EFFECT OF PARTICLE SIZES ON THE PORE BLOCKAGE OF A BRAZILIAN DOLOMITE DURING THE SULFATION REACTION

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Abstract. *The present study aims to evaluate the effect of particle sizes during sulfation reaction and correlate with changes of the physical characteristics of dolomite. Calcination and Sulfation experiments were performed in a tube furnace for a Brazilian dolomite with average particle sizes of 385 µm and 545 µm at 850 °C at seven different times of sulfation (between 5 and 40 min). Thermogravimetric tests were performed in order to establish the reactivity variation of the dolomite with time in the sulfation reaction. The final conversion in the sulfation process for the dolomite with particle sizes of 385 µm and 545 µm were 54.2 ± 3.0 % and 49.7 ± 4.0 %, respectively. Porosimetry tests were also performed to establish the BET surface area, average pore diameter and quantity of adsorbed gas of natural, calcined and sulfated samples. The results showed that considering the process as a whole, since the sample calcined up to its full sulfation, the best fit was given by the exponential decay (first-order). Good results were obtained in this study with correlation coefficients values near 0.9 ($R^2 \geq 0.88$). Moreover, it was possible to obtain mathematical expressions that predict the behavior of pores blocking of calcined dolomite and to evaluate the effect of particle sizes during the sulfation process.*

Keywords*: dolomite; sulfation; porosimetry; BET surface area; pore blockage.*

1. INTRODUCTION

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_2 emission into the 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 into the combustion chamber, sorbing SO_2 before it is emitted to the atmosphere (Li and Sadakata, 1999; Van Houte and Delmon, 1979).

Limestones are basically calcium carbonate ($CaCO_3$). Some rocks, also called dolomites, present significant fractions of magnesium carbonate ($MgCO_3$), and others are mostly double carbonate of calcium and magnesium ($CaMg(CO_3)_2$). When introduced into a high-temperature fluidized bed, the carbonates calcined to produce a very porous solid structure of CaO/MgO (Eq. 1), which ultimately sorbs SO_2 to produce $CaSO_4$/$MgSO_4$ (Eq. 2).

$$CaCO_3 + MgCO_3 \rightarrow CaO + MgO + 2CO_2 \tag{1}$$

$$CaO + MgO + 2SO_2 + O_2 \rightarrow CaSO_4 + MgSO_4 \tag{2}$$

The formed calcined during the calcination reaction (Eq. 1) 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 $CaCO_3$ (~ 36.9 cm^3 mol^{-1}) and CaO (~16.9 cm^3 mol^{-1}) (Hartiman and Couchlin, 1976; Simon et al., 1987; Dam-Johansen and Ostergaard, 1991).

The kinetic parameters of the limestone decomposition are strongly dependent on systems, and operating conditions used (Mai and Edgar, 1989; Khraisha and Dugwell, 1991; Fuertes et al., 1993; Crnkovic et al. 2006). Several models to explain the limestone decomposition mechanism have been showed in the literature. In general, proposed models seek to determine the conversion rate of $CaCO_3$ calcination and the time to complete its process. It is assumed that $CaCO_3$ particles react according to the "shrinking-core model" or "unreacted-core model" (Borgwardt, 1985; Dennis and Hayhurst, 1987;Cheng et al., 2003).

During sulfation reaction (Eq. 2), the pores of the CaO particle are filled with products ($CaSO_4$, $CaSO_3$, 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 $CaSO_4$ (~ 46 cm^3 mol^{-1}) and $CaCO_3$ (~36.9 cm^3 mol^{-1}) (Dam-Johansen and Ostergaard, 1991; Crnkovic et al., 2008).

The actual mechanism leading to the formation of $CaSO_4$ is still a controversial subject among researchers. However, it is generally accepted that the reaction between the porous solid CaO and the gas SO_2 (in oxidizing atmosphere) is first-order related to SO_2 concentration. It is also agreed that the sulfation rate is maximum at temperatures around 850 °C (Allen and Hayhurst, 1996).

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 Garciá-Labiano, 1993; Davini, 2002), 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 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 µm limestone particles there was significant resistance to intra-particle gas diffusion at 980 °C. They concluded that SO_2 diffusion through $CaSO_4$ 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 $CaSO_4$, which imposes loss of internal superficial area and makes the internal layers of CaO inaccessible.

It is clear that the limestone's porosity plays a crucial role in the sulfation rate. However, the knowledge about the development of the physical structure of the sorbent during sulfation is still limited. From this perspective, the present study aims to evaluate the effect of particle sizes during sulfation reaction and correlate with changes of the physical characteristics of dolomite. For this purpose, techniques including nitrogen adsorption porosimetry and thermogravimetry were used.

2. EXPERIMENTAL CONDITIONS

2.1. Limestone Characterization

A Brazilian dolomite from São Paulo State was used in this work. The dolomite rock was ground and sieved for two average particle sizes of 385 µm and 545 µm. The average size of the particles was determined as the arithmetic mean between the mesh apertures of two consecutive ASTM laboratory sieves. Table 1 shows its elementary chemical compositions determined by atomic emission spectrometry (ICP-AES).

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

Ca	Mg	Fe	Al	Sr	K	Mn
17.07	11.73	0.32	0.42	0.08	0.13	0.09

The data from the X-ray diffraction analysis of dolomite, presented in Fig. 1, respectively, show the peaks indicating the major compounds present in the samples.
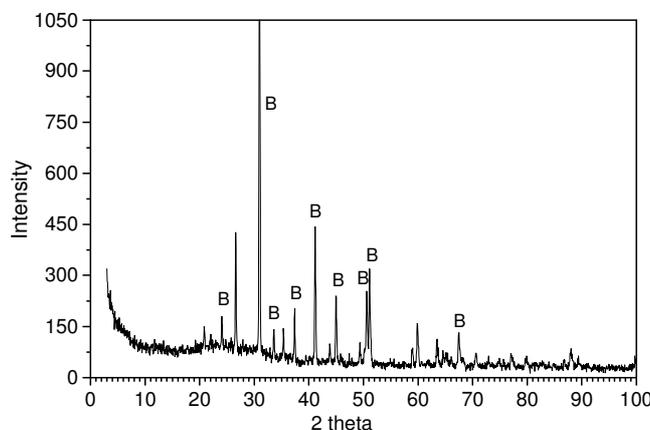
Figure 1. X-ray diffraction of the natural dolomite - B: $CaMg(CO_3)_2$

2.2. Thermogravimetric Experiments

To evaluate the sorption capacity of the dolomite, experiments were carried out under isothermal conditions in a

Shimadzu 51H Thermogravimetric Analyzer (TGA). Dolomite samples weighing 10.0±0.5 mg were used in all experiments. These small samples allowed minimizing inter-particle mass transfer resistances by spreading the particles on a monolayer at the bottom of the alumina crucible (Ø 6 mm × 2.5 mm). Alumina crucibles were used because this material supports high temperatures and does not produce catalytic effects on the sulfation reaction (Wieczorek-Ciurowa, 1992). Prior to sulfation, the sample was submitted to a heating rate of 30 °C min^{-1}, from around 20 ^{o}C to 850 °C, in air atmosphere at a flow rate of 80 mL min^{-1}. After 5 min of isothermal conditions, SO$_2$ (100 %v/v) was injected at a flow rate of 20 mL min^{-1} for 30 min. This flow rate was set to guarantee differential conditions (Borgwardt and Bruce, 1986). The sorption capability of the sorbents was established on the basis of a conversion, defined as the ratio between the mass of calcined reactant fed in the process and the mass of solid reactant which effectively reacts (Eq. 3),

$$X = \left(\frac{M_S - M_C}{M_C} \right) \times 100 \qquad (3)$$

where X is the conversion, M$_C$ is the mass of the sample after calcination and M$_S$ is the variation of the mass of the sample during SO$_2$ injection obtained from the TGA.

2.3. Preparation of Samples in a vertical tubular furnace

In order to provide enough samples for porosimetry tests, experiments of calcinations and sulfation for dolomite were carried out in a vertical tubular furnace (VTF) with volume of 3817 cm^3. In the sulfation experiment samples of natural dolomite were positioned within the furnace (electrically heated and controlled), and the samples were submitted to a heating rate of 30°C min^{-1} under a flow rate of 80 mL min^{-1} of synthetic air. When the desired temperature of 850 ^{o}C had been reached, the isothermal conditions were maintained. Under these conditions SO$_2$ was injected at a flow rate of 20 mL min^{-1}. Several samples were prepared at seven different sulfation times, i.e., 5, 8, 11, 14, 17, 20 and 40 min. In all the cases samples of 1.5±0.1 g were used.

2.4. Porosimetry by Nitrogen Gas Adsorption

Experiments of porosimetry by nitrogen gas adsorption were carried out in a Micromeritics porosimeter (ASAP - 2020). Prior to degassing, samples prepared were dried in an oven for approximately 12 h under a temperature of 110 ^{o}C. Samples of 0.6 ±0.05 g were used in all experiments. The conditions used to degassing and analyzing in the porosimeter are described as follows:

1. Degas conditions: the purpose of degassing is to remove previously adsorbed molecules from surfaces and pores (Webb and Orr, 1997). The samples were heated at rate of 10 ^{o}C min^{-1} up to 150 ^{o}C under vacuum restricted at evacuation rate of 10 mmHg.s^{-1} to 1 mmHg; the evacuation was changed to non-restricted vacuum at the same evacuating rate until 10 μmHg, remaining in these conditions for 30 min; the heating was continued at rate of 10 ^{o}C min^{-1} until 300 °C for natural dolomite or 350 ^{o}C for calcined and sulfated samples remaining in these conditions for 500 min.
2. Analysis conditions: the analysis of samples was started under vacuum restricted at evacuation rate of 5 mmHg.s^{-1} until 5 mmHg; the evacuation was changed to non-restricted vacuum at the same evacuation rate until 10 μmHg, remaining in these conditions for 6 min. Then a P/P$_0$ programming for 37 points was applied (24 points for adsorption and 13 points for desorption). P/P$_0$ is the ratio between applied pressure (P) and saturation vapor pressure of adsorbed gas (P$_0$), i.e., nitrogen.

The porosity was measured for the natural, calcined and sulfated samples of dolomite. According to Webb and Orr, 1997, convention has established that the quantity of gas adsorbed is expressed as its volume at standard conditions of temperature and pressure (0 ^{o}C and 760 torr and represented by STP) while the pressure is expressed as a relative pressure which is the actual gas pressure P divided by the vapor pressure P$_0$ of the adsorbing gas at the temperature at which the test is conducted.

3. RESULTS AND DISCUSSION

The SO$_2$ sorption capability of the dolomite was established on the basis of a conversion (Eq. 3). For this, TGA experiments were performed in three replicates and results of averaged conversion (X$_m$) were obtained. These TG curves allow evaluating the reactive behavior of the dolomite as sulfur sorbent. In addition, it is useful to determine the conversion since it quantifies this effect. Figure 2 shows conversions at temperature of 850 ^{o}C for dolomite samples with average particle sizes of 385 μm and 545 μm.

In Figure 2 the initial time was set at 3 min before the maximum peak of the DTG curve and the final time was set at 18 min 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. Although the final conversion values were different, the conversions results showed the same behavior, irrespective of particle sizes evaluated. The final conversion in the sulfation process for dolomite with particle sizes of 385 µm and 545 µm were 54.2 ± 3.0 % and 49.7 ± 4.0 %, respectively. The different behavior of the TG curves and the different conversions suggest that smaller particles improved conversion by providing larger superficial areas. In order to investigate this issue, porosimetry analyses were performed for the natural, calcined and sulfated rocks for two particle sizes of 385 µm and 545 µm.
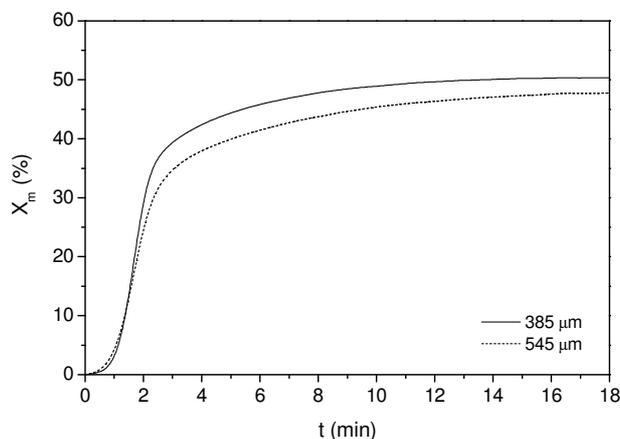
Figure 2. Average conversion (X_m) as a function of time (t) at temperature of 850 °C for dolomite samples with particle sizes of 385 µm and 545 µm.

Previously to porosimetry test, calcined and sulfated dolomite samples with particle sizes of 385 µm and 545 µm were prepared in a vertical tubular furnace (VTF) at temperature of 850 °C. Part of the samples prepared (10±0.5 mg) with particle sizes of 545 µm was subjected to sulfation in TGA to evaluate their preparation. In this case, it is advantageous to use TGA prior to the porosimetry tests in order to evaluate the methodology for preparing samples in VTF, since this technique is faster in comparison to the porosimetry. Table 2 shows the conversion obtained in TGA tests for samples prepared in VTF. The final time was set at 18 min after the initial time of sulfation.

Table 2. Conversion obtained in TGA versus time of sulfation for dolomite samples previously calcined and sulfated in VTF at 7 different times.

Time of Sulfation (min)	Conversion at 18 min (%)
0	61.92
5	46.76
8	32.30
11	24.80
14	19.58
17	12.94
20	9.21
40	0.03

As expected, samples with shorter time of sulfation had higher conversion values in TGA tests. Thus, the sample that was only calcined had the highest conversion value (around 62%) after sulfation process in TGA. On the other hand, the sulfated sample for 40 min in VTF had practically no mass increase (0.03%) after sulfation in TGA, indicating that it was completely sulfated.

It is also observed that the conversion to $CaSO_4$ obtained in TGA tests from the natural dolomite with particle size of 545 µm (49.7 % - Fig. 2) was 12 % smaller than that obtained from the previously calcined sample in the VTF. This difference of reactivity may be related to the intermediate species $Ca(OH)_2$ formed when calcined samples (VTF tests) are exposed to moisture due to differences in their pore structures. Samples not subjected to moisture (TGA tests) have cylindrical pores while those subjected to moisture (VTF tests) have slits pores or interstices between pores (platelike) and this structure allows expansion of the particles, maintaining a higher porosity (Bruce et al. 1989; Davini et al., 1991).

The results in TGA tests showed that the methodology of samples preparation for sulfation interrupt test was correct. The discussion about the methodology is described in detail by Ávila et al (2010) as well as the TGA curves related to the conversion presented in Tab. 2.

Considering the correct method of samples preparation, porosimetry experiments were performed for dolomite samples in both particle sizes of 385µm and 545 µm. A total of 18 dolomite samples were used, as follows: 2 natural, 2 calcined at 850 °C and 14 sulfated at 850 °C in interrupted tests between times of 5 and 40 min. Porosimetry techniques can be used to obtain the size and distribution pores and BET surface area. Thus it is possible to correlate the effectiveness of the sulfation process of the dolomite with changes in its physical characteristics during the reactive process. Figure 3 shows adsorption and desorption isotherms for dolomite samples with particle sizes of 385 µm in natural, calcined and partly sulfated (11 min) conditions at temperature of 850 °C.
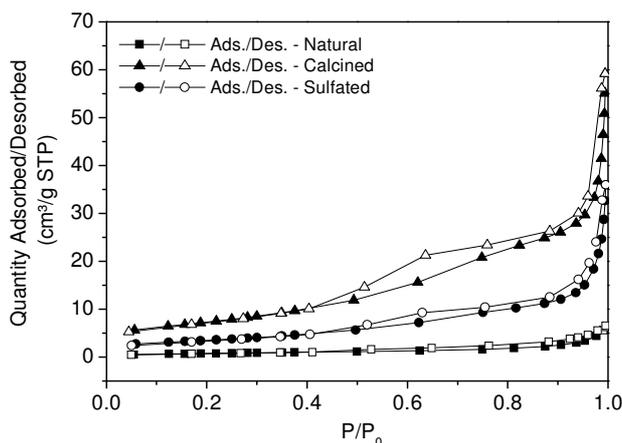
Figure 3. Adsorption and desorption isotherms for dolomite samples in its condition natural, calcined and partly sulfated (11 min) conditions at temperature of 850 °C and particle sizes of 385 µm.

Adsorption isotherms generally follow one of six forms which characterize the size of the pores of the material analyzed (Webb and Orr, 1997). Figure 3 shows that for the three samples analyzed, adsorption and desorption isotherms have similar shapes, indicating isotherms of type IV and hysteresis loops (when the curve does not coincide with the adsorption desorption). This behavior is typical of mesoporous and macroporous materials, i.e., whose pore opening is greater than 2 nm (20 Å) (Braunau, 1945, Gregg and Sing, 1982, Webb and Orr, 1997). The hysteresis behavior can be classified as type H3. According to the IUPAC, such hysteresis is observed in aggregates of particles with pore-shaped cracks (Figueiredo and Ribeiro, 1989; Rouquerol at al. 1999). It is noteworthy that the same behavior was observed for dolomite with particle sizes of 545 µm.

Table 3 shows results of physical characteristics for dolomite in its natural, calcined and fully sulfated (40 min) conditions for both particle sizes of 385 µm and 545 µm at temperature of 850 °C. The values of BET surface area (S_{BET}), average pore diameter ($D_{P.Des}$) and quantity of adsorbed gas (Q_A) were obtained. It is emphasized that the results of $D_{P.Des}$ showed in Tab. 3 refer the values obtained in desorption step, because in this step corresponds to a more stable condition (Lowell, 1984).

Table 3. Physical characteristics obtained for dolomite in its natural, calcined and fully sulfated (40 min) conditions for both particle sizes of 385 µm and 545 µm at temperature of 850 °C.

Particle Sizes	Samples	S_{BET} $(m^2 g^{-1})$	$D_{P.Des}$ $(4V/A)$ $(Å)$	Q_A $(cm^3 g^{-1} SPT)$
385 µm	Natural	2.78	97.74	6.57
	Calcined	26.54	91.86	59.24
	Sulfated (40 min)	1.25	97.90	2.83
545 µm	Natural	2.76	136.83	10.68
	Calcined	29.33	116.02	84.39
	Sulfated (40 min)	1.41	151.87	5.61

As expected, Tab. 3 shows that after calcination process, a significant increase in S_{BET} values occurred (above 9 times) for calcined samples in comparison to the natural dolomite. Nevertheless, for the samples sulfated for 40 min S_{BET}, values were below those obtained for natural dolomite samples. On the other hand, higher S_{BET} values were not expected for samples with higher particle size (545 µm). Evaluating the distribution of pores (Fig. 4), it is possible to

observe that there are no regions with different pore diameters for the sample of 385 µm, i.e., the curve presents a unimodal distribution. For sample of 545 µm two distinct regions of pore diameter (bimodal distribution) between 20-100 Å and between 300-1000 Å are noted. The bimodal distribution may have possibly contributed to higher S_{BET} values for the sample of 545 µm, although not have contributed to higher conversion in the sulfation process to this particle size (Figure 2). This behavior should be further investigated.
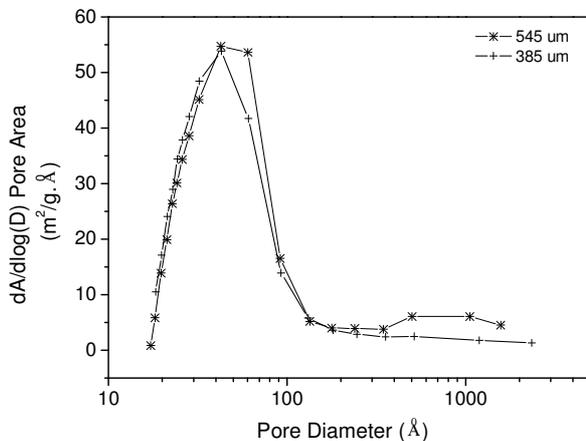
Figure 4. Pore size distributions of calcined dolomite at 850 °C in both particle sizes of 385 µm and 545 µm.

Table 3 also shows that average pore diameters were increased with calcinations process and decreased with sulfation process. Regarding the values of the maximum quantity of adsorbed gas, for calcined samples in both particle sizes they were significantly higher (above 100% and 150% to 385 µm and 545 µm, respectively) than those obtained for natural samples. In general these results were expected, because calcined dolomite has a more porous structure compared to natural dolomite, which means greater activation of the surface favoring SO_2 sorption process. As sulfation proceeds porosity loss occurs due to the growth of the product layers deposited on both internal and external surfaces. A pore blockage quickly develops all over the outer shells of a particle, making the internal regions inaccessible to reaction (Simon et al., 1987).

Figure 5 shows the pore distributions as a function of pore diameter for all porosimetry tests performed for dolomite samples with 385 µm. The same behavior was observed for dolomite with particle sizes of 545 µm (see Ávila et al., 2010).

(a)   (b)
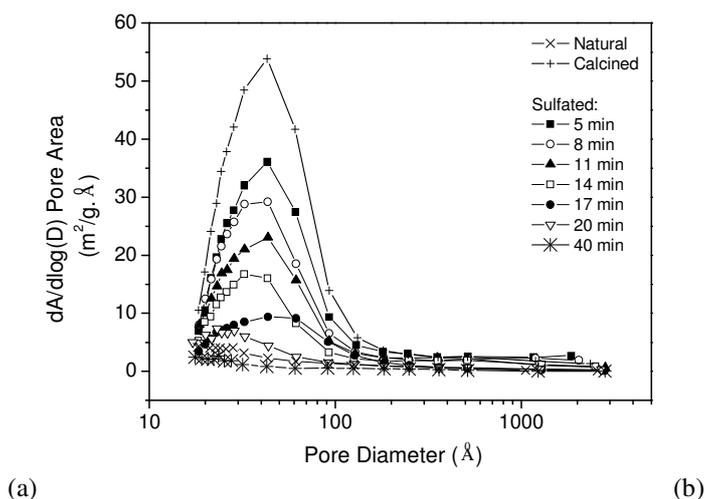
Figure 5. Distribution of pore area [dA/dlog (D)] as a function of pore diameter (Å) for dolomite samples of natural, calcined and sulfated at different times at temperature of 850 °C and particle sizes of 385 µm.

The results observed in Fig. 5 were consistent with expectations, since with the progress of sulfation process pores of sorbent particles were progressively blocked by sulfation products ($CaSO_4$/$MgSO_4$) and the internal surface area is reduced or become inaccessible (Borgwardt and Harvey, 1972; Bruce et al. 1989; Dennis and Hayhurst, 1990).

In order to evaluate the decrease of surface area during the sulfation process, surface area BET values (S_{BET}) were plotted as a function of sulfation time in both particle sizes studied. For this study, linear and exponential decay (first-order) fits were obtained as shown in Fig. 6.

Figure 6 shows that the linear fit explains only pores blocking in the initial step (until about 15 min), while the decay exponential fit explains the whole process (from dolomite calcined condition up to its blocked structure by sulfation products). Thus, considering the process as a whole, since the sample calcined up to its full sulfation, the best fit is given by the decay exponential (Eqs. 5 and 7) compared to linear fit (Eqs. 4 and 6) for particle sizes of 385 µm (Eqs. 4 and 5) and 545 µm (Eqs. 6 and 7).
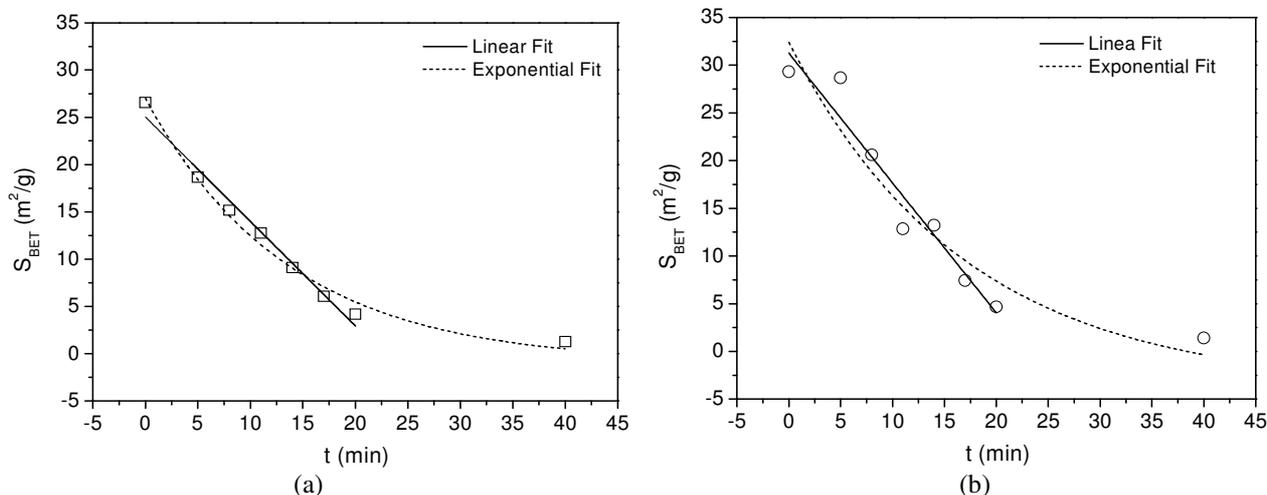
Figure 6. Curves of fits for the experimental data - Surface area BET versus time of sulfation at temperature of 850 ^{o}C and particle sizes of (a) 385 µm and (b) 545 µm.

Linear and exponential fits for average particle sizes of 385 µm:

$$S_{BET(385\,\mu m)} = 25.03 - 1.10 \cdot t \qquad\qquad R^2 = 0.98 \qquad\qquad\qquad (4)$$

$$S_{BET(385\,\mu m)} = 28.02 \cdot \exp\left(-\frac{t}{13.67}\right) - 1.01 \qquad R^2 = 0.98 \qquad\qquad\qquad (5)$$

Linear and exponential fits for average particle sizes of 545µm:

$$S_{BET(545\,\mu m)} = 31.28 - 1.36 \cdot t \qquad\qquad R^2 = 0.92 \qquad\qquad\qquad (6)$$

$$S_{BET(545\,\mu m)} = 32.71 \cdot \exp\left(-\frac{t}{16.22}\right) - 2.46 \qquad R^2 = 0.93 \qquad\qquad\qquad (7)$$

In agreement with the literature (Borgwardt and Harvey, 1972), in both linear and exponential fits the best correlation coefficients (R^2) were obtained for particle sizes of 385 µm.

The present study has provided mathematical expressions that predict the behavior of pores blocking of calcined dolomite with particle sizes of 385 µm and 545 µm at temperature of 850 ° C during the sulfation process.

4. CONCLUSIONS

This study investigated the sulfation effectiveness and correlated it with changes in the physical characteristics of limestone during the reactive process.

Thermogravimetry (TGA) experiments were applied to investigate the sorption reactivity of a Brazilian dolomite with particle sizes of 385 µm and 545 µm at 850 °C. The final conversion in the sulfation process for dolomite with particle sizes of 385 µm and 545 µm was 54.2 ± 3.0 % and 49.7 ± 4.0 %, respectively. The different behavior of the TG curves and the different conversions suggest that smaller particles improved conversion by providing larger superficial areas. TGA also showed advantageous in evaluating the samples preparation.

A total of 18 tests were performed in nitrogen adsorption porosimetry considering dolomite samples, as follows: 2 natural, 2 calcined at 850 ^{o}C and 14 sulfated at 850 ^{o}C in interrupted tests between times of 5 and 40 min. The results were consistent with expectations, since with the progress of sulfation process pores of sorbent particles are progressively blocked by sulfation products and the internal surface area is reduced or became inaccessible. From these data, it was possible to obtain mathematical expressions that predict the behavior of pores blocking of calcined dolomite with particle sizes of 385 µm and 545 µm at temperature of 850 ° C during the sulfation process. The results showed

that considering the process as a whole, since the sample calcined up to its full sulfation, the best fit is given by the exponential decay (first-order).

This study obtained good results with correlation coefficients values near 0.9 ($R^2 \geq 0.88$) indicating that the methodology applied for samples preparation to calcination and sulfation in vertical tubular furnace was adequate. Moreover, the results showed that it is possible to predict the reactivity decrease behavior of dolomite for SO_2.

5. ACKNOWLEDGEMENTS

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