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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

PECULIARITIES OF INTERACTIONS IN THE $CaCO_3$/CaO–SO_2/SO_3–AIR SYSTEM
A review

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Abstract

The reactions occurring between $CaCO_3$/CaO and SO_2/SO_3 in oxidizing atmospheres are discussed. Calcination and sulphation were carried out in a thermobalance under conditions relevant to atmospheric fluidized bed combustion. It is suggested that the quality of limestones as potential SO_2 sorbents can be assessed on the basis of tests carried out in a TG apparatus adapted for use with corrosive gases. Limestone calcined under different conditions including the treatment with NaCl leads to changes in surface texture. Sulphated samples were examined in a SEM by energy dispersive X-ray and backscattered electron imaging. Two sulphur-bearing solids ($CaSO_4$ and CaS) were identified. The sulphation rate and extent are determined by the product layer diffusion. The amount of CaS present at the end of the process depends on the particle size of the sorbent.

Keywords: calcination, limestone, phase analysis, porosity, reactivity, SEM, sulphation, sulphur oxide capture, texture, TG

Introduction

The main reactions occurring in $CaCO_3$/CaO–SO_2/SO_3–air systems at higher temperatures can be represented schematically as follows [1]:

$$A_{(s)} \leftrightarrow B_{(s)} + C_{(g)} \tag{1}$$

$$B_{(s)} + D_{(g)} \rightarrow E_{(s)} \rightarrow F_{(s)} + G_{(s)} \tag{2}$$

Reaction (1) corresponds to calcination of $CaCO_3$, whereas reaction (2) represents sulphation of CaO by SO_2 with the formation of $CaSO_3$, which then disproportionates to CaS and $CaSO_4$. Detailed studies of these are undertaken at various laboratories, because of obvious practical relevance. The SO_2 generated during the combustion of coal at 850–950°C in a fluidized bed can react with cal-

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cium-based sorbents before being emitted to the atmosphere [2]. Due to the relatively low price of naturally occurring limestones, they are often used in fluidized bed combustors (FBC) giving solid compounds containing calcium and sulphur. The major disadvantage of using limestone is the environmental impact of quarrying limestone and of utilization or disposing of large quantities of solid waste material. The problem is made worse by the fact that only part of the $CaCO_3$ present in the limestone is converted to sulphur-bearing compounds, although the thermodynamics of every stage of reaction (2) is favourable [2]. If the amount of sulphated products formed per unit mass of $CaCO_3$ could be substantially increased, the environmental impact and cost could be reduced. This problem is still under consideration.

The heterogeneous reactions (1) and (2) are high-temperature topochemical solid – gas reactions. It is a particular feature of these reactions that the reactants involved have significantly different molar volumes (V) [3]. The inequalities can be expressed as:

$$V_B < V_A \tag{3}$$

$$V_F, V_G > V_B \tag{4}$$

for reactions (1) and (2), respectively. Such molar volume relationships can affect the mechanism and kinetics of the sulphation process to a considerable extent.

Structural changes during the calcination of limestone

There are numerous varieties of limestones with different impurities [4]. The behaviour during thermal dissocation is the most important chemical property of limestones. Certain limestones decrepitate into dust during calcination. These are not suitable as SO_2 sorbent in fluidized bed coal combustion. The reactivities of different limestones towards SO_2 could possibly be explained by the physical properties of the calcines, since the chemical composition of raw limestones is of secondary importance. The free volume left in the $CaCO_3$ structure after CO_2 loss (reaction (1)) appears as an intricate network of pores and the originally relatively nonporous limestone with small surface area can become a calcine (CaO) with about 59% porosity. The quantitative pore-structure characteristics of calcines obtained under different conditions can be found by determining the apparent density, the pore volume, the pore area and pore size distribution. The calcines with large internal surface area and pore volumes are the most reactive, because the rate of gas–solid reactions is determined primarily by the total area accessible to the gas and by the space available for the reaction product [5]. Thus, the physical properties of a calcine depend largely on the calcination conditions (e.g. temperature, time, atmosphere) and on the presence of impurities in the limestone or on the addition of certain salts.

Microphotographs of the external surface of limestone Z (from Zabierzow, Poland) obtained using a scanning electron microscope (JEOL JSM-35) are shown in Fig. 1. The raw limestone Z (Fig. 1a) is practically nonporous and the particles are irregular with rough external surfaces. A SEM microphotograph of the surface of limestone Z calcined up to 900°C in an atmosphere of 15% CO_2 in air is shown in Fig. 1b. Calcine grains with small pores (radius 0.12 μm) can be seen. Figure 1c also shows that the presence of NaCl during the calcination of limestone Z completely changes the appearance of the surface. The pores become bigger (1.59 μm) and larger crystallites with smooth surfaces appear. This is associated with a sintering effect, which causes a reduction in the surface area of the sample. The above observations are in agreement with porosity measurements by mercury porosimetry [1, 6] (Fig. 2). For example, the calcination of

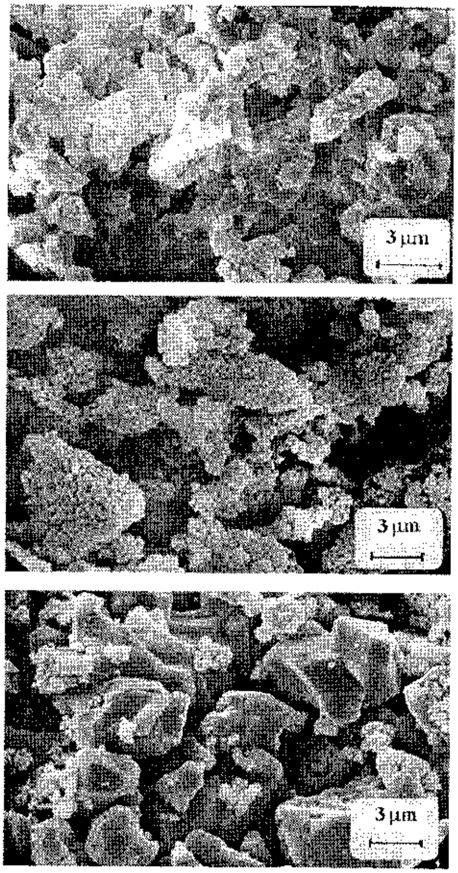

Fig. 1 SEM microphotographs of the external surface of particle of (a) raw limestone Z, (b) calcine of limestone Z, (c) calcine of limestone Z with NaCl, (grain size ca. 0.5 mm)

limestone Z at 900°C gives a calcine which is very reactive towards sulphur oxides, whereas calcination followed by sintering at 1500°C yields an almost dead-burned product (Fig. 3) [7]. At higher temperatures, strains and defects in the newly formed crystallites of CaO are removed by sintering, i.e. with atom movements. Then the crystallites are joining together, their number falls and their average size increases, so that the internal surface area shrinks. An increase in time at a fixed temperature leads to increased sintering. It has been observed that the specific surface area decreases (from about 5.5 to 2.0 $m^2 g^{-1}$) at constant pore volume (0.35 $cm^3 g^{-1}$), if the pore diameter, i.e. also the crystallite size increases. Relevant data can be found in published papers [1, 6, 8].

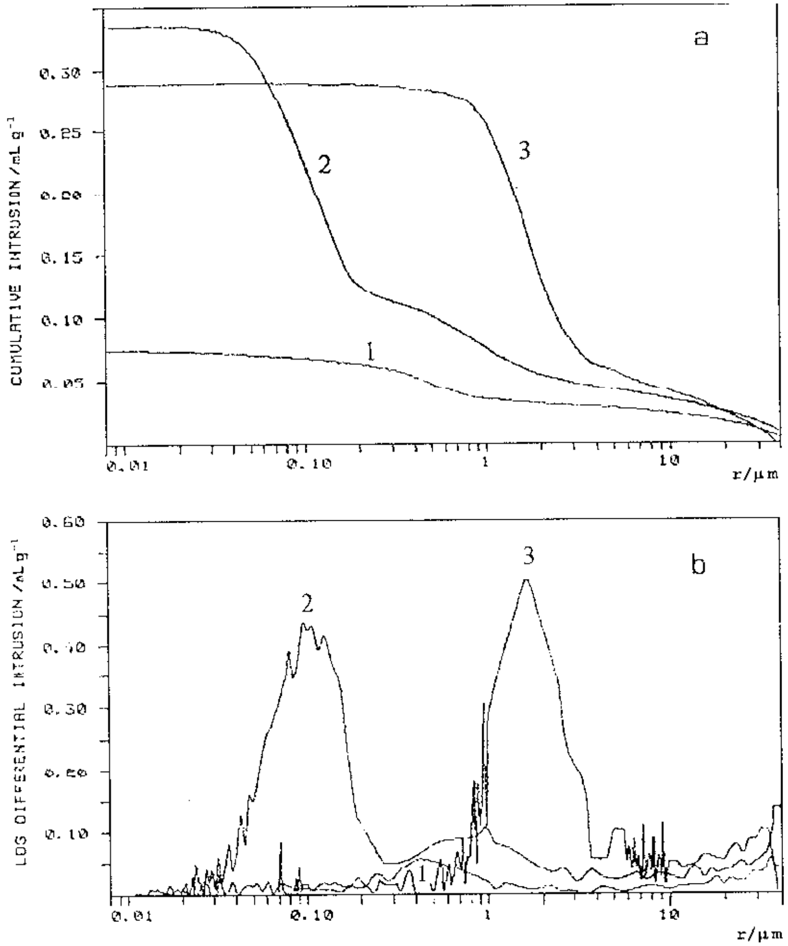

Fig. 2 Effect of calcination on the pore volume – pore size distribution: 1 – raw limestone Z, 2 – calcine of limestone Z, 3 – calcine of limestone Z with NaCl, (grain size ca. 0.5 mm)

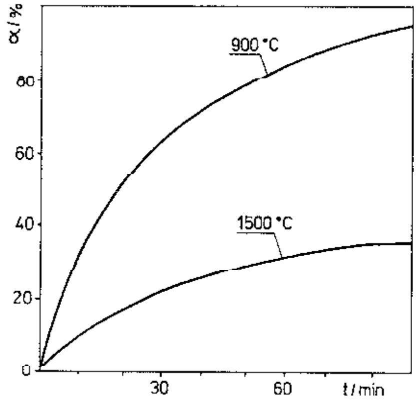

Fig. 3 Effect of calcination temperature on the sulphation of limestone Z (grain size ca. 0.15 mm) (after [8])

The use of thermogravimetric analysis in the characterization of calcium-based sorbents as fluidized bed desulphurizing agents

Thermogravimetric studies of gas solid reactions in which the sample examined reacts with non-corrosive gases can readily be performed. It is much more difficult, however, to react the sample with SO_2/SO_3 gases, particularly at high temperatures (e.g. in the 800–1000°C range) because of the danger of damaging the thermobalance. This is the problem with the thermal sulphation of limestone under conditions corresponding to those in an atmospheric fluidized bed combustor (e.g. [9, 10]).

Sulphation studies were undertaken by the author several years ago [7] using a Q-derivatograph (Hungarian Optical Works (MOM), Budapest) with a modified operation method [11] and continued using Mettler thermoanalyzers TA-2 and TA-3000 System also suitably modified to withstand atmospheres containing SO_2. The gas flow systems are illustrated schematically in papers [12, 13].

The behaviour of limestones to be used as SO_2 sorbents is difficult to predict simply from their chemical and physical characteristics. Thermogravimetry is a suitable laboratory method which enables reliable prediction of sorbent behaviour to be made. This is important from the practical point of view. The measurements and the evaluation procedure are fast and accurate. However, such phenomena as thermal shock, decrepitation, attrition, etc., are not taken into account.

In the author's work a naturally occurring limestone Z considered as the source of the calcium carbonate to react with SO_2 was earlier used as a sorbent in fluidized bed coal combustion studies [14]. Samples were crushed and sieved to the desired range.

The use of several sets of programmed TG analyses with variable conditions has made it possible to identify several factors which influence the mechanism and kinetics of reactions in the $CaCO_3/CaO–SO_2/SO_3$–air system. There are, for instance, the effects associated with calcination, temperature and time of calcination, grain size, carbon dioxide concentration, presence/absence of water vapour and/or additives (e.g. NaCl) and those connected directly with the sulphation of CaO i.e. temperature, concentration of sulphur dioxide [7, 15–17], presence of SO_2 oxidation catalysts (e.g. Pt) [18]. Using thermoanalytical methods, with systematic changes of the experimental conditions (only a single factor at a time), one can draw conclusions as to the effect of that particular factor. Some of these factors can be interdependent.

Two contradictory examples illustrating the effect of temperature on the sulphation of lime are shown below. The TG curves in Fig. 4 [7] indicate maximum sorbent utilization (α) at 1000°C, whereas in Fig. 5 [1], when the sulphation products obtained at 830°C were heated to 900°C and higher, the mass of the products went down. It indicates that some decomposition takes place. Moreover, it was observed that the optimum temperature for desulphurization occurring simultaneously with the combustion of coal in fluidized beds in close to 850°C.

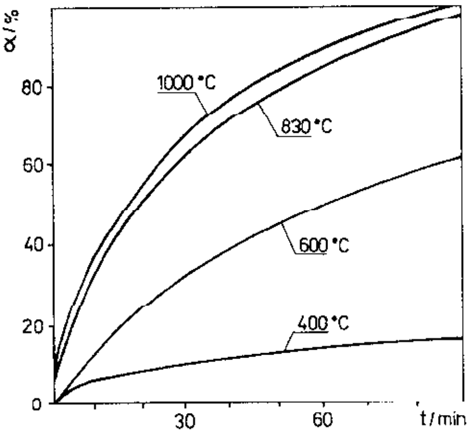

Fig. 4 Illustration of the sulphation of calcined limestone Z at different temperatures, based on measurements with a Q-derivatograph (grain size ca. 0.15 mm); (after [8])

At 950°C the desulphurization efficiency is lower (e.g. [2, 19] and literature cited herein) (Fig. 6). It is worth adding that in both cases, the procedure and the material (limestone Z) were the same, except that the limestone Z in Fig. 4 was in a powdered (grain size ca. 0.15 mm), not in a granular form (grain size ca. 0.5 mm), as for Figs 5 and 6. The explanation of this well known temperature dependence is only deceptively simple. Knowledge of the real phase composition of the products after sulphation of limestone/lime can elucidate the problem.

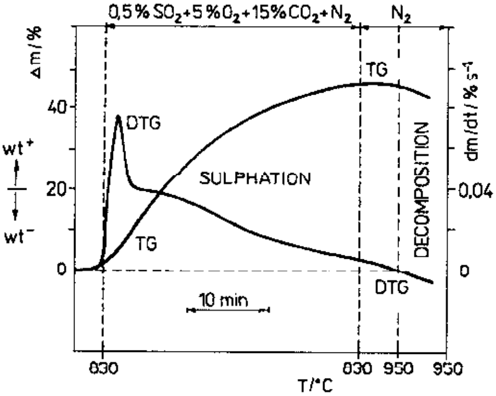

Fig. 5 Illustration of the sulphation of calcined limestone Z using a multistage heating program with a variable atmosphere, based on measurements with a thermoanalyzer TG 50 Mettler 3000 System (grain size ca. 0.5 mm); (after [1])

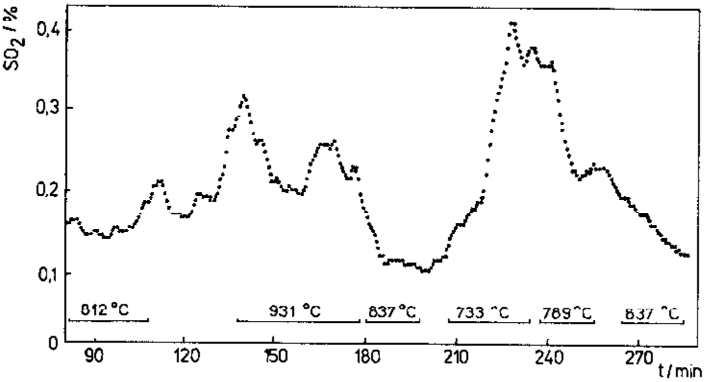

Fig. 6 Temperature dependence of the desulphurization level of gas during combustion of coal in a laboratory scale atmospheric fluidized bed using limestone Z as a sorbent (grain size ca. 0.5 mm); (after [14])

Phase analysis of the sulphation products of limestone Z

Conventional methods, such as IR spetroscopy and X-ray powder diffraction, were inappropriate here, because they can only reveal the main phases present, i.e. $CaCO_3$, CaO and $CaSO_4$. In contrast to the above techniques, backscattered electron imaging (BSE) combined with energy dispersive (EDS) X-ray microanalysis in a scanning electron microscope (SEM) can provide very detailed information on the solid products of limestone sulphation and their localization within the particles. Single particles of limestone and lime were imaged and analyzed using an optimization technique [20–22]. The results of phase analysis made it possible to distinguish two sulphur-bearing solids, $CaSO_4$ and CaS, present in the sulphation products of lime/limestone. Backscattered electron images in black and white (it could be also in colour) for a polished cross-section of a limestone particle are shown in Fig. 7. The phases containing sulphur are present in the outer layers of the particle (grey with bright areas). In the particle interior there is no conversion at all (dark area).

Fig. 7 Backscattered electron photomicrograph of the polished cross section of a sulphated particle of limestone Z (for explanation see text) (grain size ca. 0.5 mm)

Moreover, the concentration of calcium sulphide (CaS) is significantly higher away from the outer surface of a particle. Thus, the calcium sulphate ($CaSO_4$) 'coating' formed on the outside of the particles tends to protect the core against both sulphur oxides and oxygen is essential for the oxidation of CaS. The results on the thermal behaviour of $CaSO_3$ and a physical mixture of $CaSO_4$ and CaS [23] provide supporting evidence for the proposed sulphation mechanism (reaction (2)). It is thus possible to offer [1] a satisfactory explanation of the temperature optimum for flue gas desulphurization in fluidized bed coal combustion, using limestone sorbents, because $CaSO_4$, the main product, at temperatures above 950°C, partly reacts with CaS, with the evolution of SO_2 in the following reaction:

$$3CaSO_{4(s)}+CaS_{(s)} \rightarrow 4CaO_{(s)}+4SO_{2(g)} \tag{5}$$

The above results also have implications from the environmental point of view, because the presence of CaS in the sulphation products may cause difficulties with handling, disposal or utilization of the waste. The final amount of CaS in the sulphation products will be related to sorbent particle size. Thus chances for a fast oxidation of CaS to $CaSO_4$ are important. Then reaction (5) is insignificant, and SO_2 capture can occur at temperatures higher than 900°C. Similar observations were made by Zhang Hong *et al.* [24]. Reduction in particle size can have a favourable effect on the capacity of sorbent and causes the reaction with SO_2 to occur mainly at the surface (Fig. 3). Under practical conditions the presence of some CaS is usually unavoidable.

The above discussion shows that in all reactions involving the solid state, physical factors must always be taken into account, when the detailed mechanism is considered.

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