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**ORIGINAL ARTICLE**

Decomposition kinetic characteristics of calcium carbonate containing organic acids by TGA

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Abstract By means of thermogravimetric analysis (TGA), influences of organic acids such as citric acid, oxalic acid and tartaric acid on decomposition process and thermal behaviors of calcium carbonate were investigated in non-isothermal condition. Experiments were conducted from the ambient temperature to 1273 K at a heating rate of 10 K min⁻¹. Moreover, the kinetic parameters (activation energy and pre-exponential factor) of the mixtures of calcium carbonate and organic acids were determined using the Coats–Redfern method. It is indicated that the decomposition process of calcium carbonate containing different organic acids includes three or four weight loss processes. In the zone of 370–450 °C, energy is released due to the combustion of organic products decomposed from organic salts, and energy increases with the increase of molecular weight of organic acid. Activation energy of the samples containing citric acid, oxalic acid and tartaric acid is decreased by 34.9%, 28.8% and 31.9%, respectively. The results may be used to provide a useful basis for further applying industrial wastes containing different organic acids in cement industries with high-efficiency.

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1. Introduction

The thermal decomposition of calcium carbonate particles in raw meal has been the subject of intensive study over the years due to its importance in the output and heat consumption of cement clinker of cement industry. A number of researchers

reported the use of various additives with target to the effect on kinetic and thermodynamic parameters of the decomposition of CaCO₃ (Hou et al., 2005; Barros et al., 2004; Guan et al., 2004; Chen et al., 2004; Ma et al., 2005; Misra and Bopprthakur, 1992; Andradea et al., 2003; Stephan et al., 1999; Kasselouri et al., 1995). Most of the additives proposed regarded the system CaO–SiO₂. Such some inorganic additives as LiCO₃, NaCl, NaF, CaF₂, MgO etc. had been used to achieve lower temperatures in the formation of C₂S followed by a decrease of the CaCO₃ decomposition temperature. Some researchers discovered that the use of organic acids as additives can decrease energy consumption during the CaCO₃ decomposition process. The decomposition temperature of organic salts was lower than that of CaCO₃ (Qi et al., 2002).

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In this paper, influences of organic acids such as citric acid, oxalic acid and tartaric acid on the decomposition process of calcium carbonate were investigated by TGA, and the thermal behaviors of calcium carbonate containing different organic acids were also determined by differential scanning calorimetry (DSC). The decomposition kinetic parameters of the mixtures were also determined according to the Coats–Redfern method.

2. Experiments

2.1. Experimental materials

Citric acid, oxalic acid, tartaric acid and calcium carbonate are chemical reagents, which were provided by Shanghai Chemical Reagent Plant.

2.2. Experimental methods

The configuration of samples was investigated by using Scanning electron microscope (SEM, JM-840 Scanning Microscope).

Experiments on the decomposition characteristics of the mixtures were performed with a NETZSC STA-449C thermogravimetric analyzer. The furnace was heated at 10 K min^{-1} from the ambient temperature to 1273 K. The flow rate of gas (80% N_2 and 20% O_2) was 20 mL/min. The weight of the sample was monitored continuously as a function of temperature.

2.3. Preparation and characterization of mixtures of organic acids and calcium carbonate

Citric acid, oxalic acid and tartaric acid were added in a percentage of 5% w/w in the presence of 70 °C warm water for 20 min. The resulting mixtures were dried, ground and then passed through a 100 μm sieve. The SEM-images of the mixtures are shown in Fig. 1.

As shown in Fig. 1, some new reaction products are formed on the surface of calcium carbonate particles during the reaction of calcium carbonate with organic acids. Consequently, the mixtures contain calcium organic acid hydrate, organic acids and calcium carbonate.

2.4. Kinetics analysis

In this work, the activation energy (E) and pre-exponential factor (A) of the samples are determined by the Coats–Redfern method from an analysis of the thermogravimetric (TG) curves.

The decomposition rate is shown as

$$dx/dt = kf(\alpha) \quad (1)$$

where α is the fraction of decomposition of CaCO_3 and k is the rate constant, given by the expression.

$$k = A \exp(-E/RT) \quad (2)$$

For the decomposition of calcium carbonate, $f(\alpha)$ can be expressed as following

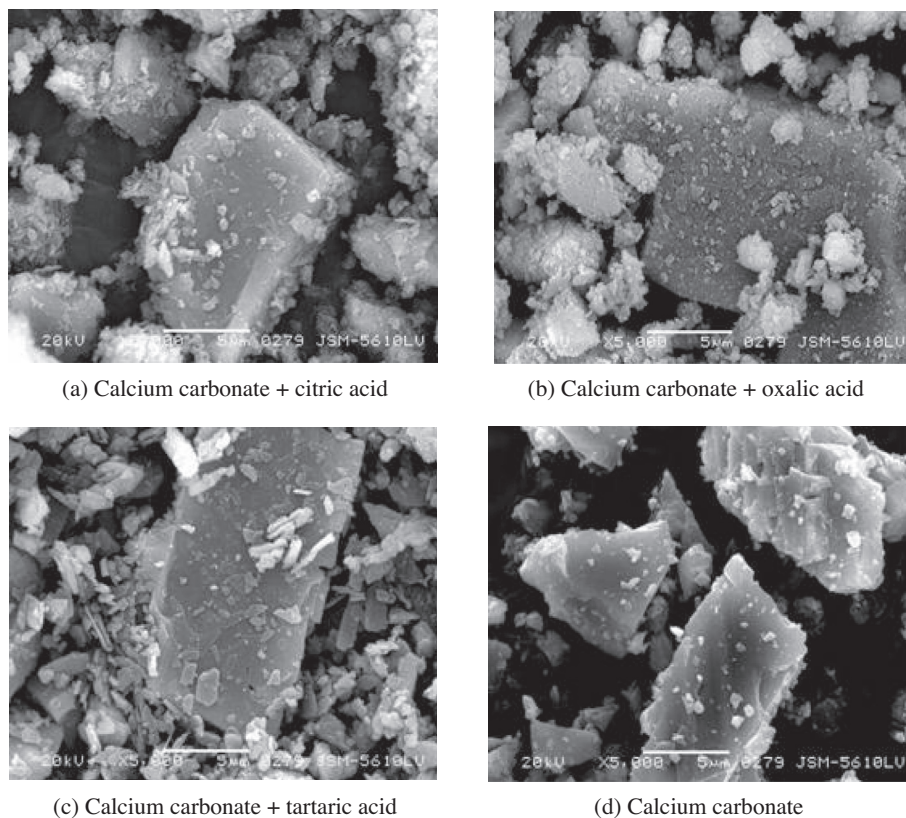


Figure 1 SEM of the mixtures containing organic acid and calcium carbonate.

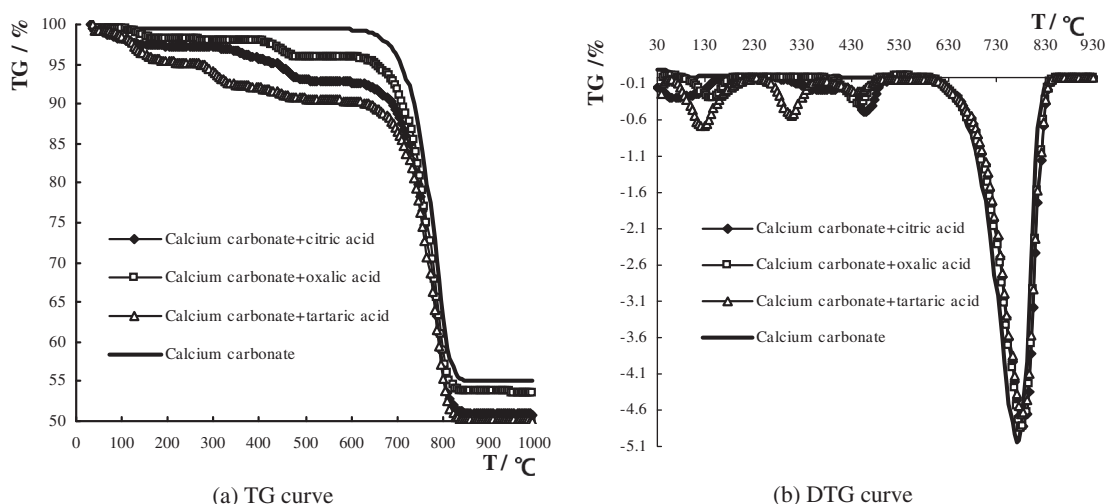


Figure 2 TG-DTG curve of the mixtures containing organic acid and calcium carbonate.

$$f(\alpha) = 1 - \alpha \quad (3)$$

If the temperature rises at a constant rate $\beta = dT/dt$, Eq. (1) becomes

$$dx/dT = A/\beta \exp(-E/RT)(1 - \alpha) \quad (4)$$

Then Eq. (4) can be integrated as

$$\ln[-\ln(1 - \alpha)/T^2] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT \quad (5)$$

In general, $RT/E \ll 1$, so Eq. (5) becomes

$$\ln[-\ln(1 - \alpha)/T^2] = \ln(AR/\beta E) - E/RT \quad (6)$$

When $\ln[-\ln(1 - \alpha)/T^2]$ was plotted against $1/T$ according to Eq. (6), E and A can be determined by linear regression.

3. Results and discussions

3.1. Influence of organic acids on decomposition process of the samples

The TG/DTG profiles of the samples with or without organic acids such as citric acid, oxalic acid and tartaric acid are presented in Fig. 2(a) and (b).

Decomposition processes of the mixtures containing different organic acids are similar. The decomposition process contains three or four phases with weight loss, but there is only one weight loss during the decomposition of calcium carbonate at 600–850 °C. The differences among the mixtures before 600 °C may be due to the decomposition of organic acids and calcium organic acid hydrate in the mixtures. Also the final weight loss of the mixtures containing citric acid, oxalic acid and tartaric acid is 48.4%, 45.8% and 49.1%, respectively. But that of pure calcium carbonate is 43.8%.

3.2. Influence of organic acids on thermal behaviors of the samples

The DSC profiles of the mixtures are presented in Fig. 3. The characteristic temperature and decomposition process are demonstrated in Table 1.

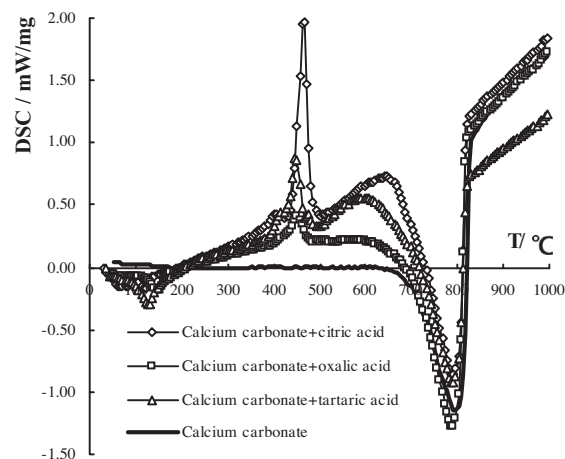


Figure 3 DSC curve of the mixtures containing organic acid and calcium carbonate.

Table 2 and Table 3 are presented the energy change of the mixtures during the decomposition process and thermal analysis of the decomposition of calcium carbonate, respectively.

The decomposition processes of the mixtures can be divided into three parts, such as dehydration of organic salts and decomposition of organic acids, decomposition of organic salts and combustion of products, decomposition of CaCO_3 . The corresponding decomposition temperature of CaCO_3 decreases with the incorporation of organic acids. Heat absorption due to the decomposition of the mixtures containing citric acid, oxalic acid and tartaric acid decreases 21.4%, 2.4% and 6.9%, respectively. Moreover, with the incorporation of organic acids, the corresponding temperature of the decomposition peak of calcium carbonate decreases by 4–7 °C, which may be due to the combustion of organic products from the decomposition of calcium organic acid hydrate at 370–450 °C. And heat evolution of the mixtures increases with the increase of molecular weight of organic acid.

Table 1 Thermal behaviors of the mixtures containing organic acid and calcium carbonate.

No.	Peak	$T_{\text{peak}}/^{\circ}\text{C}$	Decomposition process
C	Heat absorption	792.8	R_1 —decomposition of CaCO_3
CC	Heat absorption	120.1	R_2 —dehydration of $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$; decomposition of $\text{C}_6\text{H}_8\text{O}_7$
CC	Heat evolution	464.4	R_3 —decomposition of $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ and combustion of products
CC	Heat absorption	787.9	R_1
CO	Heat absorption	151.1	R_4 —dehydration of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$; decomposition of $\text{H}_2\text{C}_2\text{O}_4$
CO	Heat evolution	452.8	R_5 —decomposition of $\text{Ca C}_2\text{O}_4$ and combustion of products
CO	Heat absorption	788.3	R_1
CT	Heat absorption	126.2	R_6 —decomposition of $\text{C}_4\text{H}_6\text{O}_6$
CT	Heat evolution	441.0	R_7 —decomposition of $\text{CaC}_4\text{H}_4\text{O}_6$ and combustion of products
CT	Heat absorption	785.8	R_1

Notes: C – Calcium carbonate; CC – Calcium carbonate + citric acid; CO – Calcium carbonate + oxalic acid; CT – Calcium carbonate + tartaric acid.

Table 2 The energy change of the mixtures during the decomposition process.

No.	Thermal analysis/ $\text{kJ kg}^{-1}\text{CaCO}_3$							ΔQ
	$R_1(+)$	$R_2(+)$	$R_3(-)$	$R_4(+)$	$R_5(-)$	$R_6(+)$	$R_7(-)$	
CC	998.3	13.1	226.4	–	–	–	–	785.0
CO	1129	–	–	15.8	43.0	–	–	1101.8
CT	881.9	–	–	–	–	31.6	92.4	821.1

Table 3 Thermal analysis of the decomposition of mixture containing organic acid and calcium carbonate.

No.	Temperature/ $^{\circ}\text{C}$			$\Delta H/\text{kJ kg}^{-1}$		Decrease/%
	Initial	Peak	Final	Mixture	CaCO_3	
C	600	792.8	829	1296.0	1296.0	
CC	645	787.9	824	784.98	998.3	21.4
CO	620	783.4	820	1101.77	1129.0	2.4
CT	596	785.8	815	821.05	881.9	6.9

3.3. Decomposition kinetics of the samples

The value of $\ln(g(x)/T^2)$ is plotted against $1/T$ by using Coats and Redfern (1964), Sharp and Wentworth (1969), Wang et al. (2003a,b). The linear regression results are shown in Table 4.

The activation energy of the mixtures containing citric acid, oxalic acid and tartaric acid decreases 34.9%, 28.8% and 31.9%, respectively. The decrease in the mechanism of activation energy may be due to the lower decomposition temperature and heat absorption of the mixtures (as shown in Tables 1–3), which can reduce the reaction energy barrier of the decomposition process and increase the quantity of activated molecule. And there is a linear connection between the activation energies and pre-exponential factors ($\ln A = 0.1168E - 7.7472$).

Table 4 Influence of organic acids on kinetic parameters.

No.	Activation energy $E/\text{kJ mol}^{-1}$	Pre-exponential factor $\ln A/\text{s}^{-1}$
C	180.2	13.6
CC	117.3	6.2
CO	128.1	7.4
CT	122.7	6.9

Combined with the results of peak temperature of decomposition, heat absorption or evolution and activation energy, the incorporation of organic acids can decrease the heat consumption of decomposition of calcium carbonate.

4. Conclusions

The decomposition process contains three or four phases with weight loss, but there is only one weight loss during the decomposition of calcium carbonate at 600–850 $^{\circ}\text{C}$. The differences among the mixtures are represented before the zones at 600 $^{\circ}\text{C}$. Also the final weight loss of the mixtures increases to a certain degree with the incorporation of organic acids.

In the zone of 370–450 $^{\circ}\text{C}$, energy is released due to the combustion of organic products decomposed from organic salts, and energy increases with the increase of molecular weight of organic acid.

The activation energy of the mixtures containing citric acid, oxalic acid and tartaric acid decreases 34.9%, 28.8% and 31.9%, respectively. The results agree with that of the change of decomposition temperature of the mixtures. And there is a linear connection between the activation energies and pre-exponential factors ($\ln A = 0.1168E - 7.7472$).

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References

- Andradea, F.R.D., Maringolob, V., Kihara, Y., 2003. Incorporation of V, Zn and Pb into the crystalline phases of Portland clinker. *Cem. Concr. Res.* 33, 63–71.
- Barros, A.M., Tenório, J.A.S., Espinosa, D.C.R., 2004. Evaluation of the incorporation ratio of ZnO, PbO and CdO into cement clinker. *J. Hazard. Mater.* 112, 71–78.
- Chen, Y.M., Guo, S.H., Guan, Z.F., 2004. Cement clinker with high cementing property. *J. Chin. Ceram. Soc.* 32, 873–879 (In Chinese).
- Coats, A.W., Redfern, J.P., 1964. Kinetic parameters from thermogravimetric data. *Nature* 201, 68–69.
- Guan, Z.F., Qin, S.W., Guo, S.H., Chen, Y.M., 2004. Effect of series anions on the properties of alite-rich Portland clinker. *J. Chin. Ceram. Soc.* 32, 317–320 (In Chinese).
- Hou, G.H., Shen, X.D., Xu, Z.Z., 2005. Effect of copper oxide on decomposition kinetics for calcium carbonate. *J. Chin. Ceram. Soc.* 33, 109–114 (In Chinese).
- Kasselouri, V., Dimopoulos, G., Parissakis, G., 1995. Decomposition of CaCO_3 in the presence of organic acids. *Cem. Concr. Res.* 25, 955–960.
- Ma, S.H., Shen, X.D., Huang, Y.P., Gong, X.P., Zhong, B.X., 2005. Influence of ZnO on formation and properties for high cementing clinker. *J. Chin. Ceram. Soc.* 33, 1499–1503.
- Misra K.C., Bopthakur, P.C., 1992. Role of mineralizers in alite formation in a rice husk ash– CaCO_3 raw mix. In: Proceedings of the Ninth International Congress on the Chemistry of Cement, National Council for Cement Building Materials, New Delhi, 4, pp. 301–307.
- Qi, Q.J., Ma, Y.D., Liu, J.Z., 2002. Thermogravimetric experiment research on thermal decomposition mechanics of calcium carbonate. *J. Liaoning Tech. Univ.* 21, 689–692 (In Chinese).
- Sharp, H.J., Wentworth, S.A., 1969. Kinetic analysis from thermogravimetric data. *J. Anal. Chem.* 41, 2060–2062.
- Stephan, D., Mallmann, R., Knöfel, D., Härdtl, R., 1999. High intakes of Cr, Ni, and Zn in clinker. Part I. Influence on burning process and formation of phases. *Cem. Concr. Res.* 29, 1949–1957.
- Wang, S.J., Lu, J.D., Zhou, H., 2003a. Kinetic model study on thermal decomposition of limestone particles. *J. Eng. Thermophys.* 24, 670–699 (In Chinese).
- Wang, S.J., Lu, J.D., Hu, Z.J., 2003b. Study on kinetics of decomposition of cement raw meal. *J. Chin. Ceram. Soc.* 31, 811–814 (In Chinese).