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INFLUENCE OF FOREIGN MATERIALS UPON THE THERMAL DECOMPOSITION OF DOLOMITE, CALCITE AND MAGNESITE. PART III. THE EFFECT OF THE THERMAL DISSOCIATION AND SULPHATION CONDITIONS ON THE CAPTURE OF SULPHUR DIOXIDE

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ABSTRACT

Thermogravimetric methods have been used at atmospheric pressure to obtain data on the sulphation of calcite, dolomite and magnesite under a variety of different experimental conditions. The results obtained indicate that the sulphation process may be influenced by a large number of factors. The data also suggest that in the case of calcite and dolomite the formation of sulphates may follow a more complicated reaction path then hitherto supposed.

INTRODUCTION

The influence of foreign substances upon the thermal decomposition of dolomite, calcite and magnesite has been considered in Parts I and II [1,2] of the present series because a possibility of capturing sulphur dioxide at high temperatures is offered by a reaction with the solid calcination product obtained from these carbonates.

The desulphurization of hot combustion gases is considered in connection with air pollution by sulphur dioxide. The establishment of stone selection criteria for choosing sorbents suitable for use as desulphurizing agents in fluidized beds is especially important for optimizing the fluidized bed combustion of high-sulphur coal [3].

Thermogravimetric data show that laboratory tests can be used to simulate the absorption of sulphur dioxide under practical conditions. This process is typical of solid-state—gas reactions. The environment can influence the thermal decomposition of the raw sorbents by causing a change in the

TABLE 1

Experimental conditions for the calcination and sulphation of calcite, magnesite and dolomite

D = dynamic heating; Q = quasi-isothermal heating; M = multiplate sample holder; L = labyrinth crucible; G = granular; P = powder

Fig.	Calcination							Sulphation	
	Thermogram	Curves	Heating	Max. temp. (°C)	Sample holder	Grain size	Additive	Temp. (°C)	SO_2 concn. (vol.%)
1		1	D	900	M	G		20 → 1000	2
		2	D	900	M	G		20 → 1000	2
		3	D	900	M	G		20 → 1000	2
2—4	a	1	D	900	M	G		830	6
		2	D	900	M	G		830	4
		3	D	900	M	G		830	2
		4	D	900	M	G		830	1
	b	1	D	900	M	G		1000	2
		2	D	900	M	G		830	2
		3	D	900	M	G		600	2
		4	D	900	M	G		400	2
	c	1	D	900	M	P		830	2
		2	D	900	M	P	NaCl	830	2
		3	D	900	M	G		830	2
		4	D	900	M	G	NaCl	830	2
	d	1	D	900	M	G		830	2
		2	D	900	M	G	NaCl	830	2
		3	D	1500	M	G		830	2
		4	D	1500	M	G	NaCl	830	2
	e	1	D	900	L	G		830	2
		2	Q	900	L	G		830	2
		3	D	900	L	G	NaCl	830	2
		4	Q	900	L	G	NaCl	830	2
	f	1	D	900	M	G		830	2
		2	D	900	L	G		830	2
		3	D	900	M	G	NaCl	830	2
		4	D	900	L	G	NaCl	830	2

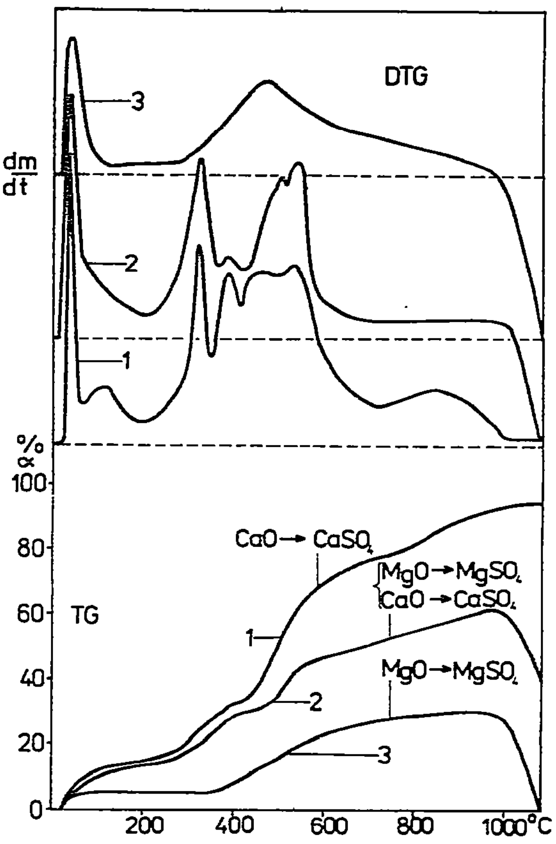

Fig. 1. The process of SO_2 capturing by CaO, MgO and their mixtures with increasing temperature.

chemical kinetics and/or by causing a change in the physical nature of the solid product [4—8].

Our experimental program consisted of laboratory studies (using thermoanalytical methods) of calcination and sulphation of calcite, magnesite and dolomite at atmospheric pressure. The aim of our investigations was to establish to what extent the absorption of sulphur dioxide is influenced by first, the conditions of the decomposition of the alkaline earth carbonates (heating rate, grain size, maximum temperature, shape of sample holder and concentration of carbon dioxide, presence of 2% sodium chloride additive [1,2]) and second, the conditions of the sulphation (temperature, concentration of sulphur dioxide). Table 1 gives information about the conditions of calcination and sulphation in the case of the curves presented in Figs. 1—4.

EXPERIMENTAL

Method

The essence of the technique used was that the given carbonate sample was decomposed in a Q-derivatograph (Hungarian Optical Works, Budapest)

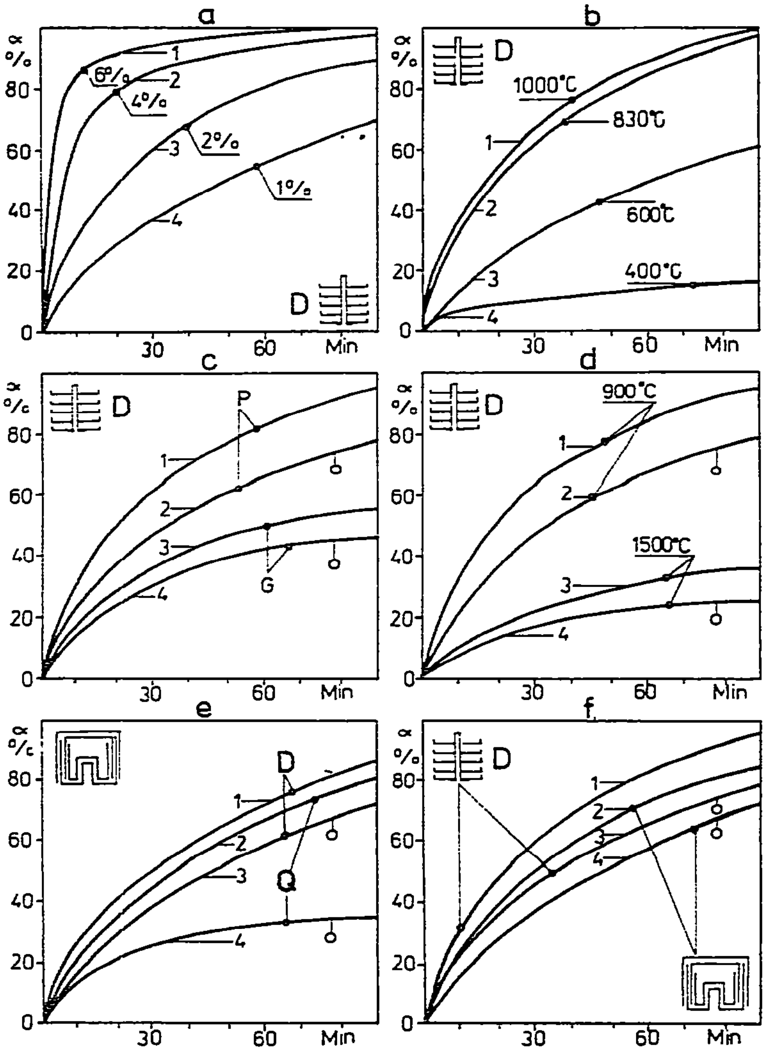

Fig. 2. The process of SO_2 capturing by CaO at constant temperature with changing concentration of SO_2 (a), temperature of sulphation (b), grain size (c), decomposition temperature (d), rate of decomposition (e), and concentration of CO_2 (f). D, Dynamic heating; Q, quasi-isothermal heating; G, granular; P, powder; o, NaCl additive.

under defined experimental conditions and at a definite temperature (Table 1). The temperature of the calcination product was then lowered or raised and kept constant, and an atmosphere of a mixture of SO_2 and air was established — the weight of the sample was followed as a function of time (Figs. 2—4).

The same calcite, dolomite and magnesite were used as in Parts I and II of this series [1,2]. All samples were either powdered (P) or in a granular form (G) (grain sizes were approximately 0.15 mm and ca. 0.5 mm, respectively).

The decomposition occurred partly in the labyrinth crucible (L) and partly on the multiplate sample holder (M), but the sulphation was carried out with samples spread very thinly on the multiplate sample holder. The sample size was about 180 mg.

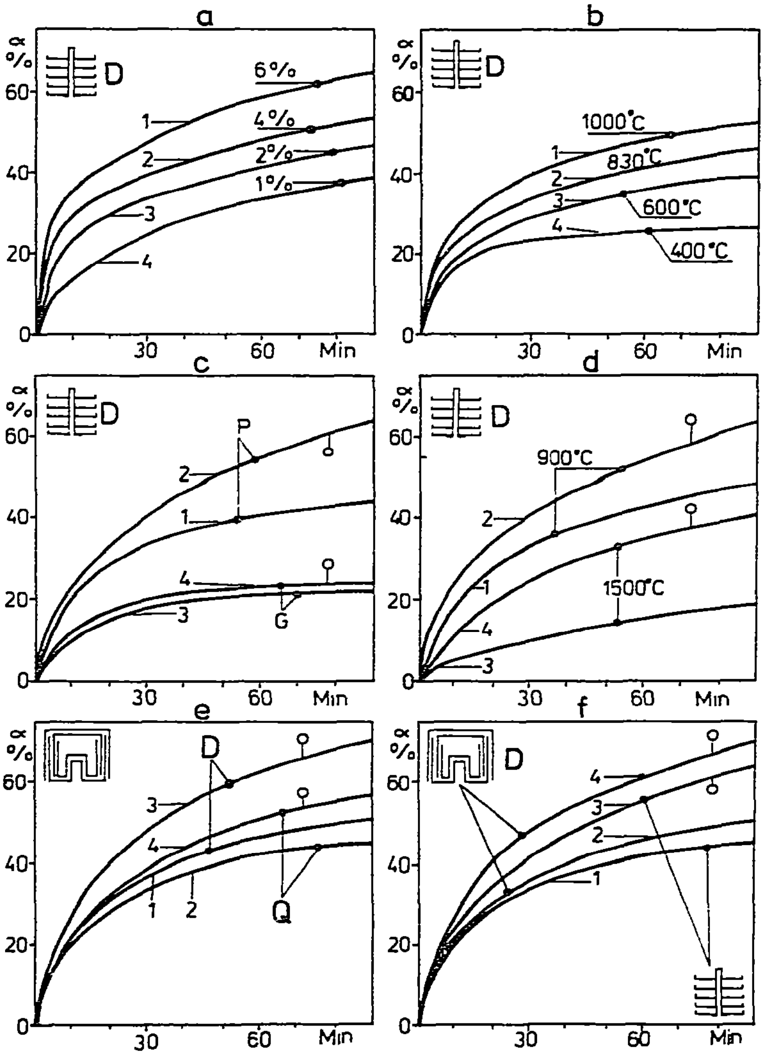

Fig. 3. The process of SO_2 capturing by CaO + MgO at constant temperature with changing concentration of SO_2 (a), temperature of sulphation (b), grain size (c), decomposition temperature (d), rate of decomposition (e), and concentration of CO_2 (f). D, Dynamic heating; Q, quasi-isothermal heating; G, granular; P, powder; ○, NaCl additive.

In the case of the dynamic heating program (D) the heating rate was 10°C min^{-1}. With the quasi-isothermal heating [9], the rate of transformation was 0.5 mg min^{-1}.

The required gas atmosphere was obtained with the help of the gas collector described in Part II [2] and shown in Fig. 1 of ref. 2. This adaptor is normally used for thermo-gas-titrimetric work [10].

The mixture of SO_2 and air (about 20 l) was prepared in advance and introduced continuously into the corundum "bell cover" (7) of the device. Here, however, the gas mixture was introduced through tube (18), and not as shown in Fig. 1 of ref. 2 through tube (6), at point (19). The gas flow rate was ca. 200 ml min^{-1} and the exhaust rate, via tube (16), 800 ml min^{-1}. Tube

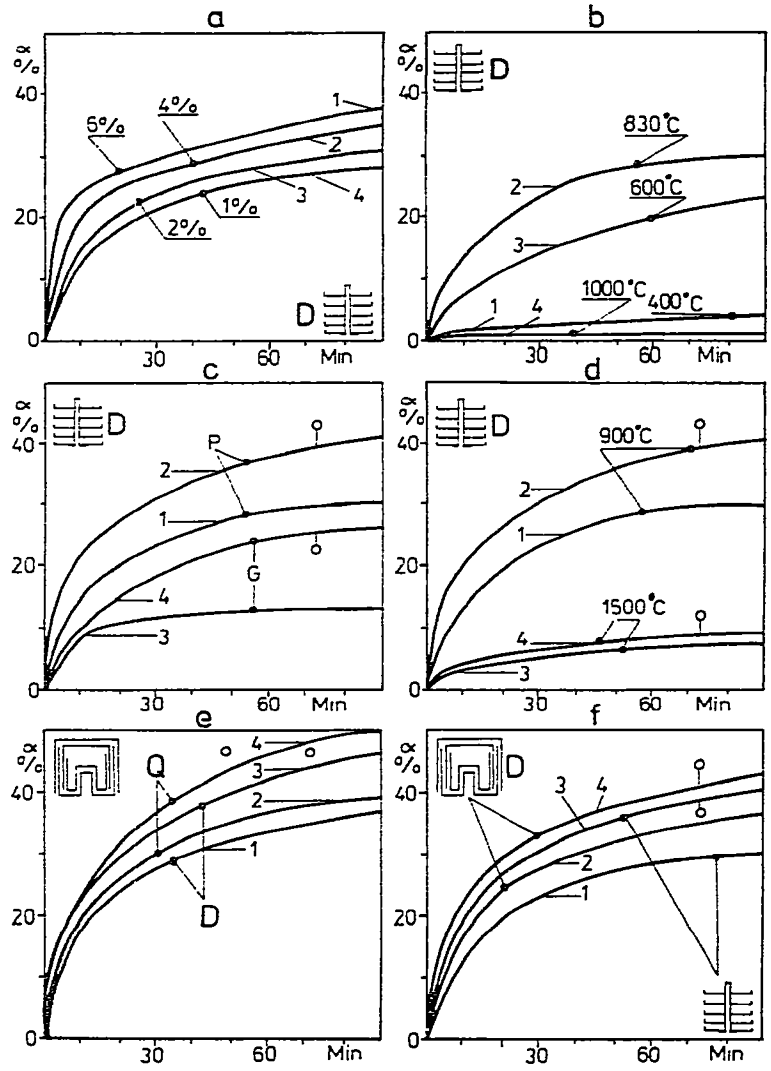

Fig. 4. The process of SO_2 capturing by MgO at constant temperature with changing concentration of SO_2 (a), temperature of sulphation (b), grain size (c), decomposition temperature (d), rate of decomposition (e), and concentration of CO_2 (f). D, Dynamic heating; Q, quasi-isothermal heating; G, granular; P, powder; o, NaCl additive.

(6) remained closed. The SO_2—air mixture was saturated with water vapour at room temperature.

The sulphation temperature was 830°C except when otherwise stated. This lies in the optimum range for desulphurization under fluidized bed coal combustion conditions [11].

The effect of temperature on the capture of SO_2 was also examined. The procedure was the same as above except that the oxides were cooled to room temperature and after the introduction of the SO_2—air mixture the temperature of the sample was gradually increased at a rate of 10°C min^{-1}. The results are shown in Fig. 1.

The results (Figs. 1—4) are expressed in terms of the percentage of the maximum theoretical degree of conversion (α). The maximum theoretical conversion is estimated on the basis of the weight loss observed in the course of calcination assuming that the reaction can be represented as

$$CaO + SO_2 + 0.5\ O_2 = CaSO_4 \quad (1)$$

$$MgO + SO_2 + 0.5\ O_2 = MgSO_4 \quad (2)$$

The total amount of SO_2 introduced during the whole duration of an experiment was at least about five times the amount of SO_2 which could be combined (curve 1 in Figs. 2a, 3a and 4).

RESULTS AND DISCUSSION

Inspection of the results shown in Fig. 1 reveals several interesting aspects of the problem. When the SO_2—air mixture is brought into contact with the calcination product (of calcite, dolomite and magnesite) reaction starts immediately at a high rate (DTG curve), and about 5—10% of the calculated amount of SO_2 is taken up (TG curve). After a short period of rapid reaction the rate slows down, probably because of the formation of a new solid phase on the surface of the grains hindering the diffusion of SO_2 towards unreacted oxide. Between 300 and 500°C the reaction accelerates several times, indicating that the changes taking place must be complex in character. At about 1000°C the conversion $CaO \rightarrow CaSO_4$ is practically complete (curve 1), i.e. the reaction takes place throughout the grain. Under the same conditions MgO takes up only 30% of the theoretical amount, but above 1000°C magnesium sulphate begins to decompose (curve 3). As could be expected, the TG curve of dolomite (curve 2) represents an intermediate case.

The results obtained under isothermal conditions are also remarkable. So, for example, the maximum conversion was nearly the same in both cases, i.e. by applying non-isothermal (Fig. 1) and isothermal (Figs. 2—4) conditions. The influence of the SO_2 concentration is shown in thermograms a. The results are as expected. Curves in thermograms b illustrate the effect of temperature (under isothermal conditions). It is clear why curve 4 of Fig. 4b does not indicate a weight increase — at 1000°C $MgSO_4$ no longer forms (Fig. 1, curve 3). In the case of different grain sizes (thermograms c) the results are also as expected — coarser grains take up SO_2 more slowly. It is also not suprising that the observed degree of conversion is lower for samples calcined at 1500°C than for those calcined at 900°C (thermograms d). In the curves of thermograms e, plots 2 and 4 are for slow calcination of the sorbent (the calcination was performed in the labyrinth crucible, i.e. in the "self-generated" atmosphere) while plots 1 and 3 are for rapid calcination. In the case of calcite and dolomite slow calcination is of no advantage. Curves of thermograms f show the effect of CO_2 pressure. Calcination was carried out under dynamic conditions, in a labyrinth crucible (curves 2 and 4) at high CO_2 pressure, and on the multiplate sample holder (curves 1 and 3) at low CO_2 pressure. Calcination under higher partial pressure was of benefit to magnesite and dolomite, but the opposite was true for calcite. It should be noted that in the case of calcination in the presence of sodium chloride additive, the degree of conversion of calcite decreases while that of dolomite and magnesite increases.

In conclusion, we can state that the method developed appears to be suitable for investigating problems such as those indicated above. However, it must be emphasized that conclusions can be drawn only on the basis of comparison. The TG curves obtained as described cannot be interpreted in an absolute sense. The course of the TG curves has been shown to be considerably influenced by the experimental conditions. The shape of an individual curve may be the result of many different effects. However, if we perform a series of experiments changing only a single factor each time, we can draw conclusions as to the effect of that factor.

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