Submitted, accepted and published by:
Fuel 137 (2014) 384-392

Sulfur retention in an oxy-fuel bubbling fluidized bed combustor: Effect of coal rank, type of sorbent and O_2/CO_2 ratio.

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Keywords: Oxy-fuel combustion; Fluidized bed; Sulfur retention; Calcium sorbents; CO_2 capture.

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ABSTRACT

In this work, SO_2 retention via calcium-based sorbents added in a continuous bubbling fluidized bed combustor (~3 kW_{th}) operating in oxy-fuel combustion mode is analyzed. Tests were performed at different operating temperatures with three sorbents, two limestones and one dolomite, and with three coals, ranging from lignite to anthracite, to analyze the influence of coal rank, type of sorbent, sorbent particle size, and O_2/CO_2 feeding ratio on the sulfation process.

It was found that the combustor temperature had a strong influence on the limestones sulfur retention with a maximum at 900-925 ºC. The behavior of the limestones was qualitatively similar with the three coals, attaining the highest sulfur retention values

working with the lignite and the lowest working with the bituminous coal. On the contrary, with the dolomite the sulfur retention was hardly affected by the combustion temperature and the sulfur retentions attained were higher than with the limestones. The sulfur retention increased with diminishing the Ca-based sorbent particle size, and it was hardly affected by the O_2/CO_2 ratio fed into the combustor.

1. Introduction

Nowadays, there is a great public awareness about the emissions of pollutant gases into the atmosphere from large power plants. The release of CO_2 and SO_2 gases from coal combustion to generate electric power causes serious environmental problems. The former contributes to the build-up of greenhouse gases and the latter to acid rain formation.

According to the IPCC 2005 [1], CO_2 capture and storage technologies could be promising to mitigate CO_2 emissions from large power plants into the atmosphere. The development of CO_2 capture technologies to obtain an outlet gas stream in energy generation processes with high CO_2 concentration seems to be one of the most reliable solutions to slow down the increase of CO_2 in the future. Currently, there are several types of CO_2 capture technologies, oxy-fuel combustion being one of them. Oxy-fuel combustion consists of burning the fuel with a mix of pure oxygen and a part of recycled flue gas, mainly composed of CO_2 (after steam condensation) [2-4]. Therefore, the CO_2 concentration in the flue gas may be enriched up to 95%, making possible an easy CO_2 recovery.

There are different types of boilers to perform this process. Fluidized bed (FB) combustors, and particularly circulating fluidized bed (CFB) combustors, are very promising for the oxy-fuel process because as well as having a great versatility to burn fuels (either fuel-lean or blend of coal with other fuels such as biomass or wastes) they allow the in-situ flue gas desulfurization via Ca-based sorbents added into the combustor, such as limestone or dolomite. This could be an advantage since sulfur containing species mean a risk of corrosion and could have impacts on the furnace, during ash collection, CO_2 compression, transport and storage [5-6]. Currently, the CFB oxy-fuel combustion technology is gaining interest. Alstom [7], VTT and Foster Wheeler [8], Metso [9], Czestochowa University of Technology [10], Canmet Energy [6, 11-13], and Fundación Ciuden [14] have carried out oxy-fuel combustion experimental tests with CFB combustors at scales up to 30 MW_{th}.

Canmet Energy research group has successfully worked with two CFB combustors of 100 kW_{th} [11-12, 15] and 0.8 MW_{th} [6,13] with flue gas recycle. They found lower sulfur retention via calcium sorbents addition in oxy-fuel combustion than in air combustion conditions at about ~850 ºC. However, further increases of temperature led to the enhancement of the sulfur retention in oxy-fuel combustion, that is, once the conditions were shifted from direct to indirect sulfation. Their results strongly support the point of view that oxy-fuel combustion technology has the same advantages as air-fired CFB. Nevertheless, the test experiences showed that operating in the oxy-fuel mode led to increase corrosion as a consequence of higher sulfur concentrations in the flue gas [6]. SO_2 concentration in the oxy-fuel mode was up to four times higher compared to the air firing mode. They suggested that the combustion mode affected limestone performance for sulfur removal and that this impact depended on combustion temperature as well as on fuel characteristics.

Our research group has performed experimental tests in a thermogravimetric analyzer (TGA) [16], in a batch fluidized bed reactor [17], and in a continuous bubbling fluidized bed (BFB) combustor (~3 kW_{th}) [18-19] to analyze the effect of temperature on the SO_2 retention by limestones under oxy-fuel operating conditions. It was observed that the main effect of increasing the CO_2 concentration in the combustor was to shift the $CaCO_3$ decomposition to CaO at higher temperatures. An optimum temperature with respect to sulfur retention in oxy-fuel conditions was found to be around 900-925 ºC whereas in oxygen enriched air combustion the optimum temperature was around 850-870 ºC.

In industrial plants, the SO_2 in the flue gas can be removed before or after the stream recirculation. In this work, the SO_2 retention via calcium-based sorbents added into a continuous BFB combustor (~3 kW_{th}) operating in the oxy-fuel combustion mode is analyzed simulating an inlet gas composition similar to one obtained when the gas cleaning is carried out before stream recirculation. Nevertheless, the effect of the SO_2 recirculation was analyzed in a previous paper [19]. Tests were performed at different operating temperatures with three sorbents, two limestones and one dolomite, and with three coals, ranging from lignite to anthracite. In addition, the influence of the sorbent particle size and O_2/CO_2 feeding ratio in the sulfation process is also analyzed.

2. Experimental section

2.1. Materials

To study the sulfation process, two Spanish coals, a lignite and an anthracite, and a Colombian bituminous coal were selected as fuels. The coals were crushed and sieved in a range of the particle size between 0.2 and 1.2 mm. Table 1 shows the proximate and ultimate analysis of the coals. Moreover, two Spanish limestones, and one Spanish dolomite were used as calcium-based sorbent for sulfur retention. The particle size of the sorbents was in the range of 0.3-0.5 mm, except for the tests where the sorbent particle size was analyzed. Table 2 gives the chemical analysis and the main physical properties of the sorbents.

To control the residence time of the sorbent in the fluidized bed combustor, inert silica sand with a particle size of 0.2-0.6 mm was also fed along with the fuel and the sorbent during the tests.

2.2. Experimental installation

The experimental installation consisted of a fluidized bed combustor (~3 kWth) and different auxiliary systems for gas supply, solid feeding, solid recovering, and gas analysis. Figure 1 shows a schematic diagram of the installation.

The combustor consisted of a stainless steel reactor of 9.5 cm i.d. and 60 cm height and a freeboard of 15 cm i.d. and 50 cm height. The height of the solids in the BFB was kept constant at 40 cm. The reactant gases, air, CO_2, and O_2, were supplied from bottle cylinders by means of electronic mass-flow controllers to simulate typical gas compositions entering the reactor in oxy-firing mode.

The gases were introduced into the reactor through a gas distributor plate and the solids by means of water-cooled screw feeders located just above the distributor plate. The O_2, CO_2, CO, and SO_2 concentrations at the exit of the combustor were continuously analyzed after water condensation by on-line gas analyzers. The installation was described in detail in a previous paper [19]. Table 3 shows the feeding rates of solids and the flow rate of gases used in the tests.

2.3. Procedure

To start-up, the bed was filled with ~1.8 kg of silica sand and hot air was fed through a gas pre-heater to reach the coal ignition temperature. Then, the coal feeding started and the bed temperature went on increasing due to the coal combustion. After reaching the desired temperature, the preheating system was turned off, the air was replaced by the typical oxy-fuel gas mixture, O_2/CO_2, sand and a coal/limestone mixture were fed into the bed and a heat exchanger was introduced into the bed to control the temperature. Once a stable operation was attained, it was maintained to reach up to the steady state operation for SO_2 retention. An important feature of the tests carried out in the continuous unit was the certainty that the results were obtained under steady state conditions. This aspect was commented in detail in a previous paper [18].

SO_2 retentions (SR) were calculated by equation (1) as the molar fraction of sulfur retained by the bed solids with respect to the sulfur contained in the coal feeding.

$$SR(\%) = \frac{\left(F_{0,coal} x_{S,coal} / M_S\right) - Q_{out} \cdot C_{SO2,out}}{F_{0,coal} x_{S,coal} / M_S} .100 \qquad (1)$$

being $F_{0,coal}$ the coal feeding rate, $x_{S,coal}$ the coal sulfur content, M_S the molecular weight of S, $C_{SO2,out}$ the SO_2 concentration in the flue gas at the exit of the reactor (dry base), and Q_{out} the gas flow rate at the reactor exit (dry base). Q_{out} was calculated by means of a mass balance, considering the coal and gas feeding flow rates and the flue gas composition. $C_{SO2,out}$ was considered as an average value of the measurements taken during the whole test duration in steady state conditions. The average concentrations of the other gases during the test were also taken into account and were calculated in the same way as for SO_2. The steady state was maintained for at least 1 h for each experimental condition.

3. Results and discussion.

FB combustors usually operate at a temperature range of 800-950 ºC, and in overall oxidizing conditions [20]. Under conventional air combustion in FB combustors, where the CO_2 concentration in the flue gas is relatively low (up to 16%), some researchers [21-22] have found the optimum temperature for sulfur retention to be nearly 850 ºC. However, under oxy-fuel operating conditions, where the CO_2 concentration is quite higher than in air combustion, up to 90 vol.%, the optimum temperature for sulfur retention was observed to be around 900-925 ºC [18]. In this work, coal combustion tests with three coals and three Ca-based sorbentes were carried out in a BFB combustor working in oxy-fuel combustion conditions at different temperatures between 830 and 975 ºC. In most of the tests, an inlet gas composition ratio of O_2/CO_2 =35/65 (vol./vol.) was used. The coal feeding rate was controlled to maintain the O_2 concentration at 4.0±1.0 vol.% at the combustor exit (dry basis).

Tables 4-6 summarize the experiments performed with the different coals and Ca-based sorbents, including the operating conditions (temperature, Ca/S molar ratio, particle size and O_2 feeding concentration), as well as the O_2 and SO_2 concentrations measured at the gas exit in each case. These data correspond to the average values recorded during at least 1 hour working under steady state operation.

To calculate the SR, coal combustion efficiencies of 100 % were assumed. This simplification was made because the carbon combustion efficiencies determined in tests carried out without limestone addition, taking into account the carbon fed to the combustor and the losses of carbon in the solids collected in the cyclone and in the solids collected in the drainage deposit, were always >99 % working with lignite, >98 % working with anthracite, and >97 % working with bituminous coal.

3.1. Effect of calcium-based sorbent type on sulfur retention.

Two limestones and one dolomite were selected to analyze the behavior of different calcium based sorbents for sulfur retention. Limestones are mainly composed of $CaCO_3$ whereas dolomite is almost formed in the same molar proportion by $CaCO_3$ and $MgCO_3$. When a limestone or a dolomite is added to a FB combustor, temperature and CO_2 partial pressure are the most important parameters affecting the SO_2 retention process because sorbent calcination is highly dependent on the temperature and CO_2 partial pressure. At the conditions existing in FB combustors, the $MgCO_3$ always decomposes into MgO, but the MgO remains inactive due to $MgSO_4$ being unstable at FB operating conditions [20]. Likewise, $CaCO_3$ can decompose into CaO and CO_2 or can remain as $CaCO_3$ depending on the temperature and the CO_2 partial pressure in the boiler.

The conditions existing in FB boiler during conventional combustion with air lead to a previous sorbent calcination (R1 or R2) and to the sulfation of calcines (R3 or R4), so-called indirect sulfation:

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad \text{(R1)}$$

$$CaCO_3 \cdot MgCO_3 \rightleftharpoons CaO \cdot MgO + CO_2 \quad \text{(R2)}$$

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons CaSO_4 \quad \text{(R3)}$$

$$CaO \cdot MgO + SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons MgO \cdot CaSO_4 \quad \text{(R4)}$$

In oxy-fuel combustion, CO_2 concentration in the flue gas may be enriched up to values as high as 90 vol.%. Therefore, in our case, during the coal combustion the sorbent can be surrounded by high CO_2 concentrations, from 65 to 90 vol.%. Under such high CO_2

concentrations, the $CaCO_3$ can react in two ways depending on the operating temperature. At 850 ºC, the sulfur retention will be produced under direct sulfation (R5 or R6), requiring higher temperatures to reach calcining conditions, i.e. indirect sulfation (R1 and R3 or R2 and R4).

$$CaCO_3 + SO_2 + \frac{1}{2} O_2 \rightleftharpoons CaSO_4 + CO_2 \quad \text{(R5)}$$

$$MgO \cdot CaCO_3 + SO_2 + \frac{1}{2} O_2 \rightleftharpoons MgO \cdot CaSO_4 \quad \text{(R6)}$$

To analyze the influence of different Ca-based sorbents on sulfur retention, several tests were carried out keeping constant the Ca/S molar ratio and the O_2 concentration entering the reactor. Tables 4-6 and Figure 2 show the sulfur retentions reached by the different sorbents during anthracite combustion as a function of the combustor temperature. With both limestones, as it was observed in a previous work [18], the sulfur retention increased by increasing combustion temperature up to a maximum of 900-925 ºC and then, a further increase in temperature caused a decrease in the sulfur retention values. Previous studies outlined by Anthony and Granatstein [20], attribute this maximum in the sulfur retention with the temperature to several theories or hypothesis. Among them the most reliable are: 1) the sintering of sorbent particles is enhanced at higher temperatures reducing the overall conversion of limestone; 2) high temperatures result in an enhanced sulfation rate which causes small pores to be blocked, hence preventing the entry of SO_2/SO_3 into the interior of the calcined limestone particle, and 3) the possibility of reverse sulfation reaction as a consequence of alternative oxidizing and reducing conditions into the reactor. Operating with FB combustors in the oxy-firing mode, oxidizing conditions are expected along the combustor where sulfation reaction product, $CaSO_4$, is thermodynamically stable.

However, it is likely to find reducing conditions in localized parts of the bed in which the overall reactions that could take place are:

$$CaSO_4 + 4\ CO \leftrightarrow CaS + 4\ CO_2 \qquad (R7)$$

$$3\ CaSO_4 + CaS \leftrightarrow 4\ CaO + 4\ SO_2 \qquad (R8)$$

In tests carried out in a TGA using Granicarb limestone [16], it was observed that this limestone achieved a maximum sulfur retention capacity at 900 ºC. This maximum was explained as a consequence of hypotheses 1 and 2. In similar tests also performed in a TGA with Horcallana limestone, whose results are shown in the Figure 3, it is observed that the sulfation conversion of the limestone rises with increasing temperature up to 900 ºC, and this conversion is maintained at higher temperatures. However, as can be seen in Figure 2, Horcallana limestone demonstrates the same behavior in the BFB combustor as Granicarb limestone with an optimum temperature with respect to sulfur retention working about 900 ºC. So, this behavior can not only be explained by hypotheses 1 and/or 2 and thus, it is likely that hypothesis 3 plays an important role during the sulfation process in oxy-fuel combustion conditions, as was also seen in conventional air combustion [23-24].

To corroborate this last assumption, experimental tests feeding pure $CaSO_4$ together with the coal-limestone mixture at 925 and 950 ºC were performed. The tests were started feeding anthracite and Granicarb limestone up to reach steady state operating condition. Subsequently, the $CaSO_4$ along with the coal/limestone mixture was supplied. Figure 4 shows the results obtained. As can be seen, at both temperatures, the SO_2 concentration increased by adding pure $CaSO_4$. The SO_2 concentration was raised in 200 and 250 vppm working at 925 and 950 ºC respectively. So, it can be concluded that $CaSO_4$ reduction plays an important role on the sulfur retention at high temperatures under oxy-fuel operating conditions.

It can also be observed in Figure 2 that the sulfation conversions achieved by the limestones under indirect sulfation (reactions R1 and R3) were always higher than those achieved under direct sulfation (reaction R5). Working in calcining conditions (indirect sulfation), the sulfur retentions reached with the limestone Horcallana were slightly higher than reached by the limestone Granicarb. Figure 5 illustrates the pore size distributions of the three calcined Ca-based sorbents used in the tests. As can be seen, Horcallana limestone has a wider pore size distribution than Granicarb limestone, being able to reach higher overall sulfation conversions in calcining conditions.

With the dolomite, the sulfur retention was hardly affected by the combustion temperature. The sulfation conversions attained under indirect sulfation (reactions R2 and R4) were almost the same as those achieved under direct sulfation (reaction R6). In addition, for the same Ca/S molar ratio and with the sorbent particle size used, the sulfur retentions obtained with the dolomite were higher than those with the limestones. This fact was very significant in conditions of direct sulfation. Anthony and Granatstein [20] and Hu et al. [25] suggested that MgO acts as an inert component favoring the formation of $CaSO_4$ from nascent CaO or from $CaCO_3$ since there is no $MgSO_4$ formation. From data of Figure 2, it seems that MgO is an inert compound or impurity that significantly promotes the sulfation reaction in non-calcining conditions because, according to the $MgCO_3$/MgO equilibrium diagram (Figure 6), the $MgCO_3$ decomposition temperature is much lower than that of $CaCO_3$ at the same CO_2 partial pressure. Therefore, in direct sulfation an increase in the particles porosity of the dolomite is generated because of the early $MgCO_3$ decomposition (see Table 2) favoring the sorbent sulfation conversion. Figure 7 shows the sulfur distribution along the diameter of sectioned particles of Granicarb limestone and dolomite removed from the bed. As can be seen, the sulfation pattern of the dolomite was different from that of the limestone. The dolomite exhibited a uniform sulfur distribution in the overall particle whereas Granicarb limestone presented a sulfur distribution according to the shrinking core model. This different sulfation pattern is responsible for the higher conversion reached by the dolomite. Finally, it is worth mentioning that no evidence of decrepitation was noted in the dolomite. Despite the fact that previous studies [26] point out that the superiority of the dolomites is masked by their tendency to decrepitate to a fine powder which suffers elutriation before absorbing much sulfur, strong elutriation of fine particle sizes to the cyclone was not noticed.

Figure 8 shows the sulfur retentions achieved with the Granicarb limestone and the dolomite for different Ca/S molar ratios. Obviously, for both sorbents, the sulfur retention increased by increasing the Ca/S molar ratio, and for the same Ca/S molar ratio, the sulfur retentions attained with the dolomite were higher than those with the limestone.

3.2. Effect of sorbent particle size on sulfur retention.

Sorbent particle size has been found to affect the sorbent sulfation during the operation of fluidized bed combustors because pore plugging produces a decrease in the sulfation reaction rate and prevents sulfation of the inner parts of the particle. As a consequence, a lower sorbent utilization is likely to be reached with increasing the sorbent particle size.

In this work, different particle sizes of the “Granicarb” limestone and “Sierra de Arcos” dolomite, using the anthracite as fuel, were fed into the BFB combustor to analyze its behavior with respect to sulfur retention. As shown in Tables 5 and 6, the tests were carried out at 925 ºC, with an inlet O_2/CO_2 gas stream composition of 35/65, and a Ca/S molar ratio of 3 and 2 for Granicarb limestone and dolomite respectively.

Figure 9 shows the sulfur retentions achieved for the different calcium-based sorbent particle sizes. As expected, for the limestone, the sulfur retention, and therefore, the sorbent utilization decreased as the particle size increased. The lower utilization of the larger limestone particles is mainly due to the blockage of pores by $CaSO_4$ formation. As seen in Figure 7, the sulfation reaction took place in an external layer around the particles because the molar volume of the $CaSO_4$ is higher than the molar volume of the $CaCO_3$ or CaO and thus the pores were blocked and the inner core of the particle remained essentially unreacted. So, as the unreacted inner volume of larger particles is proportionally higher than that of the smaller particles, the sorbent utilization decreased by increasing the particle size.

Regarding the dolomite, since MgO acts as inert material improving the access of SO_2 towards the inner part of the particles (see Figure 7), it could be expected that the particle size had less influence on the sulfation rate. However, as can be seen in Figure 9, the influence of the sorbent particle size on the sulfur retention was very similar working with the limestone and the dolomite.

3.3. Effect of the O_2 concentration fed to the combustor.

An important feature in oxy-fuel combustion is the O_2/CO_2 ratio in the inlet gas stream. It is known that higher inlet O_2 concentration leads to reducing the boiler size, and therefore capital expenses, and to reducing the recycled flue gas which diminishes energetic penalty [27]. However, to get the aim of using high O_2/CO_2 ratios it is still necessary to solve some drawbacks, such as the strength of the materials to resist high temperatures and/or corrosion.

In this section, the effect of O_2 concentration entering the reactor on the sulfur retention is analyzed. Experimental tests with O_2 concentrations in the feeding from 27 to 45 vol.% were performed. The tests were carried out using anthracite as fuel, the Granicarb limestone as Ca-based sorbent, at the temperature of 925 ºC with a Ca/S molar ratio of 3, and keeping constant the inlet gas velocity into the reactor. In order to maintain an O_2 concentration around 4.0 vol.% in the flue gas exit, the amount of coal introduced into the combustor was varied depending on the oxygen concentration fed into the boiler, that is, the coal fed to the combustor was increased as the O_2 concentration in the inlet gas increased.

It might be expected that an increase in O_2 concentration led to higher SO_2 concentration and consequently higher sulfur retention. However, as can be seen in Figure 10, the sulfur retention was hardly affected by the O_2 concentration fed into the combustor. This fact could be due to the effect of compensation between the increase of the coal feeding or SO_2 concentration generated, and the decrease of the residence time of the solids inside the combustor. Moreover, since a higher inlet oxygen concentration rate involves a higher fuel feeding, a locally more elevated SO_2 concentration near the feeding point can be found and SO_2 plumes can be generated in the bed. The SO_2 plumes could pass without reacting with the limestone, due to a poor mix of SO_2 and limestone in the bed, decreasing the sulfur capture.

3.4. Influence of coal rank on sulfur retention.

Three coals of different rank and with different sulfur content, lignite, bituminous, and anthracite, were selected to analyze the influence of the type of coal on the sulfur retention in oxy-firing conditions in the fluidized beds. Figure 11a) shows a comparison of the sulfur retentions obtained with the Granicarb limestone working at the same operating conditions with the three coals. It can be observed that the behavior of the limestone was qualitatively similar with the three coals with maximum sulfur retention at 900-925 ºC. The highest sulfur retention values, and therefore the highest limestone sulfation conversions, were achieved working with the lignite whereas the lowest were achieved working with the bituminous coal.

Previous studies carried out under oxy-fuel combustion conditions in a TGA [16] and in a batch FB reactor [17] demonstrated that the sulfation conversion of the sorbent increased as the SO_2 concentration increased. Consequently, the highest SO_2 concentration present in the FB combustor during lignite combustion was responsible for the highest sulfur retention values achieved in the combustor. However, it is worth mentioning that higher sulfur retention does not mean lower SO_2 emission (see Figure 11b) because the coals have very different sulfur content (see Table 1), the lignite having the highest and the bituminous the lowest sulfur content. The low sulfur retentions achieved at the highest temperatures with the bituminous coal were also remarkable. With this coal, in addition to the lowest sulfur content, and thus, the lowest SO_2 concentration present in the FB combustor during the combustion, other factors must be contributing to achieve the very low sulfur retention values. One of them is likely to be the substantial amount of unburned gases generated because numerous peaks of CO concentration were recorded during the combustion process. For this reason, two possibilities could occur: 1) the generation of plumes of volatiles which prevented good contact between the SO_2 and the limestone and/or 2) the $CaSO_4$ reduction as a result of the existence of high CO concentration caused by reducing conditions [27].

4. Conclusions.

This paper summarizes the experimental tests carried out in a BFB combustor operating under oxy-fuel combustion conditions in order to analyze the sulfur retention via Ca-based sorbents addition using different coals and sorbents.

With the limestones the sulfur retention became greater by increasing the combustion temperature up to 900-925 ºC and then, a further rise in temperature caused a decrease in the sulfur retention values due to sorbent sintering and $CaSO_4$ reduction. However, the sulfur retention with the dolomite was hardly affected by the combustion temperature in the interval 830-950 ºC.

The sulfur retentions reached with the dolomite were higher than those obtained with the limestones. This fact was very significant under conditions of direct sulfation. Therefore, the dolomite can be an adequate sorbent for SO_2 retention.

The sulfur retentions were hardly affected by the O_2/CO_2 ratio fed to the combustor, and increased by diminishing the Ca-based sorbent particle size.

The behavior of the limestones was qualitatively similar with three different coals. However, the sulfur retention values depended on the sulfur content of the coal used. The highest coal sulfur content involved the highest sulfur retention due to the highest SO_2 concentration inside the reactor. It was remarkable the low sulfur retentions achieved at the highest temperatures (>925 ºC) working with the bituminous coal.

Acknowledgements.

This research has been supported by Spanish Ministry of Science and Innovation (MICINN, Project: CTQ2008-05399/PPQ) and by FEDER. M. de las Obras-Loscertales thanks MICINN for the F.P.I. fellowship and A. Rufas thanks CSIC for the JAE fellowship.

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Table 1. Proximate and ultimate analysis of coals.

	Lignite	Anthracite	Bituminous
Proximate analysis (wt %)			
Moisture	12.6	2.3	5.2
Ash	25.2	31.7	12.9
Volatiles	28.7	5.6	32.7
Fixed C	33.6	60.4	49.2
Ultimate analysis (wt %, wet)			
C	45.43	59.64	65.63
H	2.50	1.67	4.06
N	0.65	0.93	1.5
S	5.17	1.52	0.77
LHV (kJ/kg)	16252	21807	25398

Table 2. Chemical composition and physical properties of Ca-based sorbents.

Sorbent	**Granicarb**		**Horcallana**		**Dolomite**		
	Raw	**Calcined**[a]	**Raw**	**Calcined**[a]	**Raw**	**Semi-calc**[b]	**Calcined**[a]
Physical properties							
Porosity (%)	3.7	49.0	2.8	49.8	9.5	30.6	51.7
Apparent density (kg m^{-3})	2573	1578	2601	1589	2512	1912	1454

Chemical composition wt.%	**Granicarb**	**Horcallana**	**Dolomite**
$CaCO_3$	97.1	92.7	52.5
$MgCO_3$	0.2	1.0	40.5
Na_2O	1.1	<0.1	---
SiO_2	<0.1	2.0	3.8
Al_2O_3	<0.1	0.8	1.7
Fe_2O_3	<0.1	0.8	0.6

[a] Calcined in N_2 atmosphere at 900 ºC for 10 min.

[b] Calcined in 60 vol.% CO_2 and 40 vol.% N_2 at 850 ºC for 10 min

Table 3. Feeding rates of solids and flow rate of gases used in the tests.

	Anthracite	Lignite	Bituminous
Q_{in} (l_N/h)	2230	2230	2230
F_{coal} (g/h)	576 ± 14	700 ± 15	510 ± 20
$F_{0,limestone}$ (g/h)	82 ± 2	339 ± 8	28 ± 1
$F_{0,dolomite}$ (g/h)	105 ± 2	-	-
$F_{0,sand}$ (g/h)	900 ± 20	900 ± 20	900 ± 20

Table 4. Experimental tests performed in the BFB combustor using “Granicarb” limestone and different coals.

	T (ºC)	Ca/S (mol/mol)	O_2/CO_2 (vol./vol.)	dp (mm)	$O_{2,exit}$ (%)	$SO_{2,exit}$ (vppm)	SR (%)
Lignite							
	850	3	35/65	0.3-0.5	5.0	5700	48.5
	850	3	35/65	0.3-0.5	4.4	6560	41.8
	875	3	35/65	0.3-0.5	4.1	3828	66.4
	900	3	35/65	0.3-0.5	3.8	2463	78.5
	920	3	35/65	0.3-0.5	3.9	2429	78.8
	925	3	35/65	0.3-0.5	3.5	2651	77.1
	950	3	35/65	0.3-0.5	4.3	3595	68.2
	950	3	35/65	0.3-0.5	4.4	3028	73.0
Anthracite							
	820	3	35/65	0.3-0.5	4.0	2046	24.7
	850	3	35/65	0.3-0.5	3.8	1866	31.6
	875	3	35/65	0.3-0.5	3.6	1460	48
	900	3	35/65	0.3-0.5	3.5	1026	62.7
	900	3	35/65	0.3-0.5	3.4	931	66.3
	925	3	35/65	0.2-0.3	3.7	575	79.0
	925	3	35/65	0.2-0.3	4.2	570	78.9
	925	3	35/65	0.3-0.5	3.7	789	71.1
	925	3	35/65	0.3-0.5	3.7	938	65.7
	925	3	35/65	0.3-0.5	3.2	1005	63.9
	925	3	35/65	0.5-0.63	3.9	978	64.0
	925	3	35/65	0.63-0.8	3.9	1086	60.0
	925	3	27/73	0.3-0.5	3.2	585	71.6
	925	3	45/55	0.3-0.5	4.0	925	74.7
	940	3	35/65	0.3-0.5	3.6	1155	58.0
	950	3	35/65	0.3-0.5	3.2	1328	52.3
	975	3	35/65	0.3-0.5	3.7	1529	44.2
	850	2	35/65	0.3-0.5	4.3	2012	25.2
	925	2	35/65	0.3-0.5	3.6	1162	57.7
	950	2	35/65	0.3-0.5	3.7	1477	46.0
	925	1	35/65	0.3-0.5	3.2	1778	36.2
Bituminous							
	850	3	35/65	0.3-0.5	4.6	891	24.8
	900	3	35/65	0.3-0.5	4.8	705	40.2
	925	3	35/65	0.3-0.5	4.3	761	36.5
	950	3	35/65	0.3-0.5	5.2	1068	8.0

Table 5. Experimental tests performed in the BFB combustor using "Horcallana" limestone and anthracite coal.

T (ºC)	Ca/S (mol/mol)	O_2/CO_2 (vol./vol.)	dp (mm)	$O_{2,exit}$ (%)	$SO_{2,exit}$ (vppm)	SR (%)
825	3	35/65	0.3-0.5	3.0	2198	20.0
850	3	35/65	0.3-0.5	3.5	1955	29.2
900	3	35/65	0.3-0.5	3.6	833	69.7
925	3	35/65	0.3-0.5	3.9	664	75.6
950	3	35/65	0.3-0.5	3.6	789	71.2
975	3	35/65	0.3-0.5	3.6	1072	61.0

Table 6. Experimental tests performed in the BFB combustor using "Sierra de Arcos" dolomite and anthracite coal.

T (ºC)	Ca/S (mol/mol)	O_2/CO_2 (vol./vol.)	dp (mm)	$O_{2,exit}$ (%)	$SO_{2,exit}$ (vppm)	SR (%)
850	3	35/65	0.3-0.5	3.8	92	96.6
925	3	35/65	0.3-0.5	4.3	15	99.4
830	2	35/65	0.3-0.5	3.9	431	84.1
850	2	35/65	0.3-0.5	4.1	390	85.5
850	2	35/65	0.3-0.5	3.9	369	86.4
900	2	35/65	0.3-0.5	3.5	344	87.5
920	2	35/65	0.3-0.5	3.8	364	86.6
925	2	35/65	0.2-0.3	3.8	188	93.1
925	2	35/65	0.3-0.5	4.0	310	88.5
925	2	35/65	0.5-0.63	3.9	516	81.0
950	2	35/65	0.3-0.5	3.9	329	88.0
975	2	35/65	0.3-0.5	3.9	433	84.0
925	1	35/65	0.3-0.5	3.6	1385	49.2

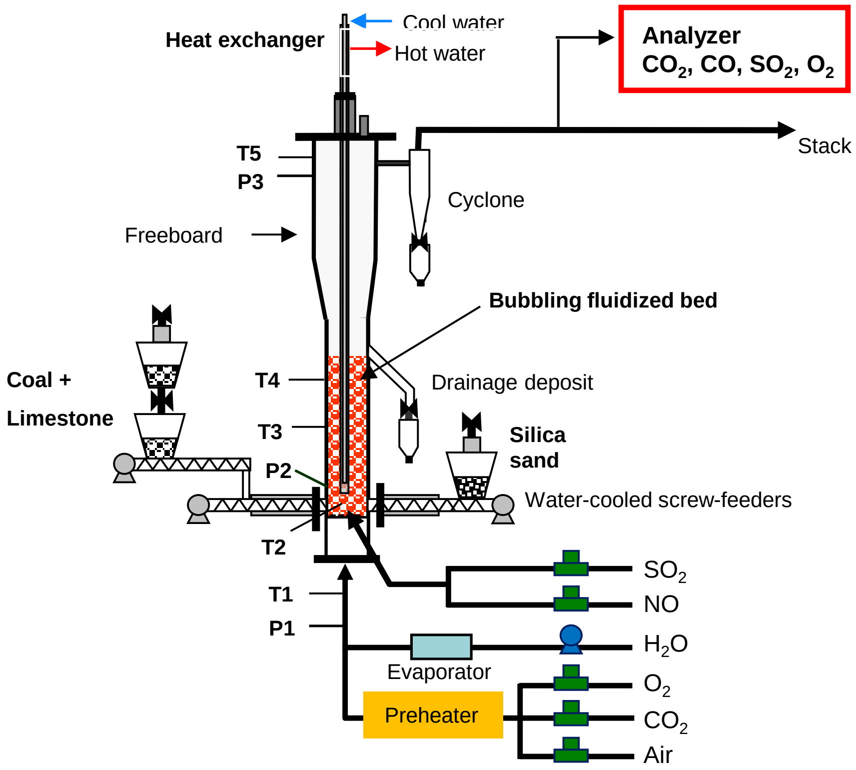

Figure 1. Scheme of the BFB combustor (ICB-CSIC).

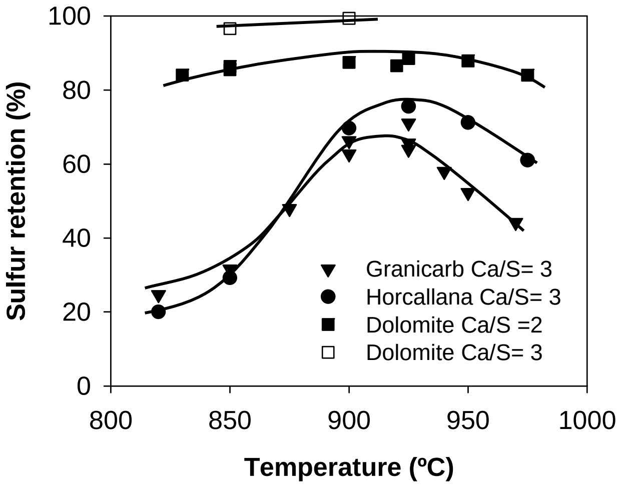

Figure 2. Influence of combustion temperature on sulfur retention using different Ca-based sorbents and anthracite as fuel. O_2/CO_2=35/65, dp =0.3-0.5 mm

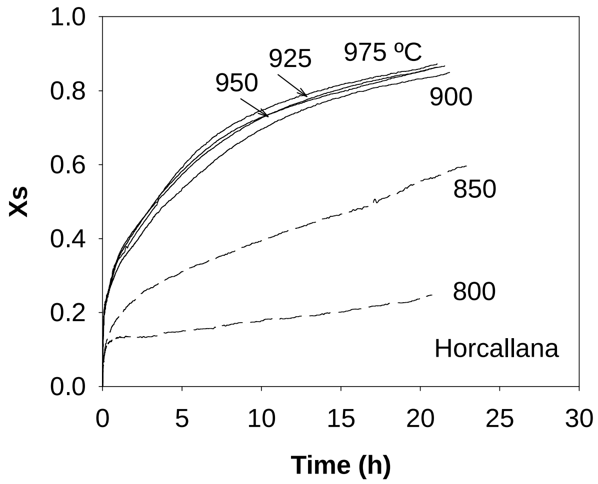

Figure 3. Effect of temperature on the Horcallana sulfation conversion in TGA. dp = 0.1–0.2 mm; 60 vol.% CO_2, 20 vol.% O_2, 3000 vppm SO_2 (N_2 to balance). Indirect sulfation (—) and direct sulfation (- - -).

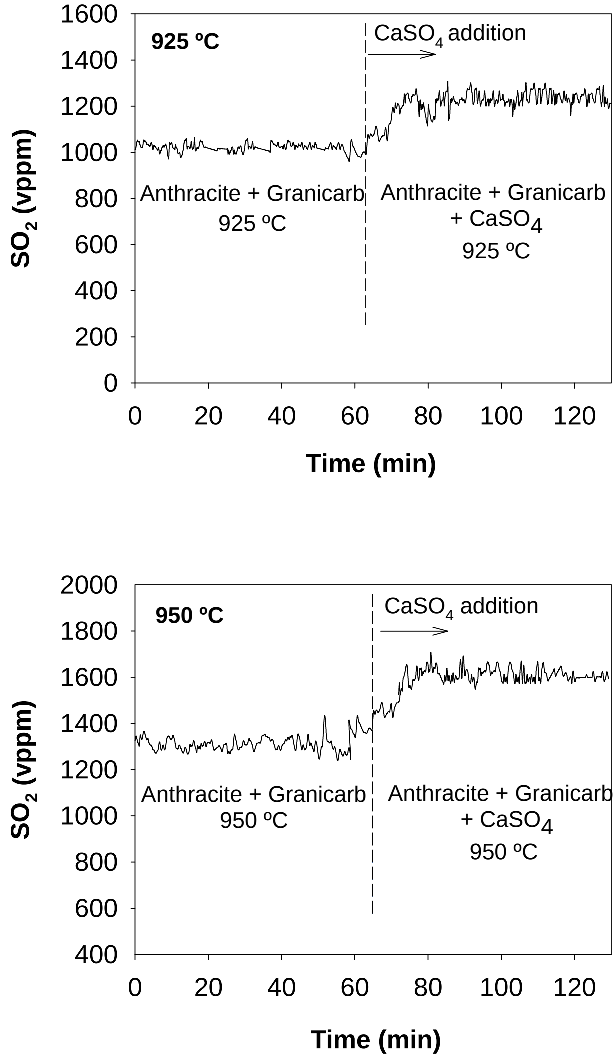

Figure 4. Increase in SO_2 concentration at the exit of the combustor due to the feeding of $CaSO_4$ at 925 and 950ºC in oxy-fuel combustion conditions. O_2/CO_2=35/65, Ca/S= 3.

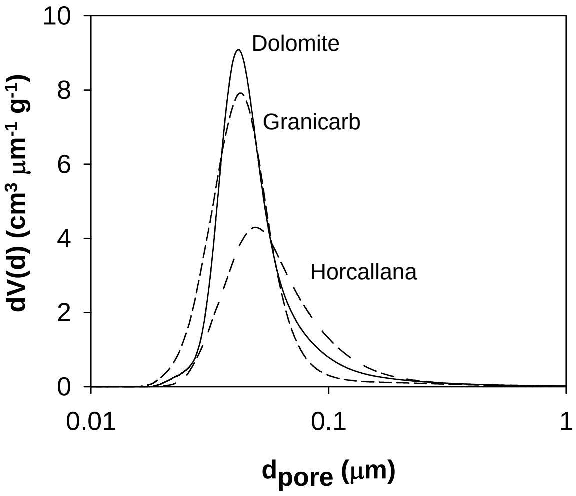

Figure 5. Pore size distribution of Horcallana and Granicarb limestones and dolomite calcined in N_2 atmosphere at 900 ºC for 10 min.

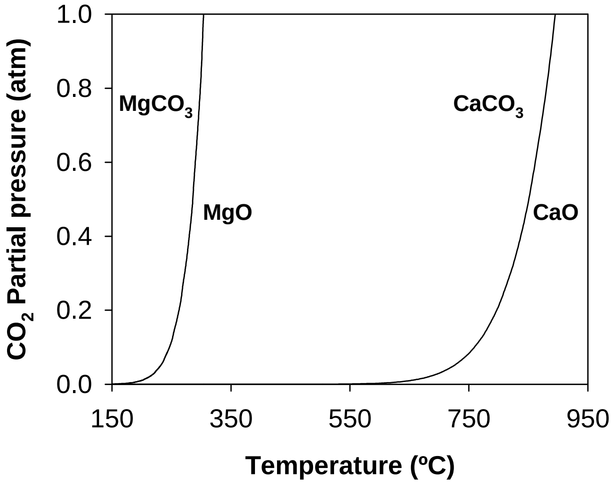

Figure 6. Equilibrium diagram of $MgCO_3$/MgO and $CaCO_3$/CaO

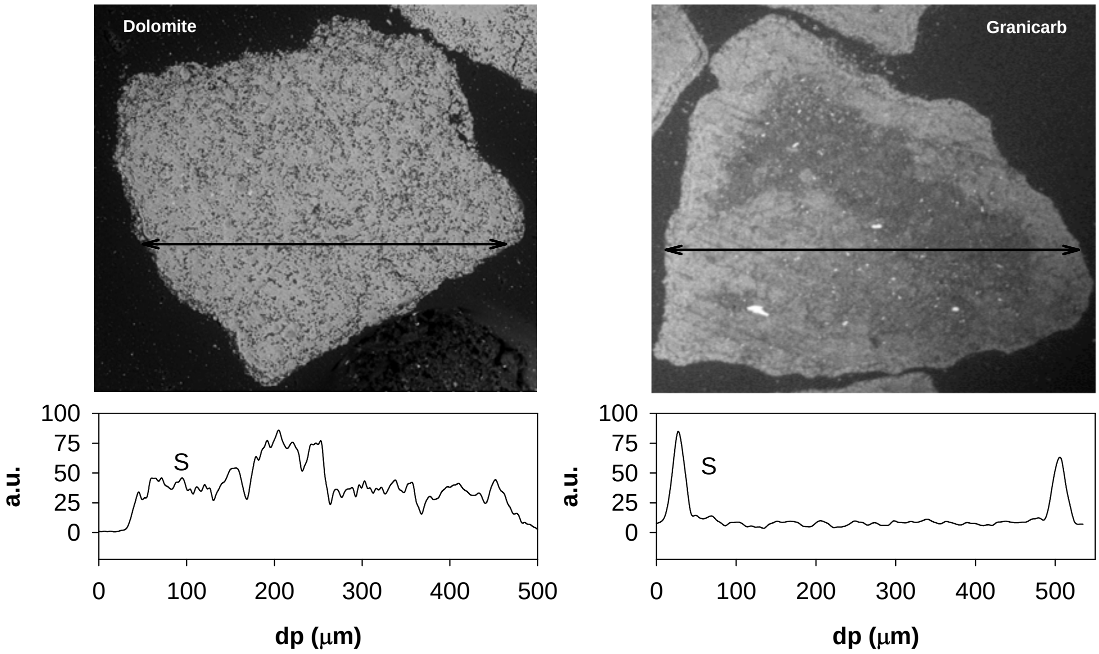

Figure 7. Sulfur distribution along the diameter of sulfated particles removed from BFB combustor. Fuel = Anthracite, T= 925ºC, Ca/S = 3.

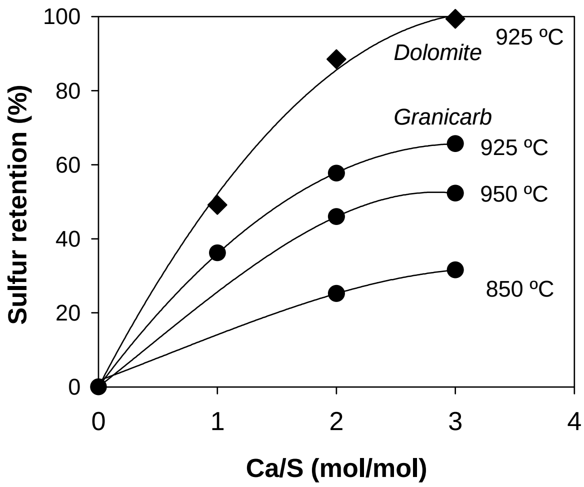

Figure 8. Effect of Ca/S molar ratio on sulfur retention for dolomite and Granicarb limestone. Fuel = Anthracite, O_2/CO_2 = 35/65.

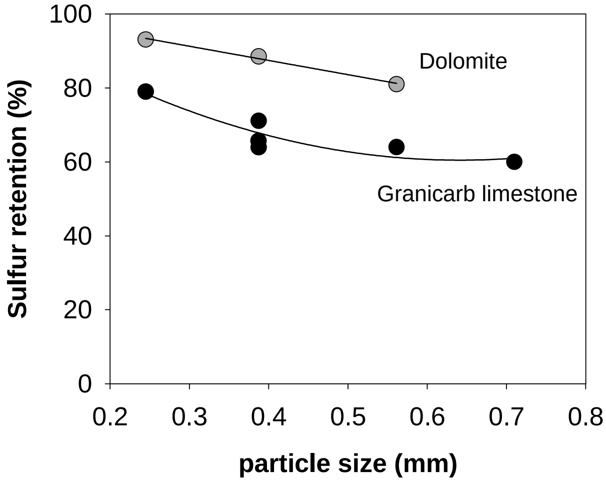

Figure 9. Influence of the particle size of Granicarb limestone and dolomite on sulfur retention. Fuel = anthracite, T= 925 ºC, O_2/CO_2= 35/65, Ca/S= 3.

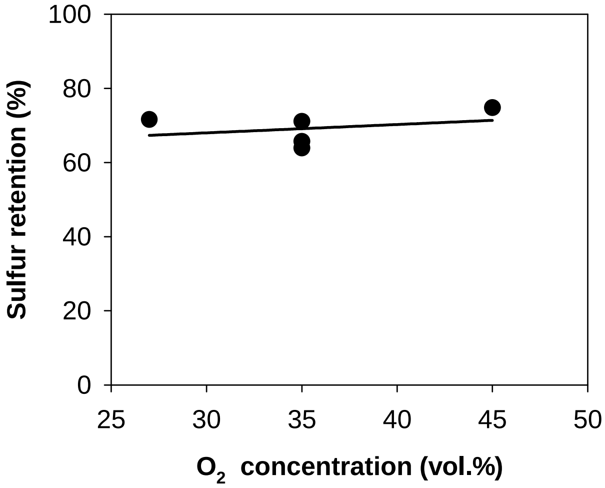

Figure 10. Effect of the O_2 concentration fed into the combustor on sulfur retention, working with anthracite and Granicarb limestone. T= 925 ºC, Ca/S= 3.

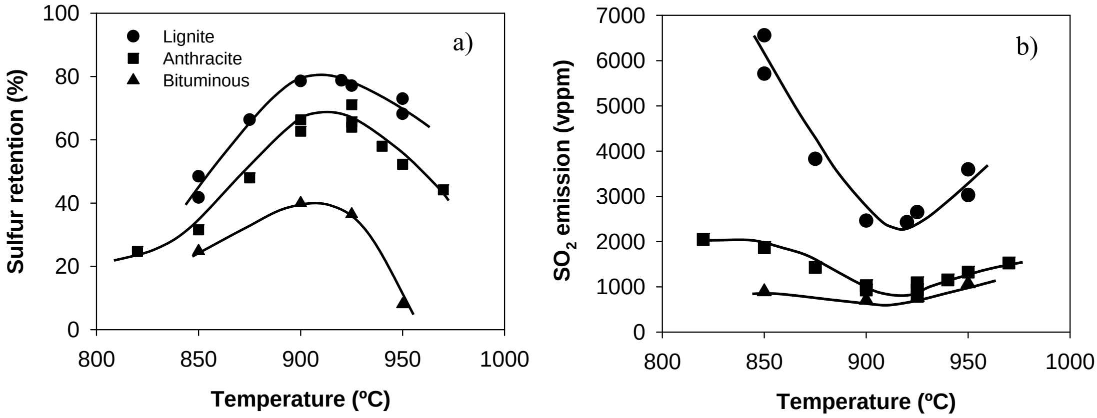

Figure 11. Influence of the temperature on a) sulfur retentions and b) SO_2 emissions using different coals with Granicarb limestone. O_2/CO_2=35/65, Ca/S= 3