

# **A STUDY ON THE KINETICS OF THERMAL DECOMPOSITION OF $\text{CaCO}_3$**

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## **Abstract**

By means of TG, the thermal decomposition of the powdered  $\text{CaCO}_3$  was tested with its various dispersities, range of size, and the different content of  $\text{CO}_2$  in flowing nitrogen. Formulae for calculating the rate and time of decomposition were obtained.

**Keywords:** dispersity, kinetics  $\text{CaCO}_3$ , range of size, TG, thermal decomposition

## **Introduction**

When the advanced techniques of heating and decomposing were applied in cement industry in the 70's, various devices were introduced and there appeared great development in the cement industry. Meanwhile, the study on  $\text{CaCO}_3$  under special conditions attracted many research workers. Vosteen [1] and Muller [2-3] published a series of papers on the kinetics of thermal decomposition of  $\text{CaCO}_3$  in the suspended state. But relatively the research on  $\text{CaCO}_3$  is scanty, limiting the advancement of technique and equipment. In this work, we used TG, a simple and fast apparatus, to study the influence of dispersity and size of  $\text{CaCO}_3$ , and the content of  $\text{CO}_2$  in flowing nitrogen, and to calculate the rate and time of decomposition.

## **Experimental**

### *Materials*

Limestone (produced in Fuping, Shaanxi),  $\text{CaCO}_3$  content,  $98\pm 0.05\%$ ;  $\text{CaCO}_3$  (A.R.), purity: 99.99%.

### *Apparatus*

LCT thermobalance (made by the Plant of Beijing Optical Instrument) with a thermocouple of PtLa-Pt.

### *Procedure*

#### The influence of packing of sample on thermal decomposition

##### Simulation the piling state

70 mg of sample and reference material were placed in cell, respectively with a heating rate of  $5.0 \text{ deg}\cdot\text{min}^{-1}$ . The atmosphere is static air and  $60.0 \text{ ml}\cdot\text{min}^{-1}$  nitrogen, respectively.

##### Simulation the dispersing state

A special cell of volume  $10\times 10\times 5 \text{ mm}$  was designed and made of stainless steel with 200 mesh screen, through which the gas may flow. In the cell added 10 mg of sample which was dispersed relatively and packed by flowing gas.

#### The influence of sample size on thermal decomposition

Weighed about 15 mg samples of different sizes and placed into sample cells respectively, then tested them one by one. The sample must have similar sizes.

#### The influence of $\text{CO}_2$ percentage in the flowing gases on thermal decomposition

The atmosphere with different contents of  $\text{CO}_2$  were obtained by adding  $\text{CO}_2$  into pure  $\text{N}_2$ , whose percentage were 10, 15, 20, 25 and 30%, respectively. The samples were tested under conditions of dispersing state, heating rate:  $10 \text{ deg}\cdot\text{min}^{-1}$ , the velocity of flowing gases:  $100 \text{ ml}\cdot\text{min}^{-1}$ , and different percentages of  $\text{CO}_2$  in the flowing gases.

## **Results and discussion**

### *Comparison between piling state and dispersing state*

The kinetic data of powder  $\text{CaCO}_3$  and particle limestone in both piling state and dispersing state were obtained under the both atmosphere of static air and flowing nitrogen conditions. The plots of  $\ln k$  vs.  $T$  are shown in Fig. 1. In Fig. 1, the curves are divided into two groups by different dispersing state. The higher the temperature, the more different the slopes between two states. In dispersing state, the sample was dispersed each other and packed by flowing gases that was similar to suspended state. So it was used to simulate the suspending state.

### *The influence of grain size on decomposition time*

The data of thermal decomposition kinetic parameter for different grain size of limestone are listed in Table 2. The plots of the fraction of decomposition

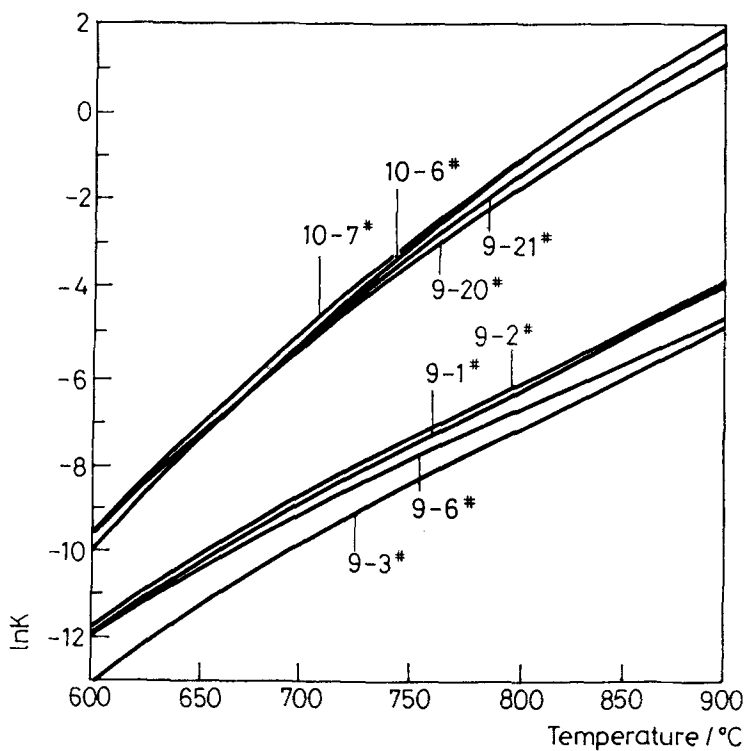


Fig. 1 The plots of  $\ln k$  vs.  $T$  of both pilling state and dispersing state

Table 1 The data for kinetic parameter of decomposition for samples of different state

Sample	No.	State	Atmosphere	$r$	$n$	$E / \text{kJ} \cdot \text{mol}^{-1}$	$A / \text{sec}^{-1}$
CaCO <sub>3</sub>	9-1	ps	Static air	0.999	2/3	213.5	$4.43 \times 10^7$
(A.R)	9-2	ps	N <sub>2</sub> (60 ml·min <sup>-1</sup> )	0.999	2/3	214.3	$5.63 \times 10^7$
Lime-	9-3	ps	Static air	0.998	2/3	225.5	$7.33 \times 10^7$
stone	9-6	ps	N <sub>2</sub> (60 ml·min <sup>-1</sup> )	0.999	2/3	199.5	$6.10 \times 10^4$
CaCO <sub>3</sub>	9-20	ds	Static air	0.999	2/3	318.6	$5.98 \times 10^{14}$
(A.R)	10-6	ds	N <sub>2</sub> (60 ml·min <sup>-1</sup> )	0.998	2/3	327.9	$2.37 \times 10^{14}$
Lime-	9-21	ds	Static air	0.998	2/3	297.4	$4.39 \times 10^{13}$
stone	10-7	ds	N <sub>2</sub> (60 ml·min <sup>-1</sup> )	0.999	2/3	310.9	$3.31 \times 10^{14}$

ps, pilling state; ds, dispersing state;  $r$ , linear correlation coefficient;  $n$ , reaction order;  $E$ , apparent activation energy;  $A$ , pre-exponential constant

**Table 2** The data for kinetic parameter of decomposition of different grain size of limestone

Sample no.	AGS	$r$	$n$	$E / \text{kJ}\cdot\text{mol}^{-1}$	$A/\text{sec}^{-1}$
9-21	81	0.998	2/3	297.4	$4.39 \times 10^{13}$
6-29	81	0.998	2/3	297.9	$4.75 \times 10^{13}$
6-28-2	93	0.998	2/3	290.5	$1.53 \times 10^{13}$
6-28-1	111.5	0.999	2/3	288.1	$9.18 \times 10^{12}$
6-27-2	139.5	0.998	2/3	284.6	$4.76 \times 10^{12}$
6-27-1	202	0.998	1	276.3	$1.50 \times 10^{12}$
6-26	350	0.999	1	244.0	$1.74 \times 10^{10}$
6-30	2280	0.999	1	161.9	$9.32 \times 10^4$

AGS, average grain size;  $r$ , linear correlation coefficient;  $n$ , reaction order;  $E$ , apparent activation energy;  $A$ , pre-exponential constant

( $\alpha$ ) vs. time ( $T$ ) are shown in Fig. 2. From Fig. 2, we found that at the higher fraction of decomposition, the slopes of plots were steeper, especially for large size limestone. So for large size limestone, very high decomposition fraction was not desirable and usually controlled at 85–95%.

#### *The relationship among $t$ , $T$ and $\text{CO}_2\%$*

$\alpha$ - $T$  curves of limestone under atmosphere of different  $\text{CO}_2\%$  are shown in Fig. 3. In Fig. 3, it is shown that the curves are divided into two stages. The first stage is fast, so the rate determining stage is the second stage, whose kinetic parameters are listed in Table 3. In Fig. 4, the plots of  $\text{CO}_2$  content vs. decomposition time are presented under isothermal condition. In Fig. 5, the plots of decomposition temperature vs. decomposition time are present under atmosphere of different  $\text{CO}_2$  content. From the plots in Figs 4 and 5, the relationship of the decomposition time, the decomposition temperature and the  $\text{CO}_2$  percentage are obtained. The equation is:

$$\log t = [-0.1 + 1.65 \times 10^{-2}(900 - T)] + [2.90 \times 10^{-2} + 9.5 \times 10^{-4}(900 - T)] \times \text{CO}_2\% \quad (1)$$

where:

- $t$  the decomposition time, s;
- $T$  the decomposition temperature,  $^\circ\text{C}$ ;
- $\text{CO}_2\%$ , the percentage of  $\text{CO}_2$ , %.

At constant temperature, the equation is:

$$\lg t = a + b \times \text{CO}_2\% \quad (2)$$

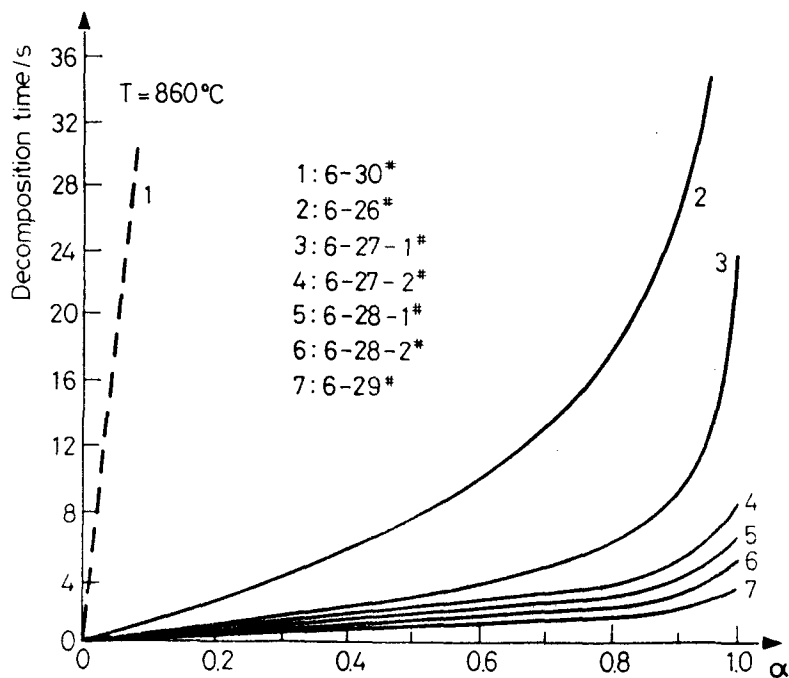


Fig. 2 The influence of grain size of limestone on decomposition time

Table 3 The kinetic parameters for limestone under different atmospheres

Sample no.	CO <sub>2</sub> %	VFG ml·min <sup>-1</sup>	<i>r</i>	<i>n</i>	<i>E</i> / kJ·mol <sup>-1</sup>	<i>A</i> / sec <sup>-1</sup>
10-7	0	60	0.999	2/3	310.9	3.31×10 <sup>14</sup>
7-02	10	100	0.998	2/3	647.3	1.54×10 <sup>27</sup>
7-13	15	100	0.999	2/3	719.5	1.00×10 <sup>22</sup>
7-09	20	100	1.000	2/3	859.0	1.67×10 <sup>22</sup>
7-12	25	100	0.999	2/3	972.4	9.83×10 <sup>44</sup>
7-10-2	30	100	1.000	2/3	1064.7	2.95×10 <sup>44</sup>

VFG, velocity of flowing gas; *r*, linear correlation coefficient; *n*, reaction order; *E*, apparent activation energy; *A*, pre-exponential constant

### *The influence of CO<sub>2</sub> content on decomposition time*

It is shown in Fig. 5 that the decomposition rate decrease with the increasing of CO<sub>2</sub>%, especially at lower temperatures.

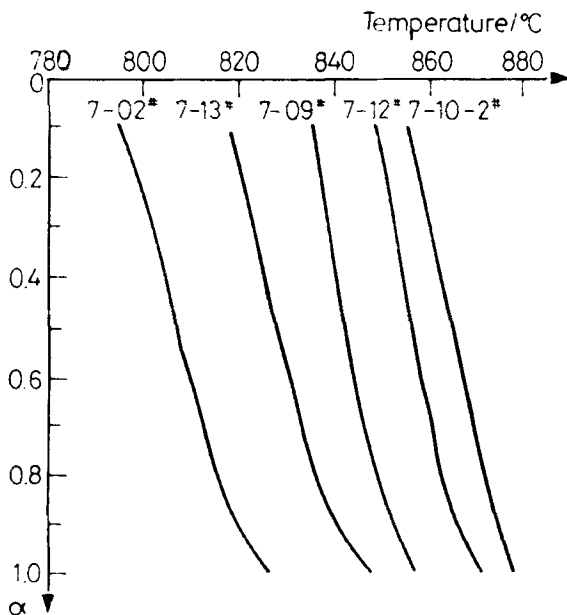


Fig. 3  $\alpha$ - $T$  curves of limestone under different  $\text{CO}_2\%$  in the flowing gases

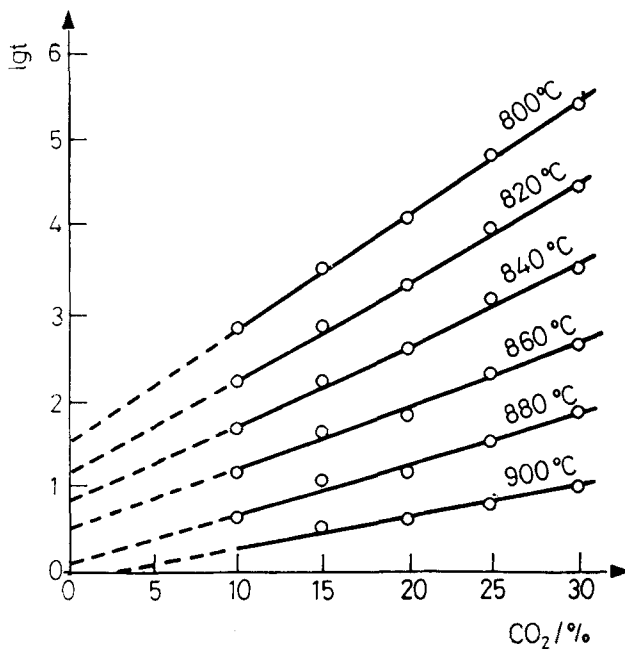


Fig. 4 The plots of different  $\text{CO}_2\%$  vs. decomposition time under constant temperature

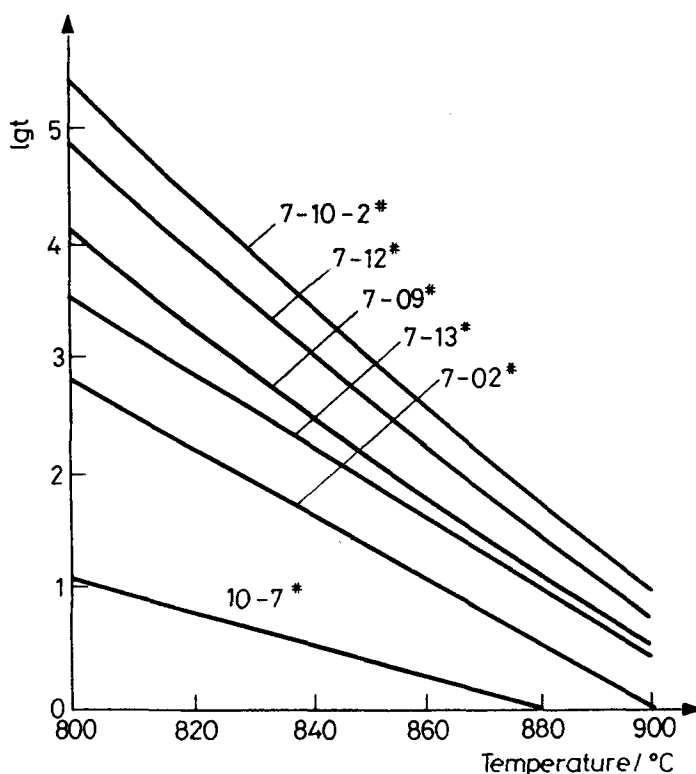


Fig. 5 The plots of decomposition temperature vs. decomposition time under same atmosphere

## Conclusions

- In TG, it is feasible and simple to simulate the suspended state by the dispersing state.
- As shown in Fig. 2, the slope of plots are very steep, so very high decomposition fraction is not suitable.
- Comparing with the static atmosphere condition, the decomposition rate of sample is faster under flowing gases condition and the temperature range of decomposition become higher and narrower.

## References

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- 2 A. Muller, B. Dabm and J. Stork, *Silikattechnik*, 1 (1977) 4.
- 3 A. Muller, B. Dabm and J. Stork, *Zement-Kalk-Gips*, 2 (1979) 78.

**Zusammenfassung** — Mittels TG wurde die thermische Zersetzung von pulverförmigem  $\text{CaCO}_3$  in Abhängigkeit vom Dispersionsgrad, Größenbereich und vom  $\text{CO}_2$ -Gehalt der Stickstoffatmosphäre untersucht. Dabei wurden Formeln für die Berechnung der Zersetzungsgeschwindigkeit und -dauer erstellt.