Journal of Thermal Analysis, Vol. 54 (1998) 85-91

PHYSICO-CHEMISTRY OF THE LIMESTONE SULPHATION PROCESS

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Abstract

Aspects of the mechanism of the overall reaction between $CaCO_3$/CaO and SO_2/SO_3 under oxidizing conditions are discussed. The limestone and lime sulphation processes were carried out in a thermobalance under conditions relevant to atmospheric fluidized bed combustion. Sulphated samples, prepared in the form of cross-section particles, were examined in a scanning electron microscope by energy-dispersive X-ray and back-scattered electron imaging. Photomicrographs are presented. The reaction proceeded from the outer surface of the particles and along the pores. Surface textural changes during the reaction were considered. The layer of products was identified as controlling both the rate and extent of limestone/lime sulphation. In the products, two sulphur-bearing solids ($CaSO_4$ and CaS) were identified. The presence of CaS, which may cause difficulties in practice, is attributed to $CaSO_3$ disproportionation.

Keywords: absorption, calcination, calcium-based sorbents, desulphurization, fluidized combustion, limestone, phase analysis, porosity, reactivity, sulphation, sulphur oxide capture, TG

Introduction

The study of limestone ($CaCO_3$) sulphation leads to a better understanding of the chemistry of the gas desulphurization process. Such processes take place when calcium-based sorbents are used to capture sulphur oxides during the combustion of coal in fluidized bed furnaces, forming dry solid waste material. Thus, fluidized combustion combined with desulphurization in the fluid bed itself is a technique that eliminates the expense and complications of the more usual wet scrubbing process (gas–liquid contact) in a separate gas clean-up system [1].

The use of natural limestones as sorbents is currently being investigated in a number of institutions with a view to optimizing the desulphurization conditions. At the same time, it is important to minimize the amount of sorbent used. Because of the nature of solid–gas reactions and the conditions during the atmo-

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

spheric fluidized bed combustion (AFBC), the utilization of the calcium remains poor. It is not possible at present to predict the limestone requirement simply from its chemical and/or physical characteristics. The physical structure of the sorbents is critically important as concerns the sulphation behaviour. The reactivity of the sorbent and the composition of the final product depend on a large number of factors, e.g. the combustion temperature, the sorbent–gas contact time, the limestone type, the impurities contained in the coal and the sorbent, the sorbent pore size, etc. Some of these factors can be interdependent. The sorbent, the coal and the ballast (silica sand) injected into the furnace have to be prepared in a desired size range, selected on the basis of the hydrodynamic properties of the fluidized layer for the temperature which is optimum for desulphurization. This temperature, in the range 850–950°C, is extremely well documented experimentally, but the explanation put forward is based on fragmentary evidence. The elucidation of the chemistry of the limestone sulphation process described in the paper offers a satisfactory explanation of the operating temperature regime and also draws attention to the possibility of the appearance of CaS, besides $CaSO_4$, in the sulphation products, which may cause difficulties in the handling, disposal or utilization of the solid wastes. None of the conventional methods, such as X-ray powder diffraction or IR spectroscopy, are appropriate in this case, because they reveal only the main phases present ($CaSO_4$, CaO and $CaCO_3$). In contrast with the above techniques, scanning electron microscopy (SEM) combined with energy-dispersive X-ray microanalysis (EDX) and back-scattered electron imaging (BSE) can provide very detailed information on the composition and localization of solids present in limestone sulphation products [2].

Thermal analysis (TA) measurements

The sulphation reactions of calcined and uncalcined limestone have been investigated by means of TA methods from many aspects [e.g. 3–9]. The capture of sulphur oxides to assess the relative merits of different limestones, the effects of additives on limestone calcination and/or sulphation, the influence of oxidizing or non-oxidizing conditions and the actions of catalysts on the limestone reactivity were studied earlier and the results have been presented extensively [7–11]. In TA experiments, the following conditions, typical of the AFBC of coal containing S at about 3% m/m, have been employed: temperature: about 850°C, and partial pressures of O_2, CO_2 and SO_2: approximately 0.04, 0.20 and 0.05 atm, respectively. A small fraction of the SO_2 can be further oxidized to SO_3, but its formation is not favoured at high temperatures. However, the TA techniques do not fully reproduce the conditions in AFBC. Thus, phenomena such as thermal shock, decrepitation and attrition are not taken into account.

Interactions in the system $CaCO_3/CaO–SO_2/SO_3–O_2$

$CaCO_3$ is unstable under the conditions in AFBC since the partial pressure of CO_2 is less than about 60% of the equilibrium CO_2 pressure and the calcination can occur at a sufficiently high rate according to the reaction

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

From a thermodynamic standpoint, CaO or $CaCO_3$ can react with sulphur oxides in the temperature range 800–950°C. It is generally assumed in the literature (e.g. [12–17]) that for calcined or uncalcined limestone, the reactions taking place are

$$CaO_{(s)} + 1/2O_{2(g)} + SO_{2(g)} \rightarrow CaSO_{4(s)} \quad (2)$$

or

$$CaCO_{3(s)} + 1/2O_{2(g)} + SO_{2(g)} \rightarrow CaSO_{4(g)} + CO_{2(g)} \quad (3)$$

Numerous model schemes have been proposed and much work has been done on the modelling of these processes, but a detailed understanding of the chemistry is still not available. From the results of the experimental work presented here, it is evident that in an oxidizing atmosphere two different pathways of reaction are possible, which depend significantly on the SO_2 catalysing or non-catalysing conditions [11, 18]. If SO_2 is the main agent (and not SO_3), then the intermediate is $CaSO_3$, which is favoured by lower temperature.

$$CaO_{(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} \quad (4)$$

At about 800°C, $CaSO_3$ disproportionates (particularly easily in the absence of air) to $CaSO_4$ and CaS, according to the equation

$$CaSO_{3(s)} \rightarrow 3/4CaSO_{4(s)} + 1/4CaS_{(s)} \quad (5)$$

However, catalytic oxidation of SO_2 to SO_3 brings about a reaction between SO_3 and CaO to form $CaSO_4$ directly and more efficiently:

$$SO_{2(g)} + 1/2O_{2(g)} \rightarrow SO_{3(g)} \quad (6)$$

$$CaO_{(s)} + SO_{3(g)} \rightarrow CaSO_{4(s)} \quad (7)$$

$CaSO_4$ is then the only solid product of limestone sulphation. However, without a reliable phase identification, no satisfactory sulphation mechanisms can be developed.

Identification of characteristics of sulphated lime and limestone particles by SEM-EDX combined with BSE imaging

Solid samples of uncalcined ($CaCO_3$) and calcined limestone (CaO) sulphated in a thermobalance (a Mettler System) under the conditions described above were analysed for Ca and S and then imaged. The specimens for SEM investigations were prepared as polished cross-section of the particles.

BSE images and elemental dot maps in SEM can show the distribution of the elements being analysed. Unfortunately, no chemical formulae can be calculated for the phases by means of these maps. Therefore, a new approach to EDX quantitative elemental analysis for Ca and S [19–21] has been used to identify the phases and to determine their proportions at the analysed points. The phase analysis results made it possible to distinguish two sulphur-bearing solids ($CaSO_4$ and CaS) present in the lime/limestone sulphation products. Back-scattered electron images in black and white (they may also be coloured) for polished cross-sections of the limestone and lime particles are shown in Figs 1a and b, respectively. Different grey levels (or many colours) associated with the BSE image by means of image-processing procedures are visible, producing in most cases sufficient contrast for discrimination of the phases as a consequence of the different average atomic numbers for the expected phases (18.2 for CaS, 13.4 for $CaSO_4$ and 12.6 for $CaCO_3$). By combining the grey level tone with the results of the quantitative microanalysis, using an optimization technique with a computer program, the phase proportions can be estimated. Representative results of the phase analysis for the four points denoted 1–4 are given in Table 1. It can be seen from Fig. 1a that the phases containing sulphur exist in the outer layers of the particle (points 1–3), the inner parts of the sorbent remaining not converted at all (point 4). Moreover, the concentration of CaS in the considered system $CaS–CaSO_4–CaO–CaCO_3$ is significantly higher at a greater distance from the outer surface of the particle (compare the analysed points 1–3).

In the case of sulphated lime (Fig. 1b), when the system $CaS–CaSO_4–CaO–Ca(OH)_2$ is considered, the $CaSO_4$ and CaS phases appear round the pores (black area) and the $CaO/Ca(OH)_2$ concentrations are higher far from the pores.

Table 1 The solid-phase proportions (%) found by an optimization procedure [21] for the measured concentrations of S and Ca

Points on Fig. 1a	1	2	3	4
CaS	5	19	21	0
$CaSO_4$	95	73	27	0
CaO	0	6	26	0
$CaCO_3$	0	2	26	100

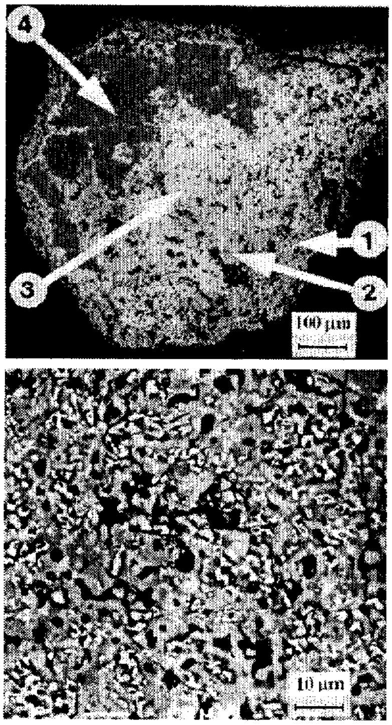

Fig. 1 Back-scattered electron micrograph of polished cross-section of a sulphated particle of (a) limestone, (b) calcined limestone. The arrows indicate the points from which the microanalyses were obtained (see explanation in the text)

Features of the mechanism and kinetics

On the basis of the phase identification and the localization of sulphation products shown in Figs 1a and b, it may be observed that the progress of lime and limestone sulphation is eventually hindered by pore blocking and the decrease or loss of the reaction surface area. This was also found by a comparison of pore size, surface area and pore volume of the raw sorbent, its calcines and the sulphation products in an earlier study [22]. In fact, in this process there are significant differences between the molar volumes of the products and reactants. The molar volumes of $CaCO_3$, CaO and CaS are about 36.9, 26.9 and 28.9 $cm^3 mol^{-1}$, respectively. $CaSO_4$, the main component in the sulphation, is formed as an anhydrate with a molar volume of 46 $cm^3 mol^{-1}$. Thus, the diffusion of SO_2 and O_2 through the compact product layer is the rate-determining step, excluding the sulphation of very small sorbent particles [7]. This means that the formation of

$CaSO_3$ (reaction (4)) and its disproportionation (reaction (5)) occur in a non-oxidizing atmosphere [2]. Furthermore, CaS cannot oxidize to $CaSO_4$. It is essential to mention the reaction between the two solid products, which can occur at temperatures above 900°C, producing calcium and sulphur oxides as follows:

$$3CaSO_{4(s)} + CaS_{(s)} \rightarrow 4CaO_{(s)} + 4SO_{2(g)} \qquad (8)$$

Final remarks

The absorption of gaseous SO_2/SO_3 by $CaCO_3/CaO$ is a rather complex topochemical process. The stoichiometric utilization of the calcium in the sorbent is impossible, not for thermodynamic but for kinetic reasons. The generation of product across the surfaces represents a barrier to gas–solid contact that prevents complete reaction of the limestone/lime particles. A wide-open pore structure may lead to a higher degree of CaO conversion.

The experimental results confirm the formation of $CaSO_4$ besides CaS during the sulphation of natural limestone in a thermobalance. This is one reason for the diminishing efficiency in the desulphurization process at temperatures above 950°C (see reaction (8)). Thus, the temperature range regime for the simultaneous combustion of coal and desulphurization when natural limestone sorbents are used can be elucidated. Moreover, the oxidizing step (for CaS) is important to allow disposal of the waste material in an acceptable manner for the environment.

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The author wishes to thank Prof. E. M. Bulewicz at the Institute of Inorganic Chemistry and Technology, Cracow University of Technology, who was the key person in the starting of this research, and Prof. Yu. G. Sirokov at the Ivanovo State Academy of Chemistry and Technology, Russia, for valuable discussions and comments on the study.

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