

## Influence of SO<sub>2</sub> on CO<sub>2</sub> capture using 13X zeolite

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### Abstract

Combustion gases, mainly from the burning of fossil fuels, are composed of a complex mixture of atmospheric pollutants, with carbon dioxide (CO<sub>2</sub>) as one of the main ones. Technologies such as adsorption are promising for capturing this pollutant, but the presence of contaminants such as sulfur dioxide (SO<sub>2</sub>) may negatively interfere with this process, requiring a detailed understanding of their impacts on the efficiency of CO<sub>2</sub> capture systems. This study investigated the effects of SO<sub>2</sub> on the CO<sub>2</sub> retention capacity of an adsorbent, using 13X zeolite in conditions like those of post-combustion. The results showed that the 13X zeolite sample has higher affinity for adsorbing SO<sub>2</sub> compared to CO<sub>2</sub> under all tested pressure and temperature conditions. While both gases may be captured and fully regenerated using appropriate methods, the impact of SO<sub>2</sub> on the textural properties of the zeolite suggests the need for a pre-treatment step to remove SO<sub>2</sub> from the gas stream. These findings indicate that it is feasible to capture and remove both CO<sub>2</sub> and SO<sub>2</sub> using a single unit, which simplifies industrial emission control processes and enhances CO<sub>2</sub> capture efficiency. The high selectivity and regeneration capacity of 13X zeolite underscore its effectiveness as an adsorbent in combustion gas capture systems, significantly contributing to the mitigation of environmental impacts caused by CO<sub>2</sub> emissions.

*Keywords: Carbon dioxide; Sulfur dioxide; Adsorption; 13X Zeolite.*

### 1. Introduction

The 20<sup>th</sup> century witnessed a sharp increase in global temperatures, mainly attributed to the greenhouse effect intensified by human activities, such as the burning of fossil fuels and deforestation. This phenomenon, known as anthropogenic global warming, has raised temperatures by 0.8 °C since 1900, with projections of an increase of between 1.4 °C and 5.8 °C by the end of the 21st century, mainly due to increased concentrations of carbon dioxide (CO<sub>2</sub>) in the atmosphere [1].

To mitigate these impacts, technologies such as Carbon Capture and Storage (CCS) have been developed to capture and store CO<sub>2</sub>, involving methods such as absorption, separation membranes, cryogenic distillation and adsorption [2]. Adsorption stands out for its low energy cost, capture efficiency and operational flexibility [3].

Power plant combustion gases have typical composition ranging from 72-74% N<sub>2</sub>, 4.8-26.9% CO<sub>2</sub>, 9-13.8% H<sub>2</sub>O, 0.7-15% O<sub>2</sub>, in addition to impurities as material particulates and sulfur and nitrogen oxides. The presence of these components may reduce the efficiency of the CO<sub>2</sub> capture processes [4,5].

Although sulfur dioxide (SO<sub>2</sub>) is present in low concentrations (between 500 and 5000 ppm), it may

interfere with the CO<sub>2</sub> capture, competing for adsorption sites on the adsorbent and reducing its adsorption capacity [6].

This study aims to evaluate the effects of the presence of SO<sub>2</sub> in gaseous flows on the performance of CO<sub>2</sub> adsorbents, using 13X zeolite as an adsorbent in conditions like those found in the post-combustion scenario. As pointed out by Li et al. [7], this zeolite is commonly used to separate CO<sub>2</sub> from combustion gases and is considered a reference material for this application.

### 2. Materials and Methodology

#### 2.1 Adsorbates

The gases used for the adsorption measurements (see Table 1) were supplied by White Martins Praxair, Inc. (São Paulo, Brazil).

Table 01 – Gases used as adsorbates.

Gases	Degree of purity	Purity (%)
Helium	5.0	99.999
Carbon dioxide	2.8	99.800
Nitrogen	5.0	99.999
Sulfur Dioxide	(4500 ppm in He)	

## 2.2 Adsorbent

The present work was conducted using 13X Zeolite Pellets supplied by Shanghai Hengye Chemical Industry Co. (Shanghai, China) as adsorbent.

## 2.3 Methodology

### 2.3.1 Adsorption Experimental Apparatus - Magnetic Suspension Balance

The adsorption isotherms of pure CO<sub>2</sub> and SO<sub>2</sub> were obtained through gravimetric measurements with a magnetic suspension balance equipped with a gas dosing unit (Rubotherm, Germany). The system includes a measuring cell coupled to the scale, pressure and temperature indicators, temperature control, vacuum pump and data acquisition system, described in Rios [8].

The measurement uses a magnetic suspension coupling with two electromagnets, detecting the mass variation during adsorption and transmitting the data to the balance. Measurements have a resolution of 0.01 mg, withstanding pressures of up to 150 bar and temperatures of up to 300 °C.

The equilibrium isotherms for CO<sub>2</sub> and SO<sub>2</sub> were obtained at 50, 70, 90, 150 and 200 °C, according to the methodology of Dreisbach *et al.* [9].

The excess amount of adsorbed gas was calculated using Equation 1.

$$m_{exc}(p, T) = \Delta m_{ads}(p, T) - (V_s + V_{sc})\rho(p, T) \quad (1)$$

where  $m_{exc}$  [g] denotes the excess adsorbed mass,  $V_s$  [cm<sup>3</sup>] represents the specific solid volume of adsorbent,  $V_{sc}$  [cm<sup>3</sup>] is the volume of suspended components,  $\rho$  [g cm<sup>-3</sup>] denotes the density of the surrounding gas,  $p$  [bar] is the total pressure and  $T$  [K] is the temperature,  $\Delta m_{ads}$  [g] indicates the mass difference between the mass at each pressure and the mass under vacuum (after regeneration).

### 2.3.2 Textural Characterization

The 13X zeolite sample was characterized using N<sub>2</sub> adsorption-desorption isotherms at 77 K with an Autosorb-iQ3 (Quantachrome Instruments, USA). The measured isotherms were used to evaluate the adsorbent textural properties, including specific surface area, total pore volume, micropore volume, and Pore Size Distribution (PSD). The specific surface area was estimated using the Brunauer-Emmett-Teller

(BET) equation (pressure range:  $10^{-6} < P/P_0 < 10^{-2}$ ;  $R^2 = 1$ ) [10], while the total pore volume was estimated at  $P/P_0 \approx 0.95$ . The micropore volume was calculated using the Dubinin-Radushkevich (DR) equation [11].

## 3. Results and discussion

### 3.1 Textural properties

Characterizing the adsorbent is crucial to initially assess its suitability for CO<sub>2</sub> adsorption in different scenarios. Furthermore, this characterization provides essential data for determining key parameters that are relevant for dynamic simulations and their application in large-scale processes. The adsorption/desorption isotherms of N<sub>2</sub> at 77 K are shown in Figure 1. The main textural properties of the 13X sample, estimated from the N<sub>2</sub> isotherms following the methodology proposed by BET [12], are presented in Table 2.

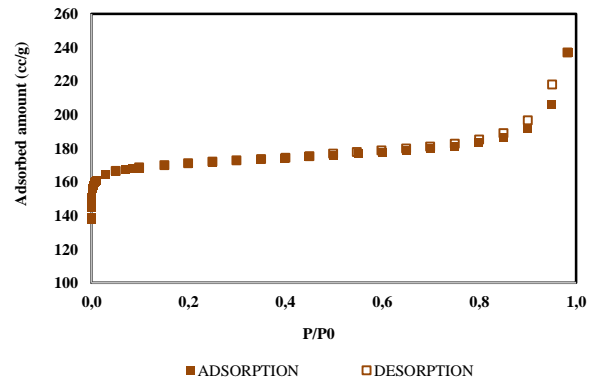


Figure 01 – Nitrogen adsorption/desorption isotherms at 77 K for the 13X zeolite sample.

Table 02 – Textural properties of the 13X zeolite sample.

Parameter	Equation	Value
Specific Surface Area (m <sup>2</sup> /g)	$S_{BET} = \sigma * nm * L$	703
Total Pore Volume (cm <sup>3</sup> /g)	$V_p = n_{as} \left( \frac{P}{P_0 = 0,95} \right) * \frac{M_{N_2}}{\rho_{N_2(l)}}$	0.34
Micropore Volume (cm <sup>3</sup> /g)	$V_{mic} = n_{p_{mic}} * \frac{M_{N_2}}{\rho_{N_2(l)}}$	0.26

Based on the N<sub>2</sub> adsorption data at 77 K and a blank run using helium at room temperature, several parameters may be estimated, including particle density, porosity, and solid density, needed for process

simulations, as shown in Table 03.

Table 03 – Adsorbent particle properties

Parameter	Equation	Value
Specific volume of solid ( $\text{cm}^3 \text{g}^{-1}$ )	-	0.41
Solid density ( $\text{kg m}^{-3}$ )	$\rho_s = 1/V_{\text{sol}}$	2450
Particle density ( $\text{kg m}^{-3}$ )	$\rho_p = 1/(V_{\text{sol}} + V_{\text{pore}})$	1594
Particle porosity	$\varepsilon_p = V_{\text{pore}}/(V_{\text{sol}} + V_{\text{pore}})$	0.35

### 3.2 Adsorption equilibrium measurements of pure $\text{CO}_2$ and $\text{SO}_2$

The adsorption isotherms of pure  $\text{CO}_2$  and  $\text{SO}_2$  at 50, 70, 90, 150 and 200 °C for the 13X zeolite sample, are presented in Figures 02 and 03, respectively. The behavior of the isotherms indicates that the predominant adsorption mechanism, for both  $\text{CO}_2$  and  $\text{SO}_2$ , is physical adsorption, since it can be observed that increasing temperatures decrease the adsorbed phase concentration of both gases. This is due to the fact that, with an increase in temperature, the molecules present in the adsorbed phase acquire enough energy to overcome the existing van der Waals adsorption forces, causing these molecules to return to the fluid phase [13,14].

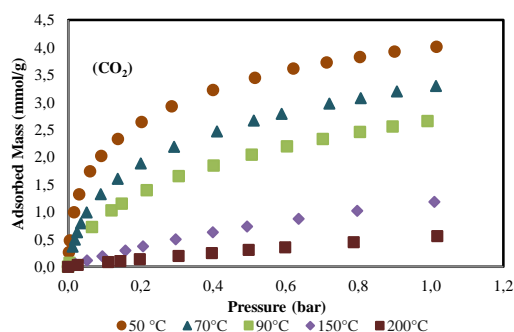


Figure 02 – Pure  $\text{CO}_2$  adsorption isotherms for the 13X zeolite sample.

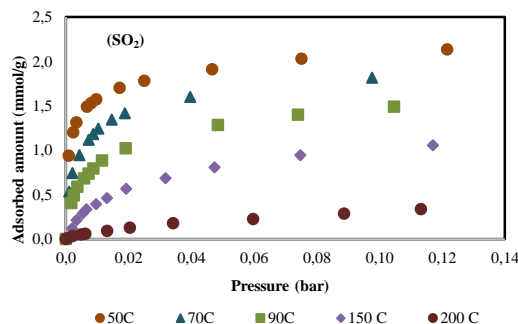


Figure 03 – Pure  $\text{SO}_2$  adsorption isotherms for the 13X zeolite sample.

It may be possible that the adsorption of  $\text{SO}_2$  may impact the simultaneous adsorption of  $\text{CO}_2$ , when in post-combustion gases processes [15]. To evaluate this effect, a second textural characterization with  $\text{N}_2$  at 77 K was performed on the 13X zeolite sample after contact with  $\text{SO}_2$  (see Figure 4).

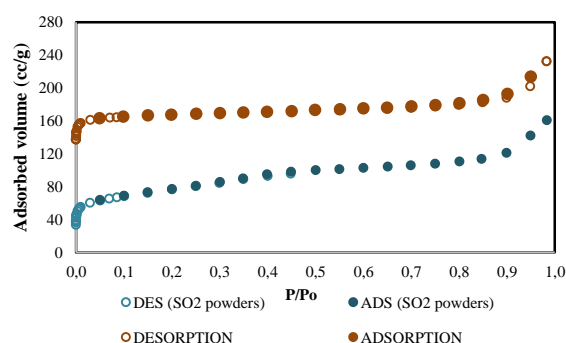


Figure 04 –  $\text{N}_2$  adsorption-desorption isotherms at  $-196^\circ\text{C}$  for 13X zeolite before (orange) and after contact with  $\text{SO}_2$  (blue). Empty symbols for desorption data.

From Figure 4, it may be noted a steep decrease of adsorbed amounts of  $\text{N}_2$  at the same pressures when compared to the original sample. This is also confirmed by the calculated data shown in Table 4. Although the used sample had been submitted to regeneration, its porous structure seems to have been affected, leading to reductions in specific surface area and pore volumes. This deterioration suggests the need for careful consideration of  $\text{SO}_2$  impacts when using 13X zeolite for  $\text{CO}_2$  capture. Remarkably the shape of the  $\text{N}_2$  isotherm at 77 K was similar to the original sample (type I isotherms according to the IUPAC classification, typical of microporous materials [12]).

Table 04 – Textural properties of the sample before and after contact with  $\text{SO}_2$ .

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	V <sub>mp</sub> (cm <sup>3</sup> /g)
Fresh	703	0.34	0.26
Spent	248	0.22	0.10

#### 4. Conclusions

The 13X zeolite sample showed high affinity for both CO<sub>2</sub> and SO<sub>2</sub>, with similar adsorption capacities if compared under the same conditions of P and T. It was also observed that contact with SO<sub>2</sub>, even at low partial pressures, seems to lead to a decrease in the textural properties of the 13X zeolite sample, which shall probably translate into a loss in CO<sub>2</sub> adsorption capacity. This decrease in textural properties may be due to chemical adsorption. It may be implied that this effect may cause successive loss of adsorption capacity of the adsorbent when used in several adsorption/desorption cycles. This may lead to the need of an additional SO<sub>2</sub> pre-treatment step in the CO<sub>2</sub> capture process to remove SO<sub>2</sub>.

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