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INFLUENCE OF FOREIGN MATERIALS UPON THE THERMAL DECOMPOSITION OF DOLOMITE, CALCITE AND MAGNESITE PART I. INFLUENCE OF SODIUM CHLORIDE

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ABSTRACT

The influence of sodium chloride on the course of thermal decomposition of calcite, magnesite and dolomite was studied partly under dynamic, and partly under quasi-isothermal heating conditions. Four different types of sample holders were applied in the experiment, i.e., the partial pressure of carbon dioxide was also different in the four cases. It was found that the presence of sodium chloride reduced the decomposition temperature in every case. The extent of this reduction amounted to about 10°C in the case of calcite, 40—80°C in the case of magnesite, and 10—40°C and 10—20°C for the first and second decomposition stages, respectively, of dolomite.

INTRODUCTION

The thermal decomposition of dolomite, calcite and magnesite is perhaps one of the most investigated problems in thermal analysis. Although the mechanism of this thermal decomposition is simple in nature, the literature gives highly contradictory data on the kinetics. The disagreement can probably be attributed to the fact that the course of the decomposition depends, to a considerable extent, on the experimental conditions and the presence of foreign substances. Since the problem is important from both the theoretical and technological points of view, we decided to undertake another investivation of the decomposition of calcium and magnesium carbonates and study the problem from a number of aspects.

The influence of sodium chloride was studied first; this influence has been studied by numerous workers [1—19]. Although the literature data do not give a consistent picture, all authors agree on one fact: that sodium chloride promotes the decomposition of dolomite, calcite and magnesite.

By changing the experimental conditions systematically we hoped to obtain further information on the decomposition. The results of this work are presented here.

EXPERIMENTAL

Materials

The chemical composition of the dolomite and calcite (both from Zabierzów, Poland) and the magnesite (from Ochtina, Czechoslovakia) is given in Table 1.

Chemical analysis, IR measurements and X-ray diffraction indicate that the principal impurity is silica (α-quartz). We must add that for dolomite, calcite and magnesite the X-ray patterns show slight deviations from those given by ASTM cards. This is caused by insertion of ferrous ions into crystalline lattices of these compounds with the formation of (Mg, Fe) $Ca(CO_3)_2$ or (Mg, Fe)CO_3.

The materials under investigation were mixed with 2% NaCl additive in the following way. 20 mg of NaCl dissolved in 2.5 ml H_2O were added to 1 g of the granulated material which was then allowed to soak for several hours. The water was next evaporated off and the material dried. The grain size of the dolomite and calcite was 0.5—0.6 mm and that of magnesite was less than 0.1 mm.

Method

The experiments were carried out using a Q-derivatograph (Hungarian Optical Works, Budapest). This instrument [20,21] made it possible to obtain data employing, on the one hand, the conventional dynamic heating program of 10°C min^{-1} (curves 9—16 in Figs. 1 and 2, curves 1—8 in Fig. 3) and, on the other, the quasi-isothermal heating technique (curves 1—8 of Figs. 1, 2 and 4). The schematic drawings of the curves refer to different sample holders depicted more fully in Fig. 5.

The essential character of the quasi-isothermal heating technique [22,23] is that the heating control system always maintains a very small temperature difference between the sample and the furnace which makes it possible for the decomposition to take place at a very slow (0.5 mg min^{-1}), strictly con-

TABLE 1

Chemical analysis of samples

Composition	Calcite (%)	Magnesite (%)	Dolomite (%)
CaO	51.3	3.1	32.4
MgO	1.9	41.1	20.5
SiO_2	1.5	4.8	4.8
Al_2O_3	1.1	0.7	0.0
Fe_2O_3	0.2	4.7	0.9
SO_3	0.1	0.1	0.1
P_2O_5	0.1	0.1	0.1
Loss on ignition	43.6	45.4	41.2

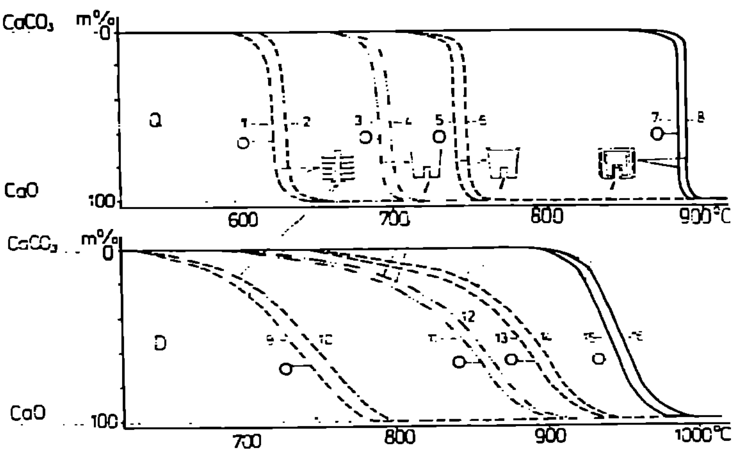

Fig. 1. Calcite. Heating techniques: Q = quasi-isothermal (curves 1—8); D = dynamic (curves 9—16). Sample holders: polyplate (curves 1, 2, 9 and 10); open crucible (curves 3, 4, 11 and 12); covered crucible (curves 5, 6, 13 and 14); labyrinth (curves 7, 8, 15 and 16). Sample: pure calcite (curves 2, 4, 6, 8, 10, 12, 14 and 16); calcite mixed with 2% NaCl, o (curves 1, 3, 5, 7, 9, 11, 13 and 15). Atmosphere: air.

stant rate. As a result of this special kind of heating, the temperature of the sample always varies in a particular way, i.e. according to the state of quasi-equilibrium. The course of the TG curve, recorded as a function of the continuously changing "pseudo-equilibrium" temperature, differs from that of the conventional TG curves and serves as a source of new information.

Every experiment was carried out employing four different sample holders

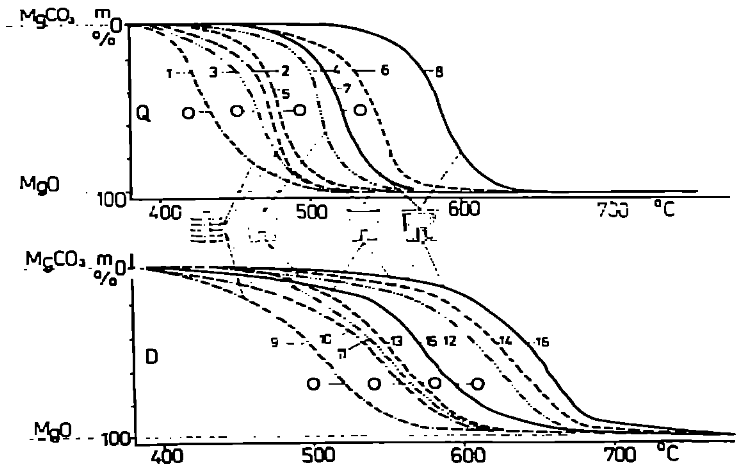

Fig. 2. Magnesite. Heating technique: Q = quasi-isothermal (curves 1—8); D = dynamic (curves 9—16). Sample holders: polyplate (curves 1, 2, 9 and 10); open crucible (curves 3, 4, 11 and 12); covered crucible (curves 5, 6, 13 and 14); labyrinth (curves 7, 8, 15 and 16). Sample: pure magnesite (curves 2, 4, 6, 8, 10, 12, 14 and 16); magnesite mixed with 2% NaCl, o (curves 1, 3, 5, 7, 9, 11, 13 and 15). Atmosphere: air.

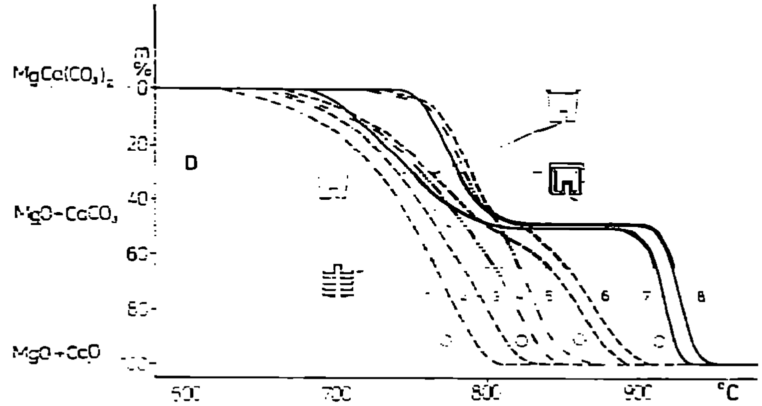

Fig. 3; Dolomite. Heating technique: D = dynamic, 10°C min^{-1} (curves 1—8). Sample holders: polyplate (curves 1 and 2); open crucible (curves 3 and 4); covered crucible (curves 5 and 6); labyrinth (curves 7 and 8). Sample: pure dolomite (curves 2, 4, 6 and 8); dolomite mixed with 2% NaCl, ○ (curves 1, 3, 5 and 7). Atmosphere: air.

(Fig. 5) in order to ascertain how the course of the decomposition changes if the partial pressure of CO_2 is altered in addition to other variables (presence or absence of additives and heating program). The partial pressure of CO_2 in contact with the solid sample depends characteristically not only on the heating program but also on the shape of the sample holder, i.e. whether the sample holder is of the labyrinth type [22,23], a covered or uncovered crucible, or polyplate type [24]. In the case of the quasi-isothermal heating technique it was possible to determine the approximate extent of these changes.

From curves 2, 4, 6 and 8 in Fig. 1, it can be seen that a relationship

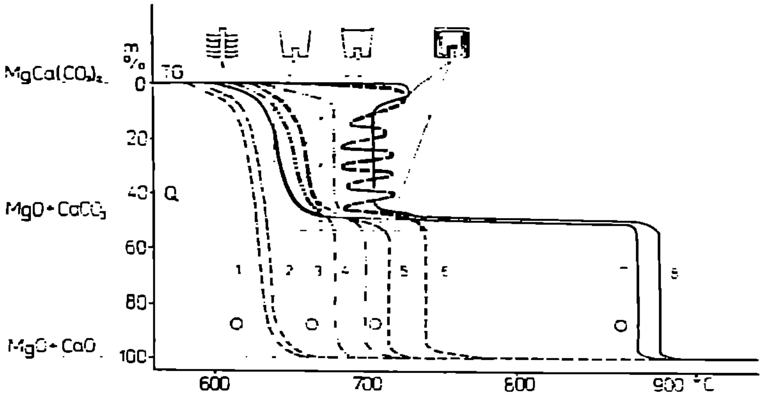

Fig. 4. Dolomite. Heating technique: Q = quasi-isothermal (curves 1—8). Sample holders: polyplate (curves 1 and 2); open crucible (curves 3 and 4); covered crucible (curves 5 and 6); labyrinth (curves 7 and 8). Sample: pure dolomite (curves 2, 4, 6 and 8); dolomite mixed with 2% NaCl, o (curves 1, 3, 5 and 7). Atmosphere: air.

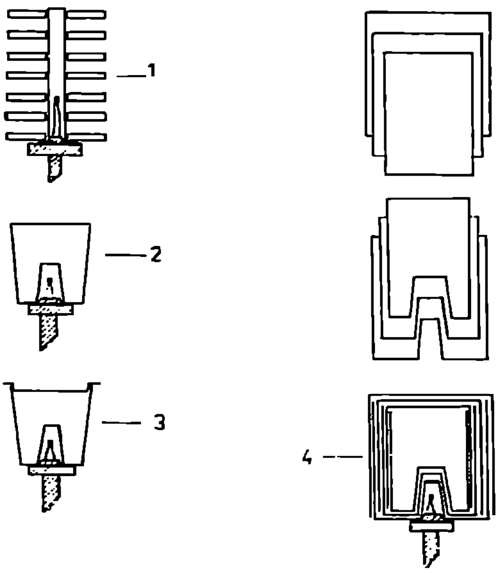

Fig. 5. Sample holders: 1, polyplate; 2, open crucible; 3, covered crucible; 4, labyrinth.

exists between the decomposition temperature and the decomposition pressure of $CaCO_3$. Under quasi-equilibrium conditions a definite value of the CO_2 pressure can be ascribed to each temperature (Table 2). Because the temperature did not change during the course of a single experiment (curves 2, 4, 6 and 8, Fig. 1) it can be stated that the partial pressure of CO_2 also remained constant. Hence, the process can be considered as having taken place not only under quasi-isothermal but also under quasi-isobaric conditions. In contrast to this situation, it is known that in the case of dynamic heating programs the partial pressure of CO_2 changes continuously, i.e., increasing during each transformation. The range within which the partial pressure of CO_2 can change may also be estimated from the temperature interval over which the process actually took place [24].

The sample weight was always constant at about 180 mg. The experiments were carried out in the presence of air.

TABLE 2

Apparent decomposition temperatures of $CaCO_3$ obtained using different sample holders [24]

Type of sample holder	Apparent temperature (°C)	CO_2 pressure (Torr)
Labyrinth	890	760
Covered crucible	750	100
Open crucible	700	20
Polyplate	630	5

RESULTS AND DISCUSSION

The TG curves in Fig. 1 represent the decomposition of pure calcite, and also the decomposition of calcite samples mixed with 2% NaCl. On the basis of a comparison between the two sets of curves the following conclusions can be drawn. In every case sodium promotes the decomposition of calcite, since the decomposition temperature of the additive-containing samples is lower than that of pure calcite under all experimental conditions. In all cases there is a parallel shift of about 10°C between the paired curves; thus the shift is not influenced either by changes in the partial pressure of CO_2 or the type of heating employed. It should be noted that the shift is the same at all stages of the reaction; sodium chloride promotes the decomposition to the same extent at all points.

It is noteworthy that with the labyrinth crucible and the quasi-isothermal heating technique (curve 8, Fig. 1) the decomposition of the pure $CaCO_3$ took place at 890°C, i.e., at nearly the theoretical decomposition temperature (895°C), while under dynamic heating conditions the decomposition in the same labyrinth crucible (curve 16, Fig. 1) occurred between 890 and 980°C, i.e., extending to temperatures considerably above the theoretical temperature. In both cases the 1 atm partial pressure of CO_2 remained constant throughout the transformation. Hence, the decomposition temperature of $CaCO_3$ could not really have risen above 895°C, and the observed temperature overshoot (curve 16, Fig. 1) can only be attributed to slow heat transport, the existence of a temperature drop within the sample [22].

We can now also state, that decomposition of $CaCO_3$ is a zero-order process. This follows from the fact that with the quasi-isothermal heating technique the decomposition temperature was stabilized during the course of every experiment (curves 1—8, Fig. 1); particularly when the labyrinth crucible was used (curves 7 and 8, Fig. 1), the temperature did not change by more than ±2°C. It was not necessary for the heating control system to bring about an increase in sample temperature as the transformation progressed with the appropriate decrease in the $CaCO_3$ concentration in order to ensure that the reaction should take place with a constant rate selected in advance. In our case, the rate of the process was controlled by the constant rate of heat transport, i.e., by a physical process, from which it follows that the process took place according to zero order.

Examination of curves 1—8 in Fig. 2 and the use of the arguments presented above lead to the conclusion that the decomposition of magnesite is not of zero order. From Fig. 2 it can be seen that the addition of 2% NaCl influences the decomposition of magnesite in the same way as that of calcite, the only difference being that in the case of magnesite the effect is significantly greater.

The decomposition curves of dolomite both with (curves 1, 3, 5, and 7), and without (curves 2, 4, 6 and 8) the addition 2% NaCl are shown in Figs. 3 and 4, respectively. They were obtained using the four different sample holders and the two heating techniques. It can be seen that the appearance of the curves is significantly different from that in the previous figures. Some of the differences were to be expected, others clearly call for an explanation.

Leaving for the moment the question of the more unusual curve shapes, it is clear that the decomposition of dolomite takes place in two steps, viz.

$$MgCa(CO_3)_2 \rightleftharpoons MgO + CaCO_3 + CO_2 \qquad (I)$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (II)$$

which, depending on the experimental conditions, may overlap to a greater or lesser extent.

The curves of Figs. 3 and 4 demonstrate, according to expectations, that sodium chloride promotes the decomposition of dolomite. During the first stage of the decomposition this effect is greater than that in the second stage. During the first stage of the decomposition the magnitude of the effect increases at higher partial pressures of CO_2. Thus, with the labyrinth crucible, the difference between the decomposition temperatures of the pure and the NaCl-containing samples (curves 7 and 8) was 70° C, while in the case of the polyplate sample holder (curves 1 and 2) this difference did not amount even to 20° C.

Over the second stage of the process sodium chloride promoted the decomposition of $CaCO_3$ practically to the same extent, independently of the experimental conditions (Figs. 3 and 4).

The two stages of the decomposition of dolomite were completely separated when the labyrinth crucible was used, i.e. in an atmosphere of pure CO_2 (curves 7 and 8, Figs. 3 and 4). With the polyplate sample holder, however, i.e. at $p_{CO_2} \cong 5$ Torr (curves 1 and 2, Figs. 3 and 4), the two stages totally overlapped. In the intermediate cases the overlapping was also intermediate. This phenomenon can be explained by the fact that the decomposition temperature of $CaCO_3$ depends much more strongly on the CO_2 pressure than that of the first decomposition step of dolomite.

A peculiar effect is observed in curve 8 of Fig. 4 over the first 10% weight change. This curve indicated that the decomposition started at 730°C, whereupon the sample temperature immediately began to decrease down to 710° C. Thereafter, the temperature of the sample spontaneously stabilized and did not change further until the end of the first decomposition stage. This overheating of the sample and the subsequent spontaneous temperature decrease are connected with nucleus formation. In all probability this particular set of conditions was not favourable to nucleation. It could start only at higher temperatures, but later, when there were already sufficient nuclei present, the nucleus growth could take place at a rate corresponding to the constant rate of weight loss of the sample which had been selected in advance. It is also understandable that with the rise in the number of nuclei, the temperature of the sample decreased until it reached the value corresponding to the state of quasi-equilibrium.

In one case, the tracing corresponding to the first decomposition stage (curve 6, Fig. 4) presents a most unusual appearance. This tracing was fully reproducible and was certainly not a result of any malfunction of the instrument. Under the conditions used in this experiment the sample temperature oscillated between 690 and 720° C.

The sequence of curves 7, 3 and 5 of Fig. 4 over the first stage of the decomposition was also unexpected. The dolomite decomposed at a lower temperature in the labyrinth crucible (≈760 Torr) than in the covered (≈100 Torr) or even uncovered crucible (≈20 Torr). The same sequence of curves was observed under dynamic heating conditions (curves 7, 3 and 5, and 8, 4 and 6, Fig. 3). This strange reversal of curve order had been observed earlier [25] but we failed to find an explanation.

In Part II of the present series [26], the problem of both the curve order and the oscillation will be answered.

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