Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Fractionated Vacuum Swing Adsorption Process for Air Separation

S. Sircarm[a]; B. F. Hanley[a]
[a] AIR PRODUCTS AND CHEMICALS INC., ALLENTOWN, PENNSYLVANIA

To cite this Article Sircarm, S. and Hanley, B. F.(1993) 'Fractionated Vacuum Swing Adsorption Process for Air Separation', Separation Science and Technology, 28: 17, 2553 — 2565
To link to this Article: DOI: 10.1080/01496399308017496
URL: http://dx.doi.org/10.1080/01496399308017496

SEPARATION SCIENCE AND TECHNOLOGY, **28**(17&18), pp. 2553–2565, 1993

Fractionated Vacuum Swing Adsorption Process for Air Separation

S. SIRCAR* and B. F. HANLEY
AIR PRODUCTS AND CHEMICALS, INC.
7201 HAMILTON BOULEVARD, ALLENTOWN, PENNSYLVANIA 18195

ABSTRACT

A novel adsorptive process for air separation using a zeolitic adsorbent is described. The process essentially consists of three simple cyclic steps, and it can be used for simultaneous production of an 80–90% oxygen-enriched gas and a 98+% nitrogen-enriched gas from ambient air. Successful operation of the process requires the use of a zeolite which exhibits high nitrogen adsorption capacity and selectivity from air. The role of nitrogen adsorption selectivity of the zeolite in the vacuum desorption process is examined, and experimental performance data for the air separation process are reported.

INTRODUCTION

Production of oxygen-enriched air containing 23–95% O_2 and nitrogen-enriched air containing 95–99.5% N_2 from ambient air by pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) processes has become a major chemical engineering unit operation during the last 25 years. Numerous process schemes have been designed, and a large number of commercial units in the size range of 100–100,000 standard cubic feet of product gas per day have been installed and operated around the world. These processes use a nitrogen-selective (based on thermodynamic equilibrium) zeolitic adsorbent or an oxygen-selective (based on differences in kinetic rates) carbon molecular sieve adsorbent for fractionation of ambient air. All these processes use a desiccant for removal of ambient

---

* To whom correspondence should be addressed.

water prior to air separation. Some of these key processes have been recently reviewed (1–3).

The growth of research and development in this area has been phenomenal. Figure 1 shows the year-by-year number of basic adsorptive air separation process patents during the last 20 years. The Derwent Patent Index was used for this survey. It may be seen that the number of patents grew almost exponentially from only a few per year in the early 1970s to about 15 per year in the early 1990s. A total of 150 basic patents were published by 60 corporations during this period. Companies from the United States, Japan, and the United Kingdom have dominated this field of research.

One key reason for this growth is that newer and better adsorbents for air separation (both zeolites and carbon molecular sieves) are continuously being introduced with improved selectivity and capacity of adsorption for either N_2 or O_2. That increases the flexibility for designing superior process schemes and obtaining improved separation performance.

Most of the adsorptive air separation processes are designed to produce a single product (O_2-enriched or N_2-enriched gas). The exception is the process developed by Air Products and Chemicals (4) which can simultaneously produce ~90.0% O_2 and 99.0+% N_2 product gases from ambient air using a zeolitic adsorbent. The purpose of this paper is to describe a new process cycle called fractionated vacuum swing adsorption (FVSA) for simultaneous production of oxygen- and nitrogen-enriched air. The

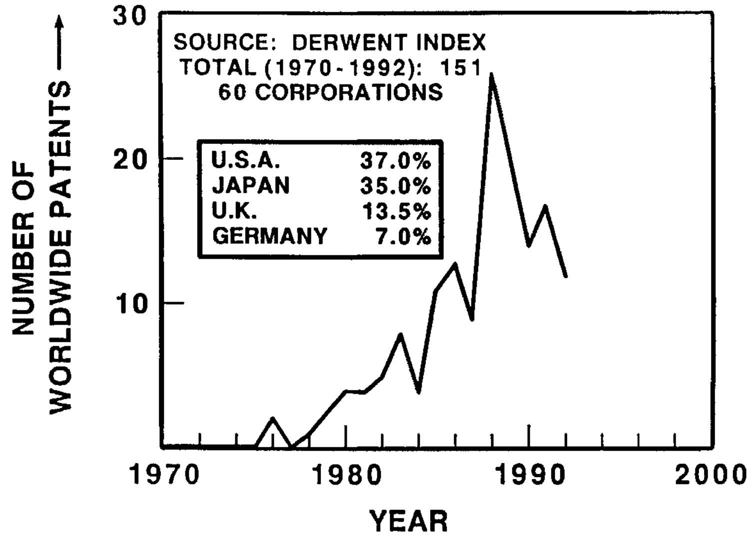

FIG. 1 Patent survey for adsorptive air separation processes.

process uses a zeolitic adsorbent; it has been patented by Air Products and Chemicals (5).

ADSORPTION OF NITROGEN AND OXYGEN ON ZEOLITES

Most aluminosilicate zeolites are polar adsorbents. Consequently, nitrogen is selectively adsorbed over oxygen from air by the zeolites because nitrogen has a larger permanent quadrupole moment than oxygen (3). The nitrogen adsorption capacity and selectivity of a zeolite, however, depend on many factors such as 1) zeolite framework structure; 2) ratio of silica to alumina in the framework; 3) nature, location, concentration, and charge density of cations present in the framework; 4) extent of zeolite dehydration; and 5) pressure, temperature, and concentration of the N_2–O_2 mixture contacted with the zeolite, etc.

Figure 2 shows the pure gas equilibrium isotherms for adsorption of N_2 and O_2 on four different commercial zeolites at 30°C in the pressure range of 0–1.5 atm. The adsorbents are (a) NaX, (b) 5A(Ca-NaA), (c) Na-mordenite, and (d) CaX. The experimental data (circles) were measured in our laboratory using a standard volumetric adsorption apparatus. The figure shows that both the N_2 and O_2 pure gas adsorption capacities of these zeolites, at any pressure, decrease in the order CaX > Na-mordenite > 5A > NaX. The N_2 adsorption isotherms of these adsorbents differ significantly while the O_2 adsorption isotherms are much less affected by the

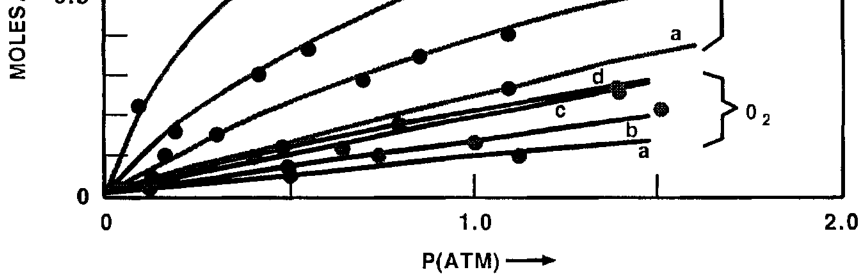

FIG. 2 Pure gas adsorption isotherms of N_2 and O_2 on various zeolites at 30°C.

zeolite structure and the cations present in them. The CaX zeolite, in particular, exhibits very high N_2 adsorption capacity because of the large charge density of the calcium ion.

The isotherms of Figure 2 can be described by the simple Langmuir adsorption model

$$n = \frac{mbP}{1 + bP} \tag{1}$$

where n is the specific amount of a pure gas adsorbed (mol/kg) at pressure P (atm) and temperature T (°K), m is the saturation adsorption capacity (mol/kg) of the pure gas, and b is the Langmuir interaction parameter (atm^{-1}) at T. The solid lines in Fig. 2 are the best fit of the data by Eq. (1). The model parameters are given in Table 1.

The same value of m can be used to describe both N_2 and O_2 isotherms in the range of the data for each zeolite. Consequently, the mixed gas Langmuir adsorption model can be used to describe the adsorption isotherms for binary N_2 (component 1) and O_2 (component 2) mixtures on these zeolites at T:

$$n_i = \frac{mb_iPy_i}{1 + \sum b_iPy_i}, \qquad i = 1, 2 \tag{2}$$

where n_i is the specific amount (mol/kg) of component i adsorbed from a mixture at total gas pressure P having a gas phase mole fraction of y_i for that component.

The selectivity of adsorption $[S = (n_1y_2/n_2y_1)]$ of N_2 over O_2 at any P, T, and y_i, according to Eq. (2), is $[b_1/b_2]$. These selectivity values are also listed in Table 1. S is independent of P and y_i for any given T by the Langmuir model. It may be seen from the table that both the affinity of

TABLE 1

Langmuir Parameters for N_2 and O_2 at 30°C

Zeolite	Saturation capacity m (mol/kg)	Interaction parameter b_i (atm^{-1}) N_2	O_2	N_2/O_2 selectivity ($S = b_{N_2}/b_{O_2}$)
(a) Na-X	3.12	0.083	0.028	2.96
(b) Ca-NaA (5A)	1.41	0.370	0.092	4.00
(c) Na-mordenite	1.47	0.602	0.126	4.78
(d) Ca-X	1.12	2.278	0.224	10.17

adsorption of N_2 (b_1) and its selectivity of adsorption over O_2 increase in the order NaX < 5A < Na-mordenite < CaX. CaX exhibits a much larger affinity and selectivity of adsorption for N_2 than the other zeolites. Interestingly, it has the smallest saturation capacity (m).

AIR SEPARATION BY ZEOLITES

The simplest process concept for separation of air by using a zeolitic adsorbent is described by Fig. 3. An O_2-enriched product gas can be very easily produced by flowing dry air at the adsorption pressure (P_A) through a column packed with the dehydrated zeolite particles which has been presaturated with an O_2-enriched gas of composition y_2^s at P_A. A nitrogen mass transfer zone (MTZ) is formed at the feed end of the adsorber, and it progressively moves toward the oxygen product end as more feed air is passed. The column effluent gas during this process has a composition close to y_2^s until the leading edge of the MTZ reaches the oxygen product end. The total quantity of effluent gas during this period is in excess of the amount of presaturating gas, and the difference can be withdrawn as an oxygen-enriched product gas. The balance can be used to presaturate another column of the process train. A typical O_2 product composition of 50–93 mol% O_2 can be produced by controlling y_2^s. Most practical processes use this simple concept for the O_2 production step. The actual

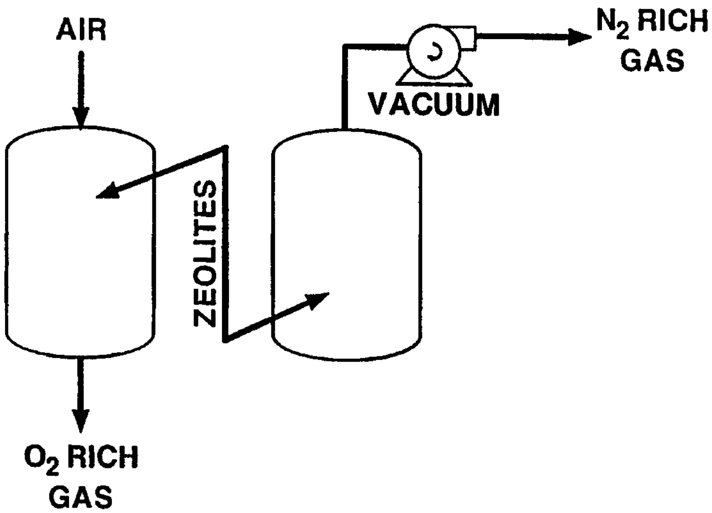

FIG. 3 Simplest concept for air separation using a zeolite.

amount of O_2 produced, however, depends on the properties of the zeolite and the operating conditions.

An N_2-enriched product gas can be obtained by desorbing the adsorbed N_2 from the air-saturated zeolite column by lowering its pressure to a preset level ($P_D < P_A$) as shown by Fig. 3. The N_2 composition of the desorbed gas, however, depends on many factors such as (a) N_2 adsorption capacity and selectivity of the zeolite from air at P_A, (b) the desorption pressure level, (c) adsorbent temperature changes during the desorption process, (d) size of the MTZ for the O_2 production step, (e) amount of intra- and interparticle void gas in the column, etc. The void gas at the end of the adsorption step has an airlike composition, and it dilutes the composition of the desorbed gas. The coadsorbed O_2 in the column saturated with air also lowers the N_2 purity of the desorbed gas. Typically, the desorbed gas has an airlike composition at the start of the desorption process and then becomes more and more N_2 enriched as the column pressure is lowered. Obviously, the larger the N_2 adsorption capacity and selectivity of the zeolite, the smaller will be the dilution of the N_2 product composition by void air and coadsorbed O_2.

ISOTHERMAL LOCAL EQUILIBRIUM MODEL FOR DESORPTION

We examined the isothermal desorption characteristics of zeolite columns saturated with air (79.0% N_2 + 21.0% O_2) at ambient pressure (P_A = 1.0 atm) by using the adsorption properties of four zeolites mentioned earlier. The desorption was actuated by evacuating the columns to a subambient pressure level.

A very simple mathematical model was formulated for this purpose by assuming that (a) the Langmuir mixed gas isotherm (Eq. 2) describes the N_2 and O_2 adsorption capacities on the zeolite at any P and y_i at constant T, (b) local thermodynamic equilibrium between the gas and adsorbed phases prevails at all points in the column during the desorption process, (c) axial mixing and pressure drops in the column are negligible, and (d) the desorption process is isothermal.

For the present case, the O_2 partial pressure (Py_2) in the column never exceeds 0.21 atm. Thus, it was further assumed that the term (b_2Py_2) in the denominator of Eq. (2) was much less than unity for all four zeolites because of the relatively smaller values of b_2. It can be shown by using Eq. (2) and the parameters of Table 1 that this assumption introduces an error of less than 1.6% in calculating n_1 and n_2 when $y_2 \leq 0.21$ and $P \leq$

1.0 atm. Thus, Eq. (2) reduces to

$$n_i = \frac{m b_i P y_i}{(1 + b_1 P y_1)}, \qquad i = 1, 2 \tag{3}$$

The total specific amount ($\bar{n}_i$) of adsorbate i (void gas and adsorbed) in the column at P and y_i is given by

$$\bar{n}_i = n_i + \alpha P y_i; \qquad \alpha = \epsilon/(\rho_b RT) \tag{4}$$

where ϵ is the total (intra- plus interparticle) void fraction in the column, ρ_b is the adsorbent bulk density (kg/L), and R is the gas constant.

The total specific amount (mol/kg) of component i desorbed (N_i) from the column, when the column pressure is P and the gas phase composition is y_i, may be written as

$$N_i = \bar{n}_i^0(P^0, y_i^0) - \bar{n}_i(P, y_i); \qquad dN_i = -d\bar{n}_i \tag{5}$$

The superscript zero in Eq. (5) and elsewhere refers to conditions at the start of the desorption process ($P^0 = 1.0$ atm, $y_1^0 = 0.79$, $y_2^0 = 0.21$).

The total specific amount (mol/kg) of all components desorbed (N) at P and y_i is given by

$$N = \sum N_i; \qquad dN = -\sum d\bar{n}_i; \qquad dN_i = y_i dN \tag{6}$$

It follows that for a binary system ($y_1 + y_2 = 1$):

$$y_2 d\bar{n}_1 = y_1 d\bar{n}_2; \qquad p_2 d\bar{n}_1 = p_1 d\bar{n}_2 \tag{7}$$

p_i (= Py_i) is the partial pressure of component i in the column when the total pressure is P.

Equations (3)–(7) can be solved simultaneously to obtain the following analytic relationships:

$$(p_1/p_1^0) = [(1 + \alpha_1) - \theta]/(\alpha_1 \theta) \tag{8}$$

$$(p_2/p_2^0) = [\{1 + \beta(1 + \alpha_1)\}e^{\chi(\theta)}]/[\theta + \beta(1 + \alpha_1)] \tag{9}$$

$$\chi(\theta) = \frac{(\beta S + 1)}{(\beta + 1)} \ln\left[\frac{\theta + \beta(1 + \alpha_1)}{1 + \beta(1 + \alpha_1)}\right] + \frac{(\beta + S)}{(\beta + 1)} \ln\left[\frac{(1 + \alpha_1) - \theta}{\alpha_1}\right] - \ln \theta \tag{10}$$

where $\alpha_i = b_i p_i^0$, $\beta = \alpha S/mb_1 = \alpha/mb_2$, and $\theta = (1 + b_1 p_1^0)/(1 + b_1 p_1)$.

Using θ as a dummy variable, Eqs. (8)–(10) can be used to calculate p_1 as a function of p_2 during the desorption process. The total gas pressure $[P = \sum p_i]$ as a function of the mole fraction of component i $[y_i = p_i/P]$ in the column can then be easily estimated. The total amount of desorbed gas (N_i and N) from the column at any pressure P can also be calculated using Eqs. (3)–(6).

Figure 4 shows the results of the model calculations. The column temperature was assumed to be 30°C, and the final evacuation pressure was assumed to be 0.092 atm. ϵ and ρ_b were assumed to be 0.69 and 0.64 kg/L, respectively, which are typical values for zeolite pellets. The N_2 mole fraction of the effluent gas from the column is plotted as a function of the fraction desorbed (between the pressure levels of 1.0–0.092 atm) in Fig. 4. The total specific amount of gas desorbed (mol/kg) and the average N_2 composition (mol%) in the mixed desorbed gas are also given in Fig. 4.

It may be seen from Fig. 4 that the effluent gas N_2 mole fraction is initially equal to 0.79 and then increases as more gas is desorbed due to progressive lowering of the column pressure. However, the N_2 composition-desorbed gas quantity profiles and the total amount desorbed are very different for the different zeolites. The desorbed gas N_2 composition increases more rapidly during the desorption process as the N_2 adsorption capacity and selectivity from the air by the zeolite increases. The total amount of desorbed gas also increases under the same conditions. The

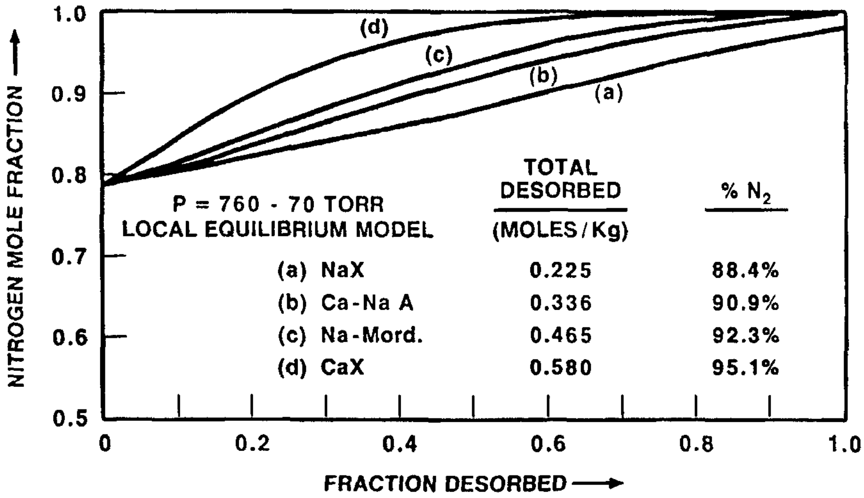

FIG. 4 Model calculation of isothermal desorption of air-saturated zeolite columns.

N_2 composition of the mixed desorbed gases for all of these zeolites, on the other hand, varies only between 88 and 95 mol%. Dilution of the desorbed gas by void and coadsorbed O_2 present in the column at the start of the desorption step prevents the mixed desorbed gas N_2 composition from being higher.

CaX zeolite has a very high selectivity and capacity of adsorption for N_2 over O_2 (Table 1) at 30°C. The adsorbed phase mole fraction of N_2 in the column saturated with air at 1.0 atm is 97.5 mol%, and the N_2 adsorption capacity is 0.71 mol/kg. Yet the dilution caused by coadsorbed O_2 (0.018 mol/kg) and column void O_2 (0.009 mol/kg) lowers the mixed desorbed-gas composition to 95 mol%. Such N_2 product purity is not practically useful. An N_2 product purity of 98% or more is desirable.

This problem was resolved in the earlier Air Products VSA process for simultaneous production of O_2- and N_2-enriched product gases by introducing an N_2-rinse step after the air adsorption step (4). The purpose of that step was to displace the void and coadsorbed O_2 remaining in the column at the end of the air saturation step by flowing a stream of pure N_2 through the column. The effluent during this step was airlike, and it was recycled as feed gas or rejected. Consequently, the column was saturated with essentially pure N_2 before the evacuation step, and the subsequent desorbed gas was high purity (99+ mol%) N_2. A part of the desorbed gas was withdrawn as the N_2 product gas, and the balance was used as the N_2-rinse gas.

FRACTIONATED VACUUM SWING ADSORPTION (FVSA) PROCESS

A closer inspection of the model air desorption characteristics of the zeolites in Fig. 4 shows that NaX, 5A, and Na-mordenite can barely make 98+% N_2-enriched gas at the very end (low pressure region) of the process. On the other hand, the CaX zeolite, with its relatively high N_2 adsorption capacity and selectivity from air, produces a decent amount of high purity N_2 at the lower pressure levels during the desorption process. This observation led to the development of the fractionated vacuum swing adsorption process described below.

Figure 5 shows a schematic flow sheet of the FVSA process. It consists of two parallel adsorbers (I and II) packed with a layer of alumina (desiccant) at the feed air end followed by a layer of zeolite (high N_2 capacity and selectivity) for air separation. It also contains two vacuum pumps (V_1 and V_2), gas storage tanks, an optional N_2 product compressor (C), and

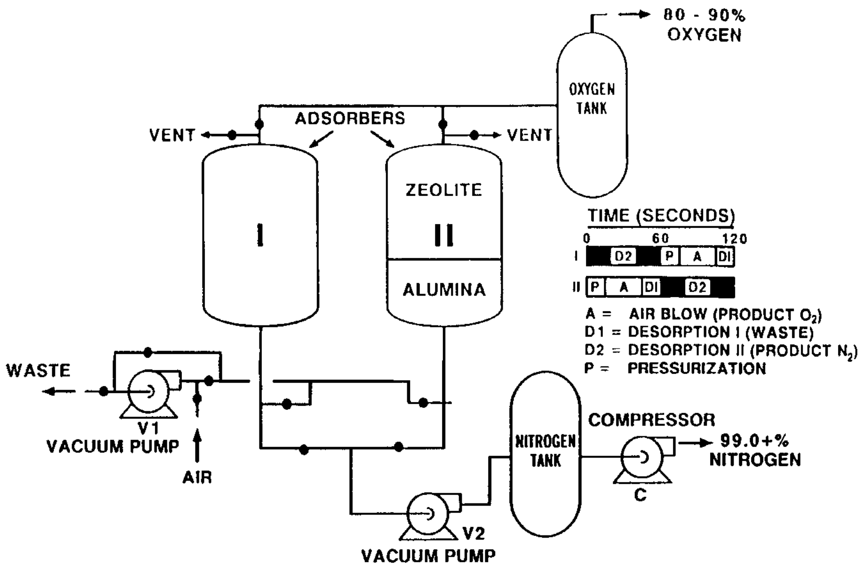

FIG. 5 Schematic flow diagram for the FVSA process.

necessary switch valves and gas headers. The cyclic process steps of the FVSA process are very simple, consisting of:

1. *Adsorption Step*: Where air at near-ambient pressure (P_A) is passed through an adsorber which is presaturated with an 80–90% O_2-rich gas. The effluent is an 80–90% O_2-enriched gas which is partly stored and the balance withdrawn as the product O_2. The step is continued until the N_2 mass transfer zone reaches the exit end of the column. The effluent is then vented until the column is saturated with air.
2. *Desorption Step I*: Where the column is evacuated countercurrently to an intermediate vacuum level (P_I) and the effluent gas is wasted.
3. *Desorption Step II*: Where the adsorber is further evacuated countercurrently to the final desorption pressure (P_D) and the effluent is collected as the 98+% N_2 product gas which may be recompressed.
4. *Pressurization*: Where the column is countercurrently repressurized to the near-adsorption pressure level with a part of the O_2-enriched gas produced and stored during Step 1. A new cycle is then started.

The process step cycle times are arranged in such a way that a continuous N_2 product gas is obtained from the system. One of the adsorbers is always undergoing Step 3 of the process, and vacuum pump V_2 is continuously engaged to carry out that step. Vacuum pump V_1 plays a double role. It acts as an air blower during Step 1 of the process and as a vacuum blower during Step 2 of the process. Figure 5 gives an example of the cycle time format for the process with a total cycle time of 120 seconds.

One of the advantages of this process is that the product N_2 is fairly dry because most of the water introduced into the adsorber during Step 1 is desorbed during Step 2 which is rejected.

The FVSA process eliminates the N_2-rinse step of our previous process for making high-purity N_2 and substantially simplifies its operation. It, however, demands that a zeolite with a high N_2 capacity and selectivity from air be used. Such requirements were not necessary for our previous process. These two processes are good examples of matching the adsorbent properties with process design.

PERFORMANCE OF THE FVSA PROCESS

We tested the FVSA process cycle using a bench-scale process development unit. The adsorber was 2.0 inches in diameter and 72.0 inches long. CaX zeolite was used as the adsorbent. The feed air pressure (P_A) was 1.1 atm, and it was supplied at the ambient temperature. The final vacuum level (P_D) in the column was 0.092 atm. Cyclic steady-state performance of the process was typically achieved after 10 cycles of operation.

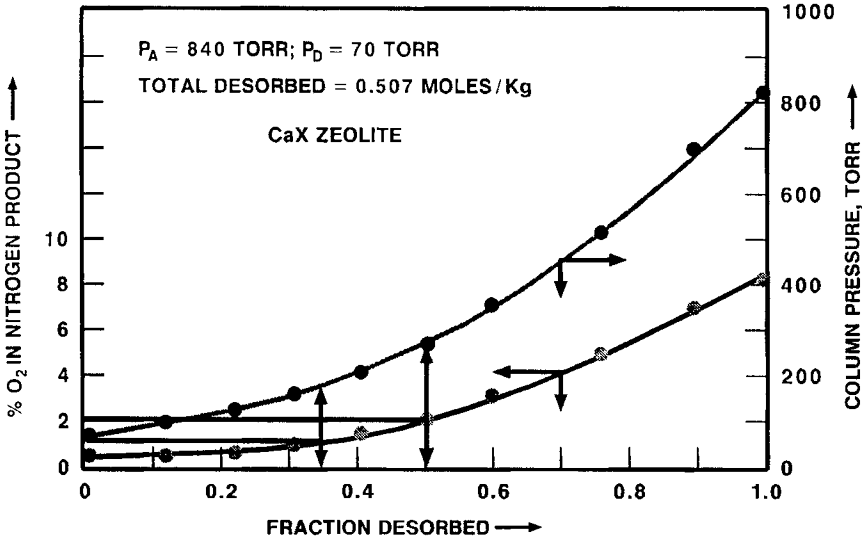

FIG. 6 Experimental desorption characteristics of CaX zeolite in the FVSA process.

TABLE 2
Performance of FVSA Process for Air Separation (CaX Zeolite)

Oxygen product			Nitrogen product		
Purity (%)	Recovery (%)	Capacity (mol/kg)	Purity (%)	Recovery (%)	Capacity (mol/kg)
90.0	24.2	0.04	99.0	30.0	0.17
			98.0	42.6	0.25

Figure 6 shows a set of cyclic steady-state performance data. It gives the mol% of O_2 in the N_2 product gas as a fraction of the total desorbed gas in Steps 2 and 3 of the process. The specific quantity of gas desorbed in these steps was 0.51 mol/kg. The figure also gives the intermediate column pressure (P_I) corresponding to the fraction desorbed.

The composition of O_2 ($\bar{y}$) in the N_2 product was calculated by integrating the experimental steady-state desorbed gas quantity–purity profile starting from the low pressure end:

$$\bar{y} = \left[\int_0^{Q(P_I)} y dQ\right] \Big/ \left[\int_0^{Q(P_I)} dQ\right] \tag{11}$$

where Q is the amount of gas desorbed between the column pressure levels of P_D and P_I. Thus, Q is set equal to zero when the column pressure is P_D. Q is equal to 0.51 mol/kg when the column pressure is P_A. y is the instantaneous O_2 mole fraction of the desorbed gas when the column pressure is P_I. y is practically equal to zero when Q is zero.

It may be seen from Fig. 6 that the process can easily make 98+% N_2 product purity. About 34.0 and 50.0% of the total desorbed gas can be collected as the product N_2 at purity levels of 99.0 and 98.0 mol% N_2, respectively. The intermediate column pressure level (P_I) for these purities are, respectively, 0.24 and 0.37 atm. Thus they represent the cutoff pressure levels between Steps 2 and 3 of the process.

The overall performance of the FVSA process for simultaneous production of O_2- and N_2-enriched product gases using the operating conditions described in Figure 6 is summarized in Table 2. It reports the net specific production capacities and the recoveries of these components from feed air at different product concentration levels. It may be seen that a very simple process like the FVSA process can be used to fractionate air with very good separation efficiency.

REFERENCES

1. S. Sircar, "Pressure Swing Adsorption Technology," in *Adsorption: Science and Technology* (NATO ASI Series E), (A. E. Rodrigues et al., Eds.), Kluwer Academic Publishers, The Netherlands, *158*, 285 (1989).
2. H. J. Schroter and H. Juntgen, "Gas Separation by Pressure Swing Adsorption Using Carbon Molecular Sieves," *Ibid.*, *158*, 269 (1989).
3. S. Sircar, *Sep. Sci. Technol.*, *23*(6&7), 519 (1988).
4. S. Sircar and J. W. Zondlo, "Fractionation of Air by Adsorption," U.S. Patent 4,013,429 (1977).
5. S. Sircar, "Vacuum Swing Adsorption Process for Production of 95–99% N_2 from Air," U.S. Patent 5,084,075 (1992).

Received by editor February 26, 1993