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CATALYTIC EFFECT OF SODIUM CHLORIDE ON LIMESTONE CALCINATION AND SULPHATION – ELECTRON MICROSCOPY AND EDS STUDIES

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Thermogravimetric studies on the influence of sodium chloride on the kinetics of limestone sulphation were supported by scanning electron microscopy and energy dispersive X-ray microanalysis.

On the basis of morphological observations on calcined and sulphated limestone and elemental microanalysis in an electron microprobe it was found that NaCl affects the sintering, favouring the formation of more compact structures of rounded crystallites during sulphation. Chlorine is largely lost during sulphation. Capacity of the sorbents under both TG and FBC conditions depends strongly on when and how the NaCl is introduced.

The SO_2 generated during the combustion of coal in fluidized beds can react with limestone to give sulphur-containing compounds. Sulphur can be thus retained in the combustor in a solid form [1]. Most investigations concerned with the SO_2/SO_3 capture by limestone sorbents aim at finding methods for reducing limestone requirements to achieve a given level of flue gas desulphurization and thus also reduce the amount of solid wastes produced.

Numerous studies have been conducted on the influence of foreign substances like sodium chloride upon lime/limestone sulphation. Although the literature does not give a consistent picture, most authors agree that sodium chloride promotes the calcination of limestone [2]. Recent work on the effect of NaCl on calcination and SO_2 capture by limestone during fluidized bed combustion of coal is summarized by Shearer et al. [3]. It is important to bear in mind that the effect of NaCl on sulphation depends on the manner in which the salt is introduced into the system.

In this paper, thermogravimetric studies on limestone sulphation are presented, supported by EDS X-ray analysis and morphological observations on calcined and sulphated limestone with and without sodium chloride.

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Experimental

Materials

Natural limestone, quarried in Zabierzow near Cracow (Poland) was used. It had been studied before, during fluidized bed coal combustion experiments [4] and using TG [5–6]. The weight loss on calcination was 43,70% (from TG curves). X-ray fluorescence analysis using Philips PW 1410 equipment gave: CaO – 57,4%, MgO – 0,4%, SiO_2 – 0,5%, Al_2O_3 – – 0,1%.

Preparation of limestone samples with NaCl.

A solution of the proper amount of salt in deionized water was added to dried granular limestone and the resultant slurry was mixed. The sample was then dried in an oven at ca. 420 K. This was a convinient method for obtaining a uniform additive distribution on the surface of the particles and within the accessible pores.

Methods and procedures

Calcination and sulphation of limestone was carried out using a Mettler Thermoanalyzer TA 3000 with a Mettler TC 10 A Processor. Experiments were planned and recorded in the processor using the so-called "method" facility. A method defines the sequence of instructions to be executed automatically during the run.. From among several methods available the basic SCREEN and/or STEP methods were adapted for the purposes of the present work. This consists of arranging a sequence of instructions suitable for the given purpose e.g. entering the operational parameters of the TG system, controlling the furnace, printing out the experimental parameters, plotting the experimental and calculated curves and setting out the results.

The Thermoanalyzer was equipped with a corrosive gas atmosphere accessory, designed by the authors and described in detail previously [6].

Approximately 20 mg sample (particle size 0,5–0,6 mm) were used. They were weighed in a standard alumina crucible (70 μl) using the thermobalance. In order to have reactions to occur without mass transport limitation, the particles were always in a single layer, without touching one another, on the bottom of the sample holder.

The limestone samples with (2%) and without NaCl were calcined at 1100 K and after ca. 10 min sulphated for ca. 60 min at the same temperature in a flow (86,5 ± 2,6 ml/min) of air containing SO_2 (4%). Sulphation was taken into account until the rate of SO_2/SO_3 gas sorption fell below

0,001 mg per sec. (i.e. ca. 0,3% Ca sulphating per minute). Although the rate criterion was used to evaluate sorbent utilization (Fig. 1), the TG data collected could be utilized for any chosen rate or time criteria. In some experiments traces of solid NaCl were injected into the system (TG/DTG) during sample sulphation, so as to act on the partially sulphated product.

Morphological observations on raw, calcined and sulphated samples were carried out using a scanning electron microscope, model JEOL JSM–35 and elemental microanalysis employing an electroprobe (EPMA, model JEOL JSXA–733) equipped with a modern energy dispersive X-ray analysis system (EDS, model Link AN10/85). For the latter measurements a few particles out of each sample investigated were positioned on a strip of double sticky tape and transferred into carbon stubs for subsequent SEM -ED analysis.

Results and discussion

TG/DTG curves for the sulphation of calcined limestone with (L,Cl) and without NaCl (L) under dry conditions are presented in Fig. 1. For the purpose of comparison, the degree of Ca sulphation was assumed to correspond to the formation of calcium sulphate, $CaSO_4$, only. Therefore, the weight increase (Δm) indicated by the TG curve was equivalent to SO_3 absorbed, even it is not quite clear whether SO_2 and/or SO_3 actually reacts.

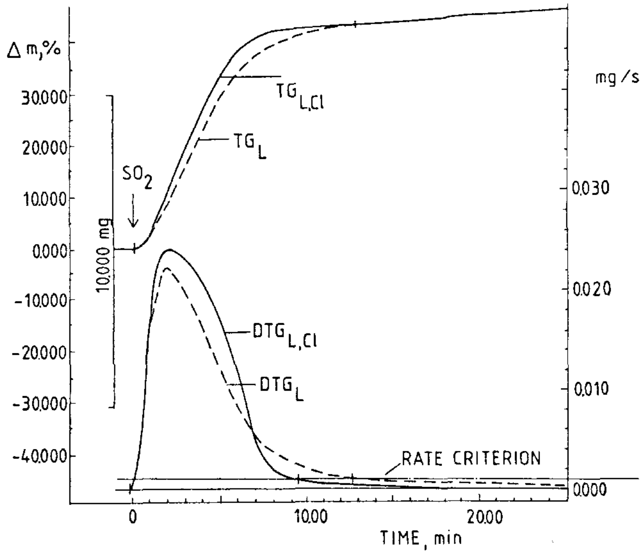

Fig. 1 TG/DTG curves of sulphation of limestone a) without NaCl (L,Cl) b) with NaCl; isothermally at 1100 K

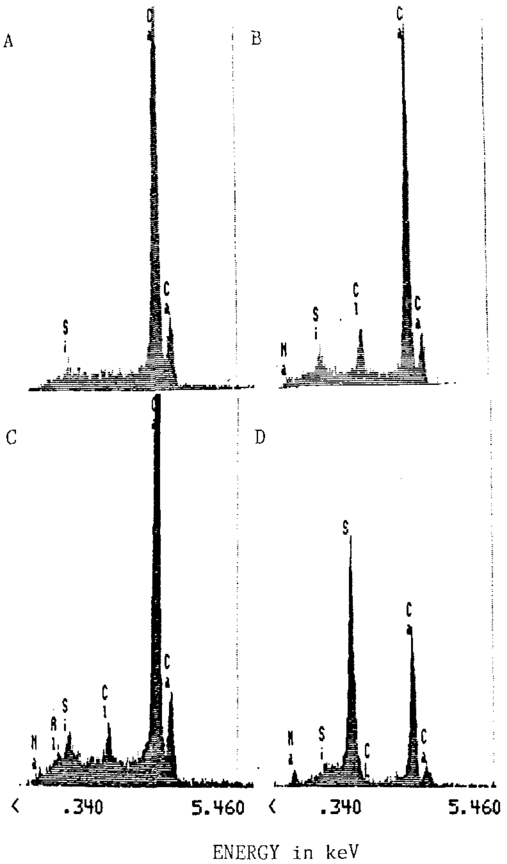

Fig. 2 Energy dispersive X-ray spectra representative of different particles: a) limestone (L) b) limestone with NaCl (L,Cl) c) calcined L,Cl d) sulphated L,Cl

From the DTG curves it can be seen that the sulphation takes place in three stages. I – $\mathrm{d}m/\mathrm{d}t$ increases up to a maximum over a period of time which is the same for both cases (1,9 min), II – $\mathrm{d}m/\mathrm{d}t$ decreases fairly rapidly, but not at the same rate – L,Cl appears to be more active towards the sulphating agent, and III – $\mathrm{d}m/\mathrm{d}t$ decreases slowly over an extended period of time. The degree of Ca utilization (α) in spite of slightly higher value of $\mathrm{d}m/\mathrm{d}t$ for L,Cl [0,02232 mg/s, 0,02268 mg/s] is close to 42%, using the rate criterion mentioned above. Differences in kinetics of SO_2/SO_3 capture by L and L,Cl are confirmed by different times of sulphation up to the value of $\mathrm{d}m/\mathrm{d}t$ = 0,3% Ca/min (9.45 min, 12,87 min, respectively). Previously used time criterion for the characterization of sorbent reactivity was unsatisfactory [5]. From detailed analysis of TG/DTG curves it can be concluded that samples of limestone impregnated with NaCl show differences in the sulphation kinetics but have similar capacity for SO_2/SO_3 capture.

Energy dispersive X-ray spectra made it possible to ascertain the fate of the sodium and chlorine introduced into the limestone by NaCl impregnation. The spectrum of Fig. 2a is typical of the majority of limestone particles investigated. All samples included particles in which silicon was present being presumably a form of quartz. The spectrum shown in Fig. 2b was obtained for L,Cl and, as expected, Cl and NaCl are present. After calcination of L,Cl both Na and Cl are still present. – Fig. 2c, but after sulphation only Na appears to the present on the surface and the evidence for the presence of Cl is weak – Fig. 2d. What is the chemical fate of Na and Cl under the present conditions – is not an academic question [7].

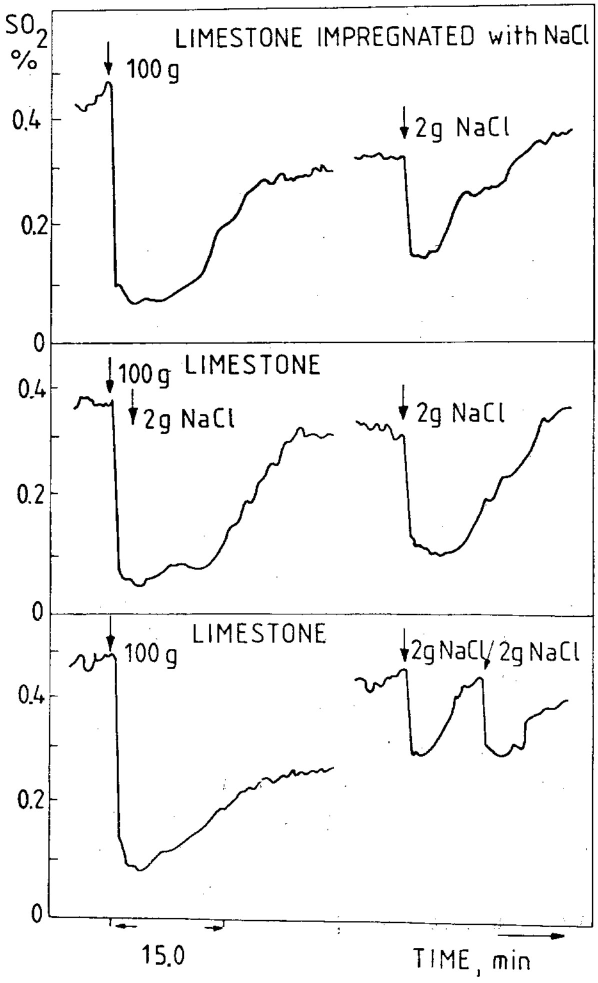

Fig. 3 Re-drawn from [9]. The effect of introducing NaCl to a FBC at various stages after batch sorbent addition. SO_2 concentration in the flue gases as function of time

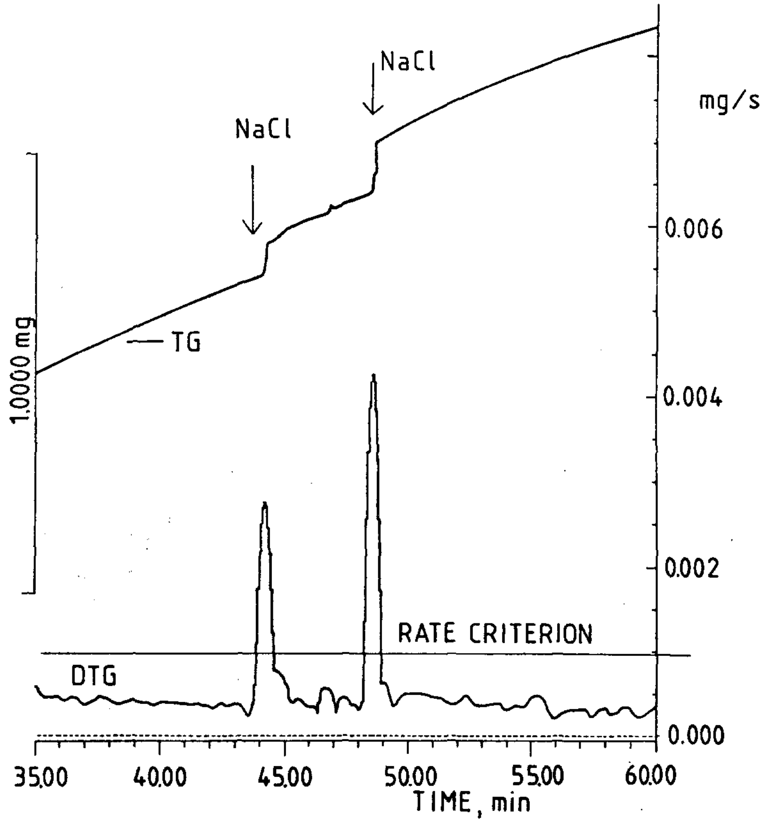

Fig. 4 TG/DTG curves of sulphation of limestone – the effect of introducing (batchwise) NaCl to partially sulphated sorbent

The morphologies of L and L,Cl after calcination and sulphation can be seen in Figs. 5–9. Calcine without NaCl (Fig. 6) shows a "brain – like" texture and is porous without any evidence of the presence of crystallites. It is a fact that the presence of small amounts of NaCl promotes sintering of the calcine which enables larger pores to be formed (Fig. 7). In general, these results are consistent with the work of Shearer et al. [8].

It is evident that sulphation reduces the porosity of the surface. For limestone, L, the surface is covered with a sponge – like network (Fig. 8). With NaCl (L,Cl) the reduction of porosity is enhanced and the structure consists of rather closely packed rounded crystallites (Fig. 9). These results should be supplemented by comparative surface area and pore – volume – pore size distribution measurements [7].

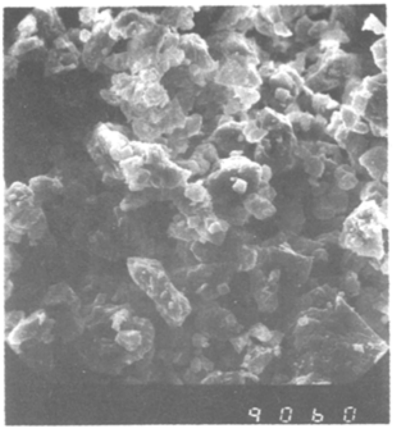

Fig. 5 Scanning electron micrograph of limestone, L

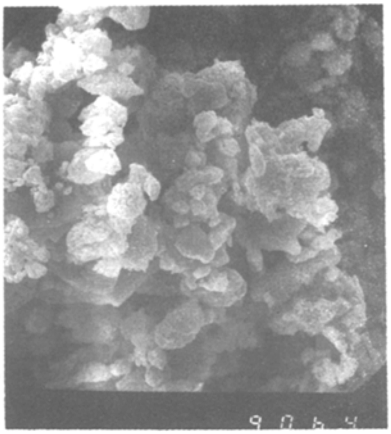

Fig. 6 Scanning electron micrograph of calcined limestone

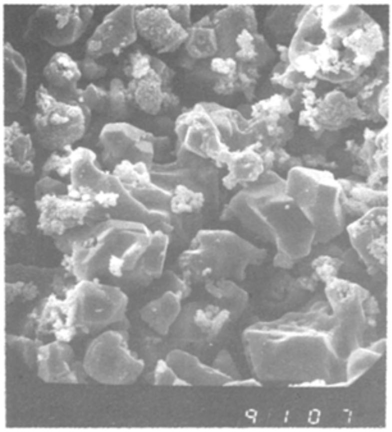

Fig. 7 Scanning electron micrograph of calcined limestone with NaCl

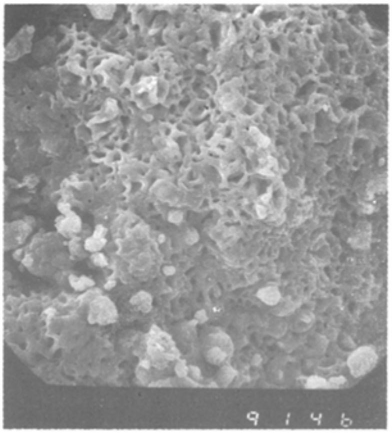

Fig. 8 Scanning electron micrograph of sulphated limestone

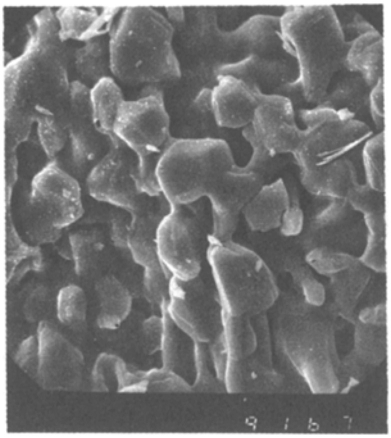

Fig. 9 Scanning electron micrograph of sulphated limestone with NaCl

It would, however, be wrong to attach too much importance to surface sintering and the effect of the additive on it, because as has been shown above (Fig. 1) the presence of NaCl modifies the sulphation kinetics and not the sorbent capacity. The presence of NaCl – together with limestone added to a FBC batchwise [9] should thus have little affect on sorbent utilization as observed – Fig. 3.

As attempt was made to reproduce the conditions when NaCl was added to partially sulphated, but already inactive sorbent [9, 10]. The results are shown in Figs. 3 and 4 – more SO_2 is taken up. The presence of pores and the size of the pores formed on calcination is important – the sulphation of calcined limestone is a strongly diffusion – limited reaction, but chemical processes, taking place at the molecular level, and the possibility of the formation of short – lived intermediates in the course of sorbent sulphation should not be overlooked.

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Zusammenfassung – In Verbindung mit Scanning Elektronenmikroskopie und Röntgenmikroanalyse wurden thermogravimetrische Untersuchungen des Einflusses von Natriumchlorid auf die Kinetik der Sulfierung von Kalkstein durchgeführt.

Auf der Grundlage von morphologischen Beobachtungen an kalziniertem und sulfiertem Kalkstein und durch Elementarmikroanalyse in einem Elektronenstrahlmikroanalysator wurde festgestellt, daß NaCl das Sintern beeinflußt. Infolgedessen wird bei der Sulfierung die Entstehung von abgerundeten Kristalliten begünstigt. Chlor wird während der Sulfierung größtenteils abgegeben. Die Kapazität der Sorptionsmittel hängt sowohl bei TG als auch bei FBC stark davon ab, wann und wie das NaCl eingebracht wurde.

Резюме – Термогравиметрические изучения влияния хлорида натрия на кинетику сульфатирования лиместона были подтверждены методом сканирующей электронной микроскопии и рентгеновским микроанализом с рассеянием энергии. На основе морфологических наблюдений и элементного микроанализа кальцинированного и сульфатированного лиместона было найдено, что хлорид натрия затрагивает спекание, способствующее образованию более компактных округленных кристаллитов в процессе образования сульфата. Хлор большей частью выделяется в процессе сульфатирования. Сорбционная способность лиместона в значительной мере зависит от того, когда и каким образом вводился хлорид натрия.