Contamination of Zeolites Used in Oxygen Production by PSA: Effects of Water and Carbon Dioxide

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Pressure swing adsorption (PSA) is one of the technologies used for producing oxygen from air. Besides the cycles employed, the adsorbent used plays an important role. Many adsorbents are nowadays available showing different adsorption properties. The adsorbent contamination that may occur in a working PSA unit has a great impact on the performance of the separation; it is then important to know the behavior of the selected adsorbent toward major contaminants such as water vapor and carbon dioxide. From the study conducted it was possible to conclude that some adsorbents are contaminated in a large extent even after being regenerated at 70 °C for 2 h. In this paper, the adsorption equilibrium data for several adsorbents used for oxygen production from air are presented. Oxysiv MDX and Oxysiv 7 from UOP as well as AgLiLSX from Air Products and Chemicals are shown to have very good selectivities for the separation of oxygen from air. The contamination study in a working laboratorial PSA unit packed with MS S 624 from Grace Davison is also presented. In the selected operating conditions, about 30% of the bed was contaminated.

Introduction

The study of the adsorption equilibrium is of great importance for simulation and selection of the adsorbent to be used in pressure swing adsorption (PSA) units for oxygen production.

The zeolites most commonly used for this separation are of type A and X. These are composed by silica and tetrahedral alumina connected in an octahedral structure. While the groups SiO_2 are neutral, the groups $(AlO_2)^-$ introduce a negative charge in the structure, which is compensated by the presence of cations, such as Na^+, Li^+, or Ca^{2+}.[1] Zeolites can be produced with smaller or greater amounts of SiO_2 than the ones that appear in natural zeolites. Larger amounts of SiO_2 generally give greater hydrothermal stability and originate more hydrophobic zeolites. Lesser amounts of SiO_2 give higher cation exchange capabilities and higher capacity to adsorb polar molecules.[2]

The first pressure swing adsorption unit (PSA), composed of two beds and using a 13X type zeolite, was patented by Skarstrom in 1966.[3] Since then, the development of zeolites with higher nitrogen adsorption capacities and higher selectivities led to improvements in PSA and in vacuum swing adsorption (VSA) processes.[2]

For taking the most out of these zeolites, it is important to understand how they behave in real conditions, i.e., if they lose performance when in contact with possible contaminants such as water vapor and carbon dioxide, present in air.

Some work has been done regarding the adsorption of water on zeolites. Ahn and Lee[4] studied the adsorption dynamics of water in layered bed for an air-drying temperature swing adsorption process and later on, in 2004,[5] studied the effect of capillary condensation on adsorption and thermal desorption dynamics of water in 13X type zeolites and layered beds with silica gel and activated alumina before the zeolite. They refer that due to the strong adsorption of water in the 13X type zeolite,

it takes a long time to regenerate the bed with a high level of energy consumption. So, they performed a study about the regeneration dynamics, but they do not mention the contamination of the zeolite or the possibility that it can occur.

Rege et al.[6] studied the air prepurification by pressure swing adsorption (PSA) using single/layered beds and mention that in this process impurities such as water (present in atmospheric air up to 3 vol %) and carbon dioxide (about 350 ppm are present in atmospheric air) are found to adsorb strongly and, to some extent, irreversibly on the adsorbents used for air separation. They also state that this effect drastically affects the capacity as well as the selectivity of the adsorbent for air separation, thus requiring frequent plant shutdowns. They concluded that in order to prevent such malfunctions in the air separation units it is critical to pretreat the feed air and reduce the impurity content to tolerable levels. They simulated a PSA unit with only three components—carbon dioxide (350 ppm) and water vapor (3000 ppm) balanced with nitrogen—and they

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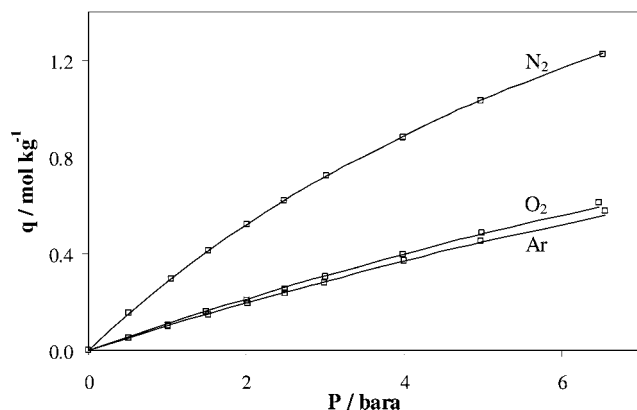
Table 1. Parameters of the Monocomponent Langmuir Equation (n = 1 in Eq 1) for Oxysiv 5 Obtained from the Adsorption Equilibrium Points Determined by the Gravimetric Method at 11.7, 19.9, and 36.4 °C

	N_2	O_2	Ar
$C_{\mu s,j}$ (mol/kg)	3.091	3.091	3.091
$b_\infty \times 10^5$ (Pa^{-1})	1.982×10^{-5}	8.823×10^{-5}	7.473×10^{-5}
$Q\mathbf{R}^{-1}$ (K)	2501.07	1767.86	1791.15
χ	0		
$\Sigma(q - q^*)^2$ /np	2.42×10^{-5}	4.07×10^{-6}	2.05×10^{-5}

Table 2. Parameters of the Monocomponent Sips Equation for Oxysiv 7 at the Reference Temperature of T_0 = 20 °C, Obtained from the Adsorption Equilibrium Experimental Points Determined by the Gravimetric Method at 11.7, 19.8, 28.2, and 44.5 °C

	N_2	O_2	Ar
$C_{\mu s,0}$ (mol/kg)	4.580	6.384	9.223
$b_0 \times 10^5$ (Pa^{-1})	5.470×10^{-2}	1.951×10^{-2}	1.095×10^{-2}
$1/n_0$	0.7100	0.9707	0.9539
$Q/\mathbf{R}$(K)	3156.82	1761.76	1829.54
α	0.3694		
χ	−0.6114		
$\Sigma(q - q^*)^2$ /np	5.21×10^{-5}	8.09×10^{-6}	1.29×10^{-6}

Figure 1. Result of the fit for Oxysiv 5 at 19.9 °C: (□) experimental data, (—) adsorption equilibrium equation.
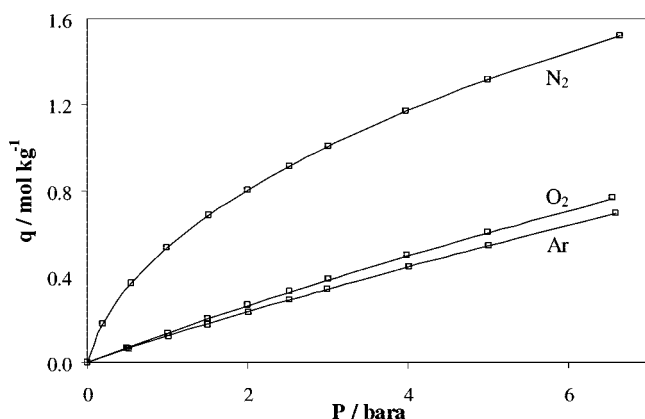

Figure 2. Result of the fit for Oxysiv 7 at 19.8 °C: (□) experimental data, (—) adsorption equilibrium equation.

Table 3. Parameters of the Monocomponent Sips Equation for MS S 624 at the Reference Temperature of $T_0 = 20$ °C, Obtained from the Adsorption Equilibrium Experimental Points Determined by the Gravimetric Method at 11.6, 19. 9, 28.3, and 44.7 °C

	N_2	O_2	Ar
$C_{\mu s,0}$ (mol/kg)	2.733	2.733	2.733
$b_0 \times 10^5$ (Pa^{-1})	2.159×10^{-1}	7.515×10^{-2}	7.042×10^{-2}
$1/n_0$	1.0711	1.0711	1.0711
Q/R(K)	2208.40	1786.28	1704.03
α	-0.4329		
χ	1.1250		
$\Sigma(q - q^*)^2 /np$	9.57×10^{-5}	2.74×10^{-5}	2.53×10^{-5}

Table 4. Parameters of the Monocomponent Langmuir Equation Monocomponent Langmuir Equation ($n = 1$ in Eq 1) for MS C 544 Obtained from the Adsorption Equilibrium Points Determined by the Volumetric Method at 9.9, 20.1, 29.8, and 39.7 °C

	N_2	O_2	Ar
$C_{\mu s,j}$ (mol/kg)	3.278	3.278	3.278
$b_\infty \times 10^5$ (Pa^{-1})	7.096×10^{-5}	1.710×10^{-4}	1.741×10^{-4}
Q/R(K)	2096.92	1559.37	1535.16
χ	0		
$\Sigma(q - q^*)^2 /np$	3.88×10^{-5}	1.60×10^{-5}	2.13×10^{-5}

assume the adsorption of each component by the adsorbents to be fully reversible. With these simulations they studied the performance of 13X type zeolite as well as γ-Al$_2$O$_3$ and chabazite as sorbents for air prepurification and concluded that no single adsorbent can provide a nitrogen product with a satisfactorily low content of water vapor and carbon dioxide impurities at a reasonable bed length. They also concluded that γ-Al$_2$O$_3$ adsorbents appear to be the best for water removal and 13X type zeolite seems to be the best choice for carbon dioxide

Table 5. Parameters of the Monocomponent Sips Equation for KEG415 at the Reference Temperature of $T_0 = 20$ °C, Obtained from the Adsorption Equilibrium Experimental Points Determined by the Volumetric Method at 10.2, 20.0, 30.0, and 39.8 °C

	N_2	O_2	Ar
$C_{\mu s,0}$ (mol/kg)	2.324	2.324	2.324
$b_0 \times 10^5$ (Pa^{-1})	2.942×10^{-1}	9.730×10^{-2}	8.448×10^{-2}
$1/n_0$	1.0913	1.0913	1.0913
Q/R (K)	1512.64	1189.13	1276.47
α	-0.3558		
χ	1.7727		
$\Sigma(q - q^*)^2 /np$	4.59×10^{-4}	3.91×10^{-5}	1.06×10^{-5}

removal. With these remarks they suggested the use of a layered bed for air prepurification, composed by a first layer of γ-Al$_2$O$_3$ followed by a zeolite layer, and after studying this system, they find that for a particular set of operating conditions the optimal alumina/zeolite ratio is 7/3. They failed, however, to discuss the effect of the irreversible adsorption of these contaminants on their results.

Wilson et al.[7] studied the effects of readily adsorbed trace component (water) in oxygen separation from air by vacuum swing adsorption (VSA). They mentioned that most molecular sieves used for oxygen VSA do not reversibly desorb water under VSA process conditions, and therefore a prelayer of activated alumina or NaX is required to protect the main adsorbent layer of a lithium- or calcium-based adsorbent from water and carbon dioxide. They performed some experiments with layered columns with activated alumina and a 13X type zeolite from UOP and removed all the carbon dioxide from the feed gas with a desiccant dryer. In these experiments they studied the length of penetration of water into the adsorption bed by removing samples of adsorbent at predefined distances and measured the nitrogen adsorption capacity of these samples and inferred the presence of water by the reduction in nitrogen loading. (This is the same method that is used in the experiments presented in this work.) They claimed that this method is better than a TGA analysis since it provides the information on the extent of nitrogen loading. They referred that levels of water above ≈ 1 wt % prevent nitrogen and oxygen from adsorbing. They concluded that in industrial practice activated alumina might be more appropriate and, in some extreme conditions, two pretreatment layers should be used, the first of activated alumina and the second of NaX. The conclusions of their study cannot, however, be applied in medical oxygen concentrators since desiccant dryers are not used, and therefore carbon dioxide along with water vapor will enter the unit and contaminate the adsorbent.

Brandani and Ruthven[8] studied the effect of small amounts of water, in regard to inhibiting the adsorption of carbon dioxide,
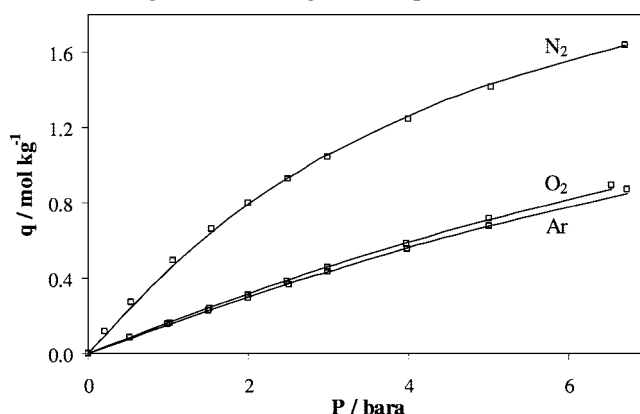

Figure 3. Result of the fit for MS S 624 at 19.9 °C: (□) experimental data, (—) adsorption equilibrium equation.
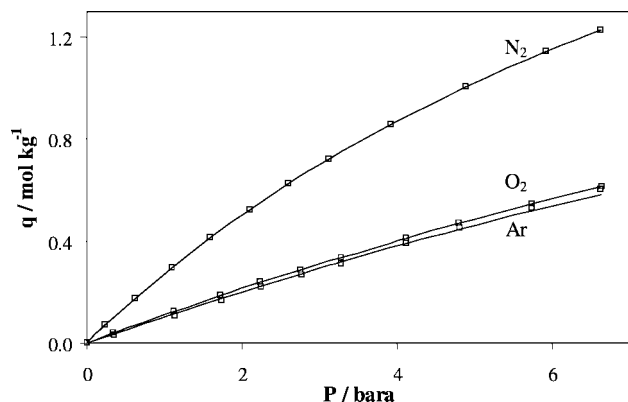
Figure 4. Result of the fit for MS C 544 at 20.1 °C: (□) experimental data, (—) adsorption equilibrium equation.

Table 6. Parameters of the Monocomponent Sips Equation for Oxysiv MDX at the Reference Temperature of $T_0 = 20$ °C, Obtained from the Adsorption Equilibrium Experimental Points Determined by the Gravimetric Method at 10.0, 20.0, 30.0, and 40.0 °C

	N₂	O₂	Ar
$C_{\mu s,0}$ (mol/kg)	3.425	6.056	7.946
$b_0 \times 10^5$ (Pa^{-1})	3.356×10^{-1}	2.665×10^{-2}	1.610×10^{-2}
$1/n_0$	0.8227	0.9797	0.9787
Q/R (K)	3160.37	1820.15	1673.81
α	0.0556		
χ	0.0213		
$\sum(q - q^*)^2 /np$	3.42×10^{-5}	7.27×10^{-7}	2.27×10^{-7}

on several different cationic forms of zeolite X (LiLSX, NaLSX, NaX, and CaX) using the zero length column technique, coupled with the temperature-programmed desorption. For all systems studied, it was observed that the Henry constant declines exponentially with the loading of water.

Some patents discloses the removal of the contaminants through a separate pretreatment material or a separate pretreatment stage for preventing the adsorbent from contaminating.[9–11]

In this paper, the adsorption equilibrium data for several new and traditional adsorbents are presented for oxygen, nitrogen, and argon as well as the results of a study of the contamination caused by water vapor and carbon dioxide. The contamination results of a laboratorial PSA unit are also presented.

Adsorbents Studied

With the aim of selecting the best adsorbents for oxygen separation from air, adsorption equilibrium data were determined
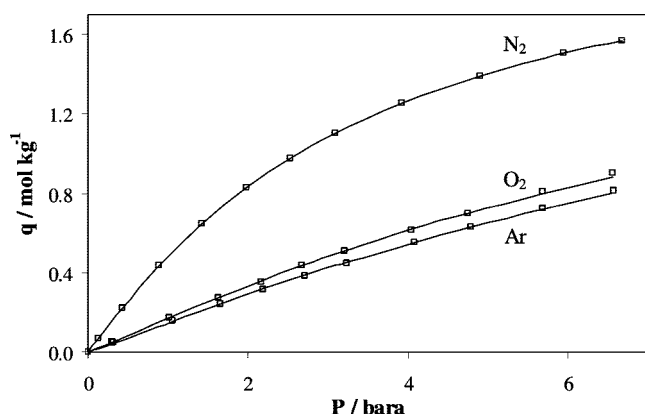

Figure 5. Result of the fit for KEG415 at 20.0 °C: (□) experimental data, (—) adsorption equilibrium equation.
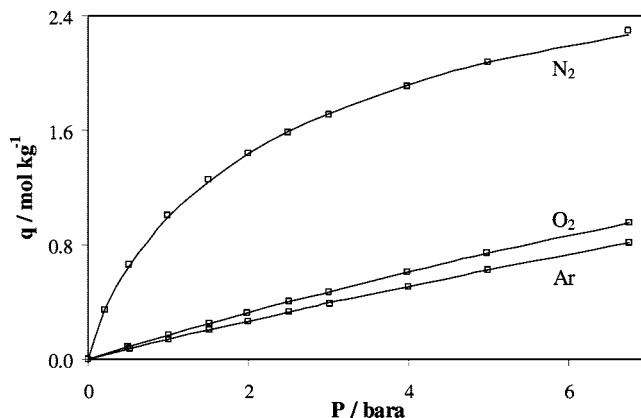

Figure 6. Result of the fit for Oxysiv MDX at 20.0 °C: (□) experimental data, (—) adsorption equilibrium equation.

Table 7. Parameters of the Monocomponent Sips Equation for AgLiLSX at the Reference Temperature $T_0 = 20$ °C, Obtained from the Adsorption Equilibrium Experimental Points Determined by the Gravimetric Method at 11.7, 23.0, 29.9, and 39.8 °C

	N₂	O₂	Ar
$C_{\mu s,0}$ (mol/kg)	2.636	5.481	7.270
$b_0 \times 10^5$ (Pa^{-1})	2.581×10^{-1}	3.013×10^{-2}	2.300×10^{-2}
$1/n_0$	0.4856	0.9484	0.9216
Q/R (K)	2740.70	1873.82	1771.33
α	0.3007		
χ	0.0112		
$\sum(q - q^*)^2 /np$	6.34×10^{-6}	8.10×10^{-5}	4.22×10^{-6}

for the following adsorbents: Oxysiv 5, Oxysiv 7, KEG415 (this adsorbent was previously from Bayer), and Oxysiv MDX from UOP; SYLOBEAD MS S 624 and SYLOBEAD MS C 544 from Grace Davison. All these adsorbents, except MS S 624, were indicated for oxygen separation from air. MS S 624, despite being indicated for natural gas purification, has nitrogen and oxygen isotherms favorable for the desired separation and was therefore included in the study.

The adsorbent AgLiLSX from Air Products and Chemicals, Inc., was also studied. This adsorbent may be used for the production of high-purity oxygen (>95%) since it adsorbs more argon than oxygen.

Oxysiv 5 is a 13X (NaX) type zeolite;[12] Oxysiv 7 is a LiX type zeolite with a ratio SiO₂/Al₂O₃ = 2.5 (Si/Al = 1.25);[13] KEG415 is a 5A type zeolite; according to the company Grace Davison, MS S 623 is a binderless 5A type zeolite; MS C 544 is also a 13X (NaX) type zeolite. Oxysiv MDX is a low silica X-type zeolite (LiLSX) with a ratio Si/Al = 1. The adsorbent AgLiLSX is a 40% silver exchanged zeolite.

Adsorption Equilibrium Data

The Sips equation was fit to the experimental data:[14]

$$q = C_{\mu s} \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \quad (1)$$

and

$$b = b_\infty \exp\left(\frac{Q}{RT}\right) = b_0 \exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)\right] \quad (2)$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1 - \frac{T_0}{T}\right) \quad (3)$$

where q is the adsorbed solute concentration at pressure P and temperature T, b is the affinity constant, b_∞ is the affinity constant at infinite temperature, b_0 is the affinity constant at

Table 8. Deactivation (%) Results after Exposure to Carbon Dioxide and/or Water Vapor and Subsequent Regeneration

		contaminant		
regeneration procedure	adsorbent	CO_2	H_2O	CO_2+H_2O
regeneration at	Oxysiv 5	5	70	35
70 °C for 2 h,	Oxysiv 7	31	82	38
evacuating and pressurizing with helium,	KEG415	17	59	29
alternately, after exposure to	MS C 544	8	18	66
the contaminant at 20 °C	MS S 624	18	95	13
	Oxysiv MDX	34	61	57
	AgLiLSX	34	91	65
subsequent regeneration	Oxysiv 5	5	8	4
at 375 °C in a muffle	Oxysiv 7	34	65	40
under nonflowing atmospheric air,	KEG415	9	2	6
after exposure to the	MS C 544	4	6	26
contaminant at 20 °C	MS S 624	0	0	0
	Oxysiv MDX	88	92	87
	AgLiLSX	28	97	70

Table 9. Dimensions of the Adsorption Columns

		mass of adsorbent (g)	
length (cm)	diameter (cm)	left column	right column
40.5	4.1	398	401
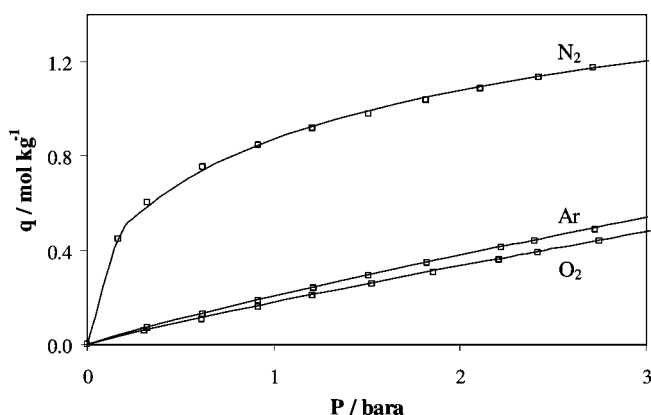
Figure 7. Result of the fit for AgLiLSX at 23.0 °C: (□) experimental data, (—) adsorption equilibrium equation.

the reference temperature T_0, n_0 is the parameter n at the reference temperature, α is a parameter of the equation, Q is the heat of adsorption, and $\mathbf{R}$ is the universal gas constant. The saturation capacity, $C_{\mu s}$, may be considered constant or the following dependency with temperature may be assumed:[14]

$$C_{\mu s} = C_{\mu s,0} \exp\left[\chi\left(1 - \frac{T}{T_0}\right)\right] \qquad (4)$$

where $C_{\mu s,0}$ is the saturation capacity at the reference temperature and χ a parameter of the equation.

These parameters were obtained by minimization of the sum of the square of the differences between the adsorbed quantity, q, and the adsorbed quantity predicted by the equation, q^*, for all gases and temperatures, divided by the number of experimental points, np (number of experimental points at each pressure for each gas and at each temperature).

The parameters obtained from the fits, for all the adsorbents studied, are presented in Tables 1–7. The plots of the fit at one of the temperatures are presented in Figures 1–7.

As can be seen from Figures 1–7, the adsorbent that presents more selectivity of nitrogen over oxygen is Oxysiv MDX. The

heat of adsorption, for each species, exhibited by this adsorbent is similar to the ones presented by Oxysiv 7.

Adsorbent Contamination and Regeneration Procedure

From the previous study it might be concluded that the best adsorbent for the oxygen production by PSA is the Oxysiv MDX, from UOP. However, the PSA feed air stream does not contain only nitrogen, oxygen, and argon. Among other components, the air feed also contain carbon dioxide and water vapor, which are known to adsorb strongly on these adsorbents. It is then of up most importance to consider these components when characterizing the adsorption equilibrium of these adsorbents. A study was then conducted with the objective of determining the causes of loss of capacity of the adsorbents after being used in a pressure swing adsorption unit. A volumetric method apparatus was used for this study.

The study consisted in exposing the adsorbent to water vapor, carbon dioxide, and to both simultaneously, at 20 °C, and, after regeneration, determining nitrogen adsorption equilibrium values at two different pressures to assess the loss of efficiency. The partial pressure of carbon dioxide (1.9 mbar) and water vapor (about 23 mbar) used are close to the ones the adsorbents are exposed to during the operation of a PSA unit at 5 bar and 20 °C. These two species were allowed to contact the absorbents separately or as a mixture. After a regeneration at 70 °C, evacuating and pressurizing with helium, alternately, two types of regeneration were considered: (a) regeneration in a muffle at 375 °C under nonflowing atmospheric air and (b) regeneration in a muffle at 375 °C passing a current of dried air (or helium) through the sample. This last procedure (type b) allowed the full recovery of the adsorbents, after they were exposed to each of the contaminants used in this study. The results obtained for the regeneration at 70 °C and for a subsequent regeneration of type a are presented in Table 8. The percentage of deactivation was defined as one minus the ratio between the quantity of nitrogen adsorbed after exposure (and regeneration) and the quantity of nitrogen adsorbed after full regeneration.

As can be seen from Table 8, carbon dioxide and water vapor contaminate the adsorbents studied. Except for MS C 544, the presence of carbon dioxide and water vapor, simultaneously, does not cause a higher deactivation than the one caused by each of these contaminants alone. When both contaminants are together, it seems that carbon dioxide protects the adsorbent from water vapor, probably by adsorbing faster and blocking the access of water vapor to the adsorption sites. As mentioned before, for MS C 544 this was not observed. For MS S 624 there seems to be a mutual blocking effect since this adsorbent
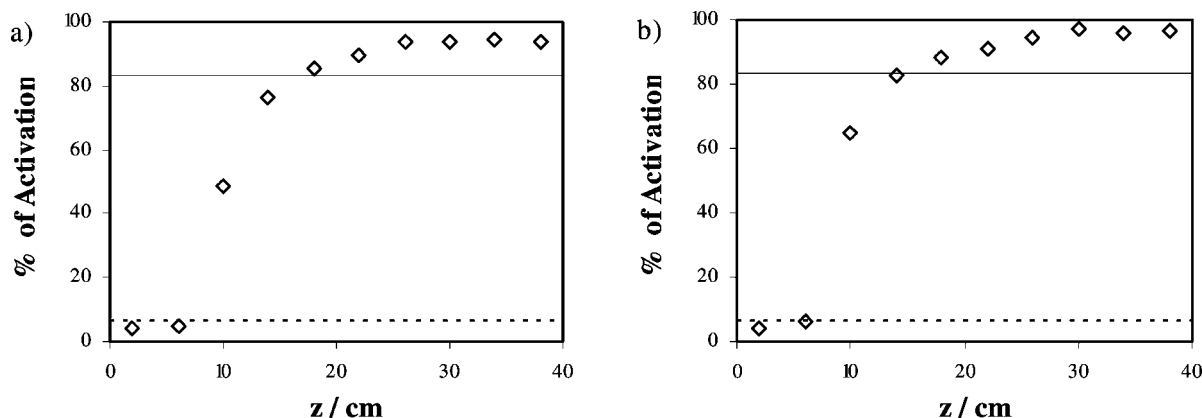
Figure 8. Percentage of activation of the adsorbent at 20 °C along the axial coordinate for the (a) left column and (b) right column. The dashed line represents the activation of the adsorbent after contamination with water, and the line represents the percentage of activation of the adsorbent after contamination with carbon dioxide.
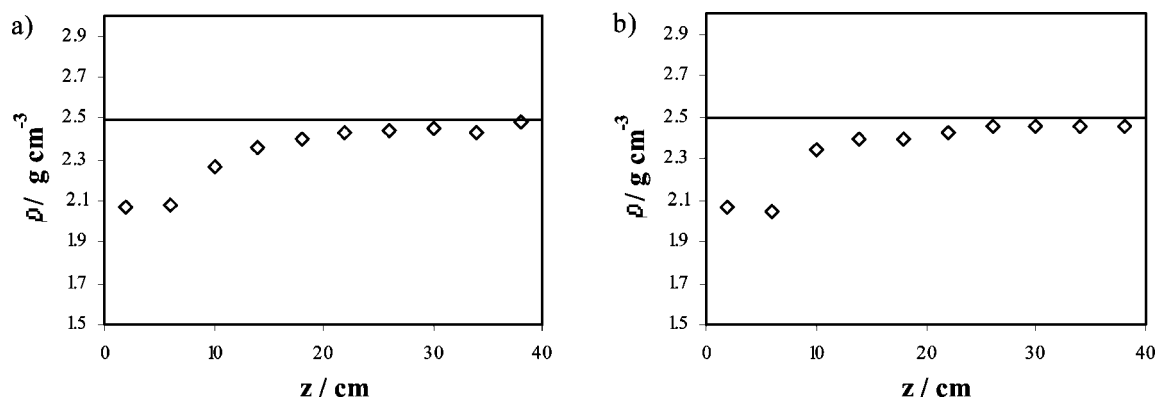

Figure 9. Density of the adsorbent in the sections of (a) left column and (b) right column. The line represents the density of the adsorbent completely regenerated.

Table 10. Operating Conditions of the Pressure Swing Adsorption Unit

	time		flow rate	
operation (h)	pressurization (s)	production (s)	production (L_{STP}/min)	purge (L_{STP}/min)
141	12	7	9.5	0.74

gets less contaminated by water vapor and carbon dioxide simultaneously than with any of these contaminants alone.

When comparing MS C 544 with Oxysiv 5, which is also a 13X type zeolite, it is possible to see that MS C 544 is more damaged in the presence of water vapor and carbon dioxide than Oxysiv 5, in the same conditions. This might be due to the different particle size of these zeolites or to differences in their composition such as the binder or size of the crystals.

The regeneration with vacuum and helium attempts to reproduce the regeneration (purge) step that occurs in a PSA unit. As can be seen, it is not enough for recovering the total capacity of the adsorbents. The regeneration at 375 °C in a muffle under nonflowing atmospheric air was also not enough, except for MS S 624. Moreover, for the other adsorbents, this last regeneration procedure caused an irreversible damage, and it was not possible to regenerate them further.

Although the starting material for AgLiLSX is a LiLSX type zeolite such as Oxysiv MDX, these zeolites behave very differently when in contact with the contaminants. Being low-silica-type X zeolites and containing lithium, these adsorbents have a strong affinity toward water vapor. This is probably the reason why water vapor causes such loss of capacity.

The adsorbent that revealed to be less affected by carbon dioxide alone was Oxysiv 5 while the one that was less affected by water vapor alone was MS C 544.

When water vapor or carbon dioxide adsorbed in the zeolite are desorbed (such as what happens when the temperature is raised) and if they are kept in the gas phase surrounding the zeolite, the crystal lattice may suffer an irreversible structural change.[15,16] This can only be avoided by continuously purging the contaminants in the gas phase surrounding the zeolite, for instance, by passing an inert gas through the bed. There is still some work to be done for identifying the precise structure of the zeolites with adsorbed water.[17]

Adsorbent Contamination in an Experimental PSA Unit

A study was conducted for exemplifying the determination of the degree of contamination of a zeolite during the operation of a PSA unit. This study consisted in operating the PSA unit at constant product flow rate for some days and following the product purity. The air was fed to the unit directly from an oil-less compressor. The dimensions of the adsorption columns used, packed with MS S 624, are presented in Table 9. The high pressure was 3 bar, and the low pressure was the atmospheric pressure. A simple Skarstrom cycle with pressurization, production, blowdown, and purge steps was used.

Table 10 presents the operating conditions of the PSA unit.

The unit started producing oxygen at 80% and stabilized producing at 65%. After the stabilization, several layers of adsorbent were removed from both columns of the PSA unit, and the nitrogen adsorption capacity at 20 °C and the adsorbent

density were determined. These measurements were performed after regenerating the adsorbent at 70 °C for 2 h with vacuum and helium, alternatively.

Figure 8 presents the percentage of activation of the adsorbent for each column along the axial coordinate, z. The percentage of activation is defined as the ratio between the concentration of nitrogen in the adsorbed phase and the maximum concentration of nitrogen in the same phase at 20 °C. The horizontal dashed line represents the percentage of activation of the adsorbent after contamination with water, and the horizontal solid line represents the activation of the adsorbent after contamination with carbon dioxide. These results were obtained from the experiments presented in the previous section.

Analyzing Figure 8, it is possible to see that the two first sections of the adsorption columns were contaminated mainly with water. The last sections appear to be partially contaminated, probably with carbon dioxide. It is also possible to see that the activation of the adsorbent along the axial direction is very similar in both columns.

Figure 9 presents the density of the adsorbent in several sections of the columns, determined by helium picnometry. Analyzing Figure 9, one may see that the density of the contaminated adsorbent is inferior to that of the regenerated sample. Since the weight of the contaminated zeolite is larger due to the presence of molecules of the contaminants, the only way for the density to decrease is if the volume of the zeolite increases. The density presented in Figure 9 is the skeleton density of the zeolite with contaminant adsorbed. Since the density of the contaminant is lower than the density of the adsorbent, the "overall" density decreases. Assuming that the contaminant is mostly water with density of 1, it is possible to estimate the loading of contaminant in the adsorbent. For the first two layers of the column, the loading is about 17 wt %, which is close to the typical maximum loading of water in 5A type zeolites (20 wt %).

It is possible then to conclude that the density of the adsorbent is a good indicator of its deactivation status.

Conclusions

From the analysis of the monocomponent adsorption equilibrium isotherms it was concluded that Oxysiv MDX, from UOP, is the adsorbent that presents the best selectivity for the separation of oxygen from air. Good results were also obtained with AgLiLSX from Air Products and Chemicals, Inc., and Oxysiv 7 from UOP. However, a significant decrease of the performance of a pressure swing adsorption unit was observed with time, using this last adsorbent. It is possible to fully regenerate all contaminated adsorbents at about 375 °C under a continuous stream of helium or dried air. However, if a continuous stream of helium or dried air is not used at this temperature, except for MS S 624 the adsorbents are irreversibly damaged.

Some of the adsorbents studied were contaminated in a large extent even after being submitted to a regeneration at 70 °C with helium and vacuum, alternately, for 2 h. Almost all adsorbent showed to get less contaminated in the presence of carbon dioxide and water vapor simultaneously than with water vapor alone, revealing a possible blocking effect by carbon dioxide, the exception being MS C 544. Also in the presence of these two contaminants, MS S 624 showed to get less contaminated than with any of the two contaminants alone, revealing a possible mutual blocking effect.

From the study of the contamination that occurs in an adsorption column with MS S 624 during the operation of a pressure swing adsorption unit separating oxygen from air, it was concluded that at the steady state operation about 30% of the column was contaminated, water vapor being the main contaminant. It was observed that the density of the contaminated adsorbents, determined by helium picnometry, is smaller than the one of the fresh adsorbent. This is because the density of the contaminants (mostly water) is smaller than the density of the adsorbent. It is possible to conclude that the density of the adsorbent, determined by helium picnometry, gives a good indication of the activation state of the adsorbent.

Supporting Information Available: Description of the experimental units for determining the adsorption equilibrium data by the volumetric method (also used for the contamination study) and by the gravimetric method as well as a comparison between the gravimetric and volumetric methods; some remarks about the calculation of the loading of the contaminant in the adsorbent using the density determined by helium picnometry. This material is available free of charge via the Internet at http://pubs.acs.org.

Nomenclature

b = affinity constant, bar^{-1}
b_0 = affinity constant at the reference temperature, bar^{-1}
b_∞ = affinity constant at infinite temperature, bar^{-1}
$C_{\mu s}$ = saturation capacity, mol kg^{-1}
n = empirical parameter from the Sips equation
np = number of experimental points
P = pressure, bar
Q = heat of adsorption, J mol^{-1}
q = adsorbed solute concentration, mol kg^{-1}
R = universal gas constant, J mol^{-1} K^{-1}
T = temperature, K
T_0 = reference temperature, K
z = axial coordinate, cm
Greek Symbols
α = empirical parameter from Sips equation or selectivity
χ = empirical parameter from the Sips equation
ρ = particle density, g cm^{-3}

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