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Versatility of the application of thermal analysis to the simulation of gas desulphurisation[1]

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Abstract

The sulphation process of pre-calcined limestone illustrates the application of programmed thermal analysis techniques using different gas sequences. The direct usage of commercial equipment (e.g. Derivatograph and Mettler thermoanalysers) is limited because the thermobalance unit must be additionally isolated to operate under a corrosive gas atmosphere. The TA methods are capable of predicting the behaviour of the potential sorbents towards SO_2/SO_3 in a larger scale installation. The thermal stability of the compounds from the Ca–S–O system and the influence of additives on sulphation have been found useful in elucidation of the limestone sulphation mechanisms. The thermoanalytical investigations had to be supplemented by independent complementary techniques such as X-ray diffraction, scanning electron microscopy with backscattered electron image followed by quantitative energy dispersive X-ray microanalysis.

Keywords: TA; Gas desulphurisation; Simulation

1. Introduction

Different techniques of thermal analysis, in which a physical property of a substance is monitored as a function of time or temperature while the temperature of the sample, in a specified atmosphere, is programmed, play an important role in the study of solid–gas reactions. Among the main techniques the most commonly used are thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and dif-

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ferential scanning calorimetry (DSC). They may be used for the determination of a single parameter, i.e. mass change of the sample, first derivative of mass change, difference in temperature between the sample and a reference material and enthalpy (difference in heat flow rate to a pan containing the sample and to the reference pan), respectively.

Techniques may apply to subsequently develop specific modifications of pre-existing methods, i.e. simultaneous thermal analysis or variable atmosphere thermal analysis whereby the furnace atmosphere conditions may be pre-selected, maintained or changed as desired between or during measurement.

An excellent example is sulphation of either calcium carbonate or calcium oxide particles in an atmosphere containing sulphur oxides. Sulphation takes place when Ca-based sorbents are used for SO_2/SO_3 capture during the combustion of coal in fluidised bed combustors. Fluidised bed combustion is a useful technology for the clean burning of high sulphur containing coals. By burning cleanly we mean that it is possible to capture most SO_2 in the fluid bed itself, without using additional equipment. Also nitrogen oxides would not be produced because the temperatures are relatively low. But it is not possible, at present, to predict the limestone requirements simply from its chemical and physical characteristics. Therefore continued development of rapid laboratory methods to simplify sorbent characterisation towards SO_2/SO_3 capture is required. These methods should enable reliable prediction of the behaviour of the sorbent to be used in a laboratory or large scale installation.

The overall chemical reaction between CaO and SO_2 is deceptively simple. However the precise chemical mechanism has still not been established and is the subject of speculation. Model schemes have been proposed, and much more work has been done modelling this process without a detailed understanding of the chemistry.

It is doubtful whether either of the two routes I and II [1] adequately describe the reaction between the gases SO_2 and O_2 with the porous solid CaO:

$$\text{I:}\quad SO_2 + 1/2O_2 \rightarrow SO_3 \qquad\qquad \text{II:}\quad CaO + SO_2 \rightarrow CaSO_3$$

$$CaO + SO_3 \rightarrow CaSO_4 \qquad\qquad CaSO_3 + 1/2SO_2 \rightarrow CaSO_4$$

to yield the product $CaSO_4$.

Therefore, the thermal stability of $CaSO_3$ up to 1200°C in air and nitrogen was examined in detail earlier [2]. The data from the X-ray diffraction analysis of the stable solid reaction intermediates at 850°C (at both atmospheres) showed the existence of calcium sulphate with calcium sulphide and the absence of $CaSO_3$ according to the reaction

$$4CaSO_3 \rightarrow 3CaSO_4 + CaS \tag{1}$$

This is in agreement with literature data that $CaSO_3$ decomposes above 700°C [3,4]. At 1100°C the X-ray data showed that calcium oxide appeared in addition to $CaSO_4$ and CaS according to the reaction

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \tag{2}$$

Moreover, by the thermal analysis study, it was shown that the introduction the catalyst of SO_2 to SO_3 (e.g. platinum) into the reaction zone brings the increased reactivity of sorbents facilitating sulphation via route I [5].

In this paper many advantages of the application of thermoanalytical techniques in the study of the elucidation of the limestone sulphation mechanism are presented.

2. Experimental

2.1. Materials and experimental procedures

Natural limestone samples quarried in Zabierzow (Poland) for sulphur oxide capture were used in the present work. These samples have been studied before during the fluidised combustion of coal [6] and by thermal analysis [7,8]. Samples were crushed and sieved to the desired size range (0.5–0.6 mm). The weight loss on calcination was 43.70 ± 0.09% (from the TG curve). X-Ray fluorescence analysis using Phillips PW 1410 equipment gave: CaO, 57.4%; MgO, 0.4%; SiO_2, 0.5%; Al_2O_3, 0.1%. Platinum asbestos was used as a catalyst for SO_2 oxidation.

Samples of CaS (98%) from Alfa Produkte (Germany) and $CaSO_4$ (anhydrous) from Merck were used.

The gas mixture, SO_2 (0.5 ± 0.08%), O_2 (5.0 ± 0.5%), CO_2 (15 ± 0.7%), the balance being nitrogen, was prepared by AGA OY (Finland).

For the thermal analysis, a Mettler 3000 Thermoanalyzer with Mettler TC 10A TA Processor and STA 2000 Thermoanalyzer (BÄHR Geratebau GmbH) with good PC-based software were employed. The Mettler Thermoanalyzer was equipped with a gas atmosphere accessory which we designed for handling corrosion gas. The flow of gases through the systems has been described in detail previously [8].

X-Ray diffraction measurements (a Siemens diffractometer D500) and microstructural examinations with elemental microanalysis (a JEOL JCXA-733 equipped with an energy dispersive X-ray spectrometer system, Link AN10/85) were used as supplementary techniques for the identification of the solid phases.

3. Results and discussion

A general example of the study of limestone sulphation is shown in Fig. 1. The heating in air up to approx. 900°C produces a weight loss due to calcination. After stabilising conditions, in the step under isothermal conditions (at 830°C) in flowing gas containing sulphur dioxide, there is a gain in weight arising from CaO sulphation. At approximately constant weight, the temperature is raised to 950°C followed by flowing nitrogen to purge the system. Finally, the sample is held isothermally at 950°C and the loss of weight is observed. This indicates that the decomposition process occurs inexplicably since calcium sulphate, $CaSO_4$, which is generally accepted as the sole limestone sulphation product is thermally stable up to 1350°C. It was necessary, therefore, to know the real phase composition of the products. None of the conventional methods such as IR spectroscopy

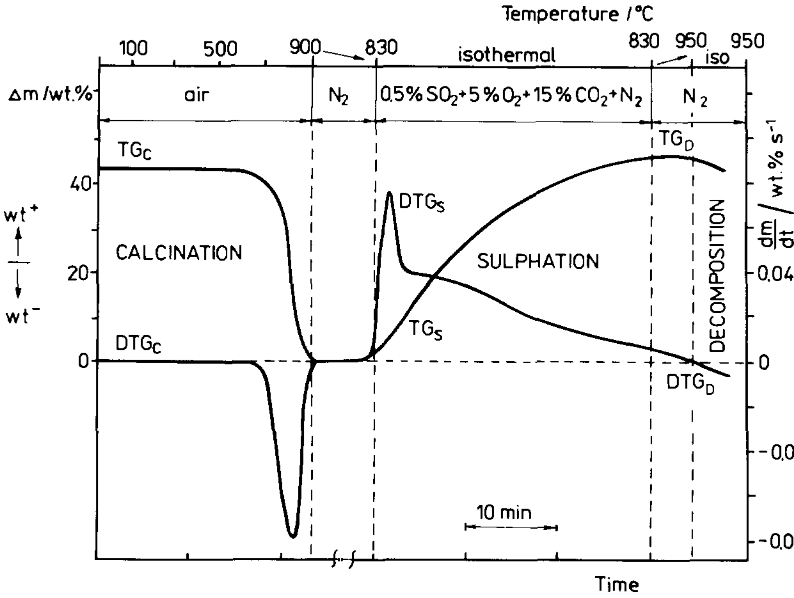

Fig. 1. Illustration of the study of the limestone sulphation process by using a multistage heating program with a variable atmosphere thermal analysis (Mettler 3000 Thermoanalyzer).

and X-ray powder diffraction were appropriate in this case because they only revealed some of the main phases present.

In contrast to the above techniques, backscattered electron imaging combined with energy dispersive X-ray microanalysis can provide very detailed information on limestone sulphation products. Single limestone particles can be imaged and analysed with a spatial resolution of a few tenths of a micrometre in an image and a few micrometres in an analysis. BSE images and elemental dot maps can reveal the distribution of the elements [9,10]. Unfortunately no chemical formulae can be calculated. When a cross section of a

Table 1

Compounds present in limestone sulphation products, characterized by the oxide concentrations of Ca and S, their average atomic numbers and grey tone levels in a BSE image; concentrations are expressed in wt%

Compound	Oxide concentration		Sum of oxides $CaO + SO_3$	Molar ratio CaO/SO_3	Average atomic number	Grey tone level in BSE image
	CaO	SO_3				
CaS	77.7	111.0	188.7	1	18.2	Bright
CaO	100.0	0	100.0	∞	16.6	Very bright
$Ca(OH)_2$	75.7	0	75.7	∞	14.3	Light
$CaSO_4$	41.2	58.8	100.0	1	13.4	Grey
$CaCO_3$	56.0	0	56.0	∞	12.6	Dark

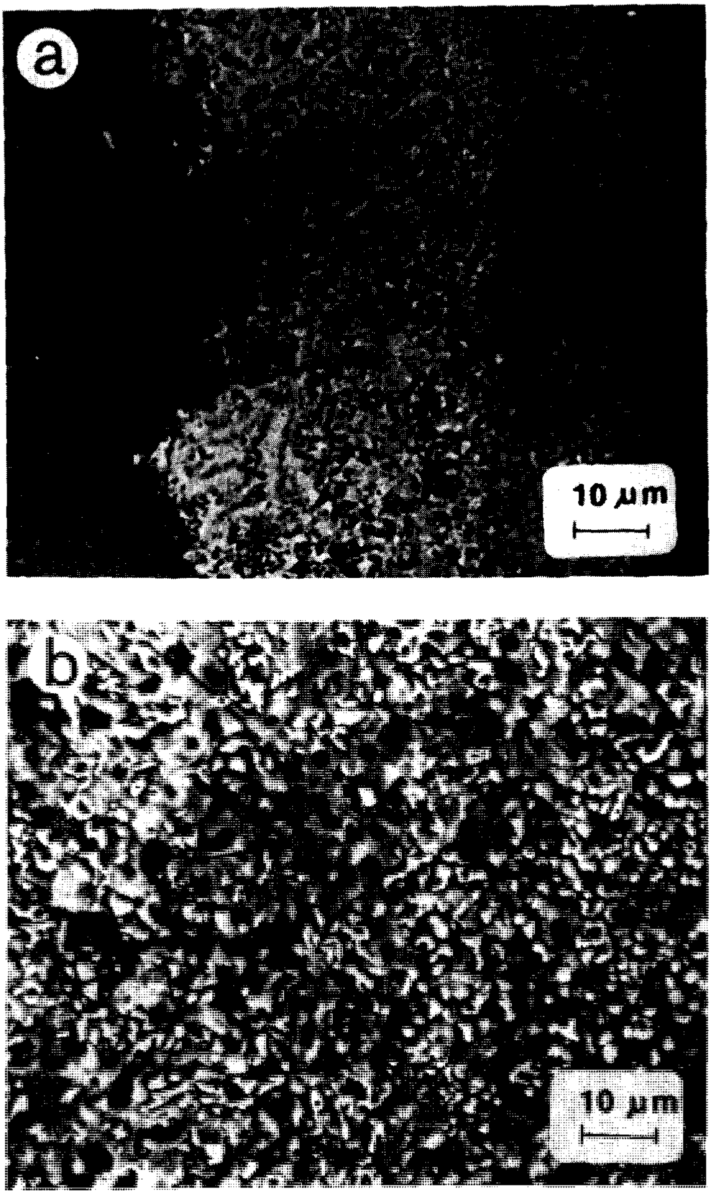

Fig. 2. Backscattered electron micrograph of the polished cross-section of a sulphated particle of (a) limestone; (b) calcined limestone. The arrows indicate the points 1–6 (see explanation in the text) from which the microanalyses were obtained. Magnification markers are at the bottom of the figure.

Table 2

The component proportions (%) found by the optimisation procedure for the measured values of the sum of oxides, *s*, and molar ration, *r*.

Fig. 2a	Point 1	Point 2	Point 3
s; *r*	104.5; 1.00	55.5; ∞	115.8; 1.16
CaS	5.1	0	18.6
$CaSO_4$	94.6	0	73.5
CaO	~0	0	6.2
$CaCO_3$	~0	~100	1.7
Fig. 2b	**Point 4**	**Point 5**	**Point 6**
s; *r*	105.0; 1.01	101.0; 1.92	99.3; 1.40
CaS	5.6	9.2	3.3
$CaSO_4$	93.9	55.9	79.0
CaO	0.4	5.5	2.7
$Ca(OH)_2$	~0	29.4	15.0

single limestone sulphated particle is examined in a scanning electron microscope, the local sulphur and calcium elemental concentrations can be measured. Since oxygen and carbon could not be determined by the EDX, the amount of calcium and sulphur were computed as elemental concentrations and then as their oxides. The sum of oxides and the molar ratios CaO/SO_3 are essential to the development of a model [11]. Characterisations of compounds which may be present in limestone sulphation products, are given in Table 1. Both elemental calcium and sulphur are thus represented as weight percentages of oxides even when no oxide is present. In such cases an excess of oxygen is calculated and the total exceeds 100%. The two quantities, sum and molar ratio can be used as a guide for solid phase identification at the analysed points. BSE micrographs are shown for polished cross-section sulphation limestone particles and lime particles in Figs. 2a,b, respectively.

Different grey levels are visible producing in most cases sufficient contrast in discrimination of the phases. This is a consequence of the different average atomic numbers for the expected phases [12]. By combining the grey level tone with the results of the quantitative microanalysis, single compounds can be quickly identified. If more than one compound is present then the procedure is more complicated but it is possible to estimate using an optimisation technique [13]. This technique identifies component proportions which minimise the differences between measured and calculated values of the sum and molar ratio. The method is developed using a computer program.

For the phase analysis, six points denoted 1–6 are shown in Fig. 2a,b and the component proportions (%) found by the optimisation procedure for the measured values of sum of oxides, *s*, and molar ratio, *r*, are given in Table 2.

The phase analysis results identified two sulphur-bearing solids, $CaSO_4$ and CaS, in the products formed in the limestone sulphation reaction. These results suggest the following explanation. The $CaSO_3$ could be formed at a relatively lower temperature while the CaO particles are being heated to gas temperature. At about 830°C, the CaS and

Fig. 3. Scanning electron micrograph showing representative sample of calcined limestone after reaction with SO_2. Magnification marker is at the bottom of the figure.

$CaSO_4$ can form according to reaction (1) as in the case of pure $CaSO_3$ decomposition, especially in an inert atmosphere. In fact, the pores of the particles have been closed by products (Fig. 3). Thus the diffusion of oxygen and SO_2 through the compact layer is hindered and disproportionation of $CaSO_3$ occurs in a non-oxidising atmosphere.

Returning to the effect of mass loss at 950°C in Fig. 1, it can be postulated that the $CaSO_4$, a main limestone sulphation product, reacts with CaS evolving SO_2 due to reaction (2). In support of this idea, the complementary thermoanalytical measurements were made on a physically prepared mixture of $CaSO_4$ and CaS (molar ratio of 3:1). As Fig. 4 shows, the decomposition in an inert gas starts at a temperature higher than 950°C resulting in the system $CaSO_4$–CaS–CaO, similar to the thermal behaviour of the $CaSO_3$ decomposition products.

4. Conclusions

With regard to the identification of limestone and lime sulphation products, if SO_2 is a main agent then CaS and $CaSO_4$ always appear together. According to the model, the intermediate product is calcium sulphite, $CaSO_3$, which disproportionates to $CaSO_4$ and CaS.

Catalytic oxidation of SO_2 into SO_3, for example by platinum, causes SO_3 to react with CaO to form $CaSO_4$ directly and more efficiently. $CaSO_4$ is the only solid product in this case.

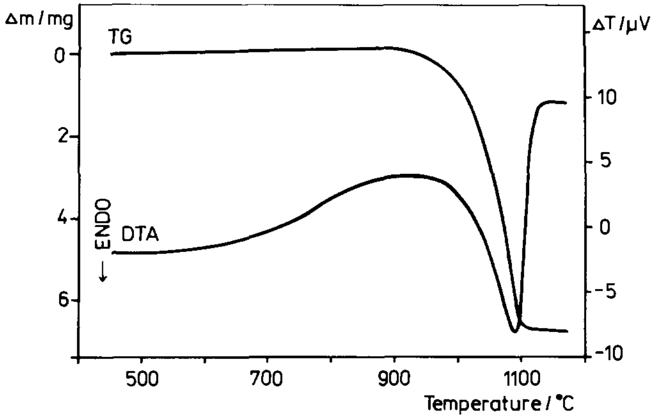

Fig. 4. TG-DTA curves (STA 2000 Thermoanalyzer) for a mixture of $CaSO_4$ and CaS (molar ratio of 3:1) in nitrogen; initial weight 27.0 mg.

In summary there are two possible documented pathways for the gas desulphurising process using Ca-based sorbents. They are significantly dependent on SO_2 catalysing or non-catalysing conditions. Particular attention was paid to obtaining direct evidence for the existence of solid intermediates and the real phase composition of products. Without this information no satisfactory mechanism can be developed.

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