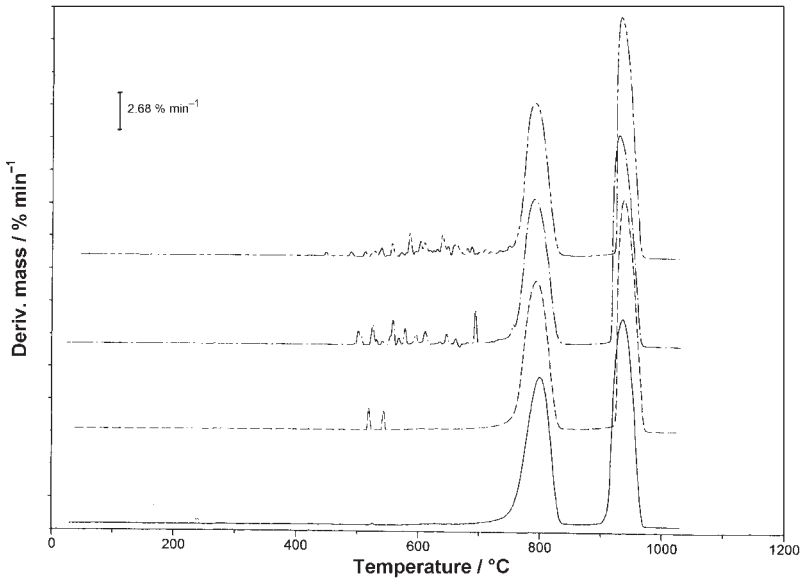

Fig. 3 DTG plots to study the impact of grain size on decrepitation behavior. Grain sizes studied include — 20 mesh, --- 40 mesh, -·-·- 60 mesh, ···· 80 mesh

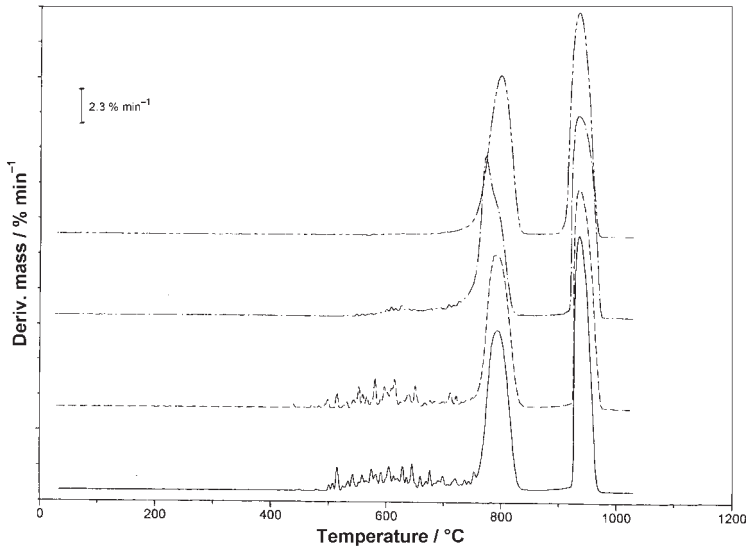

Fig. 4 DTG plots to study the impact of grain size on decrepitation behavior. Grain sizes studied include — 100 mesh, --- 120 mesh, -·-·- 140 mesh, ···· 170 mesh

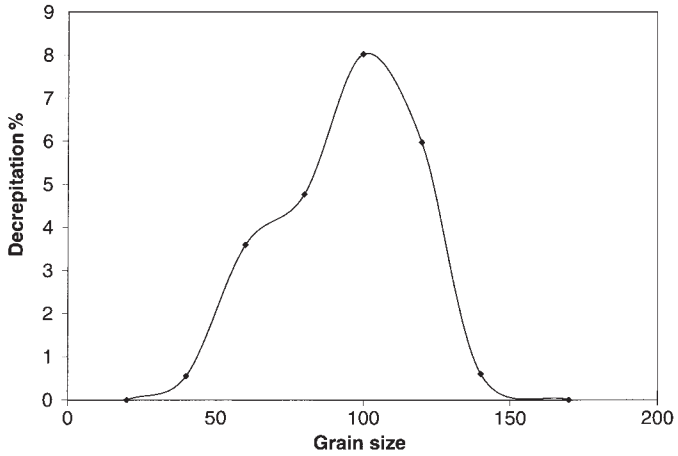

Fig. 5 Decrepitation% plotted as a function of grain size. Maximum decrepitation is observed for samples with intermediate particle size while the lower and higher size ranges exhibit minimal decrepitation

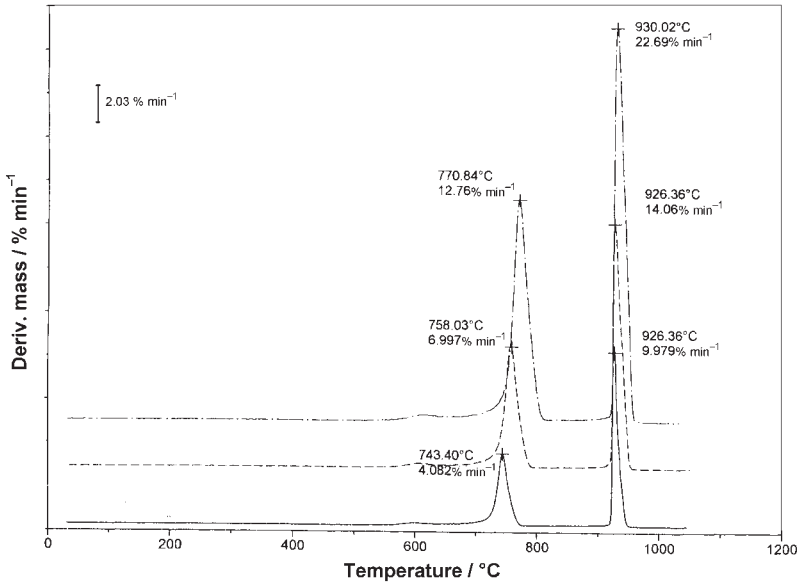

Fig. 6 The effect of heating rate on the thermal decomposition of dolomite in an atmosphere of carbon dioxide. — 5°C min^{-1}, --- 10°C min^{-1}, -·-·- 20°C min^{-1}

pressure exceeds the mechanical strength of the particle. According to McCaulay and Johnson the released pressure, in the case of the larger particles, is not enough to move them because of their higher mass. In the case of the smaller particles the pressure buildup is not enough to cause displacement of the particles. Thus, in the larger and the smaller size ranges minimal decrepitation is observed. However, in the case

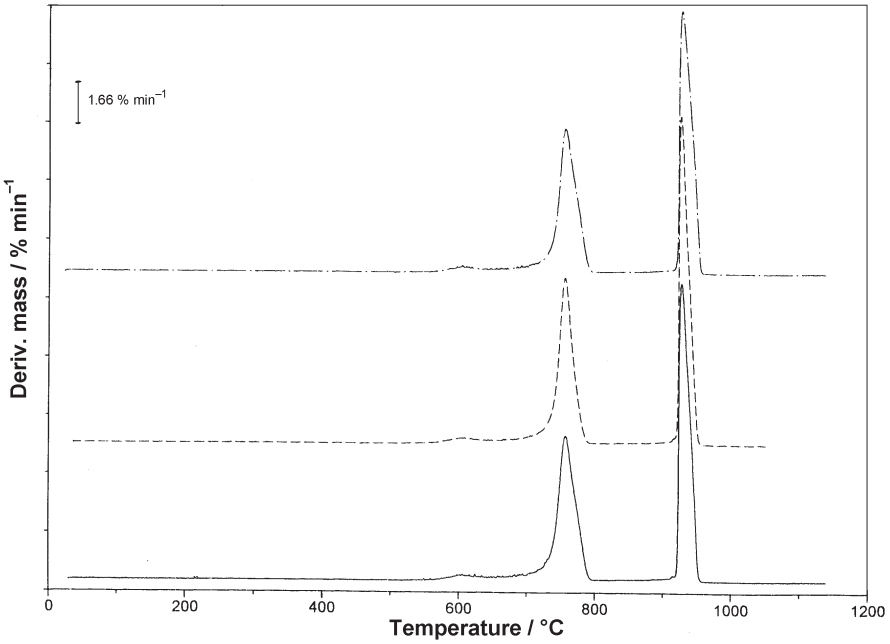

Fig. 7 The effect of flow rate on the thermal decomposition of dolomite in an atmosphere of carbon dioxide. — 25 5 mL min^{-1}, --- 50 mL min^{-1}, -·-·- 100 mL min^{-1}

of particles having intermediate grain size the pressure build up is sufficient and the mass being relatively low, maximum decrepitation is observed for these samples.

Dolomite shows the typical behavior for solids on the DTG curve when subjected to different heating rates (Fig. 6). When the heating rate is increased, the size of the peak increases and the peak temperature is displaced to a higher temperature. However, the affect of heating rate on the peak temperature of the second stage of the decomposition is marginal. The peak temperature shows an increase of approximately 4°C over the 3 heating rates employed. This can be attributed to the fact that the second stage of the thermal decomposition is a reversible reaction. In this entire study, involving different procedural variables, it was always found that this second stage occurs at a temperature of around 930°C. The reaction remains reversible up to a certain point and beyond this point the reaction can no longer sustain the energy intake. Therefore, the second stage of decomposition occurs at a drastic rate. The point of degradation remains practically constant and is not affected by variation in program design or procedural variables. Finally, three different flow rates of purge gas were used, namely 25, 50 and 100 mL min^{-1} (Fig. 7). Neither the peak height nor the peak temperature showed any change with variation in the flow rate. This indicates that the flow rate of the purge gas does not have a significant effect on the partial pressure of carbon dioxide in our experimental set up. It is well known that both stages of dolomite decomposition are sensitive to the partial pressure of carbon diox-

ide [3]. Alterations in flow rate do not lead to changes in peak temperatures for either of the two stages. Thus, we can safely conclude that the partial pressure of carbon dioxide was nearly constant for the three flow rates.

Conclusions

The study indicates that maximum decrepitation occurs at intermediate particle sizes. The coarse and fine particle samples show minimal decrepitation. A change in heating rate does affect the shape of the DTG curve. It causes the peak temperature to increase and leads to an increase in the peak height. The change in flow rate of the purge gas has no effect on either of the two stages of dolomite decomposition. This indicates that the flow rate does not affect the partial pressure of the purge gas in our experimental set up.

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