

## EFFECTS OF TEMPERATURE AND PARTICLE SIZE ON THE CONVERSION OF SULFUR DIOXIDE SORPTION BY LIMESTONES

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**Abstract.** Coals and heavy oils from petrol are burned in thermoelectric power stations and are the main source of SO<sub>2</sub> emission into earth's atmosphere. Sulfur can be removed during combustion by injecting limestone in the combustion chamber. Thermogravimetry was applied to study SO<sub>2</sub> sorption by limestone. Two types of natural limestones were used in two different particles sizes. Isothermal experiments were performed for different temperatures from 750 to 900 °C, at atmospheric pressure. The results showed the same behavior, irrespective of temperature, particle size and type of limestones. In higher temperatures resulted in lower conversions, possibly due to sintering. In all the cases, the result of the optimum conversion was between 792 and 859 °C. As expect, the conversion was higher for the dolomite. Besides temperature, limestone sulfation was considerably affected by pore size distribution, suggesting that mesopores are the key feature leading to higher conversion.

**Keywords:** thermogravimetry, limestone, sulfur dioxide, porosity.

### 1. INTRODUCTION

Acid rain is one of the most serious environmental problems in several regions of the world. This generic term covers a variety of phenomena, related to atmospheric precipitation of acids. Acid rain refers to precipitations that are significantly more acid than unpolluted rain, which is mildly acid due to the presence in it of dissolved atmospheric carbon dioxide, forming carbonic acid (Baird, 1998).

Sulfur and nitrogen oxides are present in polluted air, reacting with water to produce acids, which cause acid rain in industrialized regions. Sulfur dioxide (SO<sub>2</sub>), which is a major contributor to acid rain, is produced when sulfur or sulfur-containing fuels are burned (Kotz, 1994).

Coals and heavy oils from petrol are widely used for energy generation. Those fossil fuels are burned in thermoelectric power stations and are the main source of SO<sub>2</sub> emission into earth's atmosphere (Li and Sadakata, 1999). The development of efficient, economical and environmentally-friendly technologies is essential for the utilization of high-sulfur fuels. Fluidized bed combustion is one of such technologies. The process permits injecting limestone in to the combustion chamber, sorbing SO<sub>2</sub> before it is emitted to the atmosphere (Baird, 1998; Van Houte and Demon, 1979).

The reaction between SO<sub>2</sub> and limestone involves calcination followed by sulfation. When subjected to high temperatures, limestone decomposes into a solid mostly formed by CaO, with the release of CO<sub>2</sub>. The calcination reaction is shown in reaction (1) (Anthony and Granatstein, 2001).



The formed calcined is very porous and has the same size of the original limestone. Its high porosity is due to the difference between the molar volumes of CaCO<sub>3</sub> (~ 36.9 cm<sup>3</sup> mol<sup>-1</sup>) and CaO (~16.9 cm<sup>3</sup> mol<sup>-1</sup>) (Hartiman and Couchlin, 1976; Simons et al., 1987; Dam-Johansen and Ostergaard, 1991). Depending on temperature and SO<sub>2</sub> partial pressure, different chemical species may be produced from the reaction between CaO and SO<sub>2</sub>. The most commonly assumed routes for sulfation are:



Routes 2 and 3 were proposed by Moss (1975) and route (4) was proposed by Low et al. 1971). The reactions of route 2 predominate at low temperatures where  $\text{CaSO}_3$  is stable, while the reactions of route 3 predominate at high temperatures ( $> 850\text{ }^\circ\text{C}$ ) where  $\text{CaSO}_3$  becomes unstable (Anthony and Granatstein, 2001).

During sulfation, the pores of the CaO particle are filled with products ( $\text{CaSO}_4$ ,  $\text{CaSO}_3$ , CaS), and become progressively plugged. Even when compared to the natural limestone, the physical structure of the sulfated regions in a particle becomes more compact owing to the difference between the molar volumes of  $\text{CaSO}_4$  ( $\sim 46\text{ cm}^3\text{ mol}^{-1}$ ) and  $\text{CaCO}_3$  ( $\sim 36.9\text{ cm}^3\text{ mol}^{-1}$ ) (Dam-Johansen and Ostergaard, 1991).

Limestone sulfation is affected by porosity, pore size and size distribution of pores, intra-particle superficial area (Li and Sadakata, 1999; Borgwardt and Bruce, 1986; Adánez and García-Labiano, 1993), geological age, size and density of the particles (Yrjas et al., 1995). Another factor to consider is the presence of chemical elements that may act as catalysts or inhibitors (Moss, 1975). The first works showing the influence of internal pore structure on CaO reaction to  $\text{SO}_2$  were performed in the early 70's. Therefore, intrinsic physical features started to be considered alongside the usual external superficial effects (Borgwardt and Bruce, 1986). In one of the first works, Pigford and Sliger (1973) found that in  $96\text{ }\mu\text{m}$  limestone particles there was significant resistance to intra-particle gas diffusion at  $980\text{ }^\circ\text{C}$ . They concluded that  $\text{SO}_2$  diffusion through  $\text{CaSO}_4$  product layers controlled the sulfation rate. Borgwardt and Harvey (1972) evaluated the effect of porosity on sulfation. They defined an effectiveness factor as the ratio between the observed reaction rate and its theoretical value if the whole particle volume were available for reaction. A strong dependence was observed between effectiveness and pore structure (volume, area and shape of pores). The authors concluded that the effectiveness was dependent on the pore's external layers plugged by  $\text{CaSO}_4$ , which imposes loss of internal superficial area and makes the internal layers of CaO inaccessible.

The aim of this work is to analyze the influence of temperature, atmosphere and porosity on the conversion of a sulfation reaction applying thermogravimetry. The ranges of temperature and particle size that were applied are typical of fluidized bed coal combustion.

## 2. EXPERIMENTAL

Two types of Brazilian natural limestones were used: a calcite from Minas Gerais State, and a dolomite from São Paulo State. Table 1 shows the elementary chemical compositions of the limestones which were determined by atomic emission spectrometry (ICP-AES).

Table 1: Elementary chemical composition (% mass/mass) of the limestones.

Limestones	Chemical Composition						
	Ca	Mg	Fe	Al	Sr	K	Mn
Calcite	35.34	0.35	2.45	0.25	0.14	0.09	0.52
Dolomite	17.07	11.73	0.32	0.42	0.08	0.13	0.09

The data from the X-ray diffraction analysis of calcite and dolomite, presented in Figures 1 and 2, respectively, show the peaks indicating the major compounds present in the samples.

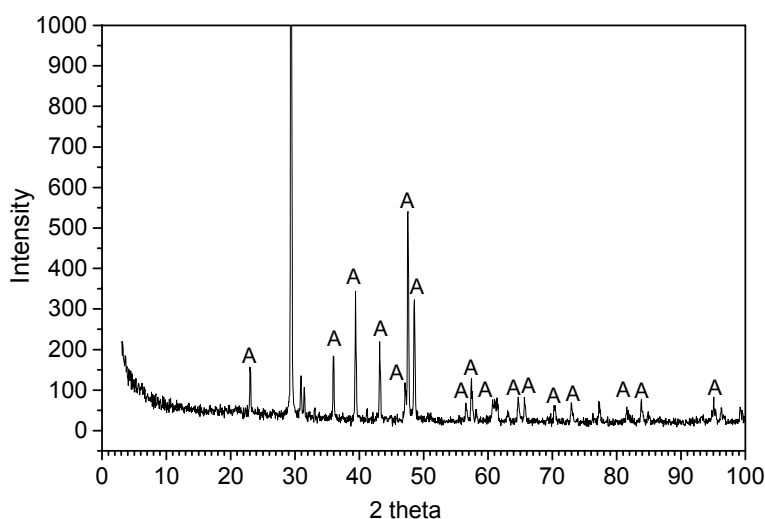


Figure 1. X-ray diffraction of the natural calcite - A:  $\text{CaCO}_3$

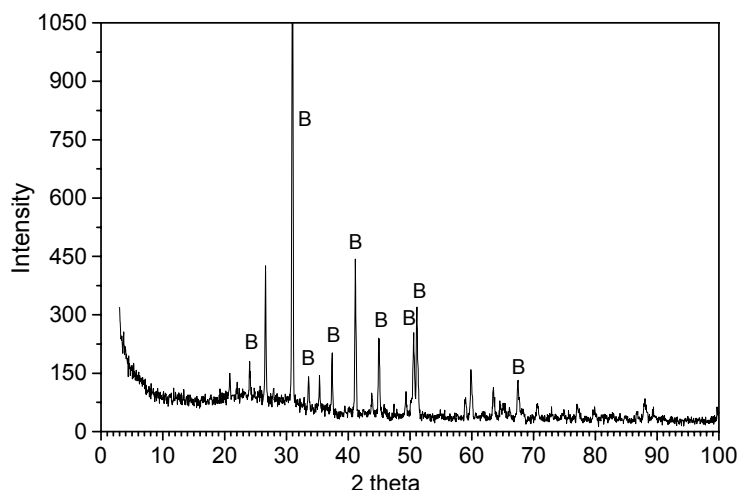


Figure 2. X-ray diffraction of the natural dolomite - B:  $\text{CaMg}(\text{CO}_3)_2$

Figure 3 shows the pore size distribution of the natural sorbents measured by mercury porosimetry. It is noted that the limestones are different regarding pore size distribution. For both cases, the range of pore sizes between 100 and 120  $\mu\text{m}$  was not considered. This range represents interstitial gaps between particles since it does not stand for porosity, but for interstitial gaps among particles (Allen, 1997). It is observed that calcite does not present mesopores, while dolomite presents a distribution in this region (around 0.050  $\mu\text{m}$ ).

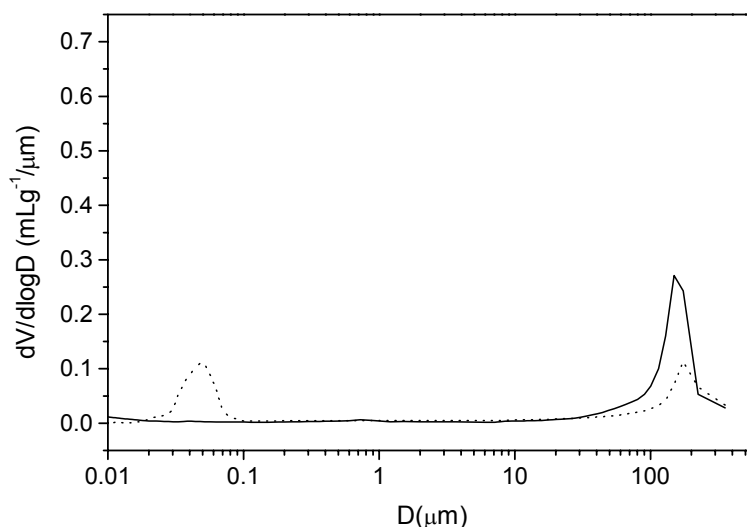


Figure 3: Pore size distributions measured by mercury porosimetry for the natural sorbents calcite (full line) and dolomite (interrupted line).

The thermogravimetric experiments were performed in a Shimadzu TGA-51H analyzer. Limestone Samples weighing  $10.0 \pm 0.5$  mg were used in all experiments. These small samples allowed to minimize inter-particle mass transfer resistances by spreading the particles in a monolayer at the bottom of the crucible (alumina,  $6 \text{ } \varnothing \times 2.5$  mm). The rock was ground and sieved for two average particle sizes of 545 and 650  $\mu\text{m}$ , respectively. The average size of the particles was determined as the arithmetic mean between the mesh apertures of two consecutive ASTM laboratory sieves. The calcite was used in two different mean sizes: 545 and 650  $\mu\text{m}$ , while the dolomite was used in 650  $\mu\text{m}$  mean size. Previously to sulfation, the sample was calcined inside the analyzer in air atmosphere at a volumetric rate of 80  $\text{mL min}^{-1}$ , applying a heating rate of 30  $^\circ\text{C min}^{-1}$  until a desired temperature had been reached and the decomposition had been complete. This condition was kept for 20 min. Then, 20  $\text{mL min}^{-1}$  of pure  $\text{SO}_2$  were added so that its volumetric fraction on the atmosphere was 20 %, and the isothermal sulfation developed. Four different sulfation temperatures were applied (750, 800, 850 and 900  $^\circ\text{C}$ ). All experiments were performed in four replicates and averaged results were produced.

### 3. METHODOLOGY

In this work, the conversion ( $X$ ) of a reactant “ $i$ ” indicates the ratio between the number of mols of the species which reacts and the number of mols of the species fed in the process. Then, the conversion is given by

$$X = \frac{\text{mols of "i" that reacts}}{\text{mols of "i" fed in the process}} \times 100 \quad (5)$$

In the present thermogravimetric sulfation experiments the conversion of Ca plus Mg is given by

$$X = \frac{(n_{Ca} + n_{Mg})_{\text{reacted}}}{(n_{Ca} + n_{Mg})_{\text{in the sample}}} \times 100 = \frac{(n_{SO_2})_{\text{sorbed}}}{(n_{Ca} + n_{Mg})_{\text{in the sample}}} \times 100 \quad (6)$$

where  $n$  stands for the number of mols of a concerning species. It should be noted that, irrespective of the considered reaction mechanism, the number of mols of  $SO_2$  that is sorbed equals the number of mols of Ca plus Mg that is reacted.

The mass variation due to the sulfation of the already calcined sample ( $\Delta M$ ) is given by

$$\Delta M = M_{SO_2} + M_{O_2} = n_{SO_2} W_{SO_2} + n_{O_2} W_{O_2} \quad (7)$$

Assuming the global reactions



one has

$$\frac{n_{SO_2}}{n_{O_2}} = \frac{1}{\frac{1}{2}} \quad \text{or} \quad n_{O_2} = \frac{1}{2} n_{SO_2} \quad (10)$$

Substituting Equation (10) into Equation (7), one has

$$n_{SO_2} = \frac{\Delta M}{(W_{SO_2} + \frac{1}{2} W_{O_2})}, \quad (11)$$

where  $W$  stands for the molecular mass of the concerning species.

The mass variation due to sulfation,  $\Delta M$ , is also given by

$$\Delta M = M - M_C, \quad (12)$$

where  $M$  is the mass of the sample during sulfation and  $M_C$  is the mass of the sample after calcination. The number of mols of calcium ( $n_{Ca}$ ) plus magnesium ( $n_{Mg}$ ) available in the sample is given by

$$n_{Ca} + n_{Mg} = M_A \left( \frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right), \quad (13)$$

where  $M_A$  is the initial sample mass of the natural limestone,  $Y$  stands for the mass fraction and  $W$  accounts for atomic masses.

Introducing Equations (11) and (13) into Equation (6), one has

$$X = \frac{\frac{M - M_C}{W_{SO_2} + W_{1/2O_2}}}{M_A \left( \frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)} \times 100 . \quad (14)$$

The required values of  $M_A$ ,  $M$  and  $M_C$  are determined from the thermogravimetric experiments. The mass fractions of Ca and Mg in the sorbents are given in Table 1.

#### 4. RESULTS AND DISCUSSION

Figure 4 shows the result of the sulfation experiments for dolomite of 650  $\mu\text{m}$  at 900  $^\circ\text{C}$ . The TG curve shows both, calcination and sulfation events, as well as DTG profile. The sets of curves for all the other experiments were similar. For the purposes of this study, the data were analyzed from complete calcination to complete sulfation, so that conversion was calculated over a time interval set from the beginning to the end of the sulfation. The initial time was set at 100 seconds before the maximum peak of the DTG curve, when the sulfation was about to begin. The final time was set at 400 seconds after the initial time when, for practicable purposes, the sulfation was assumed to be finished. In fact, above the final time sulfation proceeded, but at a very slow rate.

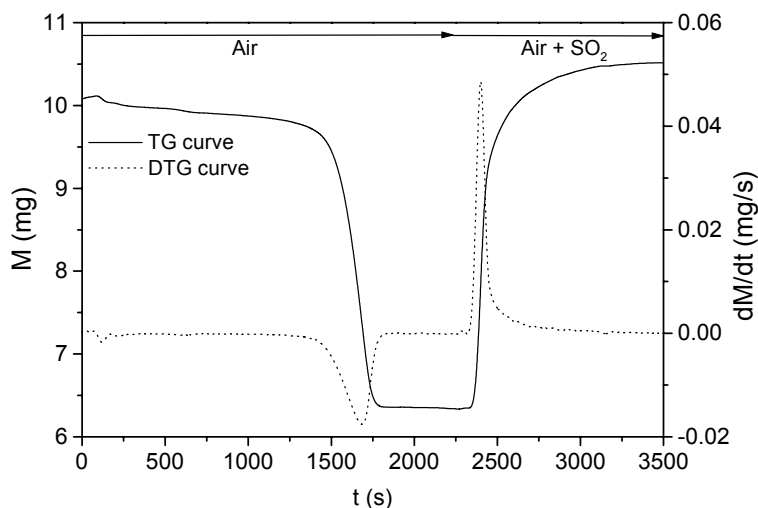


Figure 4: TG and DTG profiles of sulfation at 900  $^\circ\text{C}$ , for the dolomite of 650  $\mu\text{m}$ .

Figures 5, 6 and 7 show the average conversions at various temperatures for the calcite of 545  $\mu\text{m}$ , the calcite of 650  $\mu\text{m}$  and the dolomite of 650  $\mu\text{m}$ , respectively. The average conversions show the same behavior, irrespective of temperature, particle size and type of limestone. Otherwise, the final conversion was quite different for different temperatures. The decreasing rank of conversion regarding temperature was: 800  $\approx$  850 > 750 > 900  $^\circ\text{C}$  (for the calcite of 545  $\mu\text{m}$ ), 800 > 850  $\approx$  750 > 900  $^\circ\text{C}$  (for the calcite of 650  $\mu\text{m}$ ) and 850 > 900  $\approx$  800 > 750  $^\circ\text{C}$  (for the dolomite of 650  $\mu\text{m}$ ).

Figure 8 shows plots of the average conversion as a function of temperature, considering the conversion values in the final time of 400 seconds. The average conversion at 900  $^\circ\text{C}$  was lower than that at 800  $^\circ\text{C}$  for all limestones. For the calcite of 545  $\mu\text{m}$ , it was even lower than the one at 750  $^\circ\text{C}$ . This fact is possibly due to sintering, which causes the loss of internal superficial area and consequent conversion drop. In all cases the conversion grows up with temperature and then starts to drop as temperature further increases.

The temperature at which conversion starts to drop defines the maximum conversion, and represents the optimum sorption temperature. From polynomial fits on the curves of Figure 4, the maximum conversion temperatures were found which are: 859  $^\circ\text{C}$  (for the dolomite of 650  $\mu\text{m}$ ), 818  $^\circ\text{C}$  (for the calcite of 545  $\mu\text{m}$ ) and 792  $^\circ\text{C}$  (for the calcite of 650  $\mu\text{m}$ ). In all temperatures, the conversion was always higher for the dolomite.

Comparing the results of calcite for the different particle sizes in Figure 8, it is possible to observe that a higher conversion is found for the smaller particle, as expected. For the smaller particle a higher external superficial area is available for reaction, meaning that a larger volume of the particles is sulfated since the thickness of the sulfated layer is independent of the particle size.

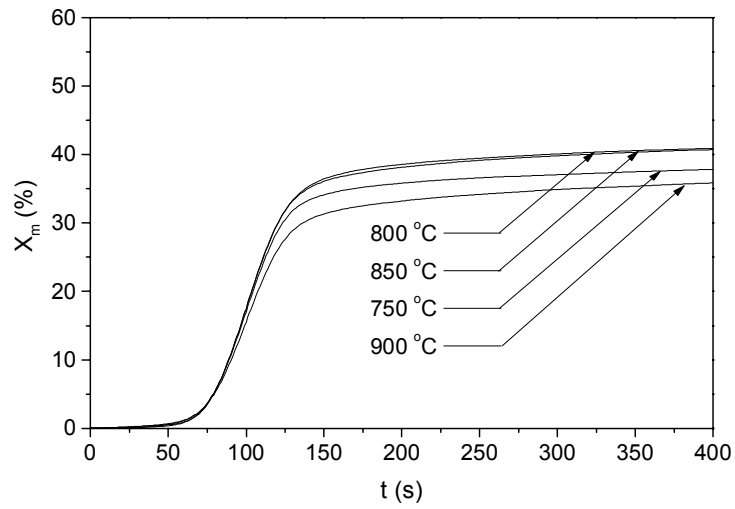


Figure 5: Average Conversion ( $X_m$ ) as a function of time ( $t$ ) at various temperatures, for the calcite of 545  $\mu\text{m}$ . Each curve accounts for the average of four replicates.

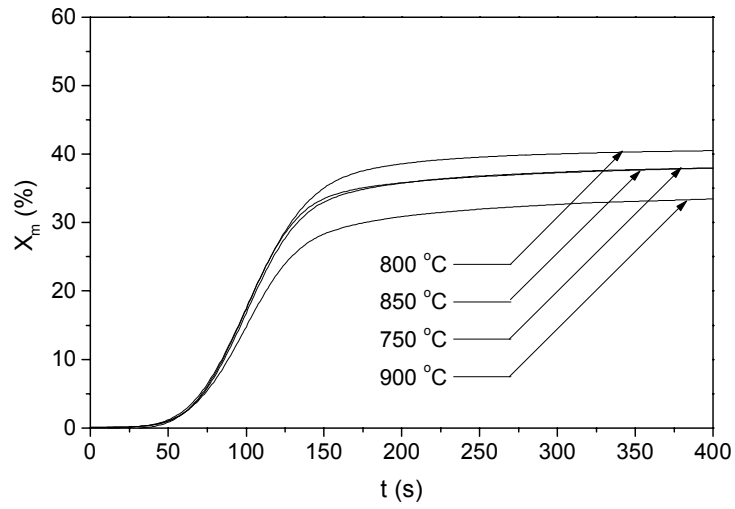


Figure 6: Average Conversion ( $X_m$ ) as a function of time ( $t$ ) at various temperatures, for the calcite of 650  $\mu\text{m}$ . Each curve accounts for the average of four replicates.

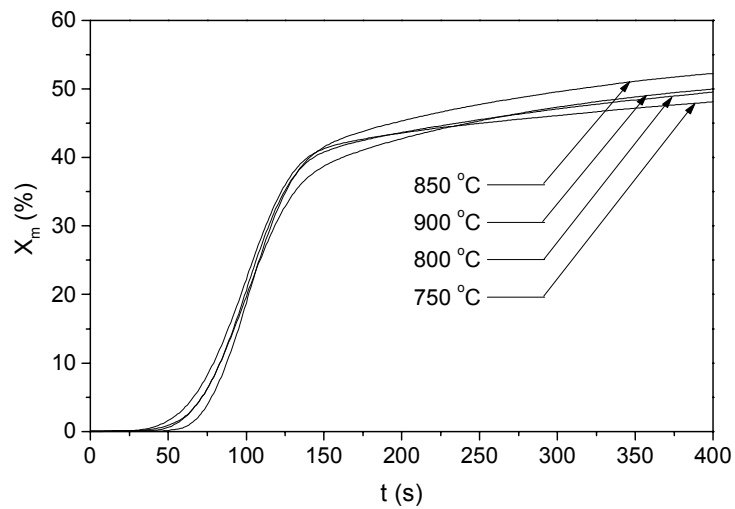


Figure 7: Average Conversion ( $X_m$ ) as a function of time ( $t$ ) at various temperatures, for the dolomite of 650  $\mu\text{m}$ . Each curve accounts for the average of four replicates.

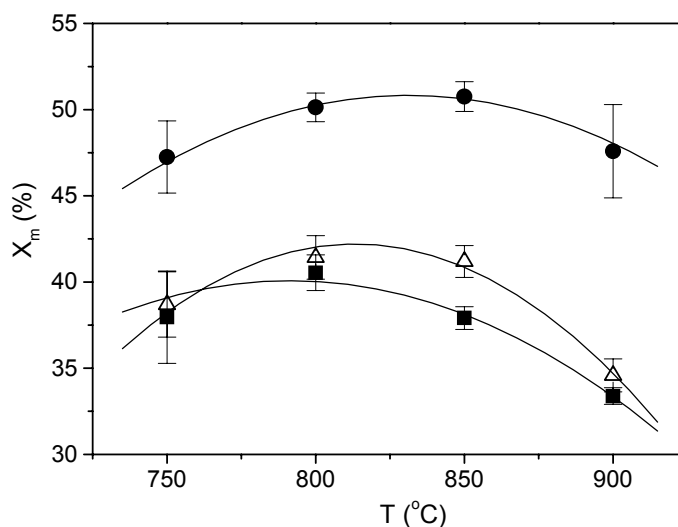


Figure 8: Average conversion ( $X_m$ ) as a function of temperature ( $T$ ) at the final time of 400 s for the calcite of 545  $\mu$ m ( $\Delta$ ), calcite of 650  $\mu$ m ( $\blacksquare$ ) and dolomite of 650  $\mu$ m ( $\bullet$ ). The bars indicate the standard deviation around the average from the experiments. The full lines stand for polynomial fits.

Regarding the type of sorbent, the conversion was always higher for the dolomite in comparison to the calcite of the same size, in all temperatures. Besides differences in the chemical composition, the superior performance of the dolomite may be due to a more favorable structure of the pores developed during calcination and sulfation.

The pore size distributions of the calcined limestones were evaluated through mercury porosimetry and are presented in Figure 9. As observed, after calcination the dolomite developed a small porosity with diameters around 9.6  $\mu$ m, while the calcite presented a range of pores between about 0.080 and about 10  $\mu$ m. Although mercury porosimetry does not allow establishing microporosity, it was observed in both limestones. The scanning electron microscopy images in Figure 10 show that, after calcination, calcite presents macro, meso and micropores. Otherwise, for the dolomite it is only possible to observe the presence of micropores.

Since micropores are present in both limestones, it seems that porosity at this range is not the main feature explains the superior conversion of the dolomite. The present results indicate that the mesopores play an important role in the limitation of conversion. In fact, it seems that mesopores are the key feature leading to higher conversion.

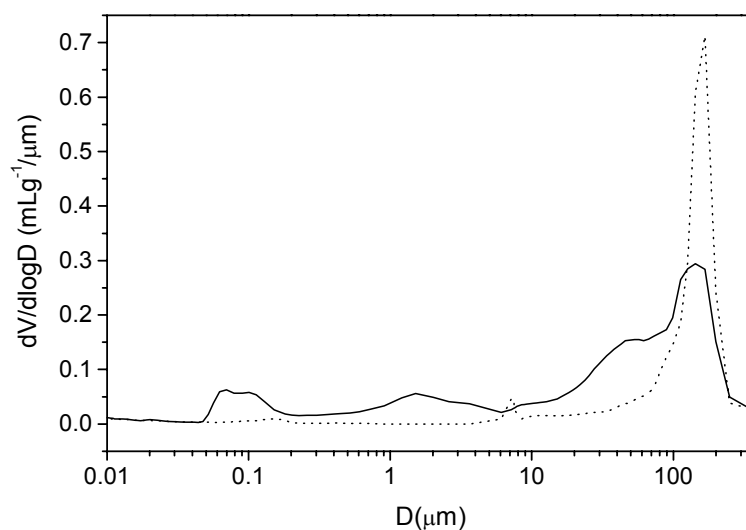
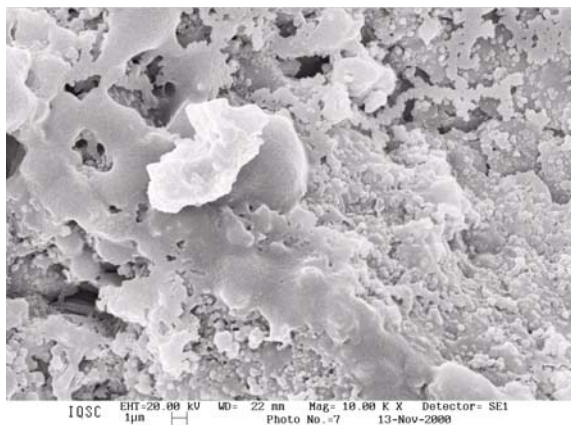
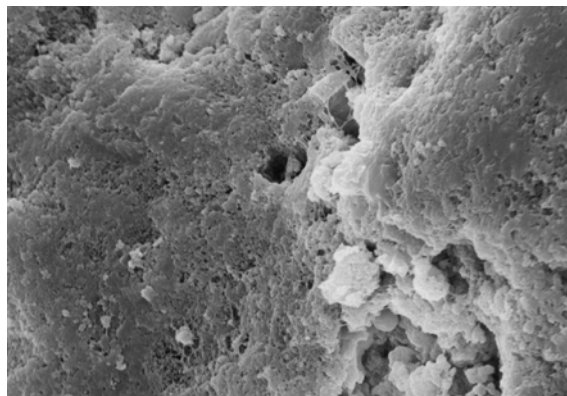


Figure 9: Pore size distribution measured by mercury porosimetry for the calcined sorbents: calcite (full line), dolomite (interrupted line).



(a)



(b)

Figure 10: SEM micrograph with 10000x of magnification for the calcined limestones: (a) calcite and (b) dolomite.

### 3. CONCLUSIONS

Thermogravimetric sulfation experiments were performed for a calcite and a dolomite. The results showed the same behavior, irrespective of temperature, particle size and type of limestone. Otherwise, the final conversion was considerably affected by all of those features.

In all the cases, conversion increased with temperature and then started to drop as the temperature was further increased, possibly due to sintering. The maximum conversion temperatures found are: 859 °C (for dolomite of 650 µm), 818 °C (for calcite of 545 µm) and 792 °C (for calcite of 650 µm).

Comparing the results of the calcite for the different particle sizes, it is possible to observe that a higher conversion was found for the smaller particles. Smaller particles improved conversion by providing larger superficial areas.

As expected, the dolomite provided better conversion than the calcite, irrespective of temperature. Besides differences in chemical composition, the superior performance of the dolomite may be due to a more favorable structure of the pores developed during calcination and sulfation. The present results suggest that mesopores are the key feature leading to higher conversion. This matter requires further investigations.

### 4. ACKNOWLEDGEMENTS

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