

## DETERMINATION OF KINETICS AND EQUILIBRIUM PARAMETERS FOR THE DESULPHURIZATION BY LIMESTONE

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**Abstract.** The sorption of  $SO_2$  into calcined limestone has been studied and is a critical point of interest related to fossil fuel combustion in energy production. An alternative to minimize the undesirable impacts of such pollutant on the environment and human health is the application of fluidized bed combustion (FBC) technology, which can achieve high combustion efficiency with low emissions of  $NO_x$  and  $SO_2$  when limestone is injected into the boiler. In this system,  $SO_2$  generated in coal combustion is removed using CaO and in this solid-gas reaction the diffusion through the product layer becomes a limiting step for the global rate of reaction. The characteristics of the sorption behavior may be interpreted in terms of both thermodynamic equilibrium and chemical kinetics. For kinetics, temporal variations of the amount of sorption are measured and the experimental data are used to obtain a proper kinetic model. For equilibrium aspects, thermodynamic parameters can be determined from sorption isotherms. The experiments related to  $SO_2$  sorption were carried out in a thermogravimetric balance and two different limestones – a calcite and a dolomite – were used. The kinetics of this process was analyzed by fitting models, such as Langmuir, Freundlich, and Modified Langmuir. The Langmuir and Modified Langmuir isotherm provided the best fitting of data for both sorbents allowing the determination of diffusion coefficients. The thermodynamics of the sorption process has been studied and the changes in Gibbs Free Energy ( $\Delta G$ ), which is an important parameter, have also been determined.

**Keywords:** sorption isotherm, desulphurization, limestone, thermal analysis

### 1. INTRODUCTION

Emissions of sulphur dioxide into the atmosphere have increased steadily due to industrial development, and increasing worldwide environmental concerns call for the limitation of such air pollutant emissions. Emissions regulations are expected to become more stringent in the future.

Technologies have been developed to control  $SO_2$  emissions, a representative acidic pollutant. Processes in which limestones are used as a sorbent of  $SO_2$  in gas treatments have been intensively investigated. After calcination, limestones develop high porosity and internal surface area, which makes those sorbents very attractive for sulfur removal in coal-fired power plants. Cheng et al (2004), for instance, reported internal surface areas of around  $30 \text{ m}^2 \text{ g}^{-1}$ .

When submitted to high enough temperatures and low enough partial pressures of  $CO_2$ , limestones calcine, as given in Eq. 1.



During coal combustion in fluidized beds, temperatures are usually between 800 and 950°C, allowing limestone to calcine, and the sulfur content of the fuel to be converted to sulfur oxides, primarily  $SO_2$ . Then, the sorbent reacts with  $SO_2$  and  $O_2$  to form  $CaSO_4$ . Both calcination and sulfation enforce considerable changes to the particles' pore structure, which significantly affects reactivity and, consequently, conversion. In general, the increasing resistances to gas diffusion due to sulfation quickly becomes so high that most of the internal volume of a particle does not sulfate (Sotirchos et al, 1992; Fuertes et. al., 1994).

The mechanism of the sulfation reaction has been described basically in two steps.  $SO_2$  and  $O_2$  diffuse into the limestone particles reacting with CaO at the interface, where sulfation takes place. Firstly the reaction is very fast and then declines markedly. This change of behavior is attributed to the plugging of pores, causing a blockage of the internal structure of the particles, and imposing high resistances to intraparticle gas diffusion.

Borgwardt and Harvey (1972) demonstrated that both pore's and particle's sizes determine the extent to which the interiors of the individual particles react; this shows that intraparticle diffusion is governed by the physical structure of the particles. The reaction occurs according to the following consecutive steps :

1. Transport of gas reactant molecules towards the limestone particles
2. Adsorption of the gases through the particles' external surface
3. Chemical reaction on the particles' internal surfaces

The overall reaction process may be predominantly limited by one or more of those steps. According to Gregg and Sing (1982), McBain (1909) proposed the term sorption to describe the successive events of adsorption on the surface, absorption by penetration into the lattice of the solid, and capillary condensation within pores. In this work steps 2 and 3 are to be referred as sorption, even though the last event is chemical reaction instead of condensation.

Adsorption is quite dependent on the interactions between gas molecules and solid surfaces. In this context thermodynamic equilibrium plays a significant role. From adsorption equilibrium observations it is possible to obtain information for better understanding the process. For instance, it is possible to establish how many different components are present in the system and how much of those components can be accommodated by a solid adsorbent. Although the expression adsorption isotherm is commonly used in the literature, in the present study we adopted the expression sorption isotherm, accounting for the fact that in sulfation the adsorption is followed by chemical reaction. From sorption isotherms it is possible to derive process parameters, including thermodynamic equilibrium constants, which can be related to thermodynamic properties such as Gibbs free energy and enthalpy of formation.

Isothermal models have been developed to describe adsorption equilibrium either at lower pressures – prior to monolayer formation – or at higher pressures – corresponding to the multilayer region in adsorption (Laidler, 1950). If the sorbents present an irregular structure, models that account for energetic heterogeneities lead to a better interpretation of the sorption data (Jaroniec, 1983).

The present paper aims to study sorption isotherms to quantitatively evaluate the sorption process between SO<sub>2</sub> and limestone. Experimental equilibrium data were fitted to the Langmuir, Freundlich, and modified Langmuir equations to determine the best fit isotherm equation. The thermodynamics of the sorption process was studied and the Gibbs free energy of formation was determined.

## 2. EXPERIMENTAL

Two different types of limestone were used, a calcite (named CI) and a dolomite (named DP), both with particle size of 545 μm. These limestones were previously tested as sorbents of SO<sub>2</sub> (Crnkovic et al, 2006). After calcination limestone CI presented 54% (wt/wt) of CaO, while limestone DP presented 31% (wt/wt) of CaO and 21% (wt/wt) of MgO. The experiments were performed on a thermogravimetric balance, and consisted of two steps. The first step was the calcination of the limestones, where the samples were submitted to a heating rate of 30°C min<sup>-1</sup> under synthetic air atmospheres, from room temperature up to the temperature desired for the sulfation to follow (750, 800, 850 and 900 °C). The system remained at this temperature for 20 minutes (establishing isothermal condition). The second step was the sulfation of the sorbets, where the reagent gas SO<sub>2</sub> (100% v/v) was injected into the furnace.

Different partial pressures of SO<sub>2</sub> were imposed by applying different flows of the reagent and the carrying gas. Table 1 presents the flows of the gases and the corresponding partial pressure for the reagent gas.

Table 1: Flows of reagent and carrier gases that were applied.

| Flow rates / mL/min <sup>-1</sup> |                                  | Partial pressure<br>SO <sub>2</sub> / atm |
|-----------------------------------|----------------------------------|---|
| Carrier gas -<br>synthetic air    | Reagent gas -<br>SO <sub>2</sub> |   |
| 60                                | 40                               | 0.400                                     |
| 65                                | 35                               | 0.350                                     |
| 70                                | 30                               | 0.300                                     |
| 75                                | 25                               | 0.250                                     |
| 80                                | 20                               | 0.200                                     |
| 85                                | 15                               | 0.150                                     |
| 90                                | 10                               | 0.100                                     |
| 95                                | 5                                | 0.050                                     |
| 96.5                              | 3.5                              | 0.035                                     |

### 2.1. Metodology

As already mentioned, the experimental data were correlated through 3 isotherm models: Langmuir, Freundlich, and Modified Langmuir. For all of the models, the maximum mass reached at equilibrium after injection of SO<sub>2</sub> was considered to be the final mass (M<sub>f</sub>) of the process. The initial mass (M<sub>i</sub>) was that immediately before the injection of SO<sub>2</sub>. Figure 1 presents the results of a typical thermogravimetric experiment, with the TG and the DTG curves for calcinations followed by sulfation, represented by loss and gain of mass respectively.

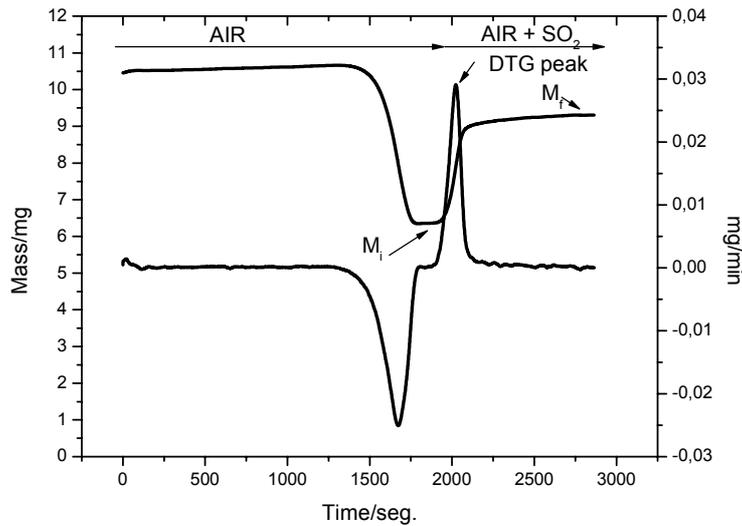


Figure 1: TG and DTG curves of calcination followed by sulfation for a typical experiment.

The normalized amount of mass gain during an sorption ( $q$ ) is usually plotted against the partial pressure of the sorbed gas for observing the behavior of the surface saturation process of the sorbent. This parameter is given by:

$$q = \frac{M_f - M_i}{M_i} \quad (2)$$

The Langmuir isotherm model, as presented in Eq. 3, is applicable to monolayer adsorption on a homogeneous adsorbent surface with negligible intermolecular force (Laidler, 1950):

$$\theta = \frac{K_L p}{1 + K_L p} \quad (3),$$

where  $\theta$  is the fraction of surface that is covered,  $p$  is the partial pressure of the reagent gas and  $K_L$  is the Langmuir equilibrium constant for the sorption process, which depends on both temperature and energy of the system. For the sorption of gases on a surface, Eq. 3 can be written as follows:

$$\theta = \frac{q}{q_{max}} = \frac{K_L p}{1 + K_L p} \quad (4),$$

where  $q$ , the amount of mass gain during sorption, is also the sorbed amount of gas.  $q_{max}$  is the sorbed amount of gas when all active sites are occupied, i.e. the maximum amount of gas that can be sorbed at pressure  $p$ . The parameter  $q_{max}$  is a constant for a sorbate-sorbent system at a given temperature and must be determined from experimental data (Riazi and Khan, 1999).

When applying Langmuir isotherm it is necessary to keep in mind that an ideal monolayer adsorption process is assumed, so that, in practice, deviations from the Langmuir equations are often observed. For multilayer sorption Freundlich isotherm can sometimes fit the empirical data, as it is generally valid in a limited range of pressure. At low pressure this isotherm equation does not show a proper Henry's law behavior and does not provide the saturation of the surface (Lu et al, 1990). Freundlich isotherm is given by Eq. 5.

$$\theta = \frac{q}{q_{max}} = K_F p^n \quad (5),$$

where  $p$  is the pressure of the sorbate,  $K_F$  is a constant related to the sorption capacity of the sorbent, and  $n$  is a constant that indicates the intensity of the sorption and is the heterogeneity factor (Mane et al., 2007)). In a linearized form, Freundlich isotherm may be expressed as

$$\ln(q) = \ln(K_F) + n \ln(p) \quad (5.1/2)$$

There is a difficulty with the Freundlich isotherm equation since a continuous increase of the adsorbate concentration may lead to a non-realistic increase of the adsorbed amounts (Adamson, 1990). The Langmuir-Freundlich isotherm was proposed to eliminate this problem. The Langmuir-Freundlich isotherm has been applied to study the adsorption on a heterogeneous surface presenting an exponential relation between sorbed amount and sorbate concentration (Selinger, 1997; Chuncai, 2000). It assumes that as the sorbate concentration increases, the concentration of sorbate on the sorbent surface also increases.

The mathematical treatment for the Langmuir-Freundlich isotherm was developed by Sips (1948). In his work, Sips derived an isotherm containing the surface heterogeneity factor ( $n$ ) (Sohn and Kim, 2005), as follows:

$$\theta = \frac{q}{q_{\max}} = \frac{(K_{LF} p)^\beta}{1 + (K_{LF} p)^\beta} \quad (6),$$

where  $q$  is the surface phase capacity (or mass gain during sorption, or sorbed amount of gas), and  $K_{LF}$  and  $\beta$  are model parameters. As described by Sips (1948),  $\beta$  is related to the adsorption energy distribution of the adsorbent and assumes values  $0 < \beta \leq 1$ . As the value of  $\beta$  decreases, the energy distribution of adsorption increases; the sorbent shows a strong heterogeneity as  $\beta$  approaches zero (Lu, 1990). When  $\beta = 1$ , the distribution function corresponds to a homogeneous adsorbent and reduces to Langmuir isotherm.

From a linear regression of  $1/q$  versus  $1/p^\beta$ ,  $K_{LF}$  and  $q_{\max}$  can be obtained from a linearized Equation (6), as follows

$$\frac{1}{q} = \frac{1}{q_{\max} (K_{LF} p)^\beta} + \frac{1}{q_{\max}} \quad (7)$$

In this model, the Langmuir constant involves the characteristic sorption energy ( $E_0$ ) (i.e.  $K_{LF} = A_0 \exp(E_0 / RT)$ ), where  $A_0$  is a pre-exponential factor. From Sips (1948) proposal, many different isotherms have been developed. Besides the above models, in the present work the Modified Langmuir model applied by Sohn and Kim (2005) is also used, which is given by

$$\theta = \frac{q}{q_{\max}} = \frac{K_{mL} p^X}{1 + K_{mL} p^X} \quad (8)$$

where  $X$  indicates the level of concentration dependence and can be associate with the physical characteristic of the sorbent. In a linearized form, Eq. (8) becomes

$$\frac{1}{q} = \frac{1}{q_{\max} K_{mL} p^X} + \frac{1}{q_{\max}} \quad (9)$$

Applying Eq. (9)  $K_{mL}$  and  $q_{\max}$  can be found from the slope and Y-axis intercept, respectively.

As described by Sohn and Kim (2005),  $X$  is a fitting parameter by which we can determine the best linear regression in a given system. The  $X$  factor represented in this model has a physical significance different from the  $n$  exponent presented in Sips model. The  $\beta$  parameter can not assume values higher than 1, while  $X$  can have any value, as it is a fitting parameter of experimental data and defines the dependency degree of partial pressure with the sorption phenomenon. As  $X$  assumes values lower than 1, the sorbent-sorbate system exhibits lower dependency on concentration and, for values higher than 1, it shows higher dependency on concentration.

### 3.RESULTS

The sorption study was conducted on a TG balance. Fig. 2 presents, for both limestones CI and DP, the values of normalized mass ( $q$ ) calculated through Eq. (2) versus partial pressure of the reagent gas ( $SO_2$ ).

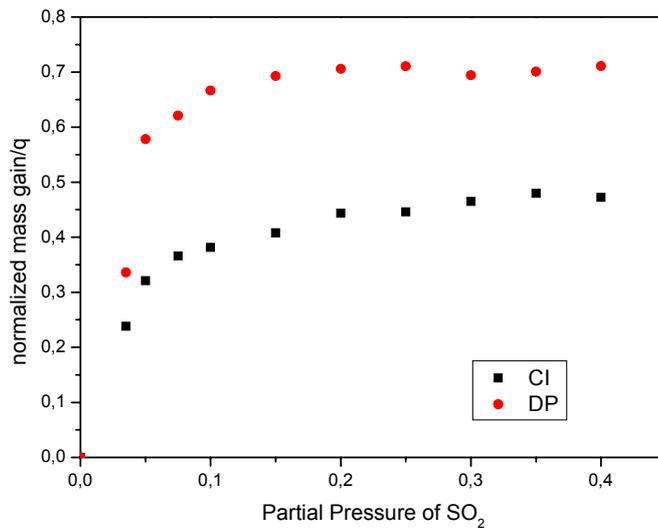
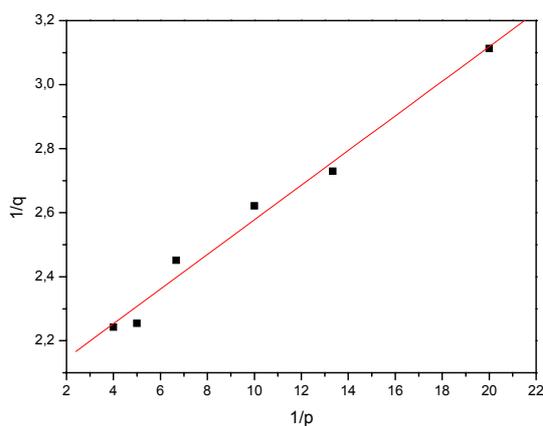


Figure 2: Normalized mass gain ( $q$ ) versus the partial pressure of the reagent gas (atm).

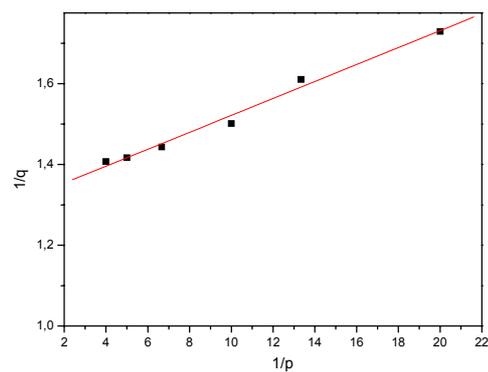
It is possible to observe that the behavior of the sulfation is different for both limestones, i.e. the sorption degree for DP is higher than that for CI. Both limestones present sorption saturation from SO<sub>2</sub> partial pressure of about 0.2, meaning that the mass gain is limited for lower pressures.

In order to perform the present analysis, three different sorption isotherm models were used, i.e. Langmuir, Freundlich and Modified Langmuir. The experimental data used in the analysis were those for SO<sub>2</sub> partial pressures between 0.05 and 0.25, since outside this range the data may be affected by measurement uncertainties due to the sensibility of the experimental technique.

Fig. 3 presents  $(1/q)$  plotted against  $(1/p)$ , and the fittings for the Langmuir model, for both the limestones CI and DP. Fig. 4 presents  $\ln(q)$  plotted against  $\ln(p)$ , and the fittings for the Freundlich model, for both the limestones CI and DP.



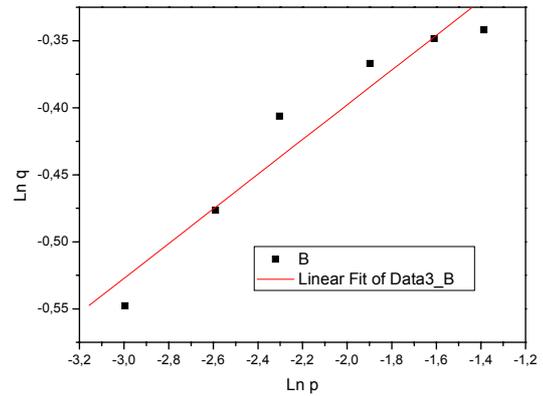
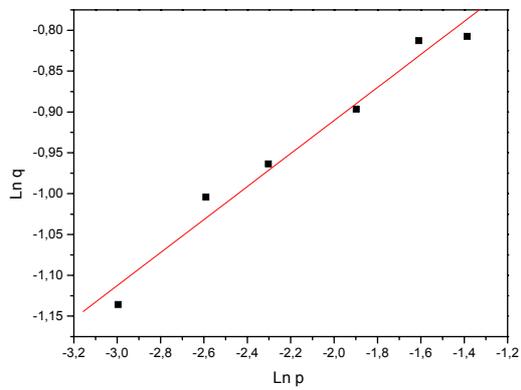
A



B

Figure 3: Fitting of the experimental data to the sorption process of SO<sub>2</sub> by limestones CI (A) and DP (B) for Langmuir model.

A



B

Figure 4: Fitting of the experimental data to the sorption process of  $\text{SO}_2$  by limestones CI (A) and DP (B) for Freundlich model..

Figures 3 and 4 show that there is a reasonable linear correlation of the experimental data with the Langmuir and the Freundlich models for both the limestones. We shall now consider the application of the Modified Langmuir model. In this model the concentration dependent factor  $X$ , which ranges between 0.2 and 2.0 must be varied in the search for the best correlation coefficient. Figures 5 and 6 show  $R^2$  versus  $X$  for the limestones CI and DP, respectively.

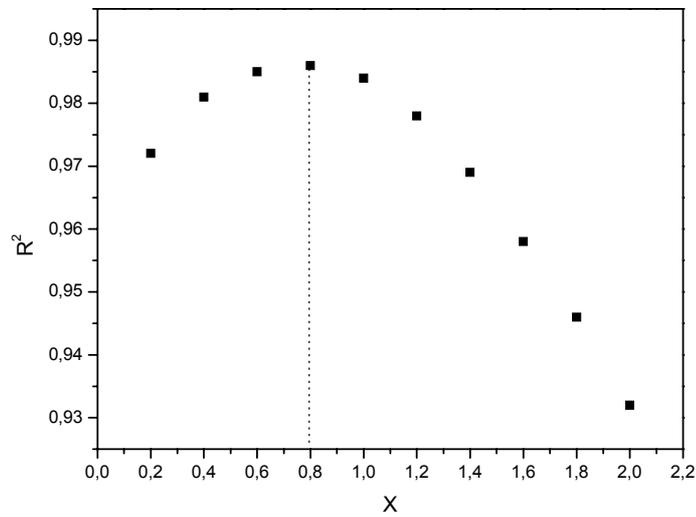


Figure 5:  $R^2$  from the least square fit versus  $X$  factor for limestone CI (applied in Eq. 9)

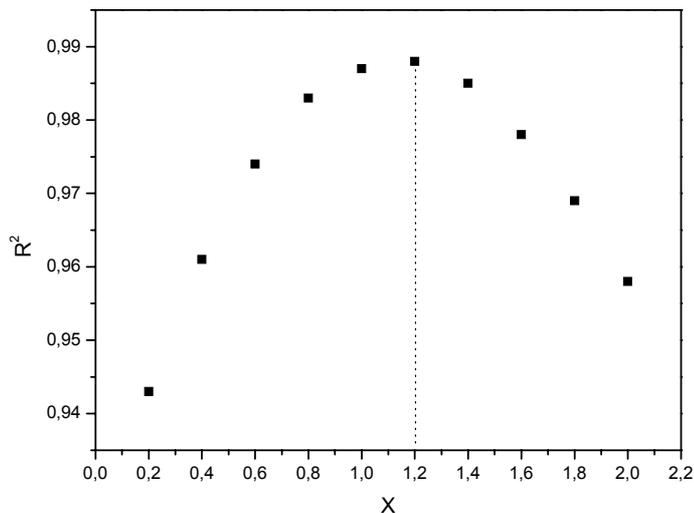


Figure 6:  $R^2$  from the least square fit versus  $X$  factor for limestone DP (applied in Eq.9)

The maximum value of  $R^2$  was obtained at  $X = 0.8$  for limestone CI and  $1.2$  for limestone DP. These values are used in Eq. (9), which corresponds to the Modified Langmuir model, to fit the experimental data and then to obtain the angular and linear coefficients for each limestone. This is done in Figure 7. The  $X$  values came from linear fitting and is suggests that this parameter can be used as an indicator of  $SO_2$  sorption in different systems.

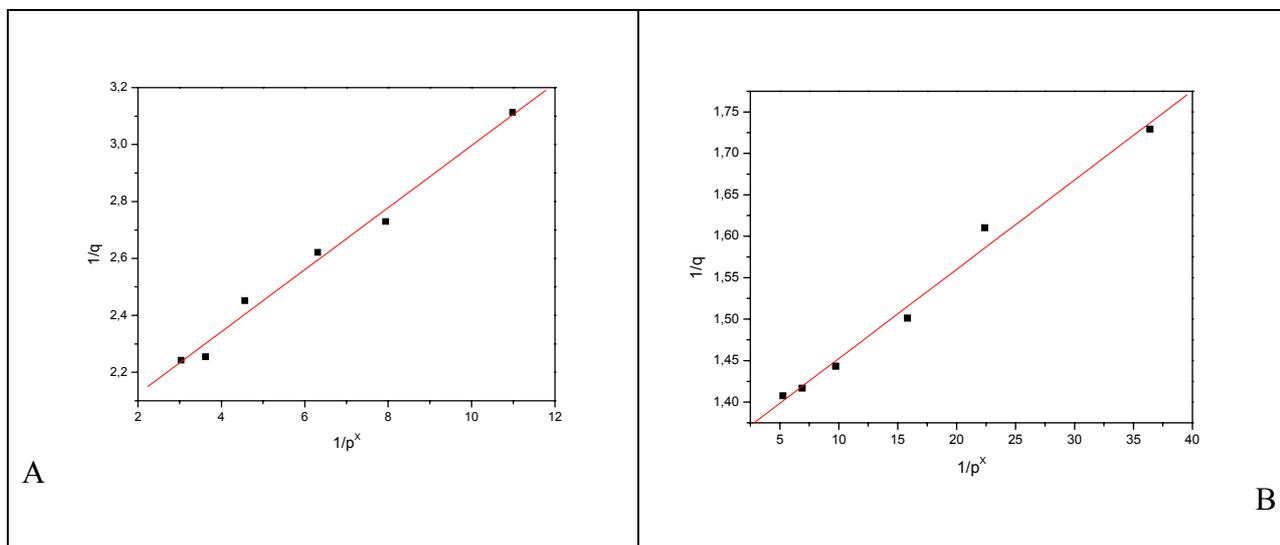


Figure 7: The fitting of experimental data of sorption process of  $SO_2$  by limestones CI (A) and DP (B) applying Modified Langmuir isotherm. Values of  $X = 0.8$  for CI and  $X = 1.2$  for DP were used.

Table 2 presents the results obtained from each kinetics model. From the equilibrium constants, the Gibbs free energy of formation ( $\Delta G^0$ ) were determined and are also shown in Tab. 2. The Gibbs free energy of formation of the sorption process is related to the equilibrium constant through Van't Hoff's equation (Eq. 11) and it is a thermodynamic parameter that indicates the availability and spontaneity of a process.

$$\Delta G^0 = -RT \ln K \quad (11)$$

Table 2: Kinetics parameters and Gibbs free energy of formation obtained from the sorption isotherms of the gas-solid process (SO<sub>2</sub>-CaO) for both the limestones CI and DP.

| Langmuir isotherm          | q <sub>max</sub> | K <sub>L</sub>  | R <sup>2</sup> | ΔG <sup>0</sup> (kJ mol <sup>-1</sup> ) |
|----------------------------|------------------|-----------------|----------------|---|
| CI                         | 0,49             | 37,703          | 0,984          | -33,90                                  |
| DP                         | 0,76             | 62,42           | 0,987          | -38,60                                  |
| Freudlich isotherm         | n                | K <sub>F</sub>  | R <sup>2</sup> |   |
| CI                         | 0,20             | 0,6029          | 0,972          |   |
| DP                         | 0,13             | 0,871           | 0,987          |   |
| Modified Langmuir isotherm | q <sub>max</sub> | K <sub>mL</sub> | R <sup>2</sup> | ΔG                                      |
| CI                         | 0,47             | 19,5            | 0,986          | -27,74                                  |
| DP                         | 0,74             | 134,4           | 0,988          | -45,76                                  |

Equilibrium constants and ΔG<sup>0</sup> were determined for the applied range of SO<sub>2</sub> partial pressures, between 0.05 and 0.25. Since the Langmuir constant is a equilibrium constant (Laidler, 1950), the Van 't Hoff equation can be obtained to describe the relation between the equilibrium constants (K<sub>L</sub> and K<sub>mL</sub>) and the Gibbs Free Energy.

Langmuir and Modified Langmuir isotherms produced negative values of ΔG<sup>0</sup>, indicating the spontaneous nature of the sorption process.

On the other hand, K<sub>F</sub> and n indicate the sorption capacity and sorption intensity respectively. Values of n less than 1 show the favorable nature of sorption. In our study, n is less than 1 for both limestones

Figures 7 and 8 show the plots of the sorption isotherms, q versus p for the sorption process for the limestones CI and DP, respectively. The experimental data are fitted in all of the models with non-linear correlation coefficients greater than 0.984. For limestone CI the Langmuir and the Freundlich isotherms provide the best fits, while for limestone DP the best fits are provided by the Langmuir and the Modified Langmuir isotherms.

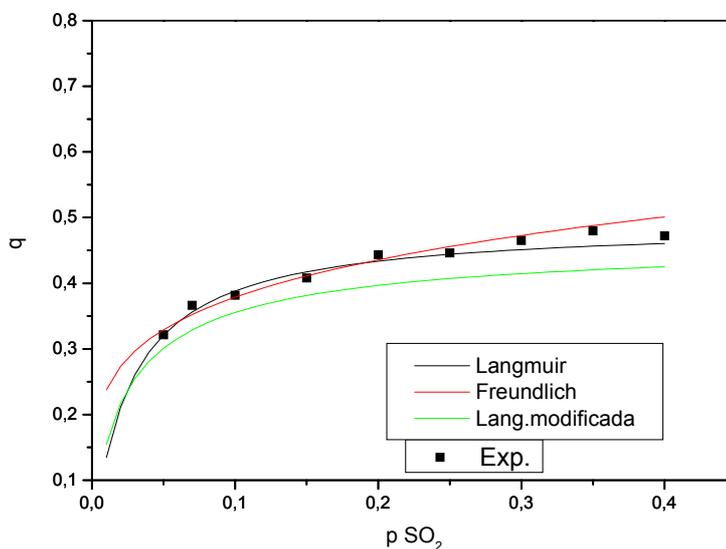


Figure 7: Isotherm plots for the SO<sub>2</sub>-CaO (CI) process.

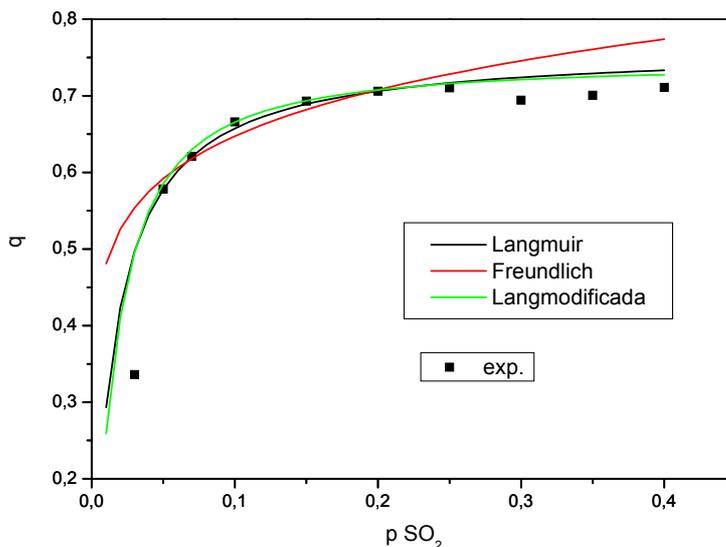


Figure 8: Isotherm plots for the SO<sub>2</sub>-CaO (DP) process.

#### 4. CONCLUSION

The sorption isotherm is the equilibrium relationship between the concentration in the gas phase ( $p$ ) and that in the sorbent particles ( $q_e$ ) at a given temperature and can provide information on the sorption strength and capacity.

The present study showed quantitatively that different limestones present different SO<sub>2</sub> sorption behavior. Both parameters equilibrium constant and Gibbs free energy of formation were determined through fitting experimental data to linearized models.

Langmuir and modified Langmuir models provided negative values of  $\Delta G^0$ , which is an indication of a spontaneous process and it is consistent with the favorable nature of the sorption process between SO<sub>2</sub> and CaO at the applied operating conditions.

These results can be explained based on the fact that Langmuir and Modified Langmuir consider that the surface of the sorbent is homogeneous and the Freundlich isotherm assumes that, as the concentration of sorbate increases, the concentration of sorbate at the surface of adsorbent also increases. From these considerations,  $K_L$  and  $K_{mL}$  were used to calculate  $\Delta G$  with Van't Hoff equation and Freundlich Model was used to determine the  $1/n$  values to elucidate about the favorable type sorption.

As previously described by other authors, the blockage of external layers of sorbent by product - CaSO<sub>4</sub> - prevents the contact of the reagent gas with the internal layers, and even increasing the partial pressure of SO<sub>2</sub>, the surface becomes saturated and then it doesn't increase the quantity of active sites.

Comparing the results obtained from Langmuir and Modified Langmuir, the reaction presents more favorable for DP limestone than CI, i.e., in both models the  $\Delta G^0$  values are more negative for DP. Related to the fitting ( $R^2$ ) the Modified Langmuir model resulted similar than the Langmuir isotherm.

Comparing the  $X$  factor of the Eq. (8) with the  $n$  factor from Sips' Equation, it should be noted that the mathematical treatment for both equations are different. The  $X$  factor considers the dependence of the partial pressure of the reagent in the sorption process, while the  $n$  factor is related to the heterogeneity of sorbent surface. Therefore, the best fit value of  $X$  which resulted 0.8 for the limestone CI means that its behavior is more independent of the reagent concentration when compared with the limestone DP, for which the best fit value of  $X$  was 1.2. This finding leads to understand that limestone DP may have more active sites available than CI during the process of the sulfation.

The performance of different limestones for sulfur capture was evaluated by considering different sorption isotherms, in an attempt to contribute to the knowledge required for minimizing SO<sub>2</sub> emissions of gas effluents and optimize of the use of raw materials.

#### 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

- Adamson, A.W. *Physical Chemistry of Surfaces*, Wiley, New York, 1990.
- Borgwardt, R. H.; Harvey, R.D. Properties of carbonate rocks to SO<sub>2</sub> reactivity. *Environ Sci. Tech*, 6, (1972) 350-360
- Chen, C.; Zhao, C.; Liang, C.; Pang, K. Calcination and sintering characteristics of limestone under O<sub>2</sub>/CO<sub>2</sub> combustion atmosphere. *Fuel Processing Technology*, 88, 171-178 (2007).
- Cheng, L.; Chen, Bo; Liu, Ni; Luo, Z; Cen, K. Effect of characteristic of sorbents on their sulfur capture capability at a fluidized bed condition. *Fuel*, 83, (2004), 925-932.
- Criado, J. M.; Gonzalez, M.; Malek J.; Ortega, A. The effect of the CO<sub>2</sub> pressure on the thermal decomposition kinetics of calcium carbonate. *Thermoc. Acta*, 254, (1995), 121-127.
- Crnkovic, P.M.; Milioli, F. E.; Pagliuso, J. D. Kinetics study of the SO<sub>2</sub> sorption by Brazilian dolomite using thermogravimetry. *Thermoc. Acta*, 447 (2006) 161-166.
- Fuertes, A. B.; Velasco. G.; Fernandez M. J.; Alvarez, T. Analysis of the direct sulfation of calcium carbonate. *Thermoc. Acta*, 242, (1994) 161-172.
- Gregg, S. J.; Sing, K. S. *Adsorption, surface Area and Porosity*, Academic Press, 1982, 303p.
- Jaroniec, M. Physical adsorption on heteroneous solids. *Adv. Colloid Interface Sci*, 18, (1983), 149-225.
- Laidler, K. *Chemical Kinetics*, 1950, 531 p.
- Mane, V. S.; Mall, I. D.; Srivastava, V. C. Kinetics and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by Rice husk ash. *Journal of Environmental Management*, 84 (2007) 390-400.
- Riazi, M.; Khan, A. A Thermodynamic model for gas adsorption isotherms. *Journal of Colloid and Interface Science*, 210 (1999), 309-319.

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