

# THEORETICAL STUDY OF CO<sub>2</sub>:N<sub>2</sub> ADSORPTION IN FAUJASITE IMPREGNATED WITH MONOETHANOLAMINE

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**Abstract** - Many efforts have been made to develop amine-based solid adsorbents for capture of CO<sub>2</sub> by adsorption. Compared with the traditional process of absorption in aqueous solutions of amines, the adsorbents with amine immobilized in solids generally result in processes with lower capital and energy costs. The literature contains some experimental studies of CO<sub>2</sub> adsorption in impregnated materials; however, few studies are devoted to the theoretical interpretation of this system in terms of CO<sub>2</sub> capture for post-combustion (N<sub>2</sub> mixture with a low partial pressure of CO<sub>2</sub>). Therefore, this study investigates the adsorption of a CO<sub>2</sub>:N<sub>2</sub> mixture on zeolite NaX impregnated with monoethanolamine (MEA), using molecular simulation. A model of NaX impregnated with MEA was proposed and the adsorption of a 15:85 (CO<sub>2</sub>:N<sub>2</sub>) mixture was investigated based on the Monte Carlo method. The simulation of the MEA impregnated zeolite at 25 °C predicted higher CO<sub>2</sub> selectivity and significant improvement in the heat of adsorption. Unfortunately, the adsorption heat improvement did not translate into corresponding increases in the amount of adsorbed CO<sub>2</sub>. Moreover, MEA concentrations higher than 12 wt% hindered the adsorption of CO<sub>2</sub> molecules. An explanation for the results in terms of occupied volumes and interaction energies is presented.

**Keywords:** Molecular simulation; CO<sub>2</sub> adsorption; Faujasite; Monoethanolamine.

## INTRODUCTION

Among the greenhouse gases, CO<sub>2</sub> emission can contribute significantly to global warming. CO<sub>2</sub> is currently the focus of several studies, where goals are directed towards enhancement of efficient processes for their capture. CO<sub>2</sub> absorption using amines is a mature technology and has proven efficient for CO<sub>2</sub> capture (Rochelle, 2009), despite being limited by high cost and technical problems such as a high equipment corrosion rate (Knudsen *et al.*, 2009). Thus, many capture processes have been studied; among these, adsorption is a very promising technology (Samantha *et al.*, 2012). In a post-combustion sce-

nario, the technological challenge is to capture CO<sub>2</sub> at low pressure in flue gas (< 1 atm) and rich exhaust streams in N<sub>2</sub> (~ 85%). For this purpose, NaX zeolite is one of the best adsorbing material in the literature. However, it has poor performance for CO<sub>2</sub> capture via adsorption at higher temperatures, since the effect of physisorption is predominant. Recent studies have focused on chemical modifications of faujasites with the immobilization of amino groups to enhance adsorption capacity, especially at elevated temperatures (Sayari *et al.*, 2011). This approach attempts to optimize the experimental conditions for impregnation in order to achieve higher levels of adsorption of CO<sub>2</sub> and CO<sub>2</sub>:N<sub>2</sub> selectivity. Thus, the aim of this

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study is to perform a theoretical study of selective adsorption of CO<sub>2</sub> on plain NaX sieve and NaX impregnated with monoethanolamine (MEA) in operating conditions of pressure and concentrations similar to the post-combustion operation.

## METHODOLOGY

### Intermolecular Interactions

The interactions between the adsorbate molecules and the adsorbent (solid-fluid) and between molecules of adsorbate (fluid-fluid) were modeled with a Lennard-Jones 12-6 potential (LJ), which takes into account geometric ( $\sigma_{ij}$ ) and energy ( $\epsilon_{ij}$ ) parameters. The contributions of electrostatic interactions are also accounted for in the calculation of the total energy of the system ( $U_{ij}$ ), as shown in Equation (1).

$$U_{ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \left( \frac{q_i q_j}{r_{ij}} \right) \quad (1)$$

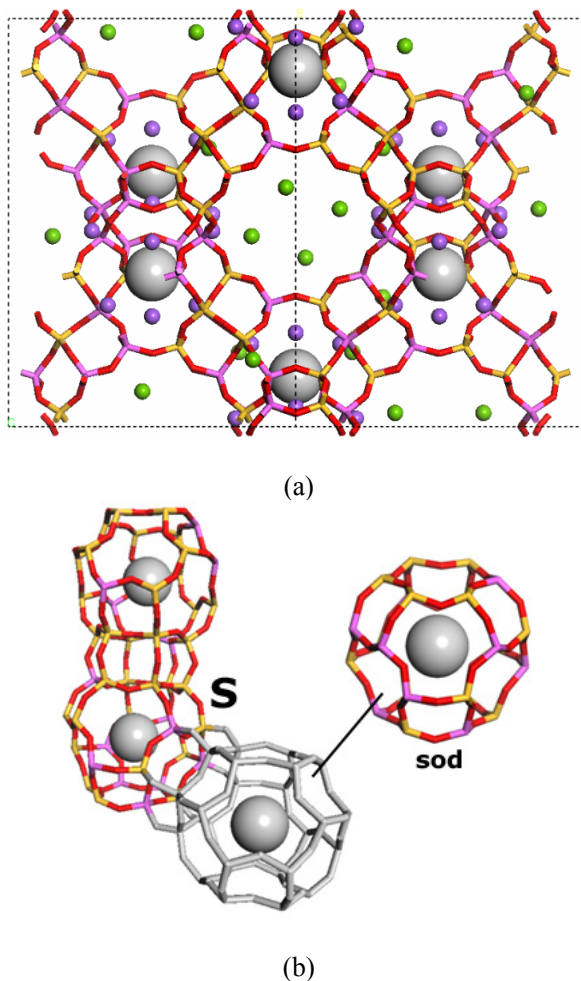
where  $r_{ij}$  is the distance between two interacting species and  $q$  the partial charge of the atoms. The Lorentz-Berthelot simple mixing rules were used to calculate the interspecies parameters.

### Faujasite

The NaX model was based on the crystallographic data reported by Zhu and Seff (1999). NaX crystallizes in the cubic space group Fd3m with a cell size parameter of 25.077 Å. The zeolite framework was built avoiding Al-O-Al connections in accordance with Lowenstein's rule. The positioning of the compensating Na<sup>+</sup> cations was randomly distributed (32 in site I', 32 in site II and 28 in site III). Then, six cations were removed at random from site III to give a Si/Al ratio = 1.23. As done previously (Maurin *et al.*, 2005; Watanabe *et al.*, 1995; Garcia-Sanchez *et al.*, 2009), the sodalite volume was blocked with large "dummy" atoms, preventing the adsorption in this region. The gas molecules adsorb only in the supercages that have a 12-ring window access with 7.4 Å of aperture. The sodalite unit can only be accessed by 6-rings windows of about 2.53 Å of diameter, which restricts the access of the gas molecules (Baerlocher *et al.* 2007). The NaX unit cell detailing cation positioning, supercage and sodalite cages is shown in Figure 1.

The distribution of partial charges was obtained by the electronegativity equalization method (Rappe

and Goddard, 1991). The simulation parameters were extracted from the Universal Force Field (Rappe *et al.*, 1992) and other parameters were adjusted empirically to best represent the experimental data. The parameters are shown in Table 1.



**Figure 1:** (a) NaX unit cell. (b) Hexagonal prism detailing supercage (S) and the sodalite cavity (sod). Atoms: Si - yellow, Al - pink, O - red. Cations colors: SI' and SII - Purple, SIII - Green. Big gray spheres - dummy atom.

**Table 1:** Force field parameters for the NaX zeolite.

Atom	$\sigma_{ss}$ (Å)	$\epsilon_{ss}$ (kcal/mol)	q (e)
Si	3.827 <sup>a</sup>	0.092 <sup>b</sup> (CO <sub>2</sub> ) 0.170 <sup>b</sup> (N <sub>2</sub> )	+1.208
Al	4.008 <sup>a</sup>	0.111 <sup>b</sup> (CO <sub>2</sub> ) 0.215 <sup>b</sup> (N <sub>2</sub> )	+1.200
O	3.118 <sup>a</sup>	0.070 <sup>b</sup>	-0.765
Na (site I', II)	2.658 <sup>a</sup>	0.030 <sup>a</sup>	+0.768
Na (site III)	2.658 <sup>a</sup>	0.030 <sup>a</sup>	+0.610

a- Universal Force Field; b - This study.

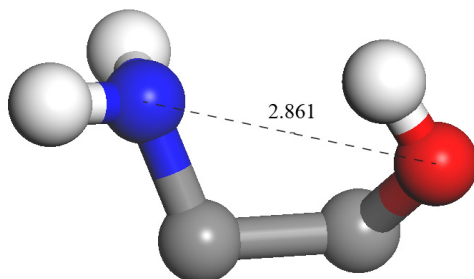
## Monoethanolamine

The model for MEA follows the molecular geometry and charges proposed by Alejandro *et al.* (2000) with bond lengths and angles similar to experimental spectroscopic measurements. The force field developed by Button *et al.* (1996) was used (Table 2) to compute LJ parameters. To reduce the time for equilibrium calculations, the central hydrogen atoms were grouped together at the center of mass of the carbon atoms (CH<sub>2</sub>-CH<sub>2</sub>) as shown in Figure 2.

**Table 2: MEA force field parameters.**

Site	$\sigma_{ff}$ (Å)	$\epsilon_{ff}$ (kcal/mol)	q (e)
HN	-	-	+0.347 <sup>b</sup>
N	3.250 <sup>a</sup>	0.169 <sup>a</sup>	-0.938 <sup>b</sup>
CH <sub>2</sub>	3.905 <sup>a</sup>	0.118 <sup>a</sup>	+0.257 <sup>b</sup>
O <sub>MEA</sub>	3.070 <sup>a</sup>	0.169 <sup>a</sup>	-0.644 <sup>b</sup>
HO	-	-	+0.374 <sup>b</sup>

a - Button *et al.* (1996); b - Alejandro *et al.* (2000).

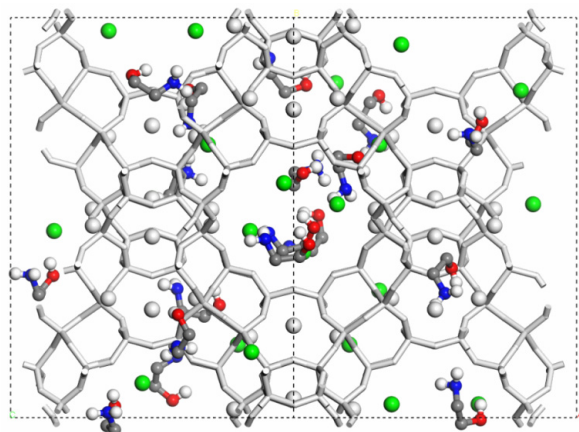


**Figure 2:** MEA molecule (H - white, N - blue, O - red, pseudo atom CH<sub>2</sub> - gray).

## Impregnation Model

The simulation cell of faujasite was impregnated with MEA at 0.05 kPa, and a temperature of 25 °C (conditions near the saturation pressure of MEA) so we could determine the zeolite maximum adsorption capacity of MEA. These calculations were performed in the grand canonical ensemble with the Monte Carlo method. Near saturation, NaX can accommodate a maximum of 60 molecules inside the pores. To obtain the other impregnation models, MEA molecules were randomly removed to match with impregnated values of the experimental studies that use different impregnation concentrations. During the adsorption of CO<sub>2</sub> and N<sub>2</sub>, the MEA molecules are considered to be fixed in their equilibrium position. Our model is an attempt to get first insight into a viable MEA impregnation model. A unit cell of NaX

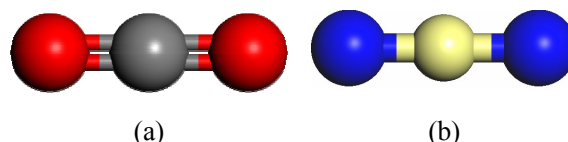
loaded with 18 molecules of MEA is shown in Figure 3.



**Figure 3:** Unit cell of an impregnation model of NaX with 18 molecules of MEA. Atoms: N - blue, H - white, CH<sub>2</sub> - gray, O - red. Cation color: SI' and SII - white, SIII - green.

## Gas Molecules (CO<sub>2</sub> and N<sub>2</sub>)

Carbon dioxide was represented by the EPM2 atom-atom model proposed by Harris and Yung (1995) with bond distance (C-O) of 1.149 Å. For N<sub>2</sub>, we used the model proposed by Murth *et al.* (1980), where the bond length (N-N) is 1.094 Å and the quadrupole moment was modeled by a three-point charge (q). In Figure 4, a representation of the gas adsorbate molecules can be seen, and in Table 3, the LJ parameters.



**Figure 4:** Molecular models of a) CO<sub>2</sub> and b) N<sub>2</sub>. (O - red; C - gray; N - blue; Dummy atom yellow).

**Table 3: CO<sub>2</sub> and N<sub>2</sub> force field parameters.**

Atom	$\sigma_{ff}$ (Å)	$\epsilon_{ff}$ (kcal/mol)	q (e)
C	2.757 <sup>a</sup>	0.055 <sup>a</sup>	+0.6512 <sup>a</sup>
O	3.033 <sup>a</sup>	0.159 <sup>a</sup>	-0.3256 <sup>a</sup>
N	3.320 <sup>b</sup>	0.072 <sup>b</sup>	-0.4050 <sup>a</sup>
Dummy	-	-	+0.8100 <sup>a</sup>

a - Harris e Yung (1995); b - Murth *et al.* (1980).

## Simulation Details

Monte Carlo simulations were performed in the grand canonical ensemble (GCMC) using the Monte Carlo method. Apart from the classical Monte Carlo

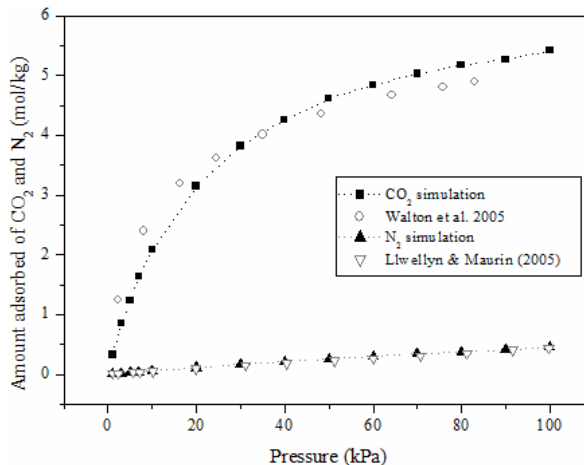
moves (rotation, translation, creation and destruction) an additional movement was implemented for mixtures. It was based on the change of identities between CO<sub>2</sub> and N<sub>2</sub> molecules. The simulation output is the absolute adsorbed quantity, which we used to chart the isotherms. All simulations were performed at 25 °C, with 2x10<sup>6</sup> equilibrium and 2x10<sup>6</sup> production steps. The Ewald Sum method was used to calculate the electrostatic contributions. The Lennard-Jones cutoff distance was 12.5 Å without long range corrections. A low cut of 0.4 Å and precision of 0.001 kcal/mol was applied. As done previously (Watanabe *et al.*, 1995; Maurin *et al.*, 2005; Pillai *et al.*, 2012), one symmetric faujasite unit cell was used as the simulation cell with periodic boundary conditions in all directions.

## RESULTS AND DISCUSSION

### Force Field Validation

The validation of the force field for the system zeolite/gases was first performed by comparing the computed monocomponent adsorption isotherm for CO<sub>2</sub> and N<sub>2</sub> and the experimental data reported by Walton *et al.* (2005) and Maurin *et al.* (2005) on NaX crystals, respectively (Figure 5). The simulated nitrogen isotherm presented a better fit than carbon dioxide. However, our fit between CO<sub>2</sub> experimental and simulated isotherms was improved if compared with other CO<sub>2</sub> simulated data on NaX (Maurin *et al.*, 2005; García-Sánchez *et al.*, 2009). Some factors that contribute to inaccuracies between simulated and experimental isotherms are: 1- experimental uncertainty regarding the cation positioning (particularly site III') and 2- the fact that simulations were performed considering a perfect and periodic crystal structure, which differs from experimental samples, where crystal imperfections may interfere in the adsorption profile. As stated in other studies (Maurin *et al.*, 2005) we also observed that, at low pressure, CO<sub>2</sub> occupies the supercage near the cations on site III'. As the pressure increases, the cations located in site II are populated.

Other parameters for validation that can be used are: adsorption heat and CO<sub>2</sub>:N<sub>2</sub> selectivity. Our simulated adsorption heat of -8.15 kcal/mol is consistent with the experimental data of 10 kcal/mol reported by Maurin *et al.* (2005). Our simulated CO<sub>2</sub>:N<sub>2</sub> selectivity (Equation (2)) for an equimolecular mixture was -12.1 (100 kPa and 25 °C) versus -13.8 (101.3 kPa and 30 °C) obtained experimentally by Pillai *et al.* (2012).



**Figure 5:** Simulated and experimental monocomponent adsorption isotherms of CO<sub>2</sub> and N<sub>2</sub> on NaX. Simulated and CO<sub>2</sub> experimental isotherms (Walton *et al.*, 2005) were performed at 25 °C. N<sub>2</sub> experimental isotherm (Maurin *et al.*, 2005) was performed at 27 °C.

### Impregnation Impact in Adsorption

As noted previously, we estimated that faujasite adsorbed a maximum of 60 molecules of MEA (21.45% wt). We then randomly deleted MEA molecules to obtain new impregnated models with 6, 18 and 30 immobilized molecules, representing a range of concentrations of 2.66, 7.57 and 12.01% by weight of the MEA inside the zeolite pores. This range of concentrations is found in experimental studies of impregnation (Jadhav *et al.*, 2007; Silva *et al.*, 2012).

First we verified how MEA modified the heat of adsorption (Figure 6). NaX without impregnation provides an average value of -8.15 kcal/mol and this value grows with the amount of amine impregnated, showing median values of -8.8 kcal/mol, -9.5 kcal/mol, -10.4 kcal/mol until reaching a maximum value of -12.4 kcal/mol for the models with 2.66, 7.57, 12.01 and 21.45 wt% MEA, respectively. This means that the presence of molecules of MEA effectively creates stronger adsorption sites. However, the simulated 15:85 (CO<sub>2</sub>:N<sub>2</sub>) mixture isotherms in the impregnation models show that the increase in heat of adsorption did not translate into a corresponding increase of CO<sub>2</sub> adsorption. This was particularly true for the models with a high loading of immobilized MEA (Figure 7).

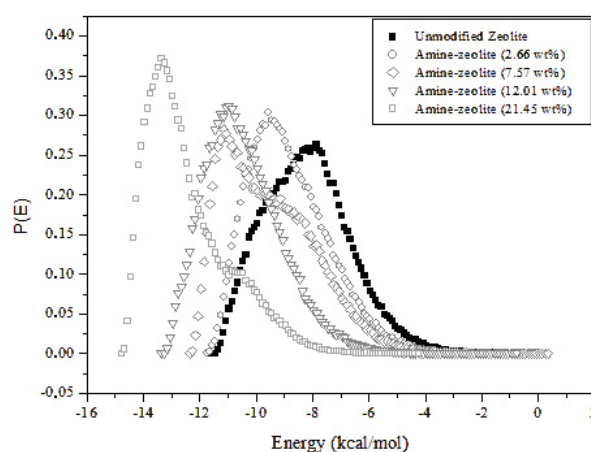
Only the model with 7.57 wt % of MEA showed a significant increase of the CO<sub>2</sub> adsorbed amount. This increase occurred in a limited range of pressure that goes from 1 to 40 kPa. The models with 2.66 and 12.01 wt % had a modest increase and, finally, the model with 21.45 wt %, which has the highest heat of

adsorption, showed a drastic decrease in its adsorption capacity. No improvement was observed for N<sub>2</sub>. With the exception of the 2.55 wt% model, the N<sub>2</sub> loading decreased for all impregnation models tested (Figure 7).

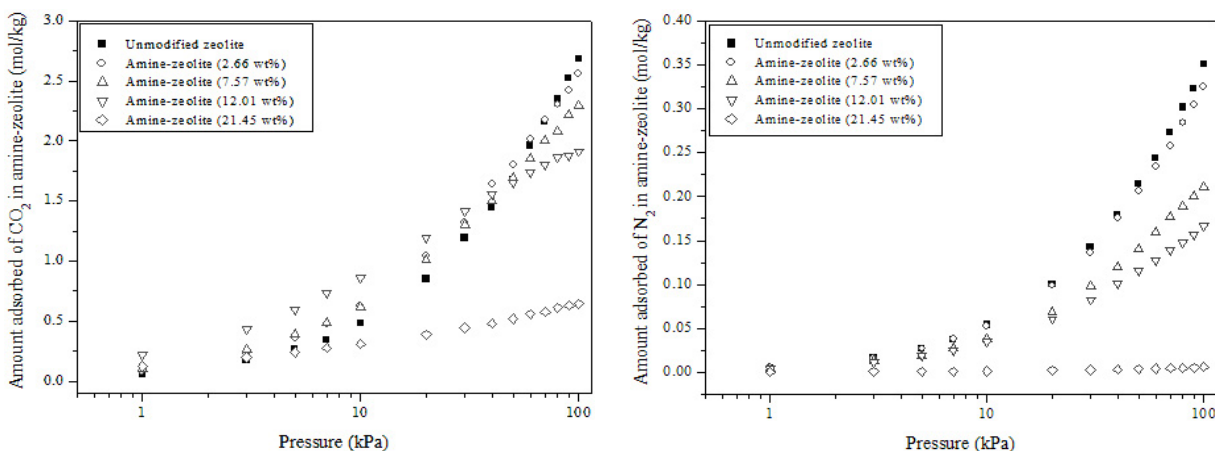
Our simulated results for the impregnated material (isotherms and adsorption heat) are similar to several experimental studies. For example, Silva *et al.* (2012) did CO<sub>2</sub> microcalorimetric measurements on NaX impregnated with MEA and found a strong peak of adsorption heat at low coverage, but the experimental isotherms with the impregnated material showed decreasing adsorption capacities with increasing concentration of MEA. Also, Jadhav *et al.* (2007) reported, via CO<sub>2</sub> breakthrough curves, de-

creasing CO<sub>2</sub> adsorption capacity in NaX with increased MEA impregnation.

The reason for the small enhancement of adsorption capacity, despite the increase in the heat of adsorption, is related to the drastic reduction of the NaX micropore volume as the MEA molecules are introduced into the pores (Table 4). With 30 molecules of MEA (12.1 wt%) the useful volume of the faujasite is reduced by almost half (43.25%). The adsorption is completely impaired for the impregnation model with 60 MEA molecules (21.45 wt%) with the available volume reduced by 90.73%. A view of the CO<sub>2</sub> and N<sub>2</sub> population in the 18 MEA (7.57 wt%) model at 10 and 100 kPa is depicted in Figure 8.



**Figure 6:** Energy histograms of CO<sub>2</sub> adsorption on zeolite NaX and in the impregnation models. Median values are: -8.15 kcal/mol, -8.8 kcal/mol, -9.5 kcal/mol, -10.4 kcal/mol and -12.4 kcal/mol for the models with 0, 2.66, 7.57, 12.01 and 21.45 wt% of MEA.

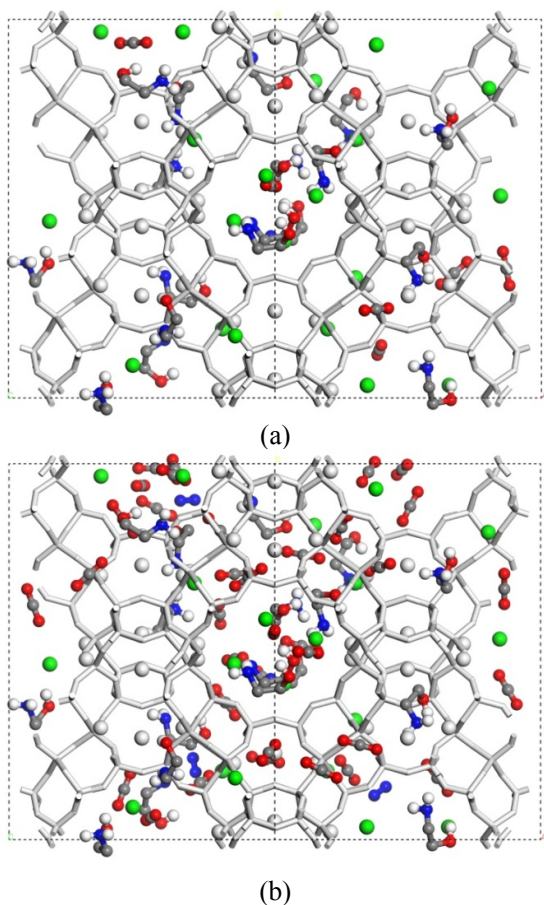


**Figure 7:** Simulated adsorption isotherms of CO<sub>2</sub>:N<sub>2</sub> (15:85) at 25 °C in NaX zeolite.



**Table 4: Micropore volume decrease with impregnation. Theoretical volume calculated by the Connolly method (Connolly, 1983) using a spherical probe with 1.8 Å radius.**

Property	Model of immobilized faujasite			
	6 MEA (2.66 wt%)	18 MEA (7.57 wt%)	30 MEA (12.01 wt%)	60 MEA (21.45 wt%)
Free volume (Å <sup>3</sup> )	5449.86	4460.44	3349.04	546.87
Reduction (%)	7.66	24.42	43.25	90.73



**Figure 8:** Snapshots of the adsorption of the 15:85 (CO<sub>2</sub>:N<sub>2</sub>) mixture in the 18 MEA (5.75 wt%) impregnation model at 25 °C and 10 kPa (a) and 100 kPa (b). H-white, N-blue, O-red, pseudo atom CH<sub>2</sub> and C-gray. Na<sup>+</sup>: SI' and SII - white, SIII - green.

Having foreseen satisfactory results for adsorption only for the 18 MEA (7.57 wt%) impregnation model, we turned to examine whether the introduction of MEA could improve the selectivity. Based on the adsorbed values of the isotherms of Figure 7, we calculated CO<sub>2</sub>:N<sub>2</sub> selectivity using Equation (2):

$$S = \frac{X_1 Y_2}{X_2 Y_1} \quad (2)$$

where  $X_i$  and  $Y_i$  are the mole fractions of CO<sub>2</sub> and N<sub>2</sub> in the adsorbed ( $i=1$ ) and gas phases ( $i=2$ ), respectively. The selectivity calculations showed that the impregnated MEA causes an increase in selectivity (Table 5). The material without impregnation has selectivity of 44.2 that increases until a maximum value of 738.1 for the model with the higher degree of impregnation (60 MEA molecules).

Our results make it clear that there exists a trade-off between the creation of stronger sites with addition of MEA molecules and the decrease of free pore volume for adsorption inside the NaX cavities. After inserted 18 MEA molecules, the effect of reduced volume available for adsorption of CO<sub>2</sub> molecules prevails, decreasing substantially the amount adsorbed.

**Table 5: Theoretical selectivity of CO<sub>2</sub>:N<sub>2</sub> in NaX and impregnated models.**

Adsorbent model	Simulated adsorption capacity (mol/kg) at 25 °C and 50 kPa		Selectivity (CO <sub>2</sub> :N <sub>2</sub> )
	Carbon dioxide	Nitrogen	
NaX (0 wt%)	1.677	0.215	44.2
6 MEA (2.66 wt%)	1.799	0.206	49.5
18 MEA (7.57 wt%)	1.696	0.141	68.3
30 MEA (12.01 wt%)	1.653	0.115	81.5
60 MEA (21.45 wt%)	0.521	0.004	738.1

## CONCLUSIONS

We applied a validated force field, able to reproduce experimental monocomponent adsorption isotherms of CO<sub>2</sub> and N<sub>2</sub> in faujasite NaX, to investigate the influence of MEA impregnated FAU zeolite on a CO<sub>2</sub>:N<sub>2</sub> mixture. Four impregnation models with increasing MEA concentration were designed. We performed adsorption theoretical studies for a binary mixture of CO<sub>2</sub>:N<sub>2</sub> (15:85) at low CO<sub>2</sub> partial pressure, similar to the scenario of post-combustion. We found that NaX impregnated with concentrations up to 12 wt% should be more efficient in CO<sub>2</sub> capture due to the best compromise between increase in heat of adsorption and reduction of available volume by the

addition of molecules of MEA. It is also observed that the adsorbents impregnated with a high concentration of monoethanolamine exhibit significant loss of adsorption capacity due to the effect of free volume reduction. The impregnation of NaX at concentrations above 12 wt% of MEA, under the investigated conditions, is not recommended to increase the capture of CO<sub>2</sub>.

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