Investigation of the pore blockage of a Brazilian dolomite during the sulfation reaction

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The influence of the temperature and reaction time on the sulfuration process of a dolomite is investigated in this paper. The sulfation effectiveness was evaluated and correlated with changes in the physical characteristics of a Brazilian dolomite during the reaction process. Calcination and sulfation experiments were performed under isothermal conditions for dolomite samples with average particle sizes of 545 μm at temperatures of 750 °C, 850 °C and 950 °C at different times of sulfation. Thermogravimetric tests were applied to establish the reactivity variation of the dolomite in function of the time in the sulfation reaction and evaluate the methodology of the samples preparation. Porosimetry tests were performed to study the pore blockage of dolomite during the sulfation reaction. The highest values of BET surface area were 25.55 m²/g, 29.55 m²/g and 12.82 m²/g for calcined samples and after their sulfation processes, conversions of 31.5%, 61.9% and 42.8% were obtained at 750 °C, 850 °C and 950 °C, respectively. Considering the process as a whole, the best fit was provided by a first-order exponential decay equation. Moreover, the results have shown that it is possible to quantify the decreasing in the dolomite reactivity for sulfur dioxide sorption and understand the changes in the behavior of the sulfation process of limestones when applied to technologies, as fluidized bed combustor, in which sulfur dioxide is present.

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1. Introduction

A critical aspect of the limestone efficiency used for the sorption of sulfur dioxide generated in coal combustion refers to its decreasing reactivity in function of the reaction time [1]. Considering the typical residence times applied to fluidized bed reactors, studies on the sorption of sulfur dioxide (SO₂) by limestones have showed that the major determining factor of the final reactivity of limestone is related to the changes in the porosity that occur in its structure during both calcination and sulfuration reactions [1–3]. Thus, for any residence time in the reactor, each calcined particle of limestone reaches a limit conversion in the sulfation process, because its internal structure becomes inaccessible due to the pores partial blockage [1,4]. The SO₂ sorption by limestones depends largely on the complex flow patterns that develop in fluidized bed combustors. This behavior is attributed to reaction rates controlled by the chemical kinetics and mass transport of the reactive gases [5,6]. The reaction in the particle as a whole is also governed by the diffusion of the gaseous reactant into the particle [7].

Several resistance characteristics are considered in the reaction: (i) transport of reactive gas through the gaseous film surrounding the reactive particles, (ii) diffusion of reactant gas through the outer layers of each reacting particle, (iii) diffusion of reactant gas through the unreacting porous core particle and (iv) chemical kinetics [8–12]. It is also possible to distinguish resistances to intrinsic reactions (intra-particle) and external part of the particles. Intrinsic resistances are difficult to evaluate individually and are generally determined in blocks, as an effective resistance results from diffusion effects and intra-particle chemical kinetics [13–15].

The composition of the intrinsic resistances with external resistances to the particles allows determining global coefficients of reaction rates. Due to the large heterogeneity and the structural complexity of limestones, it is virtually impossible to develop accurate models based on the knowledge of the physical structure evolution of the particle under reaction of both calcination and sulfation [16,17]. Such an evolution is highly transient and depends on the type of limestone, size and shape of the individual particle [14].

The kinetic parameters of the limestone (CaCO₃) and dolomite (CaCO₃-MgCO₃) decomposition are strongly dependent on the system and operating conditions used [18–20]. High temperatures and duration of thermal exposure during the calcination process lead to the sintering of the limestone particles, and a decrease
occurs in both porosity and surface areas [21–23]. According to Stanmore and Gilot [23], it is possible to anticipate that the limestone particles will exhibit a highly fused nodular surface after several hours of residence time in the circulating systems.

Thermal analysis has been widely used in the characterisation and kinetic investigation of the limestones calcination and sulfation. Kök and Smykatz-Kloss [24] studied the regular and iron-bearing dolomites based on decomposition temperatures. It was possible to identify the FeO (mass%) of all dolomite samples by DTA and the results were confirmed by atomic absorption spectrophotometer experiments. The kinetics of the thermal decomposition of limestones was investigated by Satterfield and Feakes [25]. They observed that the decomposition process is presumably determined by the interrelationship among the three major rate controlling processes: (1) heat transfer, (2) mass transfer and (3) chemical reaction kinetics. Beruto and Searcy [26] recognized the importance of the kinetic control of the process in the limestone decomposition reaction, but they did not exclude the importance of other limiting steps. Kök and Smykatz-Kloss [27] studied the behavior of four dolomite samples by X-ray diffractometer and simultaneous TG–DTA experiments. They observed three different decomposition regions and obtained activation energies in the 48–137 kJ/mol range. Ávila et al. [28] applied thermogravimetric tests under isothermal conditions to investigate the kinetics of SO₂ sorption for both calcite and dolomite. The authors concluded that the sulfation process was controlled by Knudsen diffusion for calcite and molecular diffusion of gas through the pores for dolomite.

Several models have been developed to explain the limestone decomposition mechanism. In general, they seek to determine the calcination rate of calcium carbonate (CaCO₃) and the time to complete its process. It is assumed that CaCO₃ particles react following the shrinking-core model or unreacted-core model [7,16,21,29]. According to Alfors and Svedberg [7], models that describe the limestone sulfation process should also include two stages that precede the sulfation, i.e., limestone calcination and sintering of CaO. The reaction between SO₂ and CaCO₃ in atmospheric fluidized bed combustors involves the processes of calcination following by sulfation, which occurs through the following overall reactions [23,30]:

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad \Delta H \approx +182.1 \text{ kJ/mol} \tag{1}
\]

\[
\text{CaO}(s) + \frac{1}{2}\text{SO}_2(g) \rightarrow \text{CaSO}_4(s) \quad \Delta H \approx -481.4 \text{ kJ/mol} \tag{2}
\]

The calcium oxide (CaO) formed in the calcination (Eq. (1)) is very porous and has the same size of the original particle. Its high porosity is due to the difference between the molar volumes of CaCO₃ (~36.9 cm³/mol) and CaO (~16.9 cm³/mol) [4,17,31]. During sulfation (Eq. (2)), the pores of the CaO particles are filled with products, mainly CaSO₄, and become progressively plugged; as sulfation proceeds, there occurs porosity loss 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 reactions [5,11,17,31,32]. 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 CaSO₄ (~46 cm³/mol) and CaCO₃ (~36.9 cm³/mol) [17].

Due to the characteristics of the sulfation process, some physical properties of the limestones assume large relevance in the establishment of reaction rates. Porosity, pore size distribution and BET surface area are generally considered very important factors. The limestone sulfation process is affected by porosity, pore size and size distribution of pores, intra-particle superficial area [14,33–35], geological age, size and density of the particles [36]. Another factor to consider is the presence of chemical elements, which may act as either catalysts or inhibitors [17].

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**Table 1.**

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>mass/mass</th>
</tr>
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<tbody>
<tr>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>17.07</td>
<td>11.73</td>
</tr>
</tbody>
</table>

It is clear that the limestone’s porosity plays a crucial role in the sulfation rate. However, the knowledge of mathematical equations obtained from experimental data that can evaluate the changes in the behavior of the physical structure of the limestones, depending on the sulfation time is still limited. In addition, there are no studies in the literature which clearly show the pore sizes region of dolomite that is mostly affected by the sulfation reaction. From this perspective, the present study aims to evaluate the effect of temperature on the sulfation effectiveness and correlate it with changes in the physical characteristics of a Brazilian dolomite during the reactive process. For this purpose, techniques including nitrogen adsorption porosimetry, thermogravimetry and scanning electron microscopy 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 average particle sizes of 545 μm. The average size of the particles was determined as the arithmetic mean between two consecutive ASTM laboratory sieves with mesh apertures between 590 and 500 μm. Table 1 shows its elementary chemical compositions determined by atomic emission spectrometry (ICP-AES).

2.2. Scanning electron microscopy

The morphological structures of the dolomite were determined for natural, calcined and sulfated (30 min of sulfation) samples. Morphological observations were obtained using a scanning electron microscope (SEM) in LEO Electron Microscopy 440 (ZEIS/LAIKA) with amplitude of 5000 times.

2.3. Thermogravimetric experiments

To evaluate the sorption capacity of the dolomite, experiments were carried out under isothermal conditions in a Shimadzu 51H thermogravimetric analyzer (TGA). A mass flow controller (Aalborg) specific to SO₂ was used to control the gas flow rate. Prior to the experiments, the thermogravimetric equipment was calibrated and experiments were run three times for repeatability. 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 (ϕ 6 mm × 2.5 mm). Alumina crucibles are used because they support high temperatures and do not produce catalytic effects on the sulfation reaction [3–37]. Prior to sulfation, the samples were subjected to a heating rate of 30 °C min⁻¹, from approximately 20 °C to study temperature effects at 750 °C, 850 °C and 950 °C, in air atmosphere at a flow rate of 80 mL min⁻¹. A heating rate of 30 °C min⁻¹ was adopted as it would not affect the final values of the conversion. After 5 min of isothermal conditions, SO₂ (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 [14]. All experimental conditions adopted in the TG tests and described above were evaluated and detailed elsewhere [3,28,38,39].
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)),

$$X = \left( \frac{M_S - M_C}{M_C} \right) \times 100$$  \hspace{1cm} (3)

where $X$ is the conversion, $M_C$ is the mass of the sample after calcination and $M_S$ is the variation of the sample mass during SO$_2$ injection obtained from the thermogravimetric tests.

2.4. 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 with volume of 3817 cm$^3$. The same experimental conditions of heating rate, gas flow rate and temperature of process adopted in TG tests were used. Thus, in sulfation experiments, natural dolomite samples were positioned within the furnace (electrically heated and controlled) and subjected 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 °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.

2.5. Porosimetry by nitrogen gas adsorption

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

1. Degas conditions: the purpose of degassing is to remove previously adsorbed molecules from surfaces and pores [40]. The samples were heated a rate of 10 °C min$^{-1}$ up to 150 °C under vacuum restricted at evacuation rate of 10 mmHg/s to 1 mmHg; the evacuation was changed to non-restricted vacuum at the same evacuating rate until 10 µmHg, remaining under these conditions for 30 min; the heating was continued at a rate of 10 °C min$^{-1}$ until 300 °C for natural dolomite or 350 °C for calcined and sulfated samples remaining under these conditions for 500 min.

2. Analysis conditions: the analysis of samples was started under vacuum restricted at an evacuation rate of 5 mmHg/s until 5 mmHg; the evacuation was changed to non-restricted vacuum at the same evacuation rate until 10 µmHg, remaining under 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 [40], convention has established that the quantity of gas adsorbed is expressed as its volume under standard conditions of temperature and pressure (0 °C and 760 Torr 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

In order to investigate the variation in the dolomite porosity, calcined and sulfated dolomite samples were prepared in a vertical tubular furnace (VTF) at temperatures of 750 °C, 850 °C and 950 °C for posterior porosimetry tests. After the calcination and sulfation of dolomite, part of the samples prepared (10 ± 0.5 mg) was subjected to sulfation in TGA to evaluate their preparation. In this case, it is advantageous to use the TG prior to porosimetry tests, because this technique is faster and allows evaluating the conditions of the samples preparation.

Thermogravimetry (TG) experiments of sulfuration were performed with a heating rate of 30 °C min$^{-1}$ under isothermal conditions at 850 °C for both natural and calcined samples of dolomite in VTF. Fig. 1 shows the mass loss/gain (TG curve) and derivative mass loss/gain (DTG curve) versus time profile for two samples, a natural dolomite and a calcined dolomite previously calcined at 850 °C in the VTF.

The DTG curve of the natural sample shows three peaks. The first peak of mass loss [i] occurs between 40 and 115 °C and is due to the dehydration of inter-particle water. The second peak of mass loss [ii], observed in the temperature range of 650–835 °C, is due to the calcination dolomite. The third peak of mass gain [iii] refers to the mass gained by the SO$_2$ injection into the system and further reaction under isothermal conditions at 850 °C.

For the calcined sample, two different regions of mass loss/gain can be observed and distinguished in the DTG curve, in which two peaks are obtained. The first peak of mass loss [i] occurs around
400 °C and refers to the mass loss due to the dehydroxylation. The Ca(OH)₂ specie is formed when calcined limestone (CaO) is exposed to ambient conditions of temperature and humidity. The second peak refers to the mass gained by the SO₂ injection into the TG system and further reaction under isothermal conditions at 850 °C. For all TG experiments for natural and previously calcined and sulfated samples in the VTF, similar profiles were obtained. The SO₂ sorption capability of the dolomite was established from the TG experiments and on the basis of the conversion (Eq. (3)). The TG curves show the reactive behavior of the dolomite as sulfur sorbent and the conversion quantifies this effect. 

Fig. 2 shows the conversion (X) at temperatures of 750 °C, 850 °C and 950 °C for natural dolomite samples with average particle sizes of 545 μm. 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 is assumed to be finished. All the average conversion curves show the same behavior, although the final gain of mass was different for different temperatures. It is observed that conversion grows with temperature and then starts to drop as temperature further increases. The final conversion values (18 min) were 49.7%, 53.2% and 46.8% for 750 °C, 850 °C and 950 °C, respectively.

Some authors agree that there is a maximum in the extent of sulfation reaction at temperatures around 850 °C. In agreement with these authors, Ávila et al. performed experiments in TGA in a previous study using the same dolomite with particle size of 650 μm, and a maximum conversion of 859 °C was obtained. At higher temperatures the sulfation reaction kinetics is faster and the rate of sulfation is higher. On the other hand, at sufficiently high temperatures the reaction rate decreases due to possible sintering, causing the loss of internal superficial area, and consequently the conversion falls.

Fig. 3 shows the conversion obtained in TG tests for calcined dolomite samples prepared in VTF. In general, samples with shorter sulfation time had higher conversion values in TG tests. Thus, the sample that was only calcined in VTF had the highest conversion value after the sulfation process in TGA and the sample that was partially sulfated in VTF had intermediate values of conversions. On the other hand, the sample sulfated for 40 min in VTF showed no mass increase after sulfation in TGA, indicating that the sample had been completely sulfated. Unexpected conversion values obtained for samples at some sulfation times in VTF were possibly due to the heterogeneity of the samples. The final conversion values were 51.5%, 61.9% and 42.8% for 750 °C, 850 °C and 950 °C, respectively. Comparing these conversion values with those obtained in TG tests from the natural dolomite (Fig. 2), they were 3.3% and 15.8% higher for the calcined sample in the VTF at temperatures of 750 °C and 850 °C, respectively. This difference in reactivity may be related to differences in the pore structures. In VTF tests, the calcined samples are exposed to environmental conditions, as humidity, and the intermediate specie Ca(OH)₂ is formed. According to the literature, samples not subjected to moisture usually have cylindrical pores while those subjected to moisture usually have slit pores or plate-like pores, allowing for the expansion of the particles and maintaining a higher porosity. However, this behavior was not observed for samples calcined in VTF at 950 °C, it seems that the sintering process was more effective at 950 °C in VTF than under TGA conditions.

The time in thermal exposure also affects the sintering of limestone particles, but for all temperatures studied the time in the thermal exposure during the calcination process in VTF tests was the same. Thus, the high temperature (950 °C) was possibly more effective in the sintering of calcined dolomite than the exposure time during the calcination process.

To evaluate the decrease of reactivity during the sulfation process of the samples prepared in VTF, conversion values (X) were plotted as a function of sulfation time (t) considering the
sulfation for 18 min of reaction in TGA (Fig. 4). For calcined and sulfated samples at 850 °C, the equation that best fitted the experimental points was obtained by a first-order exponential decay (Eq. (5)). However, the best fits to the experimental points were obtained by the second-order polynomial equations for calcined and sulfated samples at temperatures of 750 °C (Eq. (4)) and 950 °C (Eq. (6)). At all temperatures studied, good fits to the experimental data were obtained with correlation coefficients (R²) higher than 0.8.

\[ X_{750°C} = 0.0375 \cdot t^2 - 2.9322 \cdot t + 56.0706, \quad R^2 = 0.93 \]  
\[ X_{850°C} = 68.4747 \cdot \exp \left( -\frac{t}{13.3657} \right) - 4.7149, \quad R^2 = 0.99 \]  
\[ X_{950°C} = 0.02825 \cdot t^2 - 2.3221 \cdot t + 48.0767, \quad R^2 = 0.84 \]

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 the \( \text{SO}_2 \) sorption process. As sulfation proceeds there occurs porosity loss 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 [21,31].

The results in the TG experiments showed that the methodology for the samples preparation in interrupted sulfation test was correct. This methodology was described in details elsewhere [47]. After preparation in VTF, the samples were submitted to porosimetry experiments.

Porosimetry techniques can be used to obtain the size and distribution of pores and BET surface area. Thus, these results allow correlating the effectiveness of the sulfation reaction of the dolomite with changes in its physical characteristics during the reactive process. Dolomite samples were used in the following conditions: natural, calcined at 750 °C, 850 °C and 950 °C and sulfated at 750 °C, 850 °C and 950 °C in interrupted tests between 5 and 40 min. Fig. 5 shows the adsorption and desorption isotherms for natural, calcined and partly sulfated (11 min) dolomite samples at the three temperatures studied.

Adsorption isotherms generally follow one of the six forms which characterize the size of the pores of the material analyzed [40]. For the three samples analyzed, adsorption and desorption isotherms have similar shapes (Fig. 5), 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., materials whose pore opening is larger than 2 nm (20 Å) [40,48,49]. 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 [50,51].

Regarding the values of the maximum quantity of adsorbed gas, Fig. 5 also shows that the calcined sample at 850 °C was 46% and 171% higher than those obtained for calcined samples at 750 °C and 950 °C, respectively.

For all samples (natural, calcined and sulfated), the pore distribution results were plotted as a function of pore diameter (Fig. 6). Evaluating the distribution of pores, it is possible to observe that the curves for samples prepared at 750 °C and 950 °C presented a unimodal distribution. On the other hand, in samples prepared at 850 °C two distinct regions of pore diameter between 20–100 Å and 300–1000 Å (bimodal distribution) could be observed and the amount of pores decreased in function of the sulfation time. We believe that this behavior may be responsible for the higher conversion of sulfation at 850 °C, but this issue should be further investigated. Fig. 6 also shows that during the sulfation process of the dolomite, the region between 20 and 100 Å (mesoporous region) is the most affected by the pores blockage.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_{BET} (m²/g)</th>
</tr>
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<tbody>
<tr>
<td>Natural</td>
<td>2.84</td>
</tr>
<tr>
<td>Calcined/sulfated</td>
<td>750 °C</td>
</tr>
<tr>
<td></td>
<td>850 °C</td>
</tr>
<tr>
<td></td>
<td>950 °C</td>
</tr>
<tr>
<td>Calcined</td>
<td>25.53</td>
</tr>
<tr>
<td>Sulfated (5 min)</td>
<td>23.43</td>
</tr>
<tr>
<td>Sulfated (8 min)</td>
<td>17.62</td>
</tr>
<tr>
<td>Sulfated (11 min)</td>
<td>12.05</td>
</tr>
<tr>
<td>Sulfated (14 min)</td>
<td>10.95</td>
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<tr>
<td>Sulfated (17 min)</td>
<td>6.84</td>
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<td>Sulfated (20 min)</td>
<td>4.60</td>
</tr>
<tr>
<td>Sulfated (40 min)</td>
<td>1.15</td>
</tr>
</tbody>
</table>

These results were consistent with expectations. Due to the progress of the sulfation process, the pores of the sorbent particles were progressively blocked by sulfation products (CaSO₄/MgSO₄) and the internal surface area was reduced or became inaccessible [1,42,52]. This change in the physical structure of the natural dolomite during calcination and sulfation processes can also be observed in images of scanning electron microscope (SEM) with amplitude of 5000 times (Fig. 7).

SEM images in Fig. 7 present the external surfaces of natural, calcined and sulfated sorbents. Comparing the images of natural (Fig. 7a) and calcined dolomites (Fig. 7b), it is possible to observe that the morphological structure of the calcined one became more porous, allowing increasing the SO₂ sorption reactivity [38]. After the sulfation process (Fig. 7c), the surface became compacted and filled with products, mainly CaSO₄.

Table 2 shows the results of \( S_{BET} \) obtained for dolomite with 545 μm in its natural, calcined and sulfated (40 min) conditions at temperatures of 750 °C, 850 °C and 950 °C. As expected, there occurred a significant increase in the \( S_{BET} \) values (above 9, 10 and 4 times for calcined samples at temperatures of 750 °C, 850 °C and 950 °C, respectively) in comparison to the natural dolomite. Nevertheless, for all samples sulfated for 40 min, \( S_{BET} \) values were below those obtained for natural samples.

In order to evaluate the decrease in the surface area during the sulfation process, BET surface area values (\( S_{BET} \)) were plotted as a function of sulfation time (t) from 0 up to 40 min of reaction (Fig. 8). The best fit was provided by a first-order exponential decay equation for dolomite with particle sizes of 545 μm at temperatures of 750 °C (Eq. (7)), 850 °C (Eq. (8)) and 950 °C (Eq. (9)).

\[ S_{BET}(750°C) = 30.745 \cdot \exp \left( -\frac{t}{17.217} \right) - 3.105, \quad R^2 = 0.93 \]  
\[ S_{BET}(850°C) = 32.708 \cdot \exp \left( -\frac{t}{16.217} \right) - 2.464, \quad R^2 = 0.93 \]  
\[ S_{BET}(950°C) = 17.284 \cdot \exp \left( -\frac{t}{22.188} \right) - 2.922, \quad R^2 = 0.77 \]

Good correlation coefficients (\( R^2 > 0.9 \)) were obtained at temperatures of 750 °C and 850 °C. Considering the temperature of 950 °C, the sintering process possibly contributed to the lower value of \( R^2 \) (0.77). When the sintering occurs, the particles exhibit a highly fused nodular surface [23] and the structure cannot be assumed constant [22]. It is noteworthy that better fits can be obtained with additional points between 20 and 40 min for all temperatures studied.

The present study has provided mathematical expressions that quantify the behavior of pores blocking for a calcined dolomite with particle size of 545 μm at temperatures of 750 °C, 850 °C and 950 °C during the sulfation process. In agreement with the literature, the results showed that the \( \text{SO}_2 \) sorption rate by dolomite decreased...
Fig. 4. Fit curves to the experimental data considering 18 min of sulfation as a function of time for dolomite samples previously calcined and sulfated in VTF at temperatures of 750 °C, 850 °C and 950 °C.

Fig. 5. Adsorption and desorption isotherms for dolomite samples with an average particle size of 545 μm in their natural, calcined and partly sulfated conditions (11 min) at temperatures of 750 °C, 850 °C and 950 °C.

Fig. 6. Pore size distributions of natural, calcined and sulfated dolomite samples with an average particle size of 545 μm at temperatures of 750 °C, 850 °C and 950 °C.
exponentially as sulfation proceeded until the pores had been filled and plugged with reaction products [1].

4. Conclusions

This study investigated the sulfation effectiveness and mathematically correlated it with changes in the physical characteristics of limestone during the reactive process. The pore blockage of a Brazilian dolomite during the sulfation reaction was demonstrated by thermogravimetry and porosimetry tests.

Thermogravimetry experiments were applied to investigate the sulfur sorption reactivity of dolomite and evaluate the samples preparation. Good results were obtained indicating that the methodology applied for samples preparation for calcination and sulfation in vertical tubular furnace (VTF) was adequate. The SEM images confirmed the differences in the morphological structures when natural samples were subjected to calcination and sulfation processes.

Porosimetry tests were performed considering dolomite samples of natural and those calcined at temperatures of 750 °C, 850 °C and 950 °C, and sulfated in interrupted tests at seven different times between 5 and 40 min. The results showed that as the sulfation reaction progressed, pores of sorbent particles were progressively blocked by sulfation products and the internal surface area was reduced or became inaccessible due to the pores filling with CaSO4.

Mathematical expressions were also obtained to quantify the reactivity decrease behavior of pores blocking of calcined dolomite during the sulfation process. In agreement with the literature, the results showed that considering the process as a whole, for the sample calcined up to its full sulfation, the best fit was given by a first-order exponential decay equation.

It also was possible to show that the mesoporous region of the dolomite was the most affected region by the pores blockage during the sulfation process. In addition, possibly the high temperature (950 °C) was more effective in the calcination than the time of thermal exposure, since the latter was the same for the three temperatures studied.

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