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THERMAL DECOMPOSITION OF CALCIUM SULFATE IN CARBON MONOXIDE

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Simultaneous TG and DTA studies were performed on analytical grade calcium sulfate and on samples of natural gypsum and phosphogypsum in carbon monoxide atmosphere. The decomposition temperatures and mechanism are influenced by the mineral impurities of the sample and the heating rate as well as the CO content of the gas atmosphere.

Besides occurring in tremendous deposits in nature as gypsum or anhydrite, calcium sulfate is produced in excess of demand as a by-product in several industrial processes, especially in phosphoric acid production from apatite and phosphorite. Thus, calcium sulfate constitutes a potential source of cheap raw material for the production of sulfur based chemicals, most notably sulfuric acid.

Thermal decomposition of calcium sulfate has been studied frequently, in oxidizing, inert and reducing atmospheres. The studies performed in oxidizing and inert media have been reviewed in detail by Colussi and Longo [1], who also discussed the effect of certain added compounds. However, reductive decomposition under controlled conditions is potentially more interesting from the industrial point of view because it would allow the conversion of $CaSO_4$ into CaS and/or CaO at temperatures significantly below those required for the oxidative process [2].

Solid as well as gaseous compounds may act as reducing agents and, in a carbon-containing system, the role of carbon monoxide will be dominant. The interaction of carbon monoxide with calcium sulfate may be described by the following equations:

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \qquad (1)$$

$$CaSO_4 + 4\,CO \rightarrow CaS + 4\,CO_2 \qquad (2)$$

At 1100° reaction (1) is endothermic with an enthalpy value of 181.6 kJ/mol while reaction (2) is exothermic with a value of 202.5 kJ/mol [2].

Several groups [3–7] including ours (R. K.) [8–11], have recently reported new data on the calcium sulfate reduction process. However, the influence of $CaSO_4$

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impurities and the concentration of CO in the gaseous phase as well as the effects of temperature and heating rate on the reducing reactions have generally been overlooked. In the present study we have focused our attention on these questions.

Experimental

Materials

Calcium sulfate samples included chemically pure $CaSO_4$, natural gypsum, and phosphogypsum from the processing of various natural phosphates (Table 1).

Table 1 Origin and characteristics of the calcium sulfate samples. Contents calculated on dry material basis

Sample	$CaSO_4$, %	Impurities, % Total	Impurities, % SiO_2
1. Reactive $CaSO_4$ (chem. pure)	99.86	0.14	–
2. Natural gypsum	95.08	4.92	0.20
3. Phosphogypsum from Kola apatite concentrate	94.89	5.11	0.37
4. Phosphogypsum from Tunesian phosphorite	90.47	9.53	1.0
5. Phosphogypsum from Karatau phosphorite	80.75	19.25	14.75
6. Phosphogypsum from Toolse phosphorite	83.74	16.26	14.18

Methods

Thermal analyses of the samples were performed by simultaneous recording of the TG, DTG and DTA curves on a Mettler Thermoanalyser TA-1. The heating rate was 10 or 25 deg/min. Samples (39–41 mg) were placed in a standard platinum crucible (diam. 6 mm, depth 5 mm); in DTA measurement Al_2O_3 was used as a reference material. Measurements were carried out in a dynamic atmosphere with a flow rate of 100 ml/min. Carbon monoxide (AGA Oy, Helsinki) contained 99% CO, 0.3% H_2 and 0.7% $H_2 + O_2$. Pure nitrogen (99.9%) was used as inert component in the gas mixtures.

The composition of the solid residue was determined with a powder diffractometer (Philips PW 1050) and that of the gaseous phase with a gas chromatograph (Beckman GC-2) employing Porapack Q filled column.

Results and discussion

Experiments in pure carbon monoxide

The first peak in the TG and DTA curves of reactive $CaSO_4$ (sample 1) corresponds to the loss of water, which is complete by 200°. The decomposition of $CaSO_4$ begins at 780°, reaches a maximum at 865° and is complete at 955°. With an increasing content of impurities (samples 2–6) the decomposition temperatures are by 70 to 100° lower (cf. Figs 1 and 2).

As seen from the DTA curves, the reaction is exothermic with a measured ΔH value of 171±33 kJ/mol $CaSO_4$. Only CO_2 was found in the gaseous phase and, in agreement with this finding and equation (2), the solid residue contained sulfur in the form only of CaS.

Experiments in CO/N_2 gas mixtures

A CO content of 5–20% was selected for the gas mixtures in order to simulate the actual conditions during processing of natural and waste gypsum in a fluidized bed reactor that burns gaseous fuel with an air expenditure coefficient of 0.6–0.9.

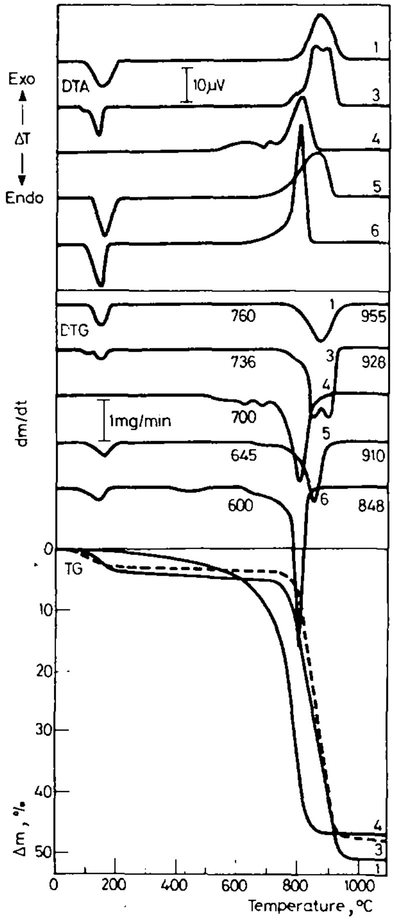

Fig. 1 Thermoanalytical curves for the decomposition of calcium sulfate samples in carbon monoxide. Heating rate is 10 °C/min. The numbers (1–6) refer to samples listed in Table 1

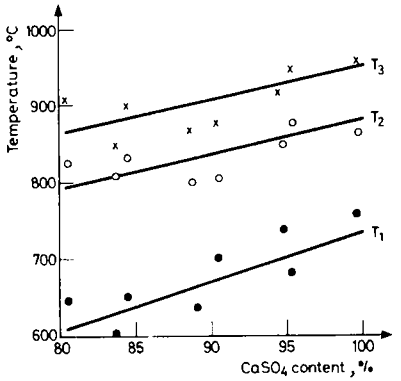

Fig. 2 The variation of decomposition temperatures as function of the $CaSO_4$ content of the samples. T_1, T_2 and T_3 are the thermogravimetric starting, maximum rate and end temperatures, respectively, of the $CaSO_4$ decomposition reaction shown in Fig. 1

It was established by X-ray diffraction analysis that, when using a heating rate of 10 deg/min and a CO content of 20% (Figs 3, 4), the solid residue contains CaS. Since no SO_2 is present in the exhaust gas according to gas chromatographic analysis, calcium sulfate must be completely transformed into calcium sulfide under these conditions. Furthermore, the measured exothermic effect of 198 kJ/mol coincides with the calculated enthalpy value of Eq. (2).

Lowering of the CO concentration to 10% decreases the exothermic effect, and at a gas composition of 5% CO/93% N_2 the overall effect is endothermic (see Fig. 4). In this CO range (5—10%) peaks due to CaO appear on the diffractogram and SO_2 is observed along with CO_2 in the exhaust gases, indicating the presence of reaction (1).

As expected, an increase in the heating rate from 10 to 25 deg/min, shifts the peaks towards higher temperatures (Fig. 3). At the same time the yield of CaO is increased and, in case of 5% CO content, the total weight change approaches the theoretical weight loss (58.8%) CaO formation from the $CaSO_4$. At the 25 deg/min heating rate calcium oxide is detected in the solid residue also when CO concentration is 20% indicating the importance of kinetic effects.

Isothermal experiments

Results from isothermal experiments on reactive $CaSO_4$ in 2—10% CO atmosphere at 1100° indicate that the decomposition reaction begins practically immediately upon feeding CO into the gas flow. The weight loss rate, however, is dependent on the gas phase composition (Fig. 5). The initial stage of the reduction process with a high rate of mass loss is always endothermic but its duration depends on the CO content. With a 10% CO content the decomposition of $CaSO_4$ proceeds during the first 6 minutes at a fast rate to CaO and SO_2, thereafter the rate decreases, and the remaining part of $CaSO_4$ decomposes according to Eq. (2) with the formation of CaS and CO_2. The reaction is completed in 20 minutes, and the overall enthalpy effect equals zero.

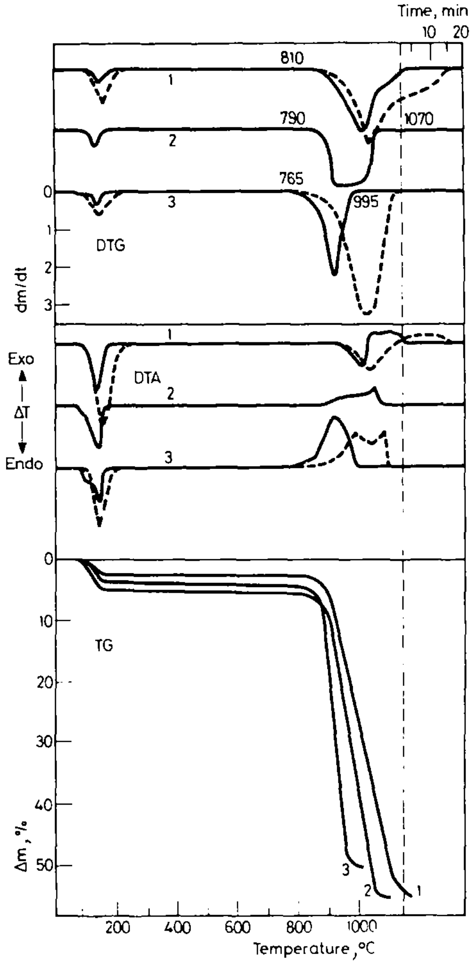

Fig. 3 The influence of CO concentration on the decomposition of pure $CaSO_4$. The numbers 1 to 3 refer to CO concentrations of 5, 10 and 20%, respectively. Time scale gives the duration of the reaction at 1150 °C. Heating rate: ———, 10 °C/min — — — 25 °C/min

When the CO concentration is lowered to 2% the reaction rate decreases, but particularly, its endothermic nature increases due to the formation of CaO and SO_2. Similarly, at higher CO concentration reaction (1) proceeds only at the beginning of the contact between $CaSO_4$ and CO. In order to promote the decomposition of calcium sulfate to get SO_2 and CaO, it is thus necessary to use finely dispersed material with a developed contact phase surface. An increase in the process temperature from 1050° to 1100° (5% of CO) increases to some extent the mass loss and the SO_2 yield, however, it does not prevent the formation of CaS. This step probably could be prevented by a further temperature increase, by the application of inhibitors for reaction (2) (e.g. CO_2), or by the presence of O_2 in the gas phase.

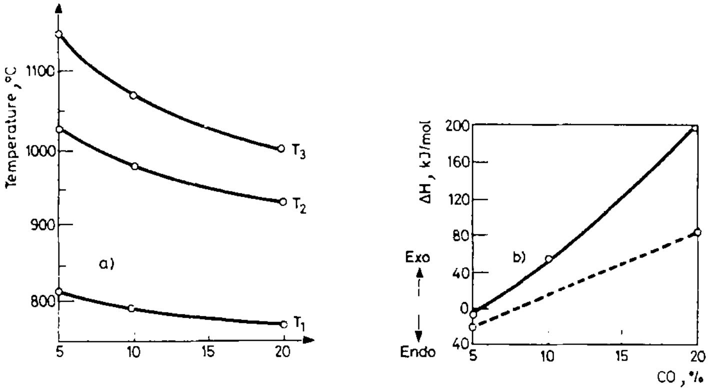

Fig. 4 The dependence of the $CaSO_4$ decomposition temperature (A) and enthalpy in kJ/mol (B) on the CO concentration of the gas phase. Temperatures T_1–T_3 are defined as in Fig. 2. Heating rate: ——— 10 °C/min, — — — 25 °C/min

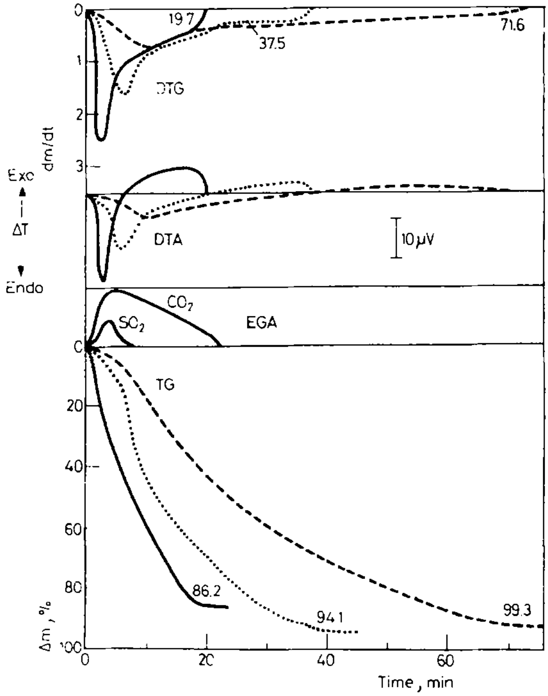

Fig. 5 Thermoanalytical curves showing the interaction of carbon monoxide at various concentrations with pure $CaSO_4$ at 1100 °C. — — — 2%, ... 5% and ——— 10% CO. EGA curves have been obtained by continuously monitoring the GC peak intensity

Conclusion

By slow heating in a gaseous medium containing 20–100% of CO, calcium sulfate is completely reduced to CaS with maximal rate just below 865°. Mineral impurities in the phosphogypsum samples considerably decrease the reduction temperature. With a CO content lower than 20% in the gas phase and at temperatures above 1050–1100°, the formation of CaO and SO_2 becomes dominant and, correspondingly, the overall exothermic effect becomes an endothermic effect.

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References

1 I. Colussi and V. Longo, Il Cemento, (1975) 75.
2 T. D. Wheelock and D. R. Boylan, Ind. Eng. Chem., 52 (1960) 215.
3 P. S. Vladimirov and N. Yu. Gavrilova, Zh. Prikl. Khim., 51 (1978) 1201; J. Appl. Chem. (Engl. Transl.), 51 (1978) 1157.
4 I. G. Kostyl'kov and V. N. Nosov, Zh. Prikl. Khim., 54 (1981) 2531; J. Appl. Chem. (Engl. Transl.), 54 (1982) 2236.
5 P. S. Vladimirov, Zh. Prikl. Khim., 55 (1982) 721; J. Appl. Chem. (Engl. Transl.), 55 (1982) 659.
6 I. G. Kostyl'kov and V. N. Nosov, Zh. Prikl. Khim., 55 (1982) 1925; J. Appl. Chem. (Engl. Transl.), 55 (1982) 1173.
7 V. N. Chentsov, T. V. Oleinikova, V. S. Epifanova and S. V. Khryashchev, Zh. Prikl. Khim., 56 (1983) 983; J. Appl. Chem. (Engl. Transl.), 56 (1983) 927.
8 E. Kärblane, A. Kuusk and R. Kuusik, Tr. Tallinn Politekh. Inst., 479 (1980) 21.
9 L. Viisimaa, A. Kuusk and R. Kuusik, Ibid., 479 (1980) 29.
10 R. Kuusik, M. Veiderma and A. Kuusk, Sbornik dokladov nauchnoteknicheskoi konferencii. Mineralnie udobrenya i ikh primenenie v selskom gosaistve, Varna 1978, p. 142.
11 R. Kuusik, A. Kuusk and M. Veiderma, Khim. Promst. (Moscow), 7 (1981) 409; Sov. Chem. Ind. (Engl. Transl.), 7 (1981) 872.

Zusammenfassung — Simultane TG- und DTA-Untersuchungen von analytisch reinem Calciumsulfat und Proben von natürlichem Gips und Phosphogips wurden in Kohlenmonoxidatmosphäre ausgeführt. Temperatur und Mechanismus der Zersetzung werden durch mineralische Verunreinigungen der Probe, durch die Aufheizgeschwindigkeit und durch den CO-Gehalt der Gasatmosphäre beeinflußt.

Резюме — Совмещенный метод ТГ и ДТА был использован для изучения в атмосфере окиси углерода аналитически чистого сульфата кальция и образцов природного гипса и фосфогипса. Температуры разложения и механизм реакций зависят от минеральных примесей в образцах, скорости нагрева, а также от содержания окиси углерода в газовой атмосфере.