

Factors affecting the thermogravimetric technique in the characterization of sorbents for AFBC

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(Received 5 August 1992)

Abstract

Thermogravimetric analysis (TGA) is a technique usually employed for characterization of sorbents used in fluidized-bed coal combustors. Different sorbent characterization studies by TGA display great differences depending on the experimental conditions used. Mercury porosimetry and sulphation experiments made with calcined sorbents indicate that sorbent reactivity is strongly affected by the calcination conditions. In this paper, the effect of the experimental technique (sample heating rate, time before sulphation, CO₂ concentration and sorbent particle size) on the sulphation is analysed. Such effects were stronger in limestones with small pores due to the sinterization effect. In addition, limestones with large pores showed the greatest capacity to react with the SO₂. A set of experimental conditions for the characterization of sorbents in order to obtain reliable results is proposed.

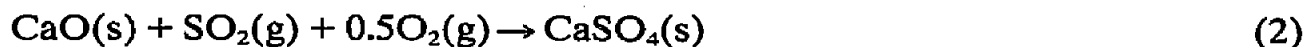
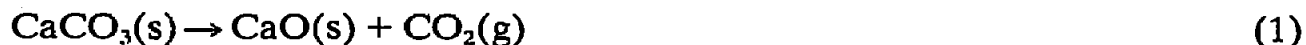
LIST OF SYMBOLS

r_s	(=2.4285), ratio between the molecular weights of CaSO ₄ and CaO
t	time (s)
t_{cal}	time from the beginning of the calcination to the beginning of the sulphation (s)
$t_{\text{cal,min}}$	time from the beginning of the calcination to the end of the calcination (s)
w	weight of the sorbent (kg)
w_{CaO}	weight of the calcined limestone (kg)
w_{CaO}^0	initial weight of the calcined limestone (kg)
x_s	sulphation conversion (kg kg ⁻¹)
Δx_s	incremental sulphation conversion from the conversion attained at $t_{\text{cal,min}}$
ρ_{ap}	apparent solid density (g cm ⁻³)

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INTRODUCTION

The use of calcium-based sorbents, such as limestone or dolomite, in fluidized-bed coal combustors (FBC) permits the reduction of the sulphur dioxide levels emitted into the atmosphere. The principal reactions that take place in the sorbent are



The sorbent calcination generates a porous solid (lime), which reacts with the SO_2 producing calcium sulphate. Because CaSO_4 has a greater molar volume than CaO , pore blockage takes place during the reaction and complete conversion of the sorbent cannot be achieved. Also, important differences between sulphur retentions reached when working at boiler scale were obtained with different limestones. Consequently, it is important to be able to predict adequately the sorbent behaviour before using it in the boiler.

The principal properties used for the sorbent characterization [1] are chemical composition, density, pore size distribution, porosity, surface area, attrition rate, and reactivity. Different techniques are used for the determination of these properties. True densities of limestones, pore size distributions and particle porosities of calcined limestone can be determined by mercury porosimetry and the specific surface area can be determined by B.E.T. The batch attrition tests give information about the sorbent strength and its possible use in FBC. Thus, limestones with high porosity which perform well with respect to their sulphur retention capacity would not be employed in some cases in FBC because of their poor physical strength.

By studying 23 limestones and dolomites, Dam-Johansen and Ostergard [2] showed that the sulphur dioxide retention capacity of the sorbents was correlated with the physical texture and, hence, with geological age. However, it was not possible to predict the performance of a given limestone from its chemical composition and physical properties alone [3] although the initial porosity and pore size distribution of the calcined lime were used as indicators of the sulphur retention capacity [4].

The principal methods to determine the reactivity of the sorbents are the batch fluidized bed reactor (FBR) and thermogravimetric analysis (TGA). The first allows sorbent characterization in conditions similar to those present in a fluidized bed combustor, even though, due to the batch character, the SO_2 concentration is not constant during the sulphation. TGA is usually applied to measure the sulphation of the sorbents because it is a rapid and easy method [5–14]. TGA must reproduce, as efficiently as

TABLE 1
Experimental conditions for sorbent characterization used by different authors

Author	Weight (mg)	Flow (Nl min ⁻¹)	Size (µm)	Heating rate (°C min ⁻¹)	Calcination		Sulphation				Notes
					T (°C)	CO ₂ (%)	T (°C)	CO ₂ (%)	O ₂ (%)	SO ₂ (ppm)	
O'Neill et al. [5]	20	0.2–0.6	420–500	–	870–950	0–60	870–950	–	4	5000	1–10 atm
Ulerich et al. [6]	19	0.2	1000–1190	10	950	–	815–900	–	4	5000	
			10	In other bed			815–900	–	4	5000	
Snyder et al. [7]	100–200	–	841–1000	–	850–950	20 or 100	900	–	5	3000	Sulphation time 5 h
Fee et al. [8]	300–400	2	1000	–	850	20	850	20	5	50–100000	
Chang and Thodos [9]	–	–	920	–	900	20	900	20	5	3000	
Barron et al. [10]	45–60	0.5	850–1000	–	870	16	870	16	2.5	3000	Cal. 1800 s, Sulphate 9600 s, 6% H ₂ O
Couturier et al. [11]	2–13	0.5	500–2000	Instantaneous	800–950	9	800–950	9	9	1000–6000	
Snow et al. [12]	5	0.2	2–10	20	To 1100*	2–95	To 1100*	2–95	5	3000	Direct sulphation; * Dynamic experiments
Mulligan et al. [13]	5	0.025	150–212	–	800–970	15	800–970	14.8	1.8	6000	Sulphation time 35 min
Shaaban [14]	3–5	0.2	6–10	10	–	–	500–850	–	–	30–3000	Sulphation 30 min after calcination
This work	5 or 20	0.25	100–2000	Instantaneous	800–900	0–20	800–900	10	5	2500	Minimum calcination time

possible, the behaviour of the sorbent in a fluidized bed combustor [1] where the phenomena of calcination and sulphation take place simultaneously. In direct sulphation by TGA, it is necessary to carry out a chemical analysis after the experiment in order to determine the final sulphation conversion achieved. However, Mulligan et al. [13] found the same sulphation conversions at 850°C when using raw and calcined samples. Snow et al. [12] found that in atmospheric fluidized bed combustion (AFBC), the temperature and concentrations are generally such that the reaction proceeds sequentially: first the calcination (reaction (1)) and then the sulphation (reaction (2)). As a result of this and due to working requirements, in TGA sulphation is normally measured on the calcined lime. Calcination and sulphation sorbent reactivity is easily analysed by the solid weight change. In the calcination, this variation is negative; in the sulphation, it is positive.

However, the sulphation reaction rate strongly depends on the calcination conditions [5, 6, 15]. There are studies of sorbent reactivities in TGA under very different working conditions. Table 1 shows the experimental conditions used by different authors. In this paper, the effect of the experimental and working conditions (temperature, CO₂ concentration, heating rate, particle size and time before sulphation) used during calcination which act on the sulphur reaction in TGA, has been analysed.

EXPERIMENTAL

A thermogravimetric analyser, the Setaram TG-85, was used for the sorbent reactivity studies (Fig. 1). The sample was placed in a basket and

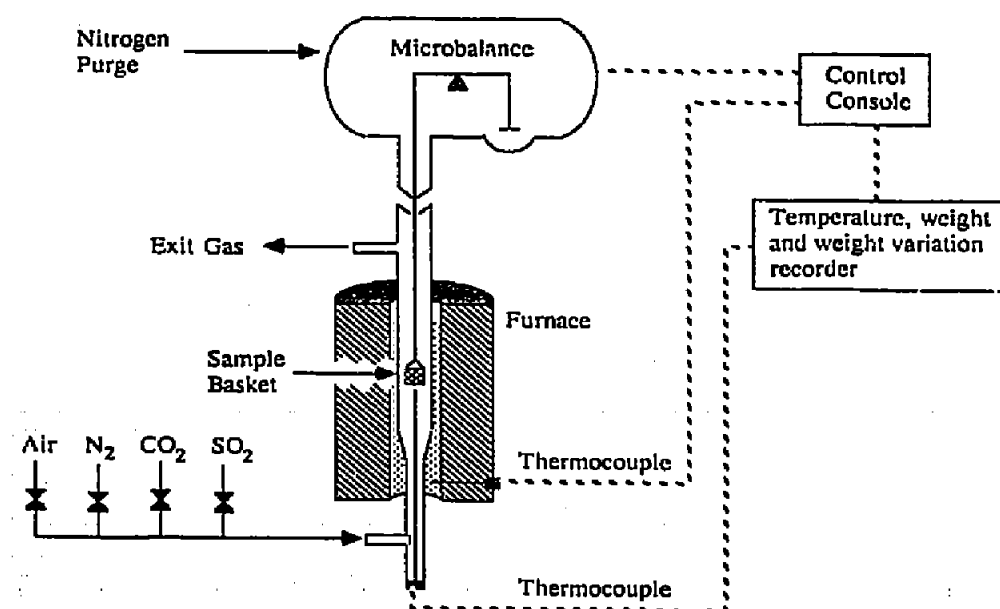


Fig. 1. Schematic diagram of the TG system.

suspended from one arm of the microbalance in a quartz reactor tube. The reactor tube was heated by a furnace which controlled the heating rate. A thermocouple placed under the basket monitored the temperature in the reaction zone. Differences of under 10°C between sample and furnace were found in the dynamics experiments, both equalizing rapidly when the desired temperature was reached (under 1 min).

The desired reactant gas (15 N l h⁻¹) was prepared by blending SO₂, CO₂, air and N₂ streams, measured and controlled by specific mass flow controllers. Also, a nitrogen purge gas that flowed through the microbalance head kept it free of the corrosive reactant gas. The gas mixture was introduced at the bottom of the quartz reactor tube (15 mm i.d.), leaving it after the mixing point with the N₂ downstream-purge from the head. The quartz reactor and the furnace can be moved down together, separating from the head. In this way, it was possible to carry out experiments with a rapid introduction of the solid sample into the reaction tube, ensuring that both temperature and gas composition in the reaction zone remain constant from the beginning (isothermal experiments). This signal, simultaneously with the sample weight and its variation with time, was collected and recorded in a microcomputer.

The textural characterization of the sorbents was made in a Micromeritics (Autopore II 9220) mercury porosimeter. Table 2 shows the porosities and characteristic pore sizes of the three sorbents used, under different calcination conditions. The preparation of calcined samples for mercury porosimetry was carried out in a horizontal quartz reactor

TABLE 2

Porosities and medium pore size of the sorbents depending on the calcination conditions

Limestone	<i>T</i> (°C)	CO ₂ (%)	Time (min)	ϵ (%)	d_{pore} (μm)	ρ_{ap} (g cm ³)
1 Blanca	Raw			3.0		2.48
2 María	Raw			21.3		1.99
3 Sástago	Raw			21.3		2.07
4 Blanca	825	0	$t_{\text{cal,min}}$	49.0	0.046	1.48
5 Blanca	850	0	$t_{\text{cal,min}}$	48.5	0.055	1.47
6 Blanca	850	0	30	47.5	0.062	1.45
7 Blanca	850	0	60	47.2	0.079	1.45
8 Blanca	850	10	$t_{\text{cal,min}}$	47.7	0.061	1.49
9 Blanca	850	20	$t_{\text{cal,min}}$	47.0	0.066	1.50
10 Blanca	850	30	$t_{\text{cal,min}}$	46.1	0.080	1.51
11 Blanca	900	0	$t_{\text{cal,min}}$	47.8	0.068	1.50
12 María	850	0	$t_{\text{cal,min}}$	55.7	4.160	
					0.053	1.20
13 Sástago	850	0	$t_{\text{cal,min}}$	51.0	0.435	1.28

TABLE 3

Chemical analysis of the limestones

(wt.%)	Blanca	María	Sástago
CaO	54.40	53.60	54.88
MgO	0.11	0.46	0.62
Na ₂ O	1.08	0.87	0.26
K ₂ O	0.00	0.15	0.05
SiO ₂	0.00	2.85	0.20
Al ₂ O ₃	0.00	0.47	0.19
Fe ₂ O ₃	0.00	0.29	0.15

(9 mm i.d.) placed in a tubular furnace. A 1.5 g sample and a gas flow rate of $9 \text{ cm}^3 \text{ min}^{-1}$ (STP) were used.

For this work, representative samples of three different limestone quarries from the Teruel area (Spain) were selected. The chemical analyses of these sorbents are shown in Table 3, where small differences in composition are observed. However, and as can be seen in Fig. 2, the sorbents considered in this work showed strong differences in their pore size distribution as measured by Hg porosimetry. In addition, the shape of these distributions is quite representative of the typical pore size distribution expected for this type of sorbent. The calcined limestone Blanca showed an internal pore structure mainly made up of small pores (unimodal size distribution); the calcined limestone María had a clear bimodal pore

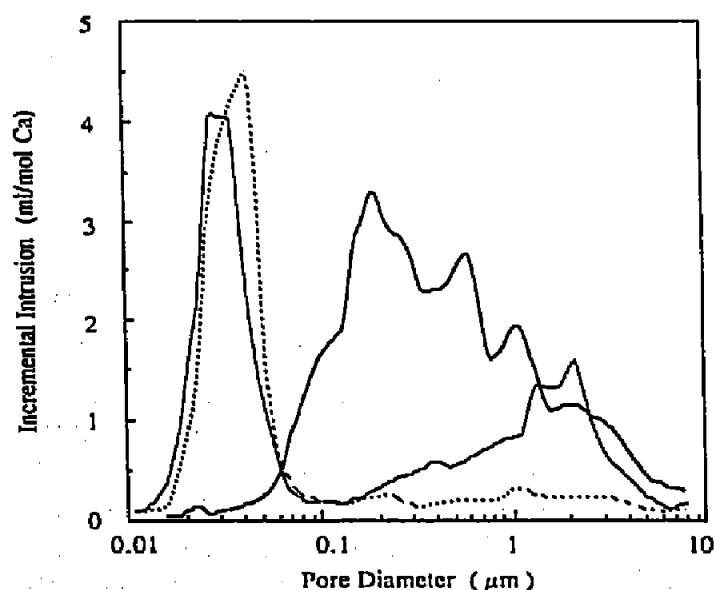


Fig. 2. Incremental pore volume as a function of the pore diameter of the calcined limestones (Blanca ····, María —, Sástago —).

size distribution; and the calcined limestone Sástago showed a widespread and continuous pore size distribution.

The effect of different operational variables acting on the sulphation was studied. Two types of experiments, isothermal and dynamic, were carried out. In the isothermal experiments, there was a rapid introduction of the solid sample into the reaction tube; in the dynamic experiments, a heating rate was applied. The calcined samples of the three different limestones were obtained in different calcination conditions (temperature, CO₂, time before sulphation, particle size, etc.); after this process they were sulphated at 850°C with 10% of CO₂ and 2500 ppm by volume of SO₂, using a linear gas velocity of 9 cm s⁻¹ in the quartz reactor. In addition, narrow particle size intervals between 100 and 2000 μm, which are usually used in fluidized bed combustors, were used in this work.

RESULTS AND DISCUSSION

As mentioned above, the reactivity of the selected sorbents was studied by TGA, yielding thermograms as shown in Fig. 3. The sulphation conversion and sorbent reactivity at any time can be obtained from

$$x_s = \frac{w_{CaO}^0 - w_{CaO}}{w_{CaO}^0} = \frac{1}{r_s - 1} \left(\frac{w}{w_{CaO}^0} - 1 \right) \tag{3}$$

$$\frac{dx_s}{dt} = \frac{1}{w_{CaO}^0 (r_s - 1)} \frac{dw}{dt} \tag{4}$$

In order to obtain correct results, the thermobalance must behave like a differential reactor, i.e. gas conversion must be low (<5%). To obtain,

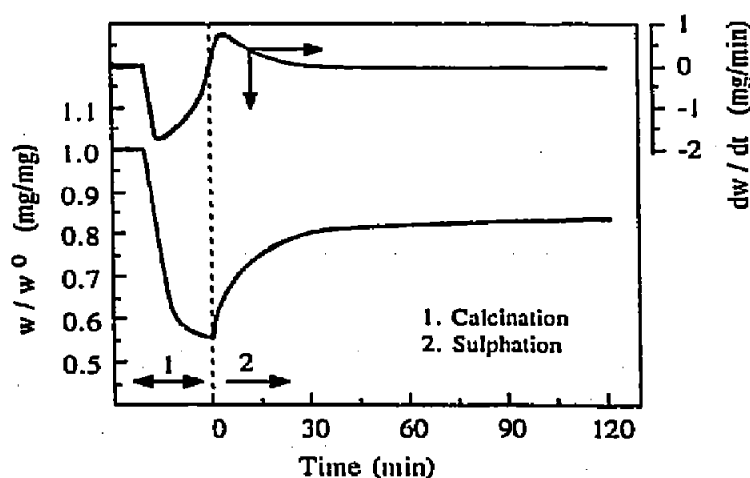


Fig. 3. Typical thermogram obtained in the TG sorbent characterization.

effective differential boundary conditions, the problems of gas diffusion into the sample must be avoided. The shape of the basket, the gas flow rate, the sample weight and size are all very important aspects in the experimental technique [5]. Some preliminary experiments were made using different sample weights, gas flow rates and basket geometries in order to find the conditions that minimized the effect of gas diffusion into the sample.

Two different basket geometries and sample weights were used to reduce a possible mass transfer resistance around the sorbent sample: a cylindrical platine plate (5 mm diameter, 2 mm height) and 5 mg of sample were employed for the experiments with particle size under 250 μm ; a wire mesh platinum basket (5 mm diameter and 5 mm height) and 20 mg of sample were used for the rest of the experiments.

Effect of the calcination conditions

There is real evidence that the calcination conditions strongly affect the sorbent sulphation. Sulphur retention and sorbent sulphation reactivity depend on the pore size distribution of the calcined lime [4] and the latter depends on the calcination conditions [5, 6, 16].

According to Stantan et al. [15], the factors affecting the development of the internal porous system of the sorbent are calcination rate which depends on sorbent size, temperature, CO_2 partial pressure and sorbent reactivity, and the sinterization rate, which basically depends on temperature.

Table 1 indicates that some authors used calcination conditions in the sorbent characterization that were very different from those present in a fluidized-bed coal combustor. In order to test the effect of the different variables on the porous system development during calcination, calcined samples of the three different limestones were obtained in different conditions in TGA, and were then sulphated in the same conditions (850°C, 10% CO_2 , 2500 ppm vol. SO_2). In this work, the instrumental and experimental TGA conditions that yield a reliable sorbent characterization, avoiding the influences of the operating method, were determined.

Heating rate

When a sorbent particle is introduced into an AFBC, rapid heating takes place up to the working temperature (800–900°C). Then the sorbent is calcined and sulphated in different environments of CO_2 (0–16%) and SO_2 (depending on the molar Ca/S ratio used).

To study the effect of the heating rate on the sorbent behaviour, dynamic

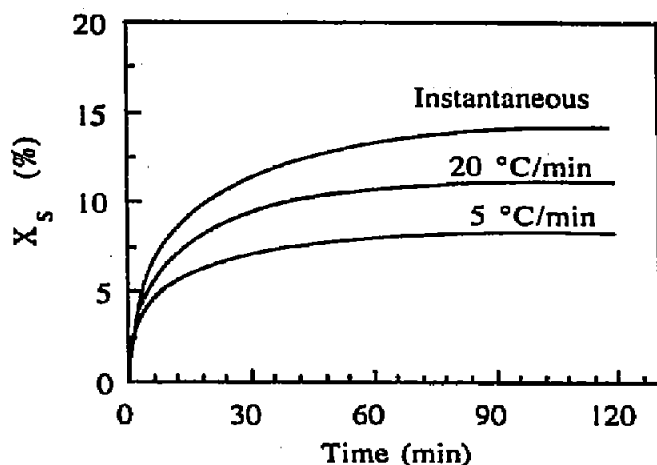


Fig. 4. Effect of heating rate on the sulphation conversion for Blanca limestone.

experiments were carried out in the TGA with different heating rates, in which sulphation began just after the calcination finished. Figure 4 shows the effect of the heating rate on the sulphation conversion for the Blanca limestone, when calcined in an atmosphere containing 10% CO₂. The instantaneous heating rate corresponded to the case when a sorbent sample was introduced rapidly into the reaction tube at the desired temperature and concentration.

As can be seen, the heating rate during calcination affects both the reaction rates and the sulphation conversion of the limestone. With the three limestones studied, higher sulphation conversions were obtained as the heating rate was increased during calcination. Due to the different calcination reactivity of the limestones (Sástago > María > Blanca), the calcination conversion achieved when the reaction temperature was reached (850°C) was different for the three limestones. Thus, the time for which particles remained at the reaction temperature until complete calcination, increased when the reactivity decreased ($t_{\text{Blanca}} > t_{\text{María}} > t_{\text{Sástago}}$). In addition, sorbent sinterization occurs simultaneously during calcination, and produces pore enlargement. The sinterization increased when the total calcination time at 850°C increased and its effect was more marked with limestone Blanca which has a small pore size distribution.

Because the heating rate affected the sorbent reactivity, a heating rate similar to that present in AFBC should be used for a satisfactory TGA characterization [1]. Consequently, the instantaneous heating rate was applied in the following experiments.

Time before sulphation

The effect of the calcination time (t^*), from the beginning of the calcination to the beginning of the sulphation, on the sulphation reactivity

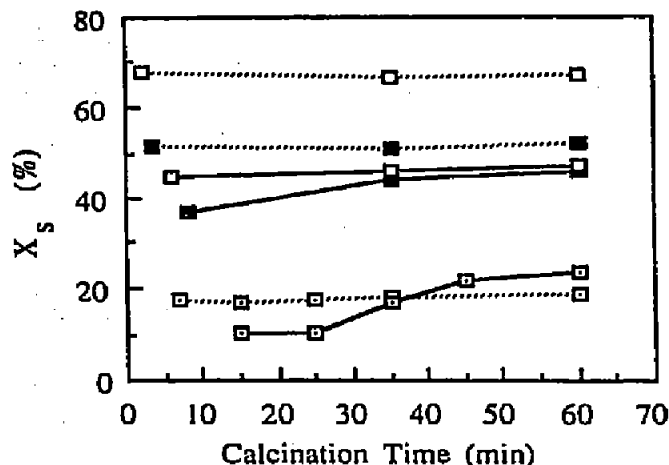


Fig. 5. Effect of calcination time on the maximum sulphation conversion for different sorbent particle sizes; Blanca, □; María, ■; Sástago, □. (+0.25–0.50 mm, ····; +1.6–2.0 mm, —).

and maximum conversion of the limestones was studied. Figure 5 shows the maximum sulphation conversions achieved plotted against t^* for the three limestones and for different sorbent particle sizes (+0.25–0.5 and +1.6–2.0 mm).

For María limestone, the differences were difficult to estimate in sizes under 1 mm, even though a small increase in the conversion was achieved for greater sizes. For Sástago limestone, there were no differences in any particle size. Blanca limestone showed greater differences in the maximum sulphation conversions when the time before sulphation (t^*) increased. These differences (ΔX_s) were higher when the limestone particle size increased, as can be seen in Fig. 6.

In the gas/solid reaction, whether controlled by chemical reaction or by diffusion, the rate of reaction is dependent on the accessible surface area of

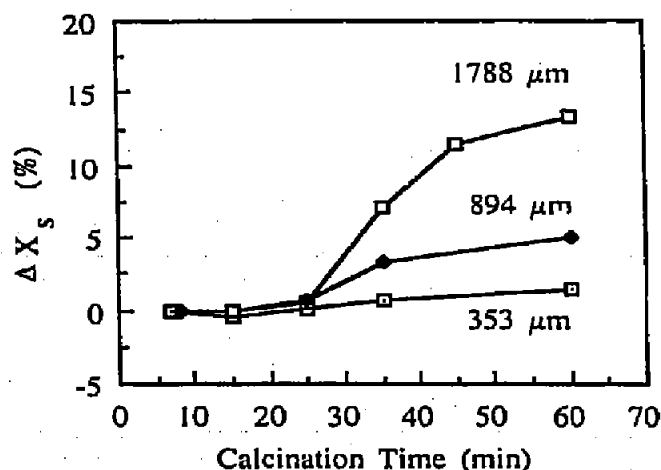


Fig. 6. Incremental sulphation conversion versus the calcination time for Blanca limestone.

the solid. A maximum is achieved in the surface area when calcination conversion is close to 1 [16] and decreases later by sintering. A smaller reaction rate is achieved for longer calcination times. Moreover, the pore size of the calcined lime increases with time, as can be seen in Table 2 (experiments 5, 6, 7), and according to results obtained by Rubiera et al. [17]. These decreases in the reaction rate in comparison with the gas diffusion rate and the pore enlarging, diminished the diffusional effects in the particle, making a higher sulphation of the sorbent possible. This explains why the greatest effect was obtained with Blanca limestone, with less effect for the other limestones with large pores.

However, the effect of the calcination time on the sulphation conversion in limestones principally made up of small pores, was greater as the particle size increased. The longer time necessary for the calcination of the bigger particles allowed the simultaneous sinterization of the pores of the calcined part and the calcination of the inner parts of the particle. The formation of larger pores diminished the pore plugging, which is assumed to be the limiting process that prevents a total sulphation of the sorbent. A higher sulphation conversion is obtained in this case.

The effect of the calcination time on the sulphation conversion was also observed at other temperatures. Figure 7 shows the effect of the calcination temperature on the sorbent sulphation at different calcination times for Blanca limestone. As above, the sulphation conversions are higher as the calcination time is increased. An optimum temperature of calcination is observed at 850°C at the same calcination time. Furthermore, an increase in the sorbent pore size (and as a result, a decrease in the specific surface area) was achieved when the temperature increased, as can be seen in Table 2 (experiments 4, 5 and 11), according to Mulligan et al [13], Rubiera et al. [17] and Zarkanitis and Sotirchos [18].

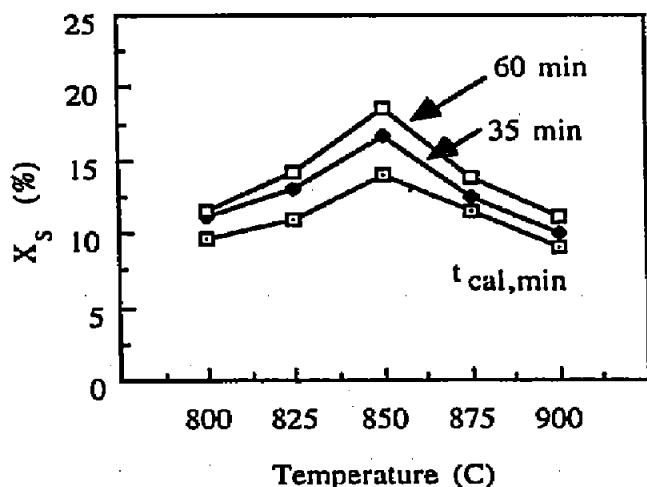


Fig. 7. Effect of calcination temperature on the sorbent sulphation at different t_{cal} for Blanca limestone.

For these reasons, it can be stated that the process of sinterization is not easy to control. In order to reduce as much as possible the effect of the calcination time on the sulphation conversion, and to simulate the sulphation process occurring during fluidized bed combustion, the sulphation in TGA must begin when the calcination of the sorbent has just finished.

Calcination and sinterization rates

As mentioned above, the development of the pore system depends on both the calcination and the sinterization rates. The calcination rate at one temperature is smaller with higher CO_2 pressures and with bigger sorbent particle sizes, whereas the sinterization rate increases with temperature.

In Table 2 (experiments 5, 8, 9 and 10) a displacement in the pore size distribution towards bigger pores can be seen in experiments with higher CO_2 concentration, which implies smaller calcination rates, according to the studies of O'Neill et al. [5], Ulerich et al. [6], Spitsbergen et al. [16] and Bhatia and Perlmutter [19].

For Blanca limestone of different particle sizes; Fig. 8 shows the sulphation conversion versus CO_2 concentration in samples calcined at 850 and 900°C and sulphated immediately following completion of calcination. At 850°C, the sinterization rate was not very high. Thus the calcination rates for particles under 1 mm, even with 20% CO_2 , were much higher than the sinterization rates. In this case, the opposite effects on porosity and surface area do not greatly affect the final sulphation of the sorbent, although different reactivities were obtained in each case. However, with

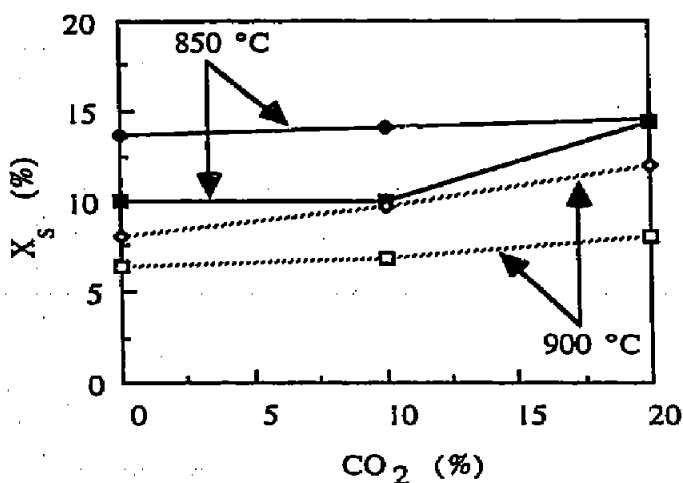


Fig. 8. Maximum sulphation conversions versus CO_2 concentration at different temperatures: +0.8–1.0 mm, \square \blacksquare ; +1.6–2.0 mm, \diamond \blacklozenge .

bigger particles (+1.6–2 mm) the calcination rate diminished, increasing the time necessary for the total calcination. In this case, the degree of sinterization was greater and higher maximum sulphation conversions were obtained.

At higher temperatures (900°C), higher sulphation was again obtained with increasing CO₂ concentrations. In this case, the effect on the maximum sulphation conversion was considerable even in sizes of 1 mm because at this temperature, sinterization rates increased, and the calcination and sinterization processes took place simultaneously.

For limestones with large pores, the effect of the relative rates of both the calcination and sinterization processes on the maximum sulphation conversion is smaller than in limestones with small pores, such as Blanca limestone.

Sorbent particle size

As the sulphation reaction occurs, the principal resistance on the reaction rate changes from pore diffusion and surface reaction to diffusion on the sulphate layer [20–22]. Also, pore blockage prevents sulphation of the inner parts of particles and diminishes the maximum conversion of the sorbent. Therefore, sorbent particle size is a very important variable in the study of the sorbent sulphation reactivity. Furthermore, the pore size distribution strongly affects the sorbent sulphation. Borgwardt and Harvey [23] showed that calcines with pore sizes $<0.2 \mu\text{m}$ only sulphated on the particle surface, and consequently, they are very sensitive to the sorbent particle size.

Figure 9 shows the maximum sulphation conversion as a function of the particle size for the three limestones in the TGA. This figure highlights the

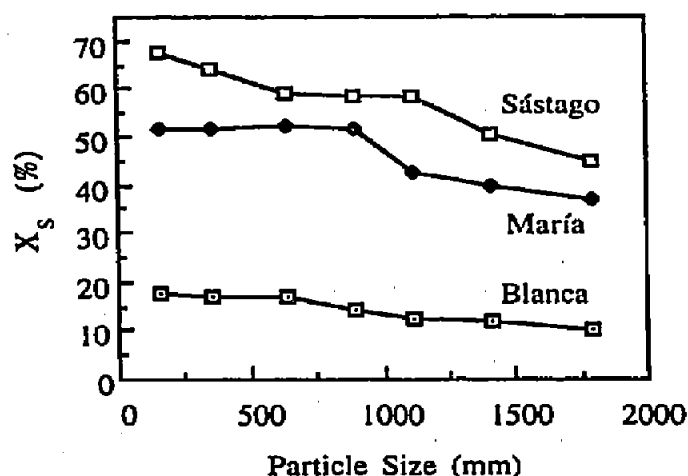


Fig. 9. Maximum sulphation conversions obtained as a function of the sorbent particle size for the different limestones.

great differences in the sulphation of sorbents depending on their pore structure. A greater degree of sulphation was obtained with limestones of greater pore size, due to the lower diffusional resistance of the sulphate layer. These results agreed with Hartman et al. [24] who found that pores with sizes greater than $0.398\ \mu\text{m}$ were the main reason for the degree of SO_2 retention by the sorbent. Shearer et al. [25] also found that the optimum pore size for the SO_2 retention was $0.2\text{--}0.3\ \mu\text{m}$ for particles of 1 mm.

As can be seen, the particle size of the sorbent is a very important process variable affecting the sulphation conversion. For this reason, particle size intervals representative of the sorbent size distribution used in the combustor have to be used in the TGA characterization.

Also, in order to avoid the internal diffusional resistance of the sulphate layer enabling the identification of intrinsic reactivities, small particle sizes of sorbent are used in TGA. In this case, a wire mesh basket cannot be employed and a plate basket must be used. But depending on the sample weight, a pile in the basket may be made, resulting in diffusional resistance inside the pile [26] and unreliable reactivity information. In this case, the sample weight must be reduced until values are reached which do not affect the results obtained (<5 mg, in this work).

CONCLUSIONS

In this paper it has been shown that sorbent sulphation in TGA depends strongly on the porous system developed in the calcination and this, in turn, depends on the equilibrium between the calcination and sinterization rates. So, if the calcination rate is rapid, sinterization begins after calcination. If the sinterization rate is fast enough, the processes are simultaneous and sorbents do not show differences in the sulphation.

The effect of sinterization was more important with limestones with small pores, which, in this work, corresponds to Blanca limestone. In this case, problems of reproducing experiments that depend on the experimental method (heating rate of the sample, calcination time, etc.) can occur. Also, a higher capacity of sulphation has been found in limestones with large pores.

In order to avoid the influence of the experimental method in TGA and to obtain reproducible results, a general set of experimental conditions for sorbent characterization in TGA is proposed: sample heating rate, instantaneous; sulphation immediately after calcination; calcination atmosphere representative of that present in a coal combustor ($\approx 10\% \text{CO}_2$); sample weight, that necessary to achieve sorbent representativity but assuring differential conditions in the TG; and sorbent particle size intervals representative of the sorbent size distribution used in the combustor.

ACKNOWLEDGEMENT

The authors thank the Dirección General de Investigación Científica y Técnica (DGICYT) (Proj. no. GEO89-0732 CO2-02) for financing this work.

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