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The effect of the porous structure on sorbent sulfation under coal-fired boiler conditions

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Abstract

A study of the behavior of different sorbents (3 limestones, a commercial calcium carbonate and a commercial calcium hydroxide) in the sulfation process has been carried out in a drop-tube, using similar conditions to those existing in sorbent injection in pulverized-coal boilers. The main variables affecting the sulfation process have been analyzed, namely, Ca/S molar ratio, SO_2 concentration, temperature, sorbent particle size and reaction time.

The work concentrates on the evolution of the porous system in the sorbents and its influence on their sulfation capacity. A direct relation between chemical structure (calcium hydroxide–calcium carbonate) and sorbent reactivity was not found. Sorbents with a widespread pore size distribution with pores above 100 Å showed the highest reactivity and sulfation capacity, maintaining pores of small size (under 80 Å) at all times and operating conditions. In the less reactive sorbents, pores less than 80 Å became blocked during sulfation, being more sensitive to the effect of the different operating variables affecting the sulfation process.

Keywords: Coal-fired boilers; Pore size; Sorbent; Sulfation

1. Introduction

It is commonly accepted that SO_2 emissions from coal-fired boilers are an important contributor to acid rain. The injection of calcium-based sorbents into the post-flame zone is used to reduce these emissions. This system can be adapted to existing boilers by not very complex modifications. In fact, the limestone-injection multistage burner (LIMB) is a potentially attractive technology for the reduction of pollutants.

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The main disadvantage of this process is the low calcium-utilization efficiency due to the adverse conditions existing in the boilers, namely, high temperature and low residence times. Several processes take place simultaneously in the sorbent when it is injected into the boiler [1]: calcination, sinterization and sorbent sulfation. The sorbent calcination generates a porous solid (lime), which reacts with the SO_2 producing calcium sulfate. Since $CaSO_4$ has a greater molar volume than CaO, pore blockage takes place during reaction. The sinterization process also affects the porous system of the sorbent, decreasing the surface area.

The sulfur retention achieved strongly depends on the material used as sorbent [2, 3]. Moreover, knowledge of the process is basic for the design of the sorbent injection in pulverized-coal boilers. In this work, a study of the behavior of several sorbents (3 limestones, 1 commercial calcium carbonate and 1 commercial calcium hydroxide) was carried out in a drop-tube system, which allowed us to simulate the conditions existing in the boiler. The main variables affecting the sulfation process have been studied, namely, Ca/S molar ratio, SO_2 concentration, temperature, sorbent particle size and residence time. To do this, the SO_2 retention, sulfation conversion and porous structure evolution were measured with these variables.

2. Experimental

The installation used in the experimental work is shown in Fig. 1. The desired reactant gas was prepared by blending N_2, CO_2 and O_2, measured and controlled by specific mass-flow controllers. The H_2O content was obtained by bubbling the gas mixture through water at the desired temperature. Finally, the SO_2 was added, yielding a gas with similar composition to an exhaust gas of a pulverized coal-fired boiler: 76% N_2, 15% CO_2, 2% O_2, 7% H_2O and a variable SO_2 concentration.

One of the most important difficulties existing in this type of experimentation is the design and operation of the sorbent-feed system, due to the small particle size of the sorbent and the small flow rates required. Several authors have proposed different systems for feeding small particles [4–6]. In this work, a volumetric syringe-type feeder with an entraining system for the solids, was used. A small flow of gas was passed through the solid inside the syringe to keep the solid expanded. The mass flow rate of the sorbent feed was proportional to the rotating rate of the rotor moving the syringe. The particle feeder was capable of injecting sorbent as small as 5 μm at a rate of between 0.1 and 1 g min^{-1}. The gas flow rate varied from 6 to 60 lN min^{-1} to control the particle residence time from 0.4 to 1.5 s respectively, at temperatures from 900 to 1100°C.

The synthetic gas and the sorbent entered at the top of the reactor and passed downward through a 4.2 cm ID × 200 cm fused alumina reactor tube. Two Nicrosil–Nisil thermocouples located at 40 and 160 cm from the top were used to measure the temperature in the reaction zone.

At the gas exit line, the SO_2 and CO_2 concentrations were measured continuously by two IR analyzers. A blast gas (N_2) was added to the exit stream to dilute the reacting

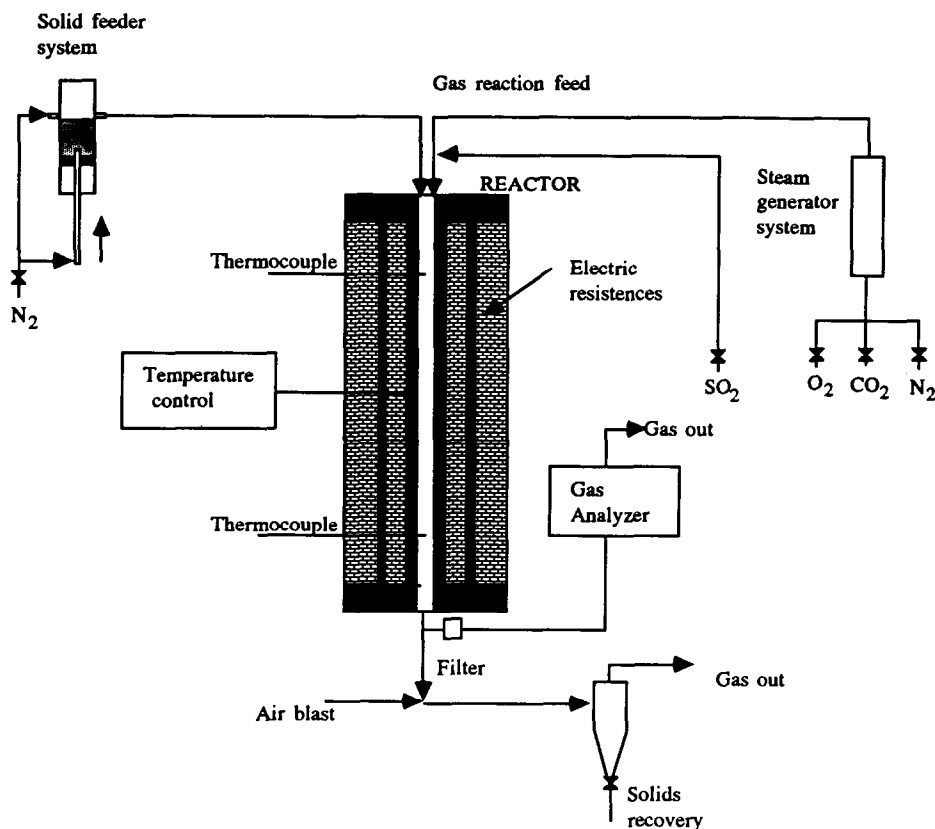Solid feeder
system

Gas reaction feed

Fig. 1. Experimental device.

gas, thus avoiding possible recarbonation of the samples. After that, the sorbents were collected in a high-efficiency cyclone, which is heated to avoid hydration of the reacted sorbent. The analyses showed that hydration during sample handling was kept within 1 % in all cases. The collected samples were later analyzed by thermogravimetry and N_2 physisorption.

A TG method [7] developed for the analysis of reaction products in coal combustion processes with limestone addition was used to determine the $Ca(OH)_2$, $CaCO_3$, CaO and $CaSO_4$ content of the sorbent. The method involves heating the sample in an N_2 atmosphere to 900°C. During the heating period, the succesive weight losses corresponded to the evolution of moisture (≈ 100°C), the dehydroxylation of $Ca(OH)_2$ (≈ 400°C), and the decomposition of $CaCO_3$ (≈ 800°C). Then, a mixture 70–30% of H_2/N_2 is introduced to reduce the $CaSO_4$ to CaS. The CaO is obtained by difference, taking into account the sorbent purity.

The sulfation conversion, X_s, for the calcium carbonate or calcium hydroxide respectively, was obtained by means of the following equations

$$X_s(\%) = \frac{n_{CaSO_4}}{n_{CaO} + n_{CaCO_3} + n_{CaSO_4}} \times 100 \tag{1a}$$

$$X_s(\%) = \frac{n_{CaSO_4}}{n_{CaO} + n_{Ca(OH)_2} + n_{CaSO_4}} \times 100 \tag{1b}$$

where n is the number of moles in the sample and the subscripts indicate the different calcium species.

The porous system of the reacted solids was measured by N_2 physisorption at 77 K, determining BET surface areas and incremental surface areas BJH.

2.1. Materials

Five sorbents of different characteristics have been employed in this work: 3 limestones (LIM1, LIM2, LIM3), a commercial calcium carbonate (CCC) and a commercial calcium hydroxide (CCH). The three limestones were selected because of their different textural systems. Fig. 2 shows the porous system of the sorbents calcined at 1000°C, 15% CO_2 and 1 s residence time. Two different types of porous systems can be distinguished: LIM1, LIM2 and CCC show a porous system mainly composed of pores
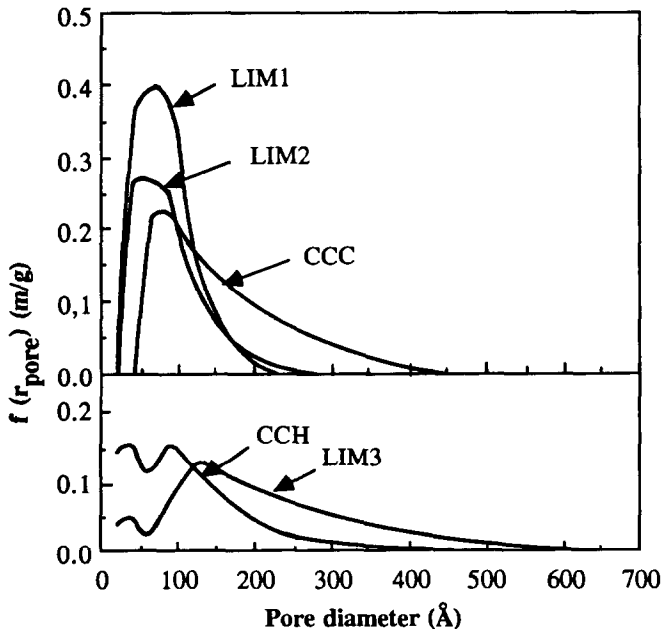
Fig. 2. Porous system of the calcined sorbents; 1000°C, 15% CO_2, 1 s.

under 200 Å, whereas CCH and LIM3 show a more widespread distribution, with pores up to 600 Å.

The limestones were sieved into samples of narrow particle size distribution by wet-screening, yielding three different particle size fractions: +5–10, +40–50 and +80–90 μm. Commercial sorbents were used as received. The mean particle diameter of these sorbents was determined by photosedimentation giving values of 36 μm for the CCC and 6 μm for the CCH, respectively.

3. Results and discussion

Since the sulfation of small particles at high temperatures is a complex process involving multiple mechanisms and changes inside the sorbent particle, the study of the sorbent behavior must be carried out in similar conditions to those existing in a coal-fired boiler. In this work, the main variables affecting the sorbent sulfation have been studied through knowledge of the sulfation conversion and the evolution of the porous system of the sorbent under different conditions.

3.1. Effect of the Ca/S molar ratio

The Ca/S molar ratio fed is a basic parameter affecting the sulfur retention in the boiler. The amount of sorbent added to the boiler to retain the SO_2 generated in the coal combustion will affect both the cost of the whole process and the amount of residue generated.

Different Ca/S molar ratios between 0.75 and 2.6 were used in the experimentation at 1000°C, 1 s residence time and 2000 ppm of SO_2. The particle size cut of +40–50 μm was used for the limestones. The sulfur retention (SR) was calculated through the gas composition at the outlet of the reactor via the equation

$$SR(\%) = \frac{C_{SO_{2i}} - C_{SO_{2f}}}{C_{SO_{2i}}} \times 100 \qquad (2)$$

where C_{SO2i} is the SO_2 concentration in the feed stream and C_{SO2f} the concentration after reaction.

Fig. 3 shows the sulfur retention (SR) obtained in the reactor as a function of the Ca/S molar ratio in the feed for the five sorbents. As expected, an increase in the Ca/S molar ratio produced an increase in the sulfur retention, which was different for each sorbent used. The highest retentions were obtained with the LIM3 and CCH sorbents.

Fig. 4 shows the sulfation conversion, X_s, obtained by using Eq. (1) for the different sorbents. In all cases, an increase in the Ca/S molar ratio produced a decrease in the sulfation conversion, mainly due to the decrease in the reaction rate by the lower SO_2 concentration present around the sorbent particles for the same residence time. The pronounced decrease in the sulfation conversion obtained with CCH should be noted. This may be due to the higher calcination rate, starting at 400°C, and the higher sulfation reactivity, which produced rapid pore shrinkage and blockage.
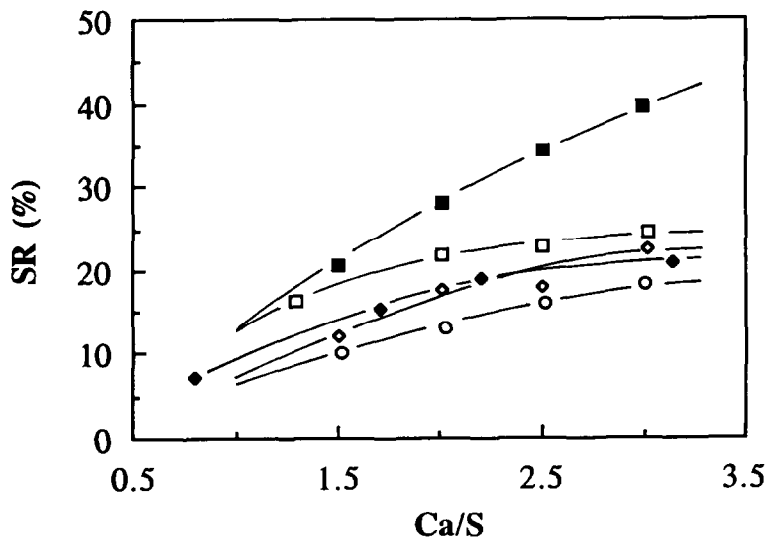
Fig. 3. Sulfur retention as a function of the Ca/S molar ratio; 2000 ppm SO_2, 1000°C, 1 s. (LIM1 ○, LIM2 ◇, LIM3 ■, CCC ◆, CCH □).
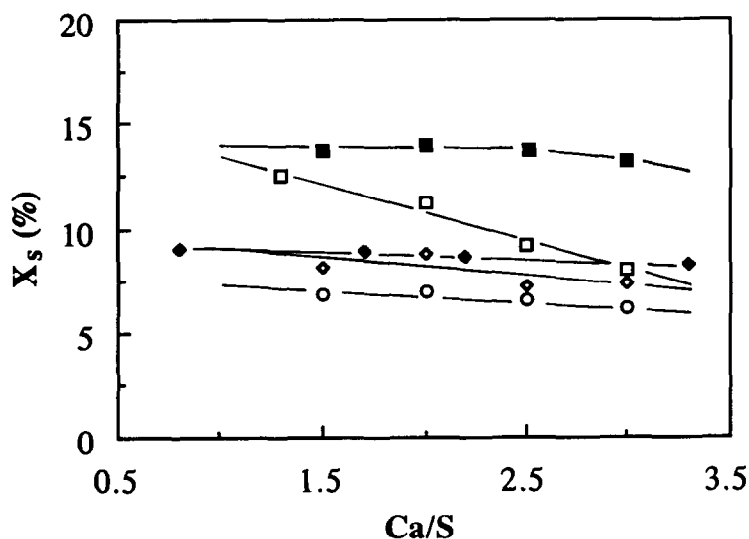

Fig. 4. Sulfation conversion as a function of the Ca/S molar ratio. (Symbols as in Fig. 3.)

3.2. Effect of SO_2 concentration

The SO_2 concentration in the boiler will depend on the sulfur content of the coal used. Concentrations of 3000 ppm or even higher can be measured when using high sulfur content coals.

In this work, three different SO_2 concentrations: 1000, 2000 and 3000 ppm, were used in the experimental work. Fig. 5 shows the sulfation conversions obtained as a function of the SO_2 concentration used in the feed for the five sorbents. An increase in the SO_2 concentration gave an increase in the sorbent conversion, except for the LIM2 sorbent, where a maximum with concentration was obtained. This maximum was also obtained in a previous work when using this limestone with higher particle sizes, typical of those used in fluidized bed combustors [8]. This can be due to the different simultaneous processes taking place in the sorbent, calcination, sinterization and sulfation, and to the specific porous system of this limestone.

In any case, an increase in the SO_2 concentration produced an increase in the mean pore size for the five sorbents used in the work. However, more information about the processes taking place inside the sorbent during sulfation is obtained when studying the porous system of the sorbent. Two different behavior types have been found in the evolution of the porous system during sorbent sulfation, the first for LIM1, LIM2 and CCC, and the second corresponding to LIM3 and CCH. For comparison, two sorbents representative of these two behavior types were subsequently investigated to determine the effect of different variables on the porous system and their relation with the sulfation capacity of the sorbent.

Fig. 6 shows the density of the incremental surface area BJH as a function of the pore diameter in the sulfation of the LIM3 and CCC sorbents when using different SO_2 concentrations. In the commercial calcium carbonate (CCC), a progressive decrease in the number of the smallest pores can be observed when the SO_2 concentration increases. This is not only due to the total pore blockage of the smallest pores but also
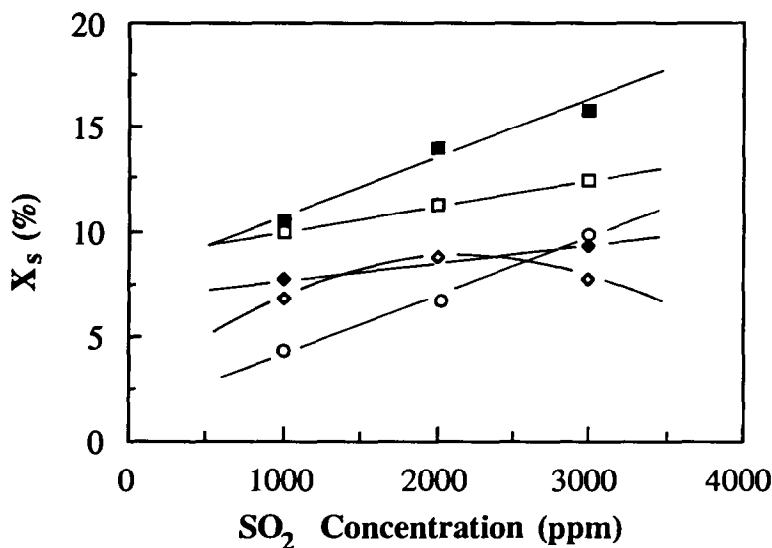

Fig. 5. Sulfation conversion as a function of the SO_2 concentration; 1000°C, 1 s. (Symbols as in Fig. 3.)
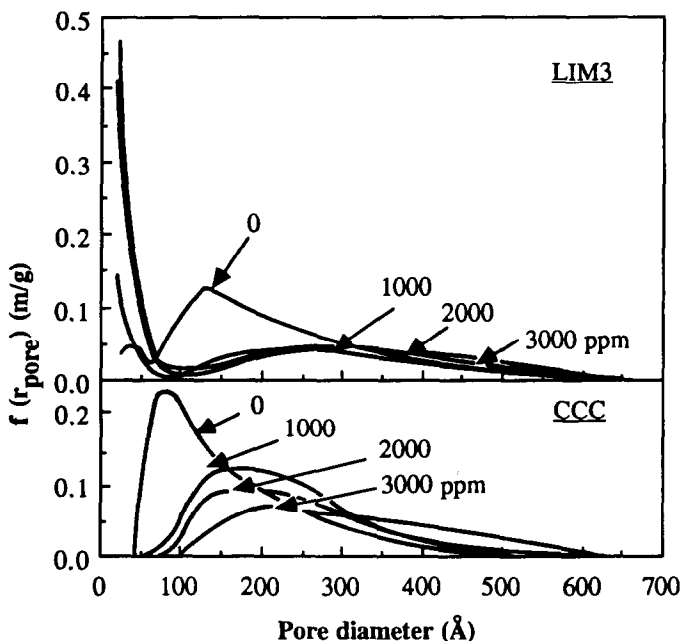
Fig. 6. Density of incremental surface area BJH as a function of the SO_2 concentration.

to the formation of pores of higher size by sinterization. Conversely, for the limestone LIM3, the smallest pores become narrower but never totally disappeared. This is due to two possible reasons: different pore shapes are formed in the different sorbents, as observed in the adsorption–desorption isotherms obtained in the physisorption analysis; Gullet and Bruce [9], Bruce et al. [10] and Beruto et al. [11] proposed plate-shaped pores in $Ca(OH)_2$ and cylindrical pores in $CaCO_3$. The second reason is that pore blockage is more difficult in these sorbents because their pores are larger.

3.3. The effect of temperature

The combustion chamber temperature determines the location of the limestone injection points in the boiler, in order to achieve maximum sorbent utilization. In this work, the effect of the temperature on the sorbent sulfation was studied. Fig. 7 shows the sulfation conversions obtained for the different sorbents when using 2000 ppm of SO_2, a Ca/S molar ratio of 2 and a residence time of 1 s. A maximum was obtained both in the sulfation conversion and, as a consequence, in the sulfur retention. This maximum was found in the range 1050–1100°C for all the sorbents, according to results obtained by other authors. Bortz and Flament [12] found the maximum at 1100°C, Milne et al. [13] at 1130°C, and Bortz et al. [14] found it at temperatures above 1180°C. The opposing effects of the calcination rate, gas diffusion into the pores and into the product layer, in one sense, and the sinterization rate and the decrease in the surface
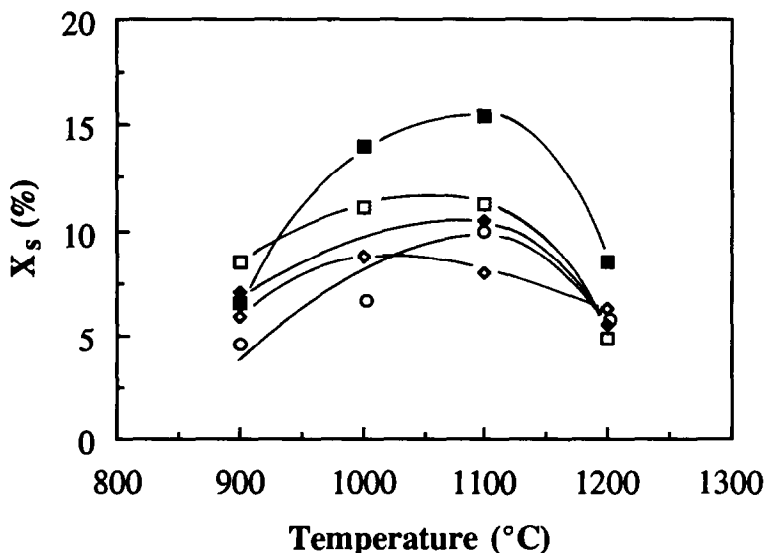
Fig. 7. Effect of the temperature on the sulfur conversion; 2000 ppm SO_2, 1 s. (Symbols as in Fig. 3.)

area affecting the sulfation rate, in the other, determine this maximum. Moreover, an increase in the equilibrium pressure of SO_2 can be found when the temperature of decomposition of $CaSO_4$ is reached. A temperature of 1125°C was proposed by Milne et al. [13] for the sulfate decomposition.

To analyze the effect of the temperature on the porous structure of the sorbent, the BET surface area was measured as a function of the temperature for the five sorbents. For the less reactive sorbents (LIM1, LIM2 and CCC), the BET surface area remained constant between 900 and 1000°C, decreasing later at higher temperatures. For the more reactive sorbents (CCH and LIM3), a sharper decrease with increasing temperature was found. This behavior was especially marked for the limestone LIM3, where a decrease from 20 m^2 g^{-1} at 900°C to 7 m^2 g^{-1} at 1200°C was found.

The evolution of the porous system of the sorbents showed important differences in the behavior of the more and less reactive sorbents. Fig. 8 shows the evolution of the porous system of LIM1 and LIM3 obtained in the sulfation at different temperatures, as representative of the behavior of the different types of porous structure. For the less reactive sorbents (LIM1, LIM2 and CCC), an increase in the porous surface with temperature was initially found due to the calcination process, with a further decrease at temperatures of about 1100°C, due to pore blockage by higher sulfation. At 1200°C, a decrease in the surface area density was found in all the ranges of pore size, although some small pores are formed by sulfate decomposition.

A different behavior was shown by the most reactive sorbents (LIM3 and CCH), where a decrease in the density of surface area was found in the range 100–600 Å when increasing temperature, due to pore shrinkage. Since small pores were found in all cases
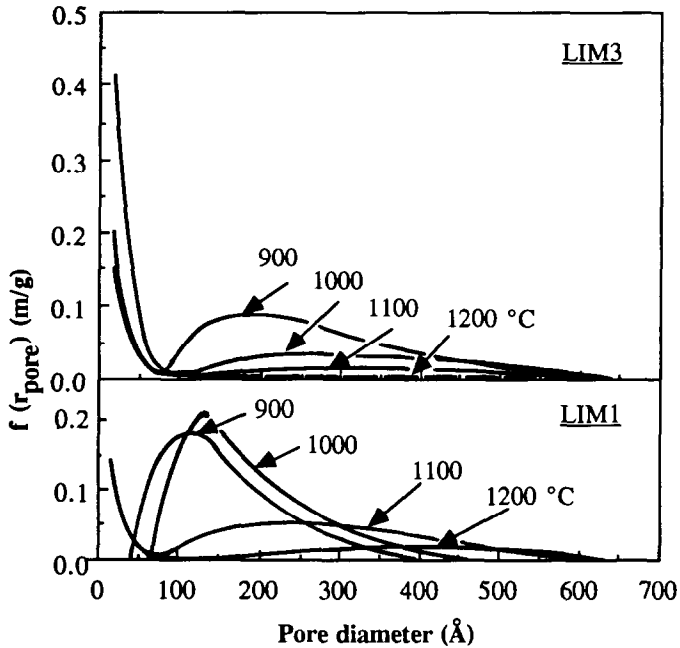
Fig. 8. Effect of the temperature on the porous system of the sorbents.

after sulfation, a dominant process of pore shrinkage over pore blockage can be observed.

3.4. The effect of sorbent particle size

The sulfation capacity of a sorbent strongly depends on the particle size, because the pore blockage makes sulfation of the inner parts of the sorbent impossible. Three different particle sizes of the limestones (LIM1, LIM2 and LIM3) were selected in order to study the effect of particle size on the sulfation process: $+5$–$10\ \mu m$, $+40$–$50\ \mu m$ and $+80$–$90\ \mu m$.

In all cases, an increase in the particle size produced a decrease in the sulfation conversion. Analysis of the recovered samples showed an increase in the BET surface area with increasing particle size of the sorbent. The variation of the pore size distribution during the sulfation for the different particle sizes of sorbent is a complex process, which depends on the initial porous characteristics of the sorbent as well as on the relative rates of the different processes involved, namely, calcination, sinterization, gas diffusion in the pores and in the product layer, and the chemical reaction. Some of these processes depend in different ways on the particle size. Calcination shows a quadratic or simple dependence on the particle diameter when diffusional or kinetic control is present. The sintering process depends on the calcination conversion through the time available after calcination. However, the smallest particles quickly reach total
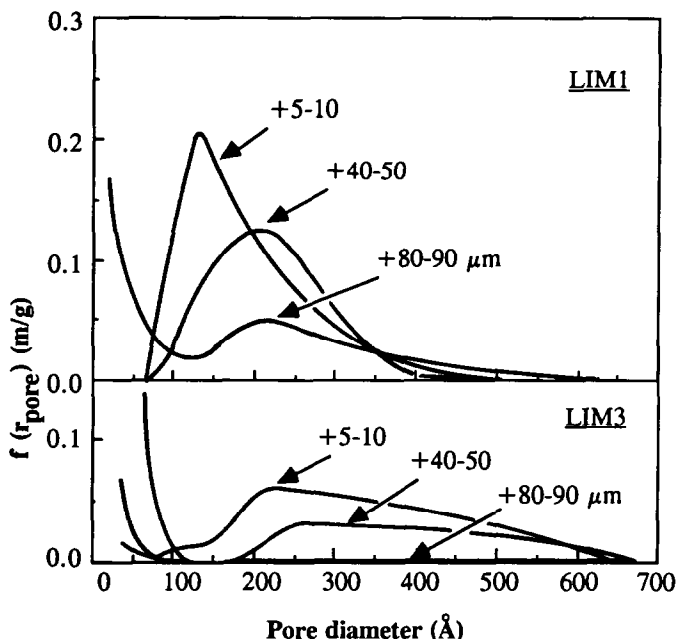
Fig. 9. Density of incremental surface area BJH for different sorbent particle sizes; 1000°C, 2000 ppm SO_2, 1 s.

calcination, allowing the later sulfation of the lime. This process will be different in larger particles in which the sulfation and calcination occurs simultaneously. Moreover, the gas diffusion in the pores will be slower as the particle size increases.

As an example, Fig. 9 shows the density of the incremental surface area BJH as a function of the pore diameter for different particle sizes and for two sorbents of different reactivity (LIM1 and LIM3). For LIM1, the particle size of +5–10 μm showed the absence of pores smaller than 80 Å due to the pore blockage and sintering suffered during the sulfation process. Particles of +80–90 μm showed an appreciable amount of pores of small size due to the small sulfation conversion and the lower sintering by the lower calcination conversion reached during the reaction time. The intermediate particles, +40–50 μm, showed an intermediate situation between those described above.

For the most reactive sorbents, such as LIM3, pores of small size, under 80 Å, were found for the three sizes. The small density of incremental surface area BJH found for the +80–90 μm particles where the porous system was not developed, mainly due to the small calcination conversion reached at this reaction time, is to be noted.

3.5. The effect of reaction time

The high temperatures existing in the combustion chamber of the pulverized coal boilers, together with the small particle sizes, allow the sulfation of the sorbents at low
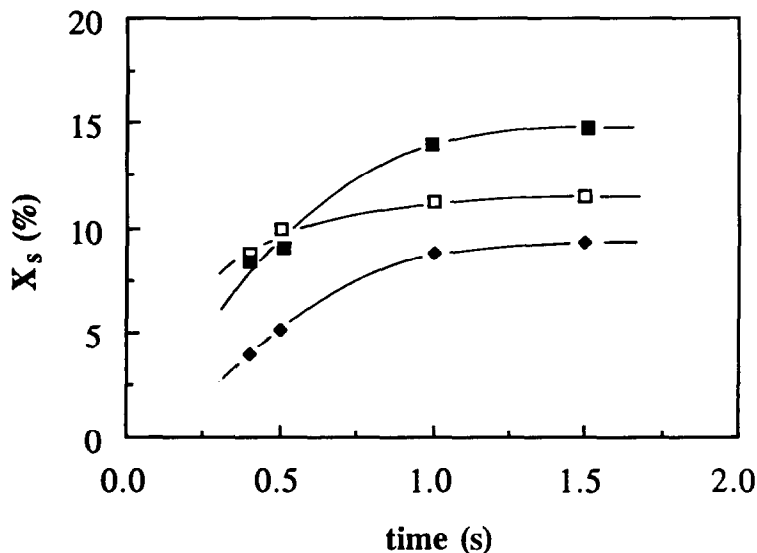
Fig. 10. Sulfur conversion as a function of the reaction time; 2000 ppm SO_2, 1000°C. (Symbols as in Fig. 3.)

residence times, generally under 2 s. Different processes take place inside the sorbent during this time: heating, calcination, sulfation and sinterization.

The effect of the residence time on the SO_2 retention was studied with three sorbents: CCC, CCH and LIM3. Different reaction times between 0.4 and 1.5 s were used by varying the linear gas velocity and keeping the other system variables constant.

Fig. 10 shows the sulfation conversion as a function of the reaction time for the three sorbents. Obviously, an increase in the reaction time produces an increase in the sulfation conversion until the maximum sulfation is reached. It must be noted that about 70% of the final sulfation is reached in the first moments of the reaction (times lower than 0.4 s). These results agree with those obtained by other authors, who found that the sulfation takes place in the first instants of the process, when the reaction is controlled by diffusion in the pores or by the chemical kinetics, decreasing later by the change to diffusional control in the product layer [1, 13, 15, 16].

The increase found in the sulfation conversion with time produced a decrease in the BET surface area, especially for the LIM3 sorbent, which showed the highest sulfation capacity. However, the study of the evolution of the porous system of the sorbents with time is more noteworthy. Fig. 11 shows the density of incremental surface area BJH for two sorbents of different reactivity at several reaction times. It can be observed how the pore size distribution moves toward pores of higher size as the reaction progresses, i.e., when the reaction time increases, for both types of sorbents. However, the smallest pores remain, even at the highest reaction times, for the most reactive sorbents.
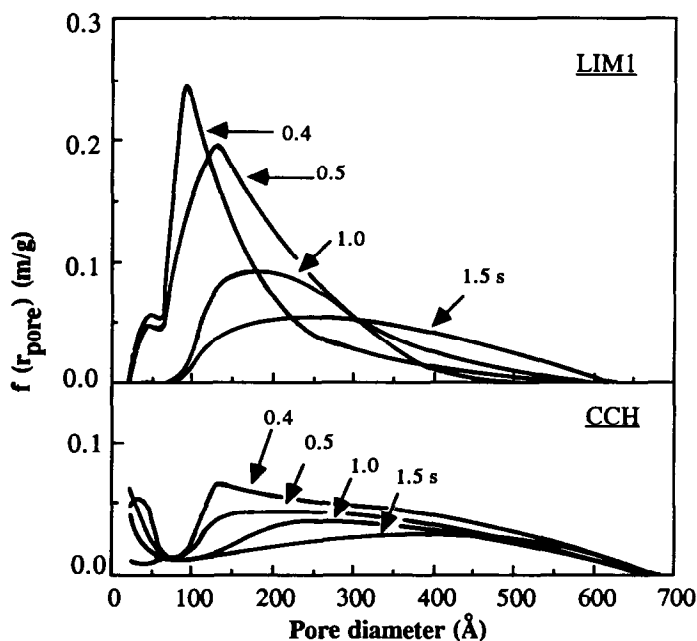
Fig. 11. Density of incremental surface area BJH at different reaction times.

4. Conclusions

The effect of the porous system on the sorbent sulfation process in conditions similar to those existing in pulverized-coal boilers has been studied by using sorbents of different characteristics. A direct relation between chemical structure (calcium hydroxide–calcium carbonate) and sorbent reactivity was not found. In this way, two different behaviors were found. Sorbents with a widespread pore size distribution with pores above 100 Å showed the highest reactivity and sulfation capacity, maintaining pores of small size (under 80 Å) at all times and operating conditions. In the less reactive sorbents, pores under 80 Å became blocked during sulfation, being more sensitive to the effect of the different operating variables affecting the sulfation process, such as the SO_2 concentration or the temperature.

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