Characterization of a limestone in a batch fluidized bed reactor for sulfur retention under oxy-fuel operating conditions.

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Abstract.

CO_2 and SO_2 are some of the main polluting gases emitted into atmosphere in combustion processes using fossil fuel for energy production. The former is one of the major contributors to build-up the greenhouse effect implicated in global climate change and the latter produces acid rain. Oxy-fuel combustion is a technology, which consists in burning the fuel with a mix of pure O_2 and recirculated CO_2. With this technology the CO_2 concentration in the flue gas may be enriched up to 95%, becoming possible an easy CO_2 recovery. In addition, oxy-fuel combustion in fluidized beds allows in situ desulfurization of combustion gases by supplying a calcium based sorbent.

In this work, the effect of the principal operation variables affecting the sulfation reaction rate in fluidized bed reactors (temperature, CO_2 partial pressure, SO_2

concentration and particle size) under typical oxy-fuel combustion conditions have been analyzed in a batch fluidized bed reactor using a limestone as sorbent. It has been observed that sulfur retention can be carried out by direct sulfation of the $CaCO_3$ or by sulfation of the CaO (indirect sulfation) formed by $CaCO_3$ calcination. Direct sulfation and indirect sulfation operating conditions depended on the temperature and CO_2 partial pressure. The rate of direct sulfation rose with temperature and the rate of indirect sulfation for long reaction times decreased with temperature. An increase in the CO_2 partial pressure had a negative influence on the sulfation conversion reached by the limestone due to a higher temperature was needed to work in conditions of indirect sulfation. Thus, it is expected that the optimum temperature for sulfur retention in oxy-fuel combustion in fluidized bed reactors was about 925-950ºC. Sulfation reaction rate rose with decreasing sorbent particle size and increasing SO_2 concentration.

1. Introduction

The emission of polluting gases into the atmosphere from combustion of fossil fuels, like coal, for energy production can cause different environmental problems like the greenhouse effect and acid rain, where CO_2 and SO_2 are the main contributors respectively. Currently new technologies for CO_2 capture are being developed to produce a gas stream with high concentration of CO_2 at the end of the process preventing its release into the atmosphere. The oxy-fuel combustion is one of them, which consists in burning the fuel with a mix of pure O_2 ($\approx$ 30%) and CO_2 recirculated from the outlet gas stream to control the operating temperature. With this technology the CO_2 concentration in the flue gas may be enriched up to 95%, therefore becomes possible an easy CO_2 recovery.

Although the majority of the researches in oxy-fuel combustion have been carried out for pulverized coal boilers, fluidized bed combustors (FBC), and specially circulating fluidized bed combustors (CFBC), are also very appropriate for this combustion system. This technology has the advantage that external solid heat exchangers can be used to extract heat from the combustion process. This allows a significant reduction of the amount of recycled flue gas required for combustion temperature control (Jia et al., 2010). Moreover, desulfurization of combustion gases can be produced in situ by supplying of a calcium based sorbent.

Calcium based sorbents have been used for removing SO_2 at high temperatures. Depending on process conditions (temperature and CO_2 partial pressure) the calcination can perform prior to or during the sulfation of the sorbent. In addition, the sorbent can not calcine and as a result direct sulfation of calcium carbonate occurs. This is due to the characteristics of the thermodynamic equilibrium of calcination.

$$CaCO_3 \longleftrightarrow CaO + CO_2 \tag{R.1}$$

Calcination reaction (R.1) is an endothermic reaction whose equilibrium constant can be obtained from (Barin, 1989):

$$P_{CO_2}^{eq} (atm) = 4.137 \cdot 10^{12} \exp\left(-\frac{20474}{T(K)} \right) \tag{1}$$

Figure 1 shows the equilibrium curve calculated with this equation as a function of the temperature and CO_2 partial pressure. Under conventional combustion conditions with air, the operating conditions are always calcining conditions because the temperature in the system is above the calcination temperature and thus sulfation of calcined sorbent or indirect sulfation (R.2) is carried out.

$$CaO + SO_2 + ½ O_2 \longleftrightarrow CaSO_4 \tag{R.2}$$

However, under oxy-fuel combustion conditions the CO_2 partial pressure in the boiler is higher than in air combustion, and as a result the calcium based sorbent can operate in

calcining or non calcining conditions. If the temperature in the system is below the calcination temperature the sorbent operates in non calcining conditions and direct sulfation (R.3) is carried out. A review on direct sorbent sulfation, discussing the influence of the reaction conditions, limestone properties and additives to the reaction kinetics, the reaction mechanism and modelling, was done by Hu et al (2006).

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \longleftrightarrow CaSO_4 + CO_2 \qquad (R.3)$$
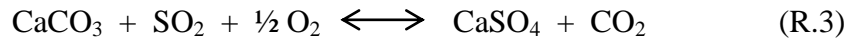
Other possibility to take into account is when the calcium based sorbent is operating in calcining conditions and the partial pressure of CO_2 is close to the thermodynamic equilibrium curve (de Diego et al., 2004). In this case, the calcination rate can be so slow that direct sulfation predominates over calcination.

Literatures and data concerning calcium based sorbent characterization under high CO_2 partial pressures are limited (Fuertes et al., 1993, 1994a, 1994b, 1995, Hajaligol et al., 1988, Liu et al., 2000, Snow et al., 1988, Tullin et al., 1993). Snow et al. (1988) and Hajaligol et al. (1988) found that direct sulfation of limestones produced a higher conversion than the sulfation of calcined limestones since the calcium sulfate layer formed during direct sulfation was porous, while the sulfate layer formed from calcined stone showed no porosity. These researchers suggested that the porosity was caused by the flow of CO_2 gas formed by the direct sulfation reaction. However, Hu et al. (2006) consider this explanation questionable since the direct sulfation reaction consumes 1.5 moles of gaseous reactants for each mole of released CO_2. So, the outward flow of the CO_2 gas should be diffusional and it is doubtful that this diffusional flow of CO_2 can be responsible for the formation of the porosity. Moreover, Ulerich et al. (1980) and Tullin et al. (1993) found that high partial pressure of CO_2 significantly reduced the rate of direct sulfation reaction under certain conditions.

Chen et al. (2007) found that the specific pore volume and the specific surface area of CaO calcined in O_2/CO_2 atmosphere were less than that of CaO calcined in air at the same temperature, and the pore diameter of CaO calcined in O_2/CO_2 atmosphere was larger than that in air. Sintering had influence on the pore structure of CaO calcined by means of influencing the grain size of CaO. The grain size of CaO calcined in O_2/CO_2 atmosphere was always larger than that in air.

Among the previous investigations on sorbent characterization, most were made with thermogravimetric analyzers (TGA) (Adánez et al., 1993, Fuertes et al., 1993, Hajaligol et al., 1988, O'Neill et al., 1976, Snow et al., 1988, Tullin et al., 1993, Ulerich et al., 1980) and with fixed bed reactors (Hu et al., 2007, Liu et al., 2000) and using very small particle sizes, smaller than used in fluidized bed reactors.

Batch fluidized bed reactors allow sorbent characterization in similar conditions to those existing in fluidized bed combustors, such as simultaneous calcination and sulfation, attrition, thermical shock and crackle. Hajaligol et al. (1988) found that the porous sulfate layers were quite fragile, and attrition in a fluidized bed could remove some of this material, reducing diffusional resistance and decreasing conversion time.

Up to now, calcium based sorbents have been characterized with batch fluidized bed reactors under air combustion conditions (Adánez et al., 1994, Suyadal et al., 2005). In this paper, the effect of the principal variables affecting sulfur retention (temperature, CO_2 partial pressure, SO_2 concentration and particle size) under oxy-fuel combustion conditions have been analyzed with this technique.

2. Experimental section

2.1. Materials

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A calcium based sorbent from Spain, "Granicarb limestone", in narrow particle size intervals between 0.2 and 0.63 mm, was used for the experimental work. Chemical composition and physical properties of this sorbent are showed in the Table 1. As can be seen the "Granicarb" raw limestone is mainly composed of calcium carbonate. Due to calcium sorbent can operate in calcining or non calcining operating conditions, the physical properties of calcined and uncalcined sorbent are showed. The porosity and density of the calcined sorbent correspond to samples calcined in nitrogen at 900 ºC and cooled just after finishing the process. This limestone, during calcination, developed an internal pore structure mainly constituted of small mesopores with unimodal size distribution and with characteristic pore diameter of 0.0420 μm.

2.2. Experimental systems

2.2.1. Batch Fluidized Bed Reactor.

The experimental tests to characterize the reactivity of the sorbent were carried out in a batch fluidized bed reactor. A scheme of the installation is shown in Figure 2. The experimental system consisted of a fluidized bed reactor, 0.1 m i.d. and 1.0 m height, externally heated by an electric oven. The bed of solids was composed of 2.8 kg of silica sand with a particle size between 0.2-0.63 mm, and the superficial gas velocity was 20 cm/s to avoid the elutriation of limestone particles. The temperature of the bed was measured by a thermocouple type K. The reacting gas was prepared by mixing air, O_2, CO_2, and SO_2 streams to simulate the flue gas generated under oxy-fuel and air coal firing. The inflow gases (without SO_2) were heated by a pre-heater, and then distributed in the bed by a bubble caps distributor. The SO_2 stream, 3000 vppm as reference case, was fed at 0.02 m from the bubble cap distributor to avoid its corrosion. Outlet gas stream went through a high efficiency cyclone and a filter, and the SO_2, CO_2 and O_2

concentrations were continuously measured by i.r. analyzers (Siemens Ultramat 23 and Siemens Ultramat/Oxymat 6).

The sorbent characterization experiments were performed by fast injection of a limestone charge (5 g) into the sand bed. The sulfation and calcination reaction rates of the sorbent were measured by means of the variation of SO_2 and CO_2 concentrations, respectively, in the outlet gas stream when a charge of calcium sorbent was introduced into the reactor. Typical profiles of CO_2 and SO_2 concentrations obtained with these kind of tests working in calcining and non calcining conditions are shown in Figure 3. When limestone was introduced into the reactor a decrease of SO_2 concentration, due to SO_2 retention by the calcium based sorbent, and an increase of CO_2 concentration, due to sorbent calcination (R.1) in calcining conditions or $CaCO_3$ reaction into $CaSO_4$ (R.3) in non calcining conditions, were observed. Subsequently, SO_2 concentration was increasing slowly and the end of the experiment was considered when the initial SO_2 concentration was achieved again. In previous studies (Abanades et al., 2000, 2003) were found that the calcium sorbents had a residual activity for long times of reaction which were more noteworthy for particle size below 1.0 mm. However, these experiments only permitted studying with precision the sorbent reactivity during the first minutes (≈30 min) due to the sensitivity of the analyzer and the few limestone charge (5 g) used in each test.

The sulfation conversion (Xs) was obtained by the following expression:

$$Xs = \frac{Q_m\,RT}{mP}\int_0^t (C_{S0} - C_S)\,dt \qquad (2)$$

where Q_m is the gas molar flow, m are the moles of limestone supplied, C_{s0} the initial SO_2 concentration and C_s the SO_2 concentration at a generic time.

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2.2.2. *Thermogravimetric analyzer*

To better understand the behaviour of calcium based sorbents during sulfation in the fluidized bed reactor, some calcination tests were carried out in a CI electronic TGA described elsewhere (Adánez et al., 2004). The calcination tests were carried out at atmospheric pressure using a inlet gas stream of 5 l_N/h, a sample weight of 50 mg with a particle size between 0.1 and 0.2 mm. Different CO_2 concentrations between 0-90 vol% and N_2 (balance) were used. Temperature was raised from room to 950ºC at 5 ºC/min. Finally, to gain some insight on the mechanism of sulfation, samples of limestone with particle sizes between 0.063 and 0.8 mm were sulfated in the TGA for observations by scanning electron microscopy (SEM).

3. Results and Discussion.

The batch fluidized bed reactor permitted to study the behaviour of the sorbent in similar hydrodynamic conditions to that found in continuous FBC. The experiments carried out to analyze the effect of temperature and CO_2 partial pressure on the limestone sulfation reaction are plotted in the Figure 1.

3.1. *Effect of CO_2 concentration*

Oxy-fuel combustion is based on introducing into the system a mix of CO_2 and O_2 like comburent. The CO_2 concentration is a factor of utmost importance because depending on it and the temperature, the calcium sorbent will be operated in calcining or non calcining conditions. To analyze the effect of the CO_2 partial pressure during the limestone sulfation reaction, tests with different CO_2 concentrations (0-90%) were performed. In these tests the SO_2 concentration was kept constant at 3000 vppm and the limestone particle size was 0.3-0.5 mm.

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Figure 4 shows the limestone sulfation conversions obtained as a function of the reaction time at different temperatures and CO_2 partial pressures. As can be seen in this Figure, there were two behaviours well-distinguished. The highest sulfation conversions were reached in operating conditions where the limestone calcined due to the higher porosity of the reagent (CaO versus $CaCO_3$) which allowed a better access of the SO_2 toward the inner part of the particle before plugging of the external pores. On the contrary, in the non-calcining operating conditions where direct sulfation of the sorbent was produced the sulfation reaction rate was lower. Nevertheless, in some operating conditions belonging to calcining conditions zone and near to thermodynamic equilibrium curve (800 ºC and 15% CO_2, 850 ºC and 40% CO_2, 900 ºC and 60-90% CO_2, and 925 ºC and 80-90 % CO_2), it was observed that the behaviour of the limestone was the same as the behaviour in non-calcining conditions. This fact seems to be due to the sulfation reaction rate was higher than the calcination rate. Calcining and non calcining operating conditions were inferred from the CO_2 concentration evolution measured during the experimental tests (see Figure 4).

It can be also observed in Figure 4 that once defined calcining or non-calcining operating conditions, the influence of CO_2 concentration on the sulfation reaction rate was negligible as much as calcining as non-calcining operating conditions. Very similar results were also found by Snow et al. (1988) in a TGA using limestone particle sizes of a few microns.

To better understand this behaviour of the limestone during sulfation in the fluidized bed reactor, some calcination tests were carried out in a TGA. For these tests the sample was heated from room temperature up to 950ºC at 5ºC/min, working with different CO_2 concentrations between 0-90 vol% (N_2 balance). Figure 5a shows the weight loss of the limestone as a function of the temperature for the different CO_2 concentrations in the gas

inlet. As expected, an increase in CO_2 concentration produced an increase in the temperature needed to start the $CaCO_3$ decomposition. From dw/dt versus temperature curves, shown in the Figure 5b, the temperature at which the calcination rate began to be fast was calculated like intersection of the tangent to the curve with the x-axis for each test.

From these values of temperature and CO_2 concentration, a new $CaCO_3$ calcination curve, which is shown in Figure 6, was obtained. In this Figure the area between the two curves corresponds to calcining operating conditions where the $CaCO_3$ of the limestone has a very low calcination rate. Therefore, in this area, although theoretically $CaCO_3$ could calcine, the sulfation rate could be faster than calcination rate and as a result the behaviour of the calcium sorbent would be similar to the behaviour of the sorbent in non-calcining condition. This hypothesis is verified with the results obtained in the batch fluidized bed because the experimental data belonging from a thermodynamic point of view to the calcining zone that showed the same behaviour as the behaviour in non-calcining conditions were in this zone. So, it was important to note that the behaviour of the sorbent was ruled by the calcination curve obtained instead of the thermodynamic equilibrium curve of $CaCO_3$-CaO.

3.1.1. Influence of sulfation process over calcination.

Due to the calcination and the sulfation processes are carried out simultaneously in the batch fluidized bed (different from that in TGA), there was the possibility of the calcination stage was affected or prevented if the blockage of the external pores of the particle prior to whole calcination of the sorbent took place. For this reason, as well as the sulfation conversion, the calcination conversion of the limestone was also calculated for the sulfation tests carried out in the batch fluidized bed. In addition, the same tests

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without presence of SO_2 in the inlet gas to the batch fluidized bed reactor were carried out to compare and analyze the influence of the sulfation process over the calcination stage. Thus, charges of limestone were injected into the sand bed and the CO_2 concentration was measured.

It was observed that the temperature and CO_2 concentration had influence in the calcination stage. The calcination rate increased with temperature and decreased with CO_2 concentration, as it is shown in the Figure 7, being these results according to results obtained in TGA.

In addition, plotting the calcination conversions achieved with and without SO_2 in the inlet gas as a function of the time, it was found that the sulfation reaction did not affect to the calcination reaction, as can be seen in the Figure 7. In all the tests, the calcination rate was so fast in comparison with sulfation rate that the influence of sulfation process could be considered negligible.

Likewise, the effect of the calcination stage over sulfation process was also analyzed. Although the calcination rate depended on the CO_2 concentration, as it was mentioned above, the sulfation conversion achieved was independent of CO_2 concentration as much as calcining as non calcining conditions. So, it can be concluded that in a fluidized bed the influence of calcination rate over sulfation process could be considered negligible too.

3.2. Effect of temperature

Many researches (Fuertes et al. 1994a, Suyadal et al., 2005, Wang et al., 2010, Zheng et al. 1982,) agree with the sulfation process was performed by two stages. The first stage was controlled by chemical reaction and/or diffusion through porous system of the particle. As the reaction proceeded, the volume of porous decreased due to molar

volume of the product ($CaSO_4$) was higher than reagent solid (CaO or $CaCO_3$) and as a result the external pores were plugged. In this moment, the second stage began and it was controlled by diffusion through product layer according to shrinking-core model.

In this work, to analyze the effect of reaction temperature on SO_2 retention, at temperatures typical of FBC boilers, tests at different temperatures between 800 and 950 ºC were carried out. The particle size used was 0.3-0.5 mm.

Figure 8 shows the conversion-time results obtained at different temperatures with different fixed CO_2 concentrations. As commented by others researchers two different stages can be observed as much as direct sulfation and sulfation of calcined. The first one it was controlled by chemical reaction and/or diffusion through porous system of the particle, and the second one it was controlled by diffusion through product layer. It can be also observed that the sulfation conversion reached by the sorbent during the first stage was higher for sulfation under calcining conditions (indirect sulfation) than for direct sulfation due to CaO is more reactive and has higher porosity and specific surface area than $CaCO_3$. Higher porosity improves the access of the reactive gas into the particle and therefore the conversion reached before pore plugging was higher. However, the effect of the temperature was different for the direct sulfation and for the indirect sulfation reactions. In direct sulfation conditions the sulfation reaction rate rose with increasing the temperature. On the contrary, in conditions of indirect sulfation the sulfation reaction rate was almost not affected by the temperature for lower reaction times, but as time went on the sulfation reaction rate decreased faster with increasing temperature. As a result the limestone sulfation conversion for longer reaction times was lower with increasing the temperature.

The influence of the temperature with different CO_2 concentrations in the flue gas on the limestone sulfation conversion for a constant reaction time of 20 minutes is shown in

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Figure 9. An optimum temperature for each CO_2 concentration was observed. Moreover, it was found that an increase in CO_2 concentration was associated with an increase in the optimum temperature which was corresponding to the minimal operating temperature working on indirect sulfation. It was also noted that a higher optimum temperature corresponded with lower sulfation conversion achieved. Therefore, it can be concluded that an increase in the CO_2 concentration has a negative influence on the sulfation conversion reached by the limestone due to a higher temperature is needed to work under conditions of indirect sulfation. This fact can be associated to the sintering of the calcium sorbent and/or the product layer, decreasing the surface area with increasing the temperature.

Under conventional air combustion in fluidized bed reactors, some researchers (Adánez et al., 1994, Lyngfelt and Leckner , 1989, Ulerich et al., 1980) found that the optimum temperature for sulfur retention was nearly 850ºC, which corresponds with a CO_2 concentration about 15 vol% in Figure 9. However, taking into account the results found in this work, it is expected that the optimum temperature from the point of view of sulfur retention in oxy-fuel combustion in fluidized beds was incremented up to 925-950ºC due to the fact that for high CO_2 concentrations it was necessary to rise the temperature to perform the calcination of the limestone.

3.3. Effect of particle size

Particle size is an important parameter for characterization of the sorbent due to pore blockage produces a decrease in the sulfation reaction rate, prevents sulfation of the inner parts of the particle, and as a result diminishes the maximum conversion of sulfation. In this work, the sulfation rate of three particle sizes of the Granicarb limestone was investigated: 0.2-0.3, 0.3-0.5, and 0.5-0.63 mm.

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Figure 10 shows the sulfation conversions reached as a function of the time for the three limestone particle sizes, under calcining and non-calcining operating conditions. For the three particle sizes the maximum conversions obtained by the sorbent in calcining operating conditions were higher than in non-calcining operating conditions due to the higher initial porosity of the calcined sorbent. An increase in sorbent particle size produced a decrease on the sulfation reaction rate and therefore a lower conversion was reached in the tests as much as calcining as non calcining conditions. This was due to the reacted volume of smaller particles before external pore plugging was greater than larger particles with respect its total volume. This means that the relevance on the sulfation reaction rate of the diffusion on the $CaSO_4$ layer increased with the particle size.

As commented in the experimental section, the experiments carried out in the batch fluidized bed only permitted studying with accuracy the sorbent reactivity during the first minutes ($\approx$30 min) due to the sensitivity of the analyzer and the few limestone charge (5 g) used in each test. However, Abanades et al. (2003) also observed a dependence of the residual activity with the particle size being this activity inversely proportional to particle size.

To gain some insight of the influence of the particle size on the mechanism of sulfation, samples of the limestone with particle sizes between 0.063 and 1.0 mm were sulfated in the TGA for observations by SEM-EDX. The sorbent samples were sulfated (direct sulfation) and calcined and sulfated (indirect sulfation) at 850-900ºC with 0.3 vol.% SO_2, 10 vol% O_2, 60 vol.% CO_2 and N_2 (balance). The sulfated samples were prepared for observation by embedding the particles in resin, curing and polishing.

Figure 11 shows microphotographs and sulfur profiles of some sulfated samples. It was observed that larger particle had lower sulfation conversions than smaller particles with thin sulfated coatings consisting of pure or nearly pure $CaSO_4$, while the core consists of

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non-sulfated CaO. Moreover, the transition from the sulfated coating to non-sulfated core was always sharp, rather than gradual, following the unreacted core model. On the contrary, smaller particles had sulfated coatings consisting of nearly pure $CaSO_4$ in external surface of the particles with a gradual transition from the high sulfated external coating to the less sulfated core, generating a more uniform sulfur distribution in the whole particle. These behaviours were in good agreement with the experimental results obtained in the batch fluidized bed reactor.

3.4. Effect of SO_2 concentration

The SO_2 concentration in a fluidized bed combustor depends on the sulfur content of the coal used. Moreover, for the same coal under oxy-fuel combustion conditions, the SO_2 concentration in the combustor is higher than air combustion conditions due to the recirculation of flue gas towards the inlet of the system providing good sulfation conditions. In this work, to analyze the effect of SO_2 concentration on sulfation reaction rate, tests with different SO_2 concentrations between 1500 and 4500 vppm were performed as much as calcining as non calcining conditions.

Figure 12 shows the sulfation conversions achieved at 900 ºC in calcining and non-calcining conditions with different SO_2 concentrations. It was observed that the sulfation reaction rate and so the sulfation conversion increased with increasing the SO_2 concentration as much as in direct sulfation and indirect sulfation.

4. Conclusions.

Sulfur retention with limestone as sorbent under oxy-fuel combustion conditions in fluidized bed reactors can be carried by direct sulfation of the $CaCO_3$ or by sulfation of the CaO (indirect sulfation) depending on temperature and CO_2 partial pressure. Once

defined calcining or non-calcining operating conditions, the effect of CO_2 concentration on the sulfation reaction rate was negligible as much as direct sulfation as indirect sulfation operating conditions.

The rate of direct sulfation rose with increasing the temperature. The rate of indirect sulfation was almost not affected by the temperature for lower reaction times, but decreased faster with temperature for longer reaction times. However, for the same reaction time the sulfation conversion reached by the limestone working in operating conditions of direct sulfation was lower than working in operating conditions of indirect sulfation.

The major effect of increasing the CO_2 concentration in the reacting gas was to delay the $CaCO_3$ decomposition to CaO until a higher temperature. Due to the higher temperature needed to work in conditions of indirect sulfation with increasing CO_2, this had a negative influence on the sulfation conversion reached by the limestone. It is expected that the optimum temperature for sulfur retention in oxy-fuel combustion in fluidized bed reactors was incremented up to 925-950ºC from 850ºC for conventional air combustion.

The sulfation reaction rate rose with decreasing sorbent particle size and increasing SO_2 concentration. Therefore, the highest sulfation conversions were reached with the smallest particle sizes and the highest SO_2 concentrations as much as indirect sulfation as direct sulfation.

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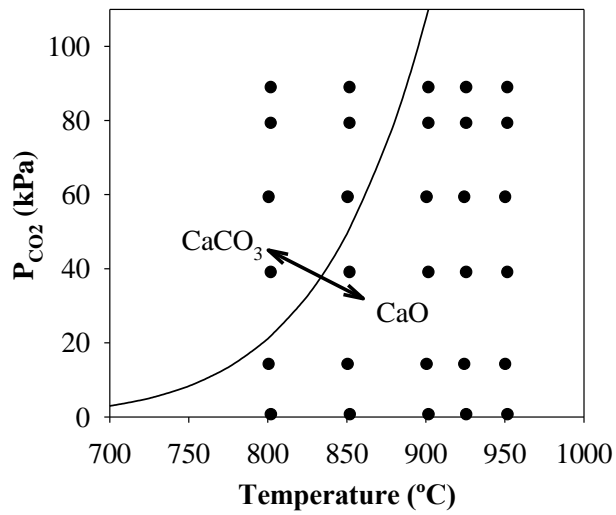
Captions of Tables and Figures

Fig. 1. $CaCO_3$-CaO thermodynamic equilibrium and main experiments performed in the batch fluidized bed reactor.
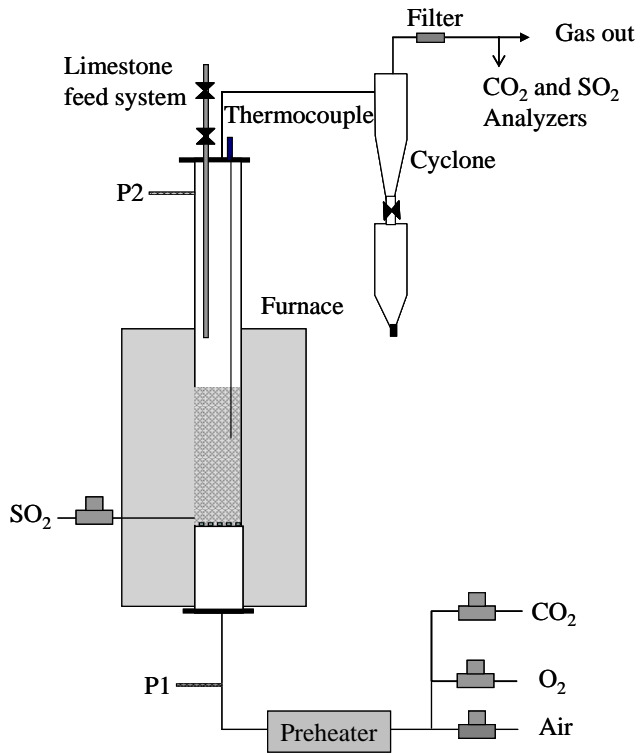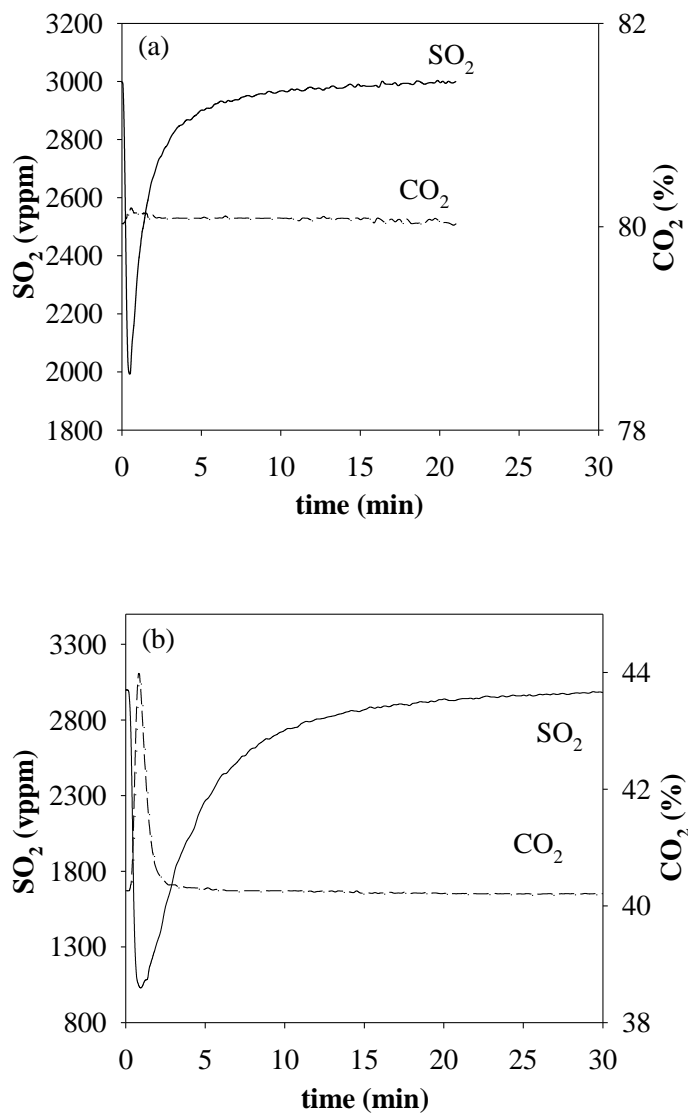
Fig. 2. Scheme of the batch fluidized bed reactor.

Fig. 3. Typical SO_2 and CO_2 concentration profiles during an experimental test. (a) Non-calcining conditions. (b) Calcining conditions.
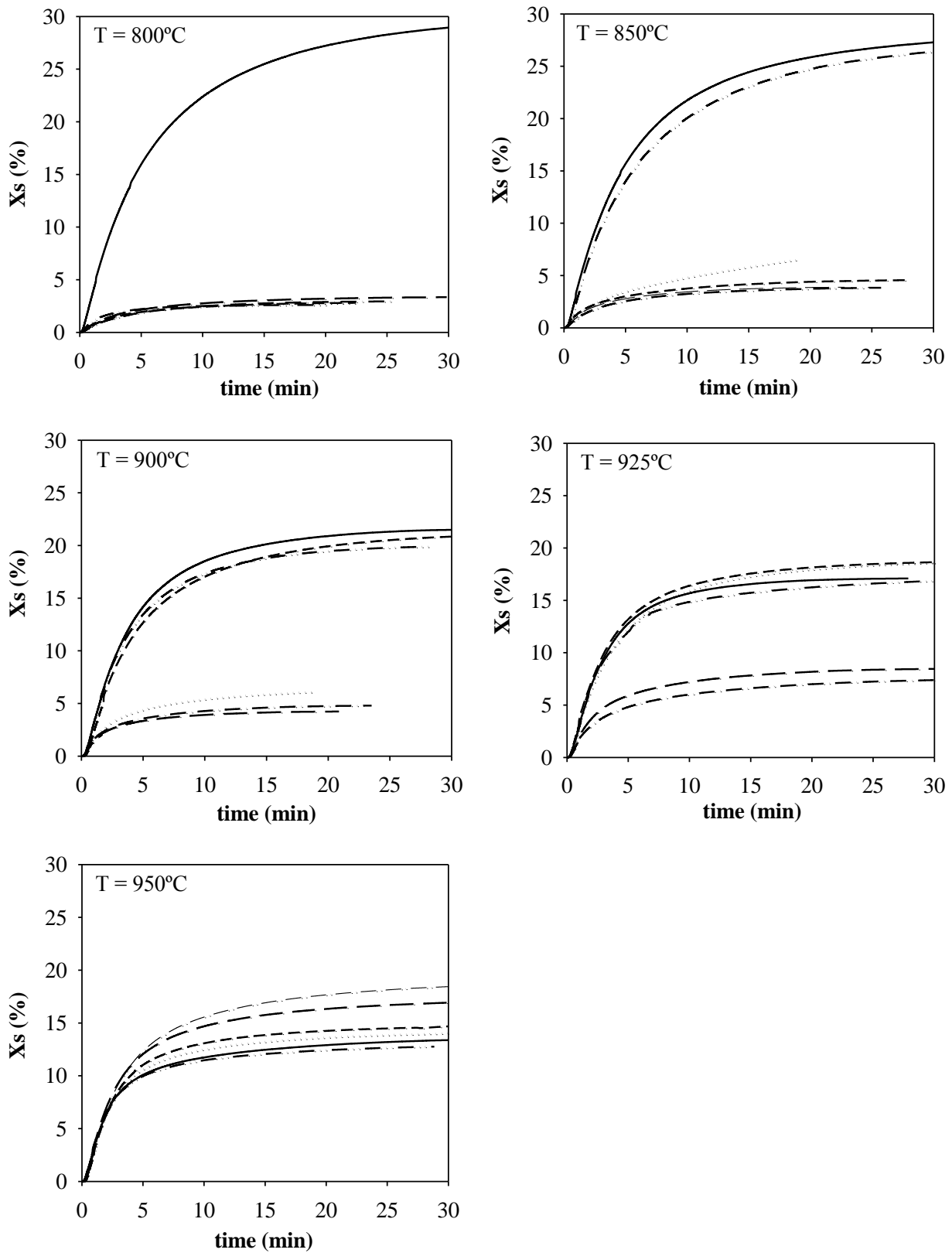
Fig. 4. Effect of CO_2 concentration on the sulfation reaction rate at different operating temperatures. dp = 0.3-0.5 mm, SO_2=3000 vppm. ——0% CO_2, ¯¯¯15% CO_2, ¯¯¯¯¯ 40% CO_2, ... 60% CO_2, ¯ ¯ ¯ 80% CO_2, ¯¯¯90% CO_2.
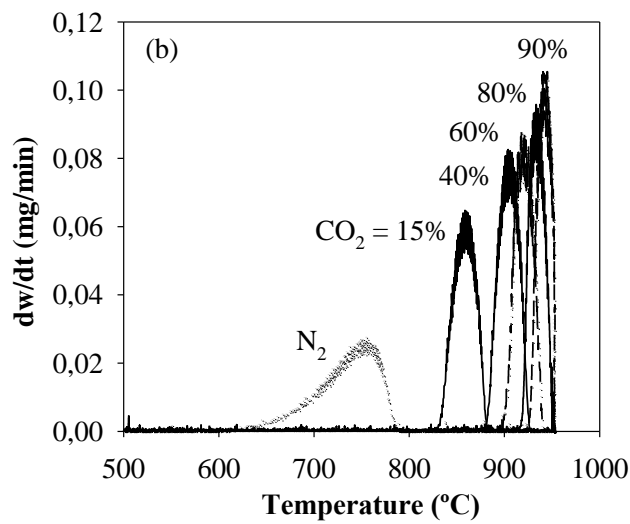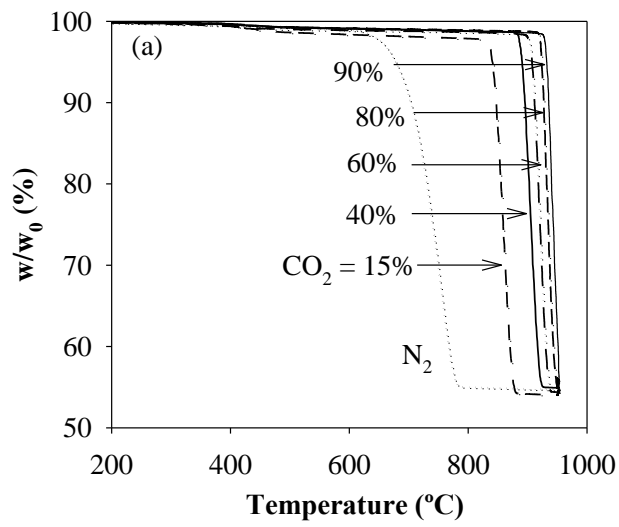
Fig. 5. Weight loss (a) and dw/dt (b) during limestone calcination with different CO_2 concentrations as a function of the reaction temperature in TGA.

Fig. 6. Comparison between the thermodynamic equilibrium curve (——) and the curve defining direct sulfation and indirect sulfation (- - - -).

Fig. 7. Effect of SO_2 in the reacting gases on the limestone calcination rate at different temperatures and CO_2 concentrations. dp = 0.3-0.5 mm (a) 40% CO_2 (b) 950ºC.

Fig. 8. Effect of temperature on the sulfation reaction rate at different CO_2 concentrations in the flue gas. dp=0.3-0.5 mm, SO_2=3000 vppm.

Fig. 9. Evolution of optimum temperature for sulfur retention with the CO_2 concentration.

Fig. 10. Effect of limestone particle size on sulfation reaction rate. T= 900ºC. SO_2=3000 vppm. Indirect sulfation: 40 vol% CO_2. Direct sulfation: 80 vol% CO_2.

Fig. 11. SEM-EDX images of sulphated limestone particles. (a) dp=0.063-0.1 mm, 900ºC, sulfation time: 2 h; (b) dp=0.8-1.0 mm, 900ºC, sulfation time: 24 h; (c) dp=0.4-0.5 mm, 850ºC, sulfation time: 24 h.

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Fig. 12. Effect of SO$_2$ concentration on sulfation reaction rate. T= 900ºC. dp= 0.3-0.5 mm. Indirect sulfation: 40 vol% CO$_2$. Direct sulfation: 80 vol% CO$_2$.

Table 1. Chemical composition and physical properties of "Granicarb" limestone.

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Chemical composition (%)	$CaCO_3$	$MgCO_3$	Na_2O	SiO_2	Al_2O_3	Fe_2O_3
	97.1	0.2	1.1	< 0.1	< 0.1	< 0.1
Physical properties		**Raw sorbent**		**Calcined sorbent**		
Porosity (%)		3.7		49		
Apparent density (kg m^{-3})		2573		1578		

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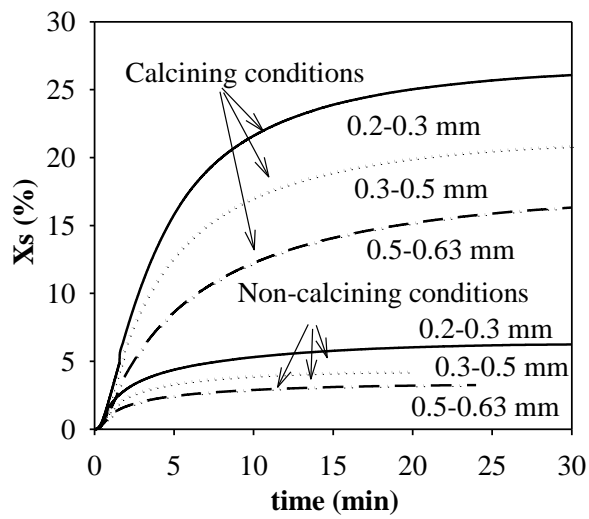**Fig. 9.** Evolution of optimum temperature for sulfur retention with the CO_2 concentration.

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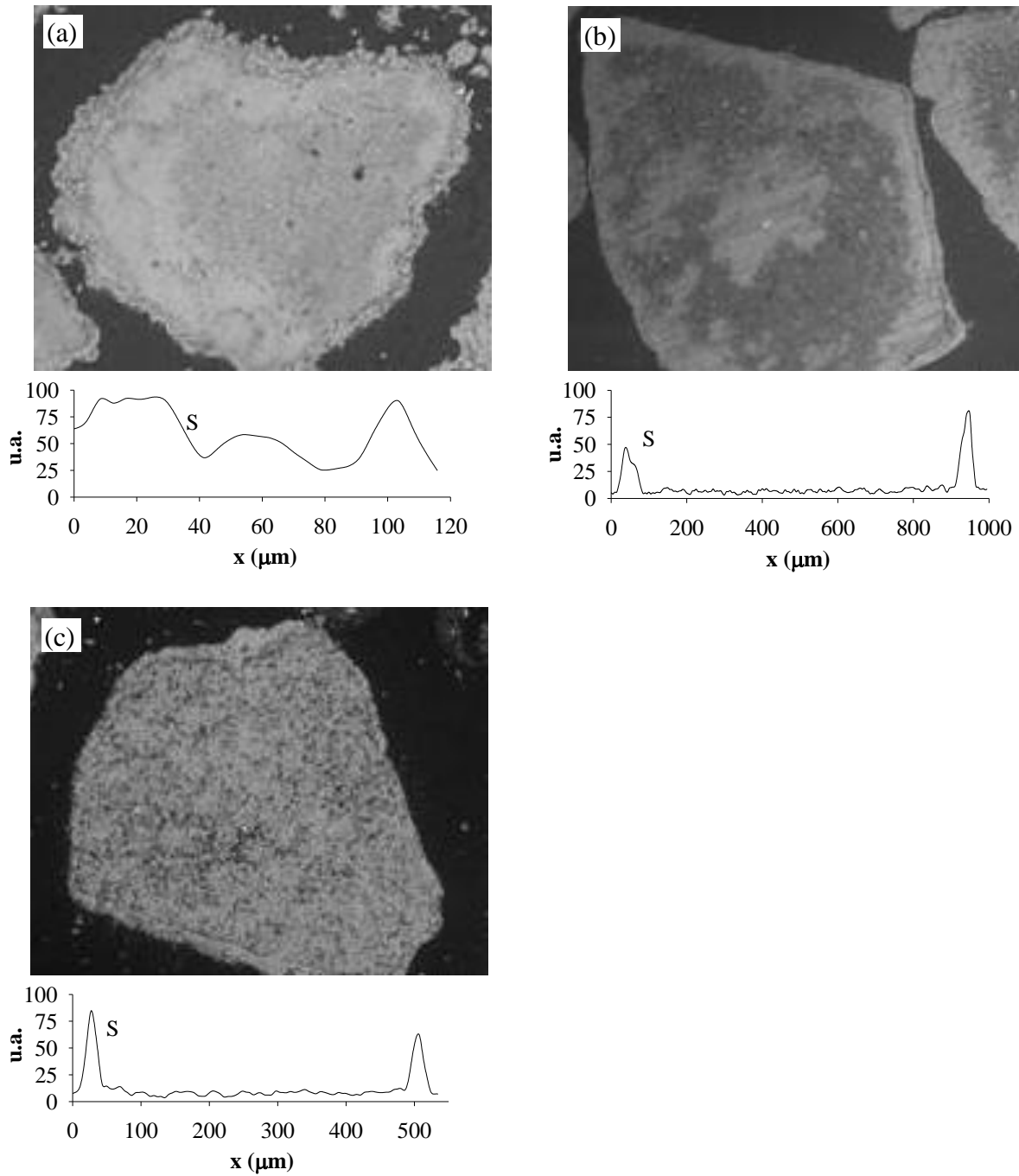
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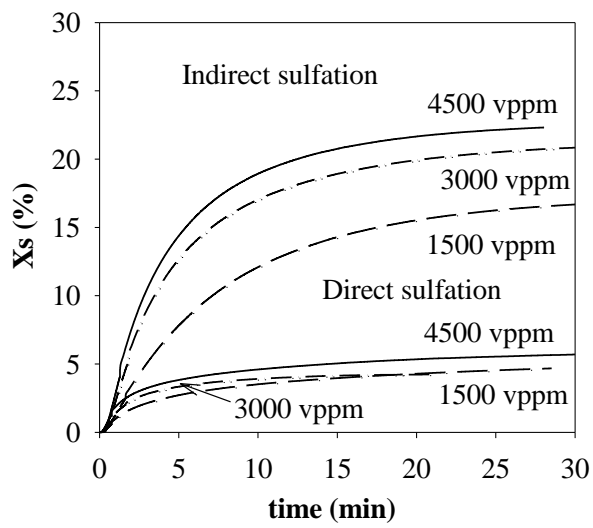
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