FBC DESULFURIZATION PROCESS USING COAL WITH LOW SULFUR CONTENT, HIGH OXIDIZING CONDITIONS AND METAMORPHIC LIMESTONES

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Abstract - A metamorphic limestone and a dolomite were employed as SO_2 sorbents in the desulfurization of gas from coal combustion. The tests were performed in a fluidized bed reactor on a bench and pilot scale. Several parameters such as bed temperature, sorbent type, and sorbent particle size at different Ca/S molar ratios were analyzed. These parameters were evaluated for the combustion of coal with low-sulfur/high-ash content, experimental conditions of high air excess and high O_2 level in fluidization air. Under these conditions, typical of furnaces, few published data can be found. In this work, a medium level of desulfurization efficiency (~60%) for Ca/S = 2 was obtained.
Keywords: Desulfurization; Low SO_2 concentration; Coal; Metamorphic limestone; Fluidized bed combustor.

INTRODUCTION

The price of petroleum has risen constantly in the last few years and therefore even the use of coal of low calorific value and high ash content has become very attractive.

Coal from Candiota mine, located in the southern region of Brazil, is a sub-bituminous and high ash coal with 50% of inorganic material, but highly reactive, and low sulfur content. Thus, the fluidized bed combustor (FBC) technology using limestone as a desulfurization agent is very appropriate to the use of this kind of coal. It is believed that FBC is the best technology, compared to other technologies such as pulverized coal (PC) combustion with flue gas desulfurization (FGD), or integrated gasification combined cycle (IGC). FBC can achieve high combustion efficiency of Candiota coal and is able to

fulfill even the strictest SO_2 emission control standards (Bragança, 1996).

The coal reserves of Candiota coal mine are approximately one billion tons. The mining conditions are excellent, ensuring low cost of production (US$ 8-10/ton). By improving the coal beneficiation system, the separation of gangue (pyrite rich particles) can be higher (Bergmann et al., 2004).

Currently, Brazilian standards (Resolução CONAMA 08/1990 and 382/2006) are quite similar to those of the Environmental Protection Agency (EPA) in the United States. Environmental problems must be carefully considered when using fossil fuels. It must be understood that the use of coal is feasible only if minimal damage is caused to the environment. Thus, the emissions of hazardous gases were limited to minimum levels, and even volatile

heavy metal emissions should be considered (Sebag et al., 2001).

After decades of studying desulfurization in fluidizations reactors, there are still many works being published about this subject. The mechanisms of the sulfation reaction are still not properly understood, and there is dispute over the explanation of the well-known temperature maximum for optimum sulfur capture found in FBC boilers (Anthony et al., 2001). Recently, studies showed the importance of limestone attrition (Chen et al., 2008; Scala et al., 2008), and reactivation of limestone sorbents by water hydration (Anthony et al., 2007; Montagnaro et al., 2004). The presence of alkali metal salts showed influence in sulfation process and kinetics of the limestones (Han et al., 2005). Those studies showed that the choice of the kind of sorbent utilized in FBC is a very complex task.

Early studies, considering the same Ca molar basis, showed that limestones with a higher content of $MgCO_3$, such as dolomites, were more reactive than calcitic limestones. This was due to a specific grain structure for the calcined material, which means a larger pore surface area for sulfur retention (Martin, 1981; Watanabe et al., 1993; Zhang et al., 1992, in: Santana et al., 1998). However, by comparing limestones of different chemical compositions, it is not easy to understand why apparently contradictory results are found in the literature, i.e., sometimes a dolomite is better than a calcitic limestone, and sometimes the opposite was found (Montagnaro et al., 2002; Kaljuvee et al., 2005; Laursen et al., 2000). This is also more complicated when comparing data obtained from dynamic and static experimental conditions. In fact, sometimes, there is no relationship between data in bench-scale and full-scale (Ford and Sage 1991; Morrison et al., 1994; in: Anthony et al., 2001).

Ford and Sage (in Anthony et al., 2001) concluded that: i) Limestone performance bears no relationship to stone geological type or chemical properties. ii) Stones obtained from different locations within the same quarry can exhibit very different SO_2 absorption properties, despite similar chemical properties. Nevertheless, different data can be found in relation to Ford and Sage's remarks (Bramer, EA, in: Valk, 1995; various authors, in: Anthony et al., 2001). Thus, despite some good results between modeling and practical data (Adánez et al., 2001), experimental work in test conditions representative of real ones is still in demand for the design of future furnace installations.

Previous investigations were realized using the same two limestones utilized in this work as desulfurization agents. It was reported that dolomite was a better SO_2 sorbent than the dolomitic limestone in a study with Recreio coal, a higher sulfur content coal than the Candiota coal used in this work (Santana et al., 1998); however, at higher Ca/S ratio, the performances of the limestones were similar. By using scanning electron microscope, the two limestones showed similar porosity after calcination (Moraes, 1998). The importance of CaO concentration in the bed, independent of the MgO concentration, was shown in a study of the kinetics of the desulfurization process (Bragança et al., 2003).

In this work, tests have been performed to investigate and characterize limestone from the surroundings of the Candiota coal mine as SO_2 sorbent. The limestones (actually, metamorphic limestone) from the main mines in southern Brazil were investigated in a bubbling fluidized bed reactor, on a bench and pilot scale. The influence of limestone type and particle size, Ca/S molar ratio and reaction temperature was investigated. Also the influence of operational conditions and reactor scale was observed.

Therefore, the main parameters of the desulfurization process in FBC were analyzed, as cited before, but considering experimental conditions typical of low initial concentration of SO_2 in a combustion gas furnace. It must be remarked that the majority of the studies investigate desulfurization under boiler conditions (low excess air). Thus, the aim of this paper was to provide useful information about the utilization of the specific limestones for desulfurization in furnace conditions (high excess air).

MATERIALS AND METHODS

In the experimental tests, one type of coal and two types of limestone were used. The desulfurization process was analyzed in two fluidized bed reactors of different capacities (bench and pilot scale).

The coal used was from the Candiota mine. The coal for bench scale tests was slightly different from that used on a pilot scale, in terms of chemical composition. This is due to the different time periods at which the tests were performed. However, the authors consider that this difference would not have had any significant influence on the results. Table 1 shows coal composition.

Two metamorphic calcareous rocks from different mines were used in this study: a dolomite (high content of $MgCO_3$) from the Pantano Grande region, and a dolomitic limestone (low content of $MgCO_3$) from the Candiota region. They were classified according to the nomenclature suggested by Pettijohn (1957). They were used at different mean particle sizes in the two fluidized bed reactors on different scales. Limestone mineralogy and particle size are shown in

Table 2, and their chemical composition is shown in Table 3. Mean particle size (Table 2) was calculated by sieve retention, and using Sauter's formula, given in Pacheco (1992).

The equipment used in pilot scale tests was a steel reactor with a pyramidal geometry, covered internally with refractory brick. The bed cross section is 0.2250 m^2 and the reactor has a capacity to process 100 kg/h of coal. The bench scale reactor is a cylindrical reactor, 0.15 m in diameter, of stainless steel covered externally with glass wool. The bed cross section is 0.0177 m^2 and it has a coal-processing capacity of 5 kg/h. The experimental conditions are summarized in Table 4.

Natural sulfur retained in ash (burning coal without limestone addition) was estimated from S (%) retained in the ash, according to ASTM D 4239.

It was found to be 0.68% and 0.56% for pilot and bench scale, respectively.

In bench scale experiments, limestone was mixed with the coal prior to injection in the reactor. In pilot scale, limestone was injected above the bed by a feeding system independent of the coal feeding system.

The mean particle size chosen for this work was 2 to 3 times particle size for the minimum fluidizing velocity, according to the fluidization equations and in agreement with the recommendations of Kunii and Levenspiel (1991).

After the bed temperature reached 850ºC and SO$_2$ emission was sufficiently stable, the SO$_2$ emission level was recorded. Gas emissions were monitored with an Infrared Continuous Analyzer (MIR 9000 - émission s.a.).

Table 1: Candiota coal analysis

Scale	Bench	Pilot
Proximate analysis		
Fixed carbon (%)	25.1	27.6
Volatile matter (%)	18.7	25.7
Ash (%)	56.2	46.8
Ultimate analysis		
Carbon (%)	31.6	38.7
Hydrogen (%)	2.1	2.5
Oxygen and others (%)	8.3	9.9
Nitrogen (%)	0.7	0.9
Sulfur (%)	1.1	1.0
Moisture (%)	11.7	11.7
Gross C.V. (kJ/kg)	11.9	15.4

Table 2: Limestone mineralogy and particle size

Sample	Mineralogy	Mean Particle size (mm)
Dolomite	Serpentine	0.47 and 0.32 (pilot)
	marble	0.35 and 0.22 (bench)
Dolomitic	Serpentine	0.42 (pilot)
limestone	marble	0.41 (bench)

Table 3: Limestone chemical composition

	Dolomite	Dolomitic limestone
MgO (%)	19.52	5.61
CaO (%)	29.00	42.62
SiO$_2$ (%)	13.54	10.27
Al$_2$O$_3$ (%)	0.56	1.84
Fe$_2$O$_3$ (%)	0.86	0.88
MnO (%)	0.02	0.06
Na$_2$O (%)	0.02	0.14
K$_2$O (%)	0.08	0.74
TiO$_2$ (%)	0.03	0.08
P$_2$O$_5$ (%)	0.01	0.04
LOI (%)	35.18	37.20

Table 4: Experimental conditions

Plant scale	Pilot	Bench
Bed temperature	850ºC +/-10ºC	850ºC +/- 15ºC
Bed initial material	Sand	Sand
Cross section area	0.225 m^2	0.0177 m^2
Static bed height (sand)	0.40 m	0.15 m
Gas residence time	0.9 s	0.6 s
Natural sulfur retained in ash	31%	28%
Air flow	410 kg/h	21 kg/h
Air velocity	0.42 m/s	0.67 m/s
Air excess	+/- 210 %	+/- 190 %
O_2 in exhausting gas	>12 %	>12 %
Coal flow	30 kg/h	2 kg/h
Coal mean particle size	0.0472 cm	0.074 cm
Coal minimum fluidization velocity	18.5 cm/s	29 cm/s

RESULTS AND DISCUSSION

Quantity of Limestone

The efficiency of the desulfurization of coal combustion gas by the addition of limestone into an FBC is presented in Fig. 1. This figure shows the investigation of the influence of quantity of limestone added in the bed on SO_2 emissions. Limestone quantity is expressed by the Ca/S molar ratio (Ca in limestone and S in coal). It can be observed (Fig. 1) that at Ca/S = 1 a significant retention of SO_2 occurred (~ 50%). At Ca/S = 2 (meaning 100% more limestone than Ca/S = 1) only another 10% of SO_2 were added to the initial retention. This behavior was observed only after the Ca/S molar ratio increased. Therefore, although total sulfur retention is increased with the rise in the Ca/S molar ratio, desulfurization efficiency decreased in relation to the increased Ca/S. Thus, it must be highlighted that the efficiency of desulfurization is strongly dependent on the initial SO_2 concentration in the bed (Fig. 1).

The addition of limestone at Ca/S = 1 promoted a reduction of the SO_2 emission from 900 ppm to ~450 ppm, shown as SO_2 retention in Fig. 1. On the other hand, the addition of a high amount of limestone (Ca/S = 4) reduced the SO_2 emission to 200 ppm. Usually, the amount of limestone utilization necessary to meet environmental norms is between Ca/S = 1 and Ca/S = 4, and a further increase will no longer be economically feasible. Otherwise, it is advisable to put a scrubber on the system.

The natural retention of sulfur in the ash was ~30%, as shown in Table 4. The natural Ca/S was ~0.4, but it may vary significantly, according to a previous study, which showed the variation of CaO amount in coal (Bergmann et al., 2004). By considering 0.4 as the natural Ca/S, and a

sufficiently stable value, the molar ratio Ca/S = 1 would be Ca/S = 1.4, and SO_2 retention would be compared to a natural Ca/S = 0.4 emission. However, the conclusions of Figure 1 are still unchanged.
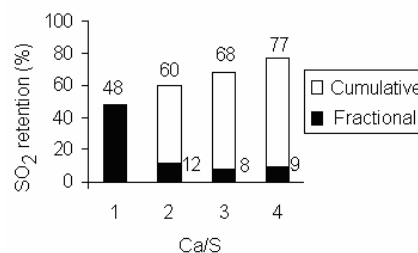

Figure 1: SO_2 retention (%) vs. Ca/S molar ratio. Dolomitic limestone, particle size 0.41 mm. Bed temperature = 850ºC. Bench scale FBC.

Chemical Composition of Limestone

The performance of limestones from different regions was evaluated. Table 3 showed the chemical composition of dolomite and dolomitic limestone. Fig. 2 shows the results of pilot scale tests, which express SO_2 emission divided by coal calorific value (SO_2 mg/kcal).
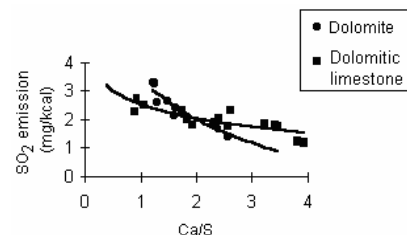

Figure 2: Effect of limestone chemical composition on SO_2 emission. Dolomite (0.32 mm) and dolomitic limestone (0.41 mm). Bed temperature = 850ºC. Pilot scale FBC.

Approximately the same SO_2 emission (2 mg of SO_2/kcal) was obtained for the dolomite and the dolomitic limestones at Ca/S = 2. According to Brazilian environmental standards, this is the level of emission allowed in a thermoelectric plant (energy production higher than 70 MW). Therefore, the higher level of MgO in the dolomite composition did not show any effect on SO_2 retention. It must be noted that, for the same Ca/S molar ratio, the quantity of CaO (and CaO activated sites) is the same but the level of MgO varies according to the limestone composition. This was also noted in bench scale tests (Fig. 3).
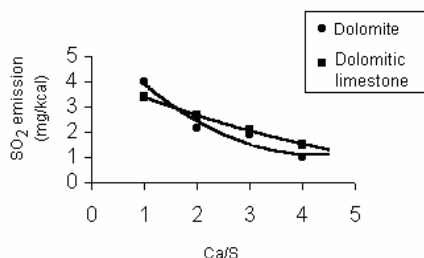

Figure 3: Effect of limestone chemical composition on SO_2 emission. Dolomite (0.35 mm) and dolomitic limestone (0.41 mm). Bed temperature = 850ºC. Bench scale FBC.

In the bench scale tests, the dolomite and the dolomitic limestone reached 2 mg of SO_2/kcal at Ca/S $\approx$ 3.0. The maximum desulfurization efficiency was $\sim$ 80% at Ca/S = 4. The behaviors of the sorbents were similar, as they were in pilot scale tests.

In dolomites (molar ratio Ca/Mg $\cong$ 1) the surface concentration of CaO activated sites is 50% lower than calcitic or dolomitic limestones. Thus, there is more space for the reaction to occur surrounding the CaO sites. It is believed that these properties of dolomites allow higher desulfurization efficiency as a consequence of the space available for $CaSO_4$ formation. It is well understood that the large molar volume of $CaSO_4$ is an obstacle to a higher SO_2 retention: the molar volume of $CaSO_4$ is large compared to the molar volume of calcium carbonate and therefore complete conversion of the limestone particle is impossible. Therefore, the MgO acts as an inert component and may help in $CaSO_4$ formation, since there is no $MgSO_4$ formation as reported in many studies (Bramer in: Valk, 1995; Han et al., 2005; Laursen et al., 2005), and also in the analysis of the sulfated ashes in a study realized before (Sebag et al., 2001). Besides, the number of sorbent particles in the reactor is higher for dolomites,

considering the same Ca/S, which would probably lead to a better mixing.

According to the discussion summarized above, a better performance is expected for dolomites. However, under the experimental conditions used in this work, i.e., low SO_2 concentration in the furnace reactor, different results were obtained and the influence of limestone chemical composition was minimized. In low SO_2 concentration a better structure that a dolomite may provide for desulfurization does not seem to be important. This highlights the importance of the SO_2 concentration in the reactor, as shown in Fig. 1, and discussed in the item "Quantity of limestone".

As expected, the kinetics of the desulfurization process is controlled by the slowest reaction step and can change upon varying experimental conditions. The mechanism which controls the sulfation reaction can be changed from reaction on the sorbent particle surface to diffusion throughout the sulfate layer formed. As postulated before, the sulfation reaction depends on the SO_2 concentration around the particles and on the mean residence time of the particles in the bed (Adánez et al., 2001).

It must be considered that the two limestones studied here have the same mineralogical characteristics (serpentine marbles – Table 2), according to a previous study (Moraes, 1998). Limestones of different ages may show different behavior, and also those that suffer high attrition rate, exposing new unreacted surface, as cited before (Anthony et al., 2001, Shimizu et al., 2003, Chen et al., 2008; Scala et al., 2008).

Limestone Particle Size

Fig. 4 shows the influence of limestone particle size on the desulfurization process performed on a FBC pilot scale. The dolomite was used in particle sizes of 0.47 mm and 0.32 mm. The finer dolomite reached 60% of SO_2 retention, while the coarser one reached 30% at the same molar ratio (Ca/S = 2.4). The higher surface area for reaction of the 0.32 mm dolomite, as a consequence of the finer particle size, was the most important factor that determined the better performance of this dolomite at this particle size. This behavior is in accordance with the results reported by Bragança et al. (2003). In this study, a higher exposed surface area for reaction was considered to be the main parameter for the dolomite. It is clear that the process is governed by the core/shell pattern of sulfation, because the longer residence time of the 47 mm fraction did not

contribute to higher desulfurization efficiency. A significant contribution of attrition of the sorbent is not expected, as pointed out in other works (Chen et al., 2008; Scala et al., 2008). The sorbents here are metamorphic limestones, what means a hard rock and low attrition rate.
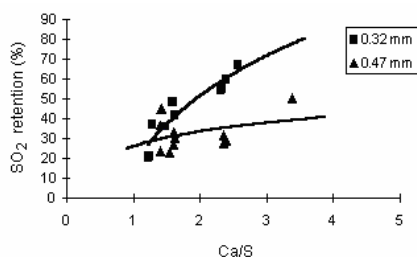

Figure 4: Particle size analysis. Dolomite 0.47 mm and 0.32 mm. Bed temperature = 850ºC. Pilot scale FBC.

Limestone particle size tests were also performed on bench scale tests. The mean particle sizes of dolomite used were 0.22 mm and 0.35 mm. The finer dolomite reached 58% of SO_2 retention (Ca/S = 2), while the coarser one reached 68% at the same molar ratio. The lower retention for the finer dolomite is accounted for by the excessive elutriation occurring at this particle size, which is a potential limitation for the investigation of finer sorbents. This was also according to previous investigation (Bragança et al., 2003).

In bubbling FBC, sorbent particle size is considered to be a key factor for the desulfurization process. Finer particles may reach higher levels of sulfur retention, since their size was kept within ideal fluidization conditions range. Particle residence time must be sufficiently long for the sulfation reaction to occur, without a significant elutriation level of limestone particles (which may occur when particle terminal velocity is higher than fluidization air velocity).

Münzner et al. (1985) remarked that the best results are obtained with either extremely fine limestone particles (large surface area) or those with a diameter just above the elutriation size (lower surface area but longer residence time). It is pointed out that the use of extremely fine particles means an extra cost to mill the limestone. Moreover, fine particles absorb more moisture than the coarser ones and can also block the limestone feeding system. This condition was not tested because the tests in this work were performed with a distribution of particle sizes more likely to be used in an industrial plant.

Bed Temperature

The evaluation of the influence of bed temperature in the desulfurization process must be performed with care, without affecting other experimental parameters such as bed height, air velocity, and Ca/S molar ratio. In the tests performed in this study only the coal feed rate was changed, varying the air/coal ratio but keeping the air flow unchanged. Although it modified the O_2 level of the bed, it was always kept higher than 5%, and variations above this level are not believed to influence SO_2 retention (Verhoeff et. al. in Valk, 1995). Thus, the experimental conditions of this work are highly oxidizing (fluidizing air $O_2 > 12\%$), which are different than the majority of data published ($O_2 \sim 3\%$).

Fig. 5 shows the analysis of bed temperature at Ca/S = 2 and Ca/S = 4 in the 750ºC to 950ºC interval.
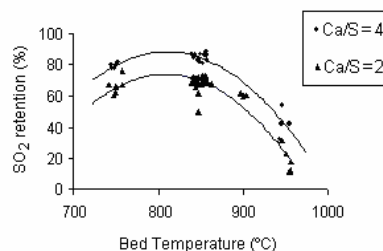

Figure 5: Effect of bed temperature on SO_2 retention. Dolomite (0.35 mm). Ca/S = 2 e Ca/S = 4. Bench scale FBC.

In the literature, it is explained that the maximum desulfurization efficiency is at 850ºC and, at higher temperatures, the SO_2 emission increases due to the decomposition of $CaSO_4$. This was shown in many studies, and is the 'preferred explanation'; according to Anthony and Granatstein's literature review (2001) "the temperature maximum can best be regarded as competition between sulfation and reduction, with reduction becoming more important at higher temperatures". These authors also highlighted that there is little published information under high oxidizing conditions, and some have not shown a sharp decreased in sulfur retention above 850ºC.

The results presented here showed that, at bed temperatures higher than 900ºC, SO_2 retention suffered a significant decrease (see Fig. 5). This is believed to be due to chemical processes associated with the sulfation reaction, and not to the $CaSO_4$ reduction mechanism.

According to the CaO-CaSO$_4$-CaS diagram (see Hansen et al., 1993), CaS is not stable under the higher oxidizing conditions of this work ($p(CO)/p(CO_2) = 2.5.10^{-3}$), and thus re-emission of SO$_2$ is not expected.

The data in Fig. 5 is accounted for by the high sulfation reaction rate at elevated temperatures. Therefore, the faster blocking of the pores is due to the formation of a calcium sulfate layer on the external surface of the sorbent particles. Consequently, it is clear that, for the limestone used here, the resistance to diffusion is high and SO$_2$ cannot reach the inner part of the sorbent where there are many CaO active sites.

The results showed that the optimum bed temperature for the desulfurization process was 850ºC, for Ca/S 2 and 4. This in accord with the results of others authors, who realized tests at higher SO$_2$ concentration in flue gas (Bramer; Verhoeff and Holtzer, in Valk, 1995; Santana et al., 1998). Further, it is believed that the total calcium utilization decreased with increasing SO$_2$ concentration (unreacted-core type sulfation) at higher temperatures, as shown in Ryu's work (2006).

Thus, according to results of Fig. 5, temperature will be a key factor for desulfurization efficiency, when it is governed by pore blockage due to CaSO$_4$ formation (a core-shell sulfation pattern is established), and also important regarding the sorbent particle diameter used. It can be inferred that, for very small limestone particle size (uniform-type sulfation) and oxidizing conditions, sulfation would not be so affected by temperature, as cited before. When a uniform-type sulfation process is established, total calcium utilization was almost independent of SO$_2$ concentration, according to Ryu's achievements (2006).

At 750ºC, the SO$_2$ retention efficiency was slightly lower than at 850ºC. Under these conditions, the rate of the sulfation reaction is slower, and the chemical reaction controls the process.

Gas Emissions

Gas emissions from coal combustion + limestone were analyzed. In the experimental conditions of this work, typical of furnace, that is, high excess air (>200%), it was observed that mainly SO$_2$ was influenced by limestone addition. The emissions of NO (200 ppm ± 20), CO (150 ppm ± 25), CO$_2$ (6% ± 0.2), O$_2$ (>12%), were almost the same between Ca/S = 0 (no addition of limestone) and Ca/S = 4. CH$_4$ and HCl were below the level of detection.

SUMMARY AND CONCLUSIONS

The two metamorphic limestones investigated in this study were approved as desulfurization agents used to control SO$_2$ emission from coal combustion. The sulfur emission standard of 2 mg of SO$_2$/kcal was reached with the addition of a reasonable quantity of limestone (Ca/S = 2 to 3). This proved to be effective in bench and pilot scale.

The dolomite and the dolomitic limestone showed similar behavior for the control of SO$_2$ emission. Under the experimental conditions used in this work (high air excess, atmospheric pressure, SO$_2$ initial concentration < 1000 ppm), it can be concluded that the higher level of MgCO$_3$ in dolomite did not show any positive effect on desulfurization, and the Ca/S molar ratio was the main parameter of the desulfurization process.

The analysis of the influence of quantity of limestone added to the FBC showed that a high SO$_2$ retention was obtained for small quantities of limestone. For the stoichiometric ratio of calcium (Ca/S = 1), the efficiency of sulfur retention was 50%, which means an addition of 4 tons of dolomitic limestone per 100 tons of Candiota coal. At Ca/S = 2, for the same limestone, only 10% more retention was added to the total sulfur retention. Thus, the importance of the initial SO$_2$ concentration in the FBC for the desulfurization process is clear.

The evaluation of limestone particle size showed that the reduction of sorbent particle size increases the desulfurization efficiency, as shown by the pilot scale tests. However, as can be seen in the bench scale tests, the finer limestone was less efficient. The presence of smaller particles, which can be easily elutriated without reaction, diminishes the desulfurization efficiency considerably. For the particle size analyzed (0.22 mm - 0.47 mm), a core-shell sulfation pattern was considered.

The maximum desulfurization efficiency was obtained at 850ºC. At bed temperatures higher than 900ºC, SO$_2$ retention suffered a significant decrease. These results confirmed the proposed mechanism that sulfur retention is low at elevated temperatures due to the high sulfation reaction rate and, therefore, the faster blocking of the pores as a consequence of the formation of calcium sulfate layer. This behavior was attributed to the high O$_2$ concentration in fluidization air used in this work, since CaS formation and then SO$_2$ release is not expected under highly oxidizing conditions.

The results obtained in this study permit scaling up to FBC industrial plants, since the time period of

each run was sufficiently long. Besides, the pilot plant data are representative and reliable due to the sample amount used in the tests (30 kg).

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