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STUDIES ON THE THERMAL DECOMPOSITION OF CALCIUM CARBONATE IN THE PRESENCE OF ALKALI SALTS (Na_2CO_3, K_2CO_3 AND NaCl)

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Mixtures of $CaCO_3$ and varying amounts of Na_2CO_3, K_2CO_3 and NaCl were subjected separately to thermal analysis. DTG, DTA, TG analyses indicate that the presence of alkali salts in $CaCO_3$ influences its decomposition behaviour. A minimum DTA peak temperature of $CaCO_3$ decomposition is noticed at low concentrations of alkali salts (K_2CO_3 and Na_2CO_3); an increase in concentration increases the DTA peak temperature. However, in the case of NaCl no appreciable lowering of the DTA peak temperature of $CaCO_3$ decomposition is observed. Similarly, the minimum temperature at which decomposition completes is found to correspond to the concentration of 1 per cent salt (K_2CO_3 and Na_2CO_3) in $CaCO_3$.

Lime is manufactured by the decomposition of limestone at about 1000°. Although the decomposition of $CaCO_3$ to CaO and CO_2 seems to be simple, complications arise due to the presence of other materials. Various lime manufacturers throughout the world examined the effect of alkali salts on limestone decomposition. Some procedures claimed improved lime quality and better fuel economy [1]. Thus, though alkali salts usually occur in natural calcium carbonate in very low percentages, it is interesting to study the decomposition behaviour of calcium carbonate in the presence of alkali salts like Na_2CO_3, K_2CO_3 and NaCl.

Earlier work [2–4] carried out on this aspect indicated possible improvements in the calcination of limestone. In the present investigation an attempt has been made to study in detail the effect of alkali salts on the decomposition of calcium carbonate with the help of a thermal analysis apparatus.

Experimental procedure

The instrument used for this study is Derivatograph, manufactured by Hungarian Optical Works (Budapest). This records simultaneously the change in weight (TG), the rate of change in weight (DTG), the differential enthalpy change (DTA) of the test specimens together with the temperature (T) of either the test sample or the reference material.

The chemicals used in this investigation were all of analytical grade. It would be difficult to analyze the results if the chemicals were of low degree of purity. The chemicals were dried for 2 hours at 100°, ground and sieved through 200 mesh BSS sieve. A number of samples were prepared by thoroughly mixing powdered $CaCO_3$ with suitable proportions of alkali salts in such a way that in each case the quantity of $CaCO_3$ was taken constant at 800 mg. Each of the samples so prepared was transferred quantitatively to the platinum crucible and was thermally analyzed under air atmosphere at a heating rate of 8° per min. Al_2O_3 previously burnt at 1500° was taken as reference material. In every analysis, the temperature was recorded in the reference material. All the operations were performed under identical experimental conditions as far as practicable.

From the thermal curves the following data were computed:

1. DTA peak temperature (from DTA and T curves).
2. Starting and finishing temperature of decomposition and also decomposition range (from DTG curve and T curve).
3. Quantity of $CaCO_3$ decomposed at DTA peak temperature (from TG, DTA and T curves).
4. Shape index of the decomposition curves (from DTA curves).

Results and discussion

The endothermic peaks observed at about 120° in some of the curves are due to the removal of adsorbed moisture from the samples. This endothermic change has no bearing on the decomposition of $CaCO_3$.

The data computed from the thermal curves of $CaCO_3$ at the decomposition peaks in the presence of varying amounts of Na_2CO_3, K_2CO_3 and NaCl are presented in Tables 1, 2 and 3, respectively.

The results indicate that the effect of Na_2CO_3 and K_2CO_3 on the DTA peak temperature (which indicates the minimum temperature at which the reaction rate

Table 1

Differential thermal data of $CaCO_3$ and its mixtures with Na_2CO_3

Sample	DTA peak temperature, °C	Temperature of decomposition, °C			Quantity decomposed up to peak temperature, %	Shape index
		Starting	Completion	Range of decomposition		
$CaCO_3$	950	700	975	275	87.0	0.111
$CaCO_3 +$ 1% Na_2CO_3	930	695	950	255	88.8	0.115
$CaCO_3 +$ 2% Na_2CO_3	930	700	955	255	87.4	0.167
$CaCO_3 +$ 5% Na_2CO_3	945	695	975	275	85.9	0.200
$CaCO_3 +$ 10% Na_2CO_3	945	680	985	305	83.3	0.269
$CaCO_3 +$ 20% Na_2CO_3	940	675	1010	335	73.1	0.380

Table 2

Differential thermal data of $CaCO_3$ and its mixtures with K_2CO_3

Sample	DTA peak temperature, °C	Temperature of decomposition, °C			Quantity decomposed up to peak temperature, %	Shape index
		Starting	Completion	Range of decomposition		
$CaCO_3$	950	700	975	275	87.0	0.111
$CaCO_3$ + 1% K_2CO_3	915	700	930	230	88.5	0.125
$CaCO_3$ + 2% K_2CO_3	925	700	945	245	86.0	0.128
$CaCO_3$ + 5% K_2CO_3	938	700	965	265	85.9	0.135
$CaCO_3$ + 10% K_2CO_3	938	710	985	275	84.4	0.160
$CaCO_3$ + 18% K_2CO_3	938	710	990	280	80.0	0.260

Table 3

Differential thermal data of $CaCO_3$ and its mixtures with NaCl

Sample	DTA peak temperature, °C	Temperature of decomposition, °C			Quantity decomposed up to peak temperature, %	Shape index
		Starting	Completion	Range of decomposition		
$CaCO_3$	950	700	975	275	87	0.111
$CaCO_3$ + 1% NaCl	945	700	975	275	90	0.117
$CaCO_3$ + 3% NaCl	945	690	970	280	89	0.136
$CaCO_3$ + 5% NaCl	940	700	970	270	86	0.158
$CaCO_3$ + 10% NaCl	945	700	975	275	85	0.175

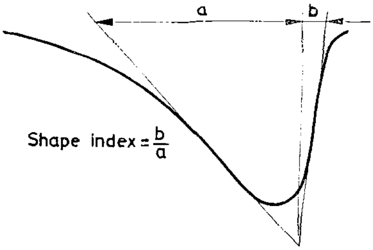

Fig. 1. Shape index of decomposition peak

is maximum) is maximum when these alkali salts are present in low concentrations. The effect is more prominent in the case of the $CaCO_3-K_2CO_3$ mixture, where the peak temperature decreases by as much as 35° (Table 2). The addition of NaCl to $CaCO_3$ has practically no effect on the DTA peak temperature (Table 3).

From the data of Tables 1 and 2 it is apparent that in all cases the temperature at which the decomposition starts is more or less the same, while the completion temperature, similar to the DTA peak temperature, has a minimum at 1 per cent concentration of the alkali salt and increases with further increase of the concentration of the alkali salt. As a result the decomposition range increases with increase in the alkali salt content or in other words more time is required for complete decomposition of $CaCO_3$. Variations of the quantity of NaCl seem to

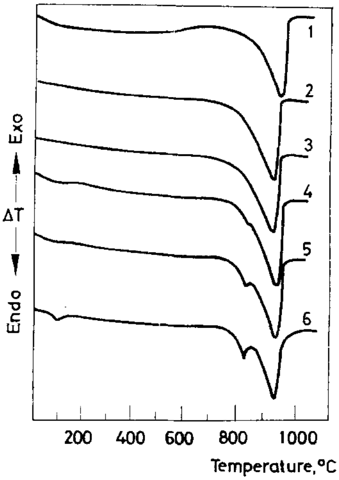

Fig. 2. DTA curve of (1) $CaCO_3$, (2) $CaCO_3 + 1\% \; Na_2CO_3$, (3) $CaCO_3 + 2\% \; Na_2CO_3$, (4) $CaCO_3 + 5\% \; Na_2CO_3$, (5) $CaCO_3 + 10\% \; Na_2CO_3$, (6) $CaCO_3 + 20\% \; Na_2CO_3$

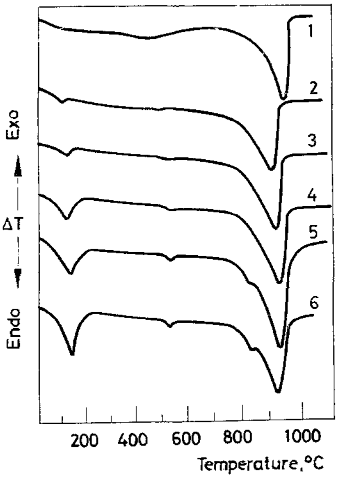

Fig. 3. DTA curves of (1) $CaCO_3$, (2) $CaCO_3 + 1\% \; K_2CO_3$, (3) $CaCO_3 + 2\% \; K_2CO_3$, (4) $CaCO_3 + 5\% \; K_2CO_3$, (5) $CaCO_3 + 10\% \; K_2CO_3$, (6) $CaCO_3 + 18\% \; K_2CO_3$

have no influence on the temperature of beginning and completion of decomposition which remains constant throughout (Table 3).

The influence of alkali salts on the quantity decomposed up to the peak temperature has also been studied. When alkali salts are present to the extent of 1 per cent the quantity of $CaCO_3$ decomposed up to the peak temperature is maximum, but with higher alkali salt content this value is reduced (Tables 1, 2 and 3). Thus it is clear from the data that more heat is required to complete the decomposition of $CaCO_3$ after attaining the peak temperature when the alkali salt concentration is higher than 1 per cent.

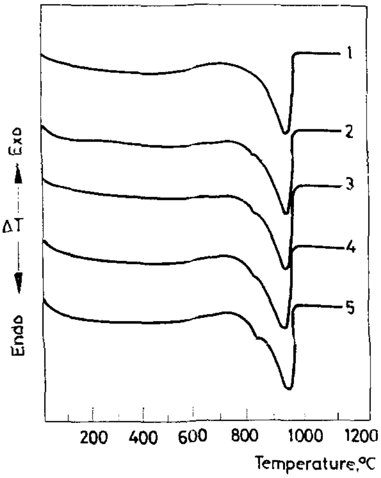

Fig. 4. DTA curves of (1) $CaCO_3$, (2) $CaCO_3$ + 1% NaCl, (3) $CaCO_3$ + 3% NaCl, (4) $CaCO_3$ + 5% NaCl, (5) $CaCO_3$ + 10% NaCl

The shape index of the decomposition peak (calculated from an endothermic peak as shown in Fig. 1) is a measure of peak symmetry. According to Kissinger [5], the order of reaction increases with increasing shape index. As in this investigation the value of shape index increases with increasing alkali salt content (Tables 1, 2 and 3), it can be anticipated that the order of reaction also increases with the rise of alkali salt content.

DTA curves in Figs 2, 3 and 4 show the effect of alkali salts on the nature of the DTA decomposition peaks of $CaCO_3$. In all decomposition curves of $CaCO_3$ there is always an inflexion in the neighbourhood of 800°. These inflexions increase with increasing content of alkali salts. This shows that these inflexions can be attributed to the presence of alkali salts in $CaCO_3$ and to the appearance of a liquid phase.

For the $CaCO_3-K_2CO_3$ system an additional, endothermic peak at 530° is observed (Fig. 3). To show the comparable effect, DTG and DTA curves of $CaCO_3$ + 4% K_2CO_3 and $CaCO_3$ + 4% Na_2CO_3 recorded at higher sensitivity are shown in Fig. 5. (sensitivity for DTG is increased from 1/20 to 1/10 and for DTA, from 1/20 to 1/2 of that of maximum) From this it is evident that there is no corresponding peak on the DTG curves in this region (530°). The areas of these endotherms increase with increasing K_2CO_3 content (Fig. 3). X-ray investigations carried out on pure $CaCO_3$ confirmed the presence of only calcite crystals and not aragonite. Therefore, this endothermic reaction in the $CaCO_3$ sample with KC_2O_3 at 530° is not due to the transformation of aragonite to calcite. The DTA of pure K_2CO_3 compound confirms that this endothermic effect is not due to changes in the K_2CO_3 structure. The X-ray data of the samples heated just up to the temperature where the peak is completed (nearly 550°) indicate that there is practically no change in the calcite system except some very weak lines comparable to those characteristic of $K_2Ca(CO_3)_2$, a solid solution product of K_2CO_3 and $CaCO_3$. The possible formation of $K_2Ca(CO_3)_2$ at such a low temperature, however, should be studied further.

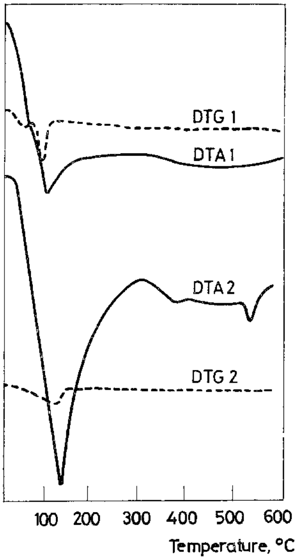

Fig. 5. DTG and DTA curves of $CaCO_3$ admixed with (1) 4% Na_2CO_3, (2) 4% K_2CO_3

Conclusions

The blending of alkali salts (Na_2CO_3, K_2CO_3 and NaCl) with calcium carbonate to the extent of 1 per cent brings about the decomposition of the latter at comparatively lower temperature. The quantity of $CaCO_3$ decomposed at this low temperature is also increased. Thus the blending results in a reduced fuel consumption and improves the economics of the lime production from limestone.

References

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Résumé — On a examiné des mélanges de $CaCO_3$ avec différentes quantités de Na_2CO_3, K_2CO_3 et NaCl par analyse thermique (ATD, TG, TGD). La présence de sels alcalins dans le $CaCO_3$ influence son comportement thermique. La température au sommet du pic d'ATD dépend de la concentration en carbonate alcalin: plus celle-ci est faible, plus la température au sommet du pic basse et, inversement, plus la concentration en carbonate augmente plus la température au sommet du pic est élevée. Cet effet ne s'observe pas avec le NaCl. L'abaissement de la température au sommet du pic se produit pour les concentrations de l'ordre de 1 pour cent en carbonate alcalin dans le $CaCO_3$.

Zusammenfassung — Gemische von $CaCO_3$ mit verschiedenen Mengen von Na_2CO_3, K_2CO_3 und NaCl wurden thermoanalytischen (DTA, TG, DTG) Prüfungen unterworfen. Man fand, daß die Anwesenheit von Alkalisalzen die thermische Zersetzung von Kalziumkarbonat beeinflußt. Je geringer die Alkalisalzkonzentration (K_2CO_3 und Na_2CO_3) war, um so niedriger lag die DTA Spitzentemperatur. Mit zunehmender Konzentration stiegen die entsprechenden Temperaturen. Mit NaCl ließ sich keine Zersetzungstemperaturerniedrigung des $CaCO_3$ beobachten. Ebenfalls ein Minimum der Beendigungstemperatur der Zersetzung des $CaCO_3$ trat bei 1% K_2CO_3 und Na_2CO_3 auf.

Резюме. — Термоаналитическими методами (ДТГ, ДТА, ТГ) исследован термораспад $CaCO_3$ с различными количествами Na_2CO_3, K_2CO_3 и NaCl. Показано, что присутствие щелочных солей оказывает воздействие на термораспад $CaCO_3$. Меньшей концентрации щелочной соли соответствует более низкая температура, пика на кривой ДТА. Соответствующие температуры возрастают с увеличением концентрации. В присутствии NaCl снижения температуры распада $CaCO_3$ не наблюдалось. Установлено, что температура, при которой заканчивается распад, наиболее низка в присутствии 1% K_2CO_3 и Na_2CO_3.