Pergamon

Cement and Concrete Research, Vol. 25, No. 3, pp. 477–484, 1995

0008-8846/95 $9.50 + .00

0008-8846(95)00035-6

EFFECT OF ACETIC AND TARTARIC ACID UPON THE THERMAL DECOMPOSITION OF $CaCO_3$

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(Communicated by F. Massazza)
(Received November 30, 1994)

ABSTRACT

In the present work the effect of acetic and tartaric acid upon the thermal decomposition of $CaCO_3$ has been studied. Mixtures of $CaCO_3$ and 5, 10 and 20% acetic and tartaric acid have been prepared. These mixtures were heated at various temperatures in order to study the progress of calcium carbonate decomposition by loss on ignition measurements. Differential Scanning Calorimetric as well as XRD studies have demonstrated that the addition of acetic or tartaric acid to $CaCO_3$ promotes its thermal decomposition.

Introduction

In previous research work the effect of oxalic and citric acid has been studied (1, 2) as a new approach to the solution of the problem of $CaCO_3$ decomposition (3-7).

The beneficial results concerning the calcination of calcium carbonate at lower temperature than the normal, led to the study of some other organic acids with the following characteristics and properties.

a. Dissociation constants,
number of carboxylic radicals,
participation of other electronegative groups and
molecular size.
b. The possibility for the above mentioned acids to be contained in industrial or agricultural wastes.
As industrial and agricultural wastes could be considered various acid compounds from the food industry or dumped fruits respectively.
c. During the calcination process the resulted substances must not have any effect upon the quality of the final product.

Experimental

Two series of mixtures from $CaCO_3$ and organic acid have been prepared. The first series included three mixtures from $CaCO_3$ with 50, 10 and 20% w/w acetic acid in the presence of 20% warm water.

The mixtures of the second series were prepared from $CaCO_3$ with 5, 10 and 20% w/w tartaric acid in the presence of the same amount of warm water.

The above mentioned amount of the water added was similar to that existing in the semi-dry process for the cement production.

The following studies have been made on the prepared mixtures.
a. Loss on ignition measurements.
b. X - Ray Diffraction (XRD) Study of the samples heated at various temperatures.
c. Differential Scanning Calorimetry (DSC) measurements of absorbed heat during the thermal treatment of the mixtures.

The XRD patterns concerning the mixtures have been prepared and thermaly treated, are presented in the Figures 1, 2, 3 and 4. The various crystalline compounds identified through XRD analysis at different thermal levels, are given in Table I.

TABLE I.
The formation of crystalline compounds during the burning of $CaCO_3$ - acic mixture

Sample	Crystalline compound	Thermal area °C
$CaCO_3 + CH_3COOH$	$(CH_3COO)_2Ca \cdot 0.5 H_2O$	20 - 250
	$3(CH_3COO)_2Ca \cdot 2CH_3COOH$	20 - 250
	β - $(CH_3COO)_2Ca$	250 - 400
	CaO	> 550
	$CaCO_3$	20 - 900
$CaCO_3 + C_4H_6O_6$	$C_4H_6O_6$	20 - 250
	$Ca C_4H_6O_6 \cdot 4H_2O$	20 - 400
	CaO	> 550
	$CaCO_3$	20 - 900

In Table II the loss on ignition of the mixtures at various temperatures is presented, while the percentages of $CaCO_3$ reacted and the calculated value of $CaCO_3$ decomposed at 550 °C, as it could be drawn from the Table II, are presented in Table III.

TABLE II.
Loss on ignition of mixtures during the burning process

Sample	Temperature °C								
	20	250	350	400	550	600	700	800	900
$CaCO_3$	0.00	0.00	0.00	0.00	0.00	0.45	12.85	24.55	44.01
$CaCO_3$+ 5%$H_2C_2O_4$	0.00	1.21	2.10	3.10	5.13	5.61	19.86	31.58	45.53
$CaCO_3$+10%$H_2C_2O_4$	0.00	2.78	4.00	6.31	10.65	11.41	24.70	32.26	47.25
$CaCO_3$+20%$H_2C_2O_4$	0.00	6.84	9.81	14.06	22.43	21.35	32.88	43.22	51.26
$CaCO_3$+ 5%$C_6H_8O_7$	0.00	1.35	3.29	3.89	5.24	5.66	18.49	30.44	46.07
$CaCO_3$+10%$C_6H_8O_7$	0.00	2.92	6.72	7.99	10.69	12.95	25.55	37.31	48.25
$CaCO_3$+20%$C_6H_8O_7$	0.00	6.84	14.40	16.22	20.57	23.89	39.46	45.18	52.88

TABLE III
Transformation of $CaCO_3$ during the $CaCO_3$ - acid reaction

Sample	% $CaCO_3$ reacted with the acid	% $CaCO_3$ transformed to CaO at 550 °C
$CaCO_3$	0.0	0.0
$CaCO_3$ + 5%CH_3COOH	3.5	3.5
$CaCO_3$ +10%CH_3COOH	7.3	7.2
$CaCO_3$ +20%CH_3COOH	12.8	12.5
$CaCO_3$ + 5% $C_4H_6O_6$	3.3	3.3
$CaCO_3$ +10% $C_4H_6O_6$	6.7	6.5
$CaCO_3$ +20% $C_4H_6O_6$	14.4	14.3

The Figure 5 shows the DSC diagrams have been drawn for the pure $CaCO_3$ and its mixtures with 5, 10 and 20% acetic and tartaric acid, respectively. The thermal behaviour of the mixtures is presented on the Table IV.

TABLE IV.
Thermal behaviour of the $CaCO_3$ - acid mixtures

Sample	Mode of reaction	Peak °C	Reaction
$CaCO_3$	endothermic	800	Decomposition of $CaCO_3$
$CaCO_3$+20%CH_3COOH (acetic acid)	exothermic	380	Decomposition of $(CH_3COO)_2$ Ca and combustion of its products
	endothermic	770	Decomposition of $CaCO_3$
$CaCO_3$+20%$C_4H_6O_6$ (tartaric acid)	endothermic	110, 130	Decomposition of $C_4H_6O_6$
	exothermic	408	Decomposition of Ca $C_4H_6O_6$ and combustion of its products
	endothermic	786	Decomposition of $CaCO_3$

In Table V the various amounts of energy absorbed during the thermal transformation, as they have been calculated from the DSC diagrams as well as the decrease in the energy demand, are presented.

Discussion

From the XRD diagrams (Fig 1) and the Table I it is shown that during the reaction of $CaCO_3$-acetic acid, calcium acetate semi-hydrate is formed. The peaks corresponding to 5.30 and 7.50 2θ° (Fig 2) indicate that this compound appears in larger amounts as the acid/$CaCO_3$ ratio increases. The compound $3(CH_3COO)_2Ca \cdot 2CH_3COOH$ (6, 43 2θ°) is well observed in the case of 20% acid/$CaCO_3$ ratio.

TABLE V

Thermal analysis data of $CaCO_3$ in the presence of acetic and tartaric acid.

Acid/ $CaCO_3$ ratio (w/w)	Temperature (°C) Start	Peak	End	ΔH values calculated by DSC (KJ/kgr $CaCO_3$)	Decrease of ΔH during the $CaCO_3$ decomposition
0.0	600	800	820	1866.7	
5.0 CH_3COOH	572	792	810	1757.9	5.9
10.0 CH_3COOH	540	780	800	1744.4	6.5
20.0 CH_3COOH	535	770	802	1666.7	10.7
5.0 $C_4H_6O_6$	542	799	809	1747.4	6.4
10.0 $C_4H_6O_6$	550	790	810	1737.0	6.9
20.0 $C_4H_6O_6$	546	786	802	1629.2	12.7

During the heating above 250 °C the calcium acetate salts are transformed to $\beta(CH_3COO)_2Ca$ (9.25 2θ°). At 550 °C the only observed compounds are $CaCO_3$ and CaO. This fact leads to the conclusion that an early decomposition of $CaCO_3$ takes place due to the complete dissociation of the calcium acetates.

The transformation of $CaCO_3$ to CaO at 550 °C increases from 3.5 to 12.5% by the increase of the acid/$CaCO_3$ ratio.

The behaviour of the mixtures with tartaric acid is similar to that of the mixtures with acetic acid. During the reaction of $CaCO_3$ with tartaric acid calcium tartrate tetrahydrate is formed (Fig. 3 peaks at 12.3, 13.2, 35.15, 2θ°) without any transformation to dehydrated salt at 250 °C. The calcium tartrate tetrahydrate is decomposed at 550 °C to CaO and CO_2 leading to a premature calcination of calcium carbonate.

At room temperature a small amount of unreacted tartaric acid is observed (20.5 2θ°). The transformation of $CaCO_3$ to CaO at 550 °C increases from 3.3 to 14.3% (Table III) by the increase of the tartaric acid/$CaCO_3$ ratio.

Concerning the DSC study, the loss on ignition measurements have been confirmed. A general remark is that while the peak corresponding to the $CaCO_3$ decomposition is slightly shifted to lower temperatures, the start of the reaction has a more intense shifting.

The various calcium-organic acid salts are dissociated at almost 400 °C and then are combusted, presenting a strong exothermic peak.

The above mentioned phenomenon causes a premature presence of CaO and assists to the decomposition of the remained $CaCO_3$.

The ΔH values showed on the Table V indicate that an energy reduction is obtained durting the $CaCO_3$ decomposition, not neccesarily proportional to the acid/$CaCO_3$ ratio.
As the above ratio increases, the analogy between it and ΔH decrease, does not exist.

Conclusions

Tartaric and acetic acids when are mixed with $CaCO_3$ lower the calcination temperature of calcium carbonate up to 50 °C. The calcium tartrate and acetate salts have been formed, are decomposed to calcium oxide at a lower temperature than 550 °C.

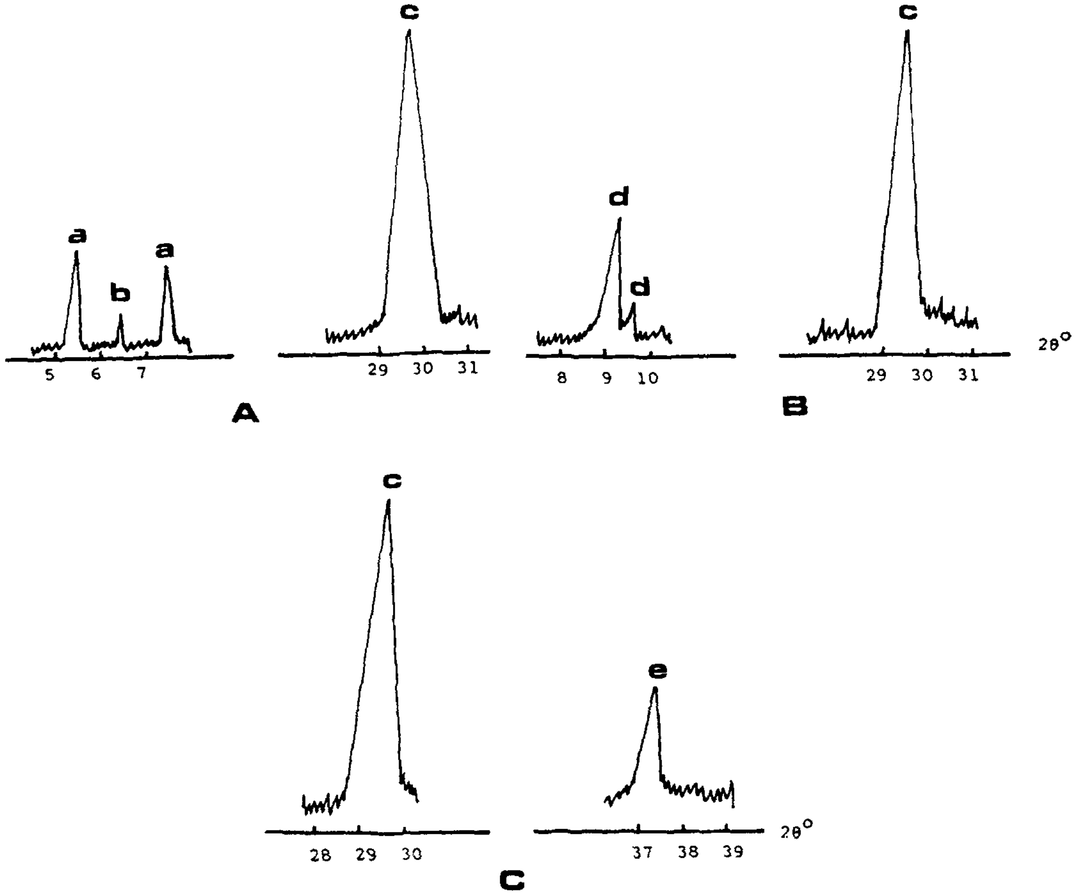

FIG. 1

XRD patterns concerning CaCO$_3$ /20% acetic acid mixtures heated at various temperatures
A : Room temperature B : 250 °C C : 550 °C
a : $(CH_3COO)_2Ca \cdot 0.5H_2O$ b : $3(CH_3COO)_2Ca \cdot 2CH_3COOH$
c : $CaCO_3$ d : $\beta(CH_3COO)_2Ca$ e : CaO

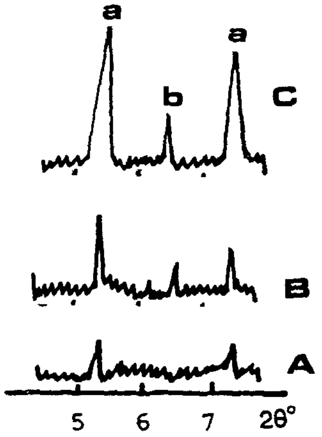

FIG. 2

XRD patterns of CaCO$_3$/acetic acid mixtures (R.T)
A : 50% B : acetic acid
C : 20% acetic acid
a : $(CH_3COO)_2Ca \cdot 0.5H_2O$
b : $3(CH_3COO)_2Ca \cdot 2CH_3COOH$

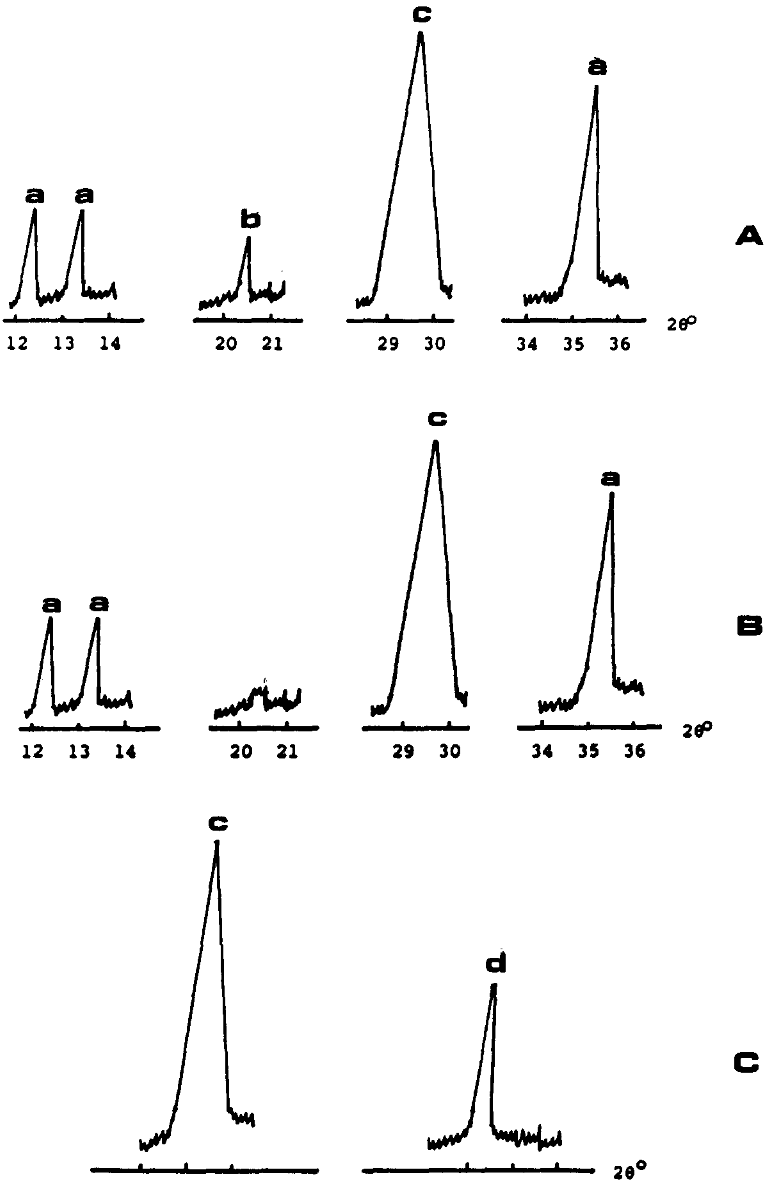

FIG. 3

XRD patterns of $CaCO_3$ /20% tartaric acid mixtures heated at various temperatures A : Room temperature B : 250 °C C : 550 °C
a : $CaC_4H_4O_6 \cdot 4H_2O$ b : $C_4H_6O_6$ c : $CaCO_3$ d : CaO

The dissociation constant (K_a) of the organic acids is one of the factors that define and explain their effect on the decomposition of $CaCO_3$.

As it is resulted from the thermograms during the DSC study of the mixtures with acetic and tartaric acid, the decomposition profile is lower, as temperature concerns, in comparison to that of pure calcium carbonate.

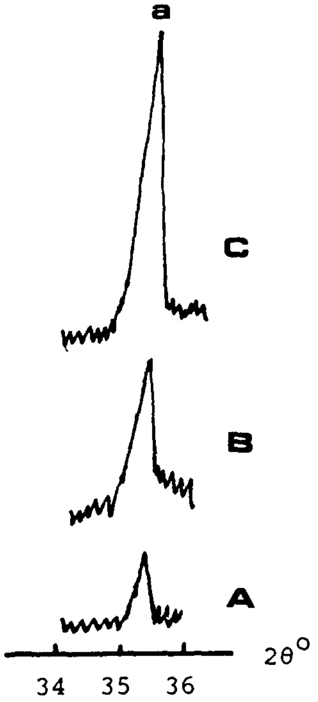

FIG. 4

XRD patterns of $CaCO_3$ /tartaric acid mixtures (R.T)
A : 5% tartaric acid, B : 10% tartaric acid
C : 20% tartaric acid
a : $CaC_4H_4O_6 \cdot 4H_2O$

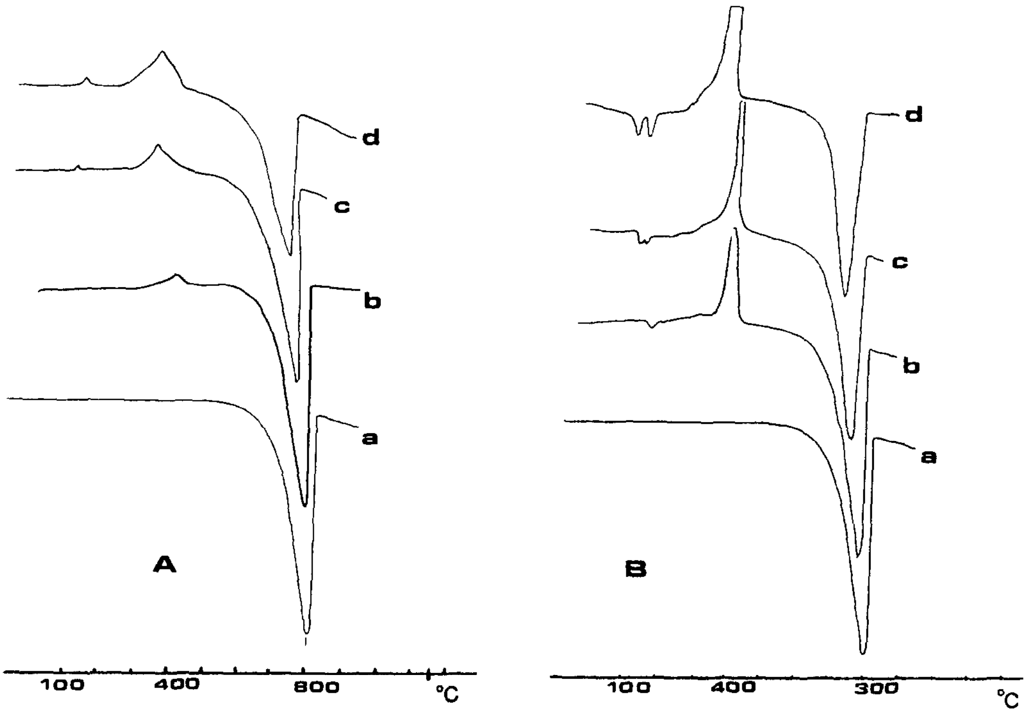

FIG. 5
DSC diagrams concerning A : mixtures of $CaCO_3$ with acetic acid B : mixtures of $CaCO_3$ with tartaric acid
a : pure $CaCO_3$ 5% acid b : 10% acid c : 20% acid

In addition, the relative required energy for the $CaCO_3$ decomposition decreases, not always proportionaly to the acid/$CaCO_3$ ratio increase. The premature calcination of $CaCO_3$ can be explained by the phenomenon of the complete decomposition of the calcium salts formed during the $CaCO_3$-acid reaction.

The heat evolution during the combustion of the organic salts assists to the $CaCO_3$ decomposition process.

The compounds produced during the decomposition of the resulted organic salts have not any effect upon the quality of the final product. Therefore the use of the examined acids during the thermal decomposition of $CaCO_3$ could be consederated as absolutely safe.

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