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REVIEW

Vacuum Swing Adsorption Process for Oxygen Production—A Historical Perspective

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ABSTRACT

Adsorbent and cycle developments for the last 25 years have resulted in the advancement of vacuum swing adsorption processes for the production of oxygen from air, and in this review are traced and critically examined. The key criteria in the past developments and for future improvements are identified.

INTRODUCTION

Oxygen is a commodity chemical in the industrial gas industry. It has numerous applications including wastewater treatment, glass melting furnaces, and the steel industry. One of the most common methods of oxygen production is by cryogenic distillation of air. However, this technology is not competitive for small size oxygen plants i.e., less than 100 TPDc (tons per day contained) oxygen, especially when high purity oxygen is not required. The technology of choice for this size range is adsorption. The two major categories of adsorption processes used in oxygen production are pressure swing adsorption (PSA) processes and vacuum swing adsorption (VSA) processes. The PSA processes carry out the feed step at pressures much higher than the ambient, and adsorbent regeneration at pressures close to ambient. The VSA processes on the other hand, carry out the feed step at pressures close to the ambient and the adsorbent regeneration at sub-atmospheric pressures. Since selectivity of nitrogen over oxygen decreases as pressure increases, a greater amount of oxygen is coadsorbed and then lost during the regeneration step in the PSA than in the VSA processes. This results in lower oxygen recovery from the PSA than the VSA processes. Also, the entire feed air stream has to be compressed in the PSA processes as compared with the evacuation of only the waste gas in the VSA processes. Those two factors result in higher energy consumption per unit of oxygen production for the PSA processes than for the VSA processes. On the other hand, the PSA process is inherently simpler and therefore has a capital advantage over VSA processes. At present, PSA is the process of choice for productions of less than ~15 TPDc oxygen. Above this, VSA is generally the process of choice for producing low purity oxygen.

In the past 25 years, significant advances have been made in the VSA technology for oxygen production. These have been both in the areas of adsorbent and process cycle development. Highlights of these advances are summarized in the following discussion.

ADSORBENT DEVELOPMENT

There are usually at least two layers of adsorbents used in oxygen VSA adsorbent beds. The adsorbent toward the feed end of the vessel is called the "pretreatment" adsorbent. Its main function is to remove water and carbon dioxide from the feed air. Alumina has generally been used as the pretreatment adsorbent. However, as the understanding about cold spots, discussed later, has advanced, alumina has been replaced by NaX-type zeolites. This helps to reduce the severity of cold spots due to its higher N_2, O_2 loading and higher heat of adsorption as compared against alumina. Higher capacity NaXs have been developed to further reduce the effect of cold spots.

The second layer of adsorbent toward the product end of the vessel is called the "main adsorbent." Its primary function is N_2, O_2 separation. It is invariably a zeolitic material which preferentially adsorbs nitrogen over oxygen due to its electrostatic field and small quadrapole moment of nitrogen. The emphasis in adsorbent development has been on improving the main adsorbent. In some instances, NaX has been used as both the main and the pretreatment adsorbent. However, CaA-type zeolitic materials have been the most commonly used O_2 VSA main adsorbents (1). The next improved class of adsorbents was the CaX-type zeolitic materials (2), and recently LiX (3–6) and MgA (7) type materials have become prominent in this application.

There are three process parameters which dictate the choice of the main adsorbent for oxygen VSAs (8): Oxygen recovery, feed processed per unit weight of the adsorbent, and cubic feet per mole of the evacuated gas (EVAC). Out of these three, oxygen recovery is the most critical parameter. If it is assumed that the process is isothermal and there is no oxygen left in the bed at the end of the evacuation step, a simplified expression can be written for oxygen recovery in terms of equilibrium parameters:

$$\begin{aligned} O_2\text{, recovery} &= 1 - \frac{\text{oxygen lost}}{\text{oxygen fed}} \\ &= 1 - \frac{n_{N2i}}{S\Delta n_{N2}} - \frac{PY_{N2i}\epsilon}{RT\rho_b\Delta n_{N2}} \end{aligned} \tag{1}$$

where

$$S = \frac{n_{N2i}}{Y_{N2i}}\frac{Y_{O2i}}{n_{O2i}}$$

The last term on the right-hand side of Eq. (1) is oxygen lost due to external bed voidage, and the second term on the right-hand side of Eq. (1) is oxygen lost due to coadsorbed oxygen. The contribution to losses due to voids is ~15%. Therefore, the main loss in oxygen recovery is due to coadsorbed oxygen which is lost during the evacuation step. Table 1 lists equilibrium properties for typical oxygen VSA adsorbents. Trends in oxy-

TABLE 1
Typical Oxygen VSA Adsorbents and Comparative Performance[a]

	Zeolitic adsorbents							
	NaX[b]		CaA[c]		CaX		LiX	
	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2
m_1, gmol/g	1×10^{-3}		0.7×10^{-3}		1.1×10^{-3}		2×10^{-3}	
b_0, 1/kPa	5.13E-07	8.88E-07	1.97E-07	1.28E-06	9.9E-08	1.18E-06	1.78E-07	8.49E-07
q_2, cal/gmol	5100	3500	6300	3500	7600	4500	6600	4000
m_2, gmol/g	6×10^{-3}		3.2×10^{-3}		5.5×10^{-3}		5×10^{-3}	
d_0, 1/kPa	4.44E-07	1.48E-06	1.38E-07	1.38E-06	3.26E-07	1.18E-06	1.18E-07	8.29E-07
q_2, cal/gmol	3800	2800	5200	3500	3800	2700	4700	3000
Feed processed (g mol/g)	2.8E-04		4.2E-04		5.1E-04		8.6E-04	
O_2, recovery (%)	47		54		71		82	
EVAC (cc/g mol)	6.71E04		6.81E04		7.29E04		6.89E04	

[a] For all cases, operating conditions: at the start of evacuation: $P = 101.3$ kPa, $T = 25°C$, Y, $N_2 = 0.79$. At the end of evacuation: $P = 20.3$ kPa, $T = 25°C$, Y, $N_2 = 1$. External bed voidage, $\epsilon = 0.37$. Bulk density, $\rho_b = 0.672$ g/cm^3.

[b] Commonly known as 13X molecular sieve.

[c] Commonly known as 5A molecular sieve.

gen recovery as calculated from Eq. (1) are also listed. As observed, significant gains have been made in oxygen recovery by improving the main adsorbent.

The second important parameter is feed processed per unit weight of the adsorbent. Neglecting the gas phase accumulation in addition to the above assumptions:

$$\text{Feed processed} = \Delta n_{\mathrm{N2}}/Y_{N2\mathrm{i}}$$

Table 1 shows the increasing trend in this parameter with main oxygen VSA adsorbents.

The third parameter, EVAC, is used to size the vacuum pump and is one of the key parameters in determining the power consumption for these processes. For systems described by a dual site Langmuir model:

$$n_{\mathrm{i}} = \frac{m_1 b_{\mathrm{i}} P Y_{\mathrm{i}}}{1 + b_{\mathrm{i}} P Y_{\mathrm{i}} + b_{\mathrm{i}} P(1 - Y_{\mathrm{i}})} + \frac{m_2 d_{\mathrm{i}} P Y_{\mathrm{i}}}{1 + d_{\mathrm{i}} P Y_{\mathrm{i}} + d_{\mathrm{i}} P(1 - Y_{\mathrm{i}})}$$

where

$$b_{\mathrm{i}} = b_{\mathrm{i0}} \exp(q_{\mathrm{i1}}/RT)$$

$$d_{\mathrm{i}} = d_{\mathrm{i0}} \exp(q_{\mathrm{i2}}/RT)$$

and

$$\mathrm{i} = \mathrm{N_2} \text{ or } \mathrm{O_2}$$

The following simplified expression can be written for EVAC if, as a further simplification, oxygen coadsorption is neglected:

$$\mathrm{EVAC} = \frac{RT}{\Delta n_{\mathrm{N2}}}\left[m_1 b\left\{\ln\frac{P_{\mathrm{i}}(1 + bP_{\mathrm{f}})}{P_{\mathrm{f}}(1 + dP_{\mathrm{i}})} - \frac{b(P_{\mathrm{i}} - P_{\mathrm{f}})}{(1 + bP_{\mathrm{i}})(1 + bP_{\mathrm{f}})}\right\}\right.$$
$$\left. + m_2 d\left\{\ln\frac{P_{\mathrm{i}}(1 + dP_{\mathrm{f}})}{P_{\mathrm{f}}(1 + dP_{\mathrm{i}})} - \frac{d(P_{\mathrm{i}} - P_{\mathrm{f}})}{(1 + dP_{\mathrm{i}})(1 + dP_{\mathrm{f}})}\right\}\right]$$

Table 1 lists values of EVAC for typical oxygen VSA adsorbents. As can be seen, EVAC has more or less remained constant for these oxygen VSA adsorbents. However, by increasing the recovery and feed processed per unit weight of the adsorbent while keeping EVAC constant, the performance of oxygen VSA processes has been continuously improved.

Reflections on the coadsorbed oxygen lost term in Eq. (1) reveal that low oxygen capacity at comparable nitrogen capacity is the key for better oxygen VSA adsorbents. In other words, simply increasing nitrogen capacity is not desirable if it is not accompanied by a more than proportional increase in selectivity.

CYCLE DEVELOPMENT

One of the first processes for producing oxygen by regenerating adsorbent under vacuum was outlined by Tamura (9). The vacuum swing adsorption (VSA) process outlined in this patent is divided into two stages. The first stage consists of a pair of adsorbent beds capable of removing water and carbon dioxide from air. These pretreatment beds are normally regenerated by pulling vacuum through them but also have the capability of being regenerated by flowing a hot purge gas over the adsorbent. While one of the pretreatment beds is regenerated by hot purge gas, the other pretreatment bed is used to process the ambient air to produce water and carbon-dioxide-free clean air. The second stage consists of one main bed per pair of the pretreatment beds, filled with an adsorbent capable of removing nitrogen from clean air and producing oxygen.

The entire process scheme consists of three main beds and six pretreatment beds. This is required to ensure continuous operation of the feed blower and the vacuum pump. The three primary process steps, shown in Fig. 1 for the main beds are:

1. Feed ambient air through the pretreatment bed and then clean air through the main bed, producing high purity oxygen
2. Countercurrent (to feed flow direction) evacuation to regenerate both the main and the pretreatment beds
3. Countercurrent repressurization from evacuation pressure to feed pressure by product oxygen from the product end

As an option, feed flow to the system could be continued at the end of the first step but the effluent, which now contains oxygen less than desired in the product but more than in the feed air and is water–carbon dioxide free, is fed to the other main bed to produce high purity oxygen. This "second-cut feed" is stopped when effluent from the main bed has oxygen concentration similar to ambient air.

Bed #			
1	Feed/Product	Evacuation	Repressurization
2	Repressurization	Feed/Product	Evacuation
3	Evacuation	Repressurization	Feed/Product

FIG. 1 Cycle chart for the proposed oxygen VSA in US Patent 3,533,221 (9).

The example in the patent quotes 60% oxygen recovery at 80% oxygen purity and requires about 608 kg of adsorbent for producing one *t*on *p*er *d*ay of *c*ontained (TPDc) oxygen. Feed pressure in the example is 1.5 atm and the evacuation pressure is 145 mmHg. The main bed was 95 cm long and had a 5-cm internal diameter, and was packed with a natural adsorbent found in the Chugoku district of Japan. This adsorbent was dehydrated at 600°C. The pretreatment bed was 10 cm long and had a 5-cm internal diameter. Use of synthetic zeolites CaA and NaX as main adsorbents and silica gel and activated alumina as pretreatment adsorbents is mentioned.

Tamura has clearly identified the possibility of producing oxygen by the VSA technique and the advantages of product repressurization before starting the feed step. He also identified the need to remove water and carbon dioxide from ambient air before processing this gas for nitrogen–oxygen separation and the possibility of regenerating adsorbent laden with water and carbon dioxide by evacuation.

Armond and Webber (10) simplified the pretreatment system by eliminating the heating step and regenerating the pretreatment beds only by evacuation. This reduced the number of pretreatment beds to one per main bed. Therefore, the total number of vessels was reduced from nine in the Tamura cycle to six in this process. Also, the possibility of combining pretreatment and main beds in a single vessel was mentioned, further reducing the total number of vessels to a total of three. They also added another step of countercurrent vent after the feed step in the Tamura cycle.

The listed examples mention the use of CaA zeolite as the main adsorbent at a feed pressure of 1.5 atm and an evacuation pressure of 150 mmHg. However, numerical values for process performance are not given.

Drissel and Sircar (11) suggested the removal of water and carbon dioxide by pulling deeper vacuum on the pretreatment beds. This is achieved by stopping the communication between the main and the pretreatment beds during the evacuation step and continuing evacuation of only the pretreatment beds. The cycle is simplified by eliminating the second-cut feed option of Tamura and the countercurrent vent step of Armond and Weber. The number of vessels is also reduced to two each for main and pretreatment beds, but an expandable ambient pressure bag is added to maintain the continuous operation of the vacuum pump. The importance and difficulty of removing water and carbon dioxide from ambient air is clearly reemphasized. For the first time, the possibility of producing 95% oxygen from air is mentioned. However, an final evacuation pressure of 10 mmHg is required in the main beds. 90% oxygen is produced by reducing it to ~20 mmHg and 80% oxygen is produced by reducing the final evacuation pressure in the main beds to 72 mmHg. 1058 kg of main adsorbent per TPDc oxygen at 90% product purity is quoted. Even though the productivity from the suggested cycle is higher than in previous processes, the capital cost advantage is more than lost due to higher power consumption required to pull the deep vacuum and the maintenance costs associated with variable volume storage tank.

Armond and Ray (12) packed the pretreatment and main adsorbents in the same vessel as hinted in US Patent 3,923,477 (10). In addition, two new concepts were introduced. First, the feed blower is eliminated and air feed is sucked into the beds by pulling air from the product end of the bed. The pressure in the bed during the feed-production step is therefore below ambient pressure. Second, the bed is purged by product oxygen while it is being evacuated. This concept takes advantage of the fact that bed purging for regeneration is more effective at lower pressures. Both two- and three-bed options are outlined. The vacuum pump is operated continuously in the three-bed option but is discontinuous for the two-bed option.

Reiss (13) extended the concept of vacuum purge by providing the purge gas by cocurrently depressurizing the bed which has just finished the feed-production step. This eliminated the need to use high purity product for purge. Also, since the purge step is followed by repressurization by the high purity product, vacuum purge by somewhat impure gas does not effect the process performance. The quoted examples, with CaA zeolite as the main adsorbent, show a reduction in adsorbent requirement from 981 to 872 to 760 kg of main adsorbent per TPDc oxygen product at 90% purity for no purge, product purge, and the above-mentioned provided purge concept, respectively. The adsorbent requirements for 80% oxygen product are 736, 688, and 650 kg per TPDc for the three cases, respectively. Another advantage of this process cycle is that by not using high purity product for purge, effective oxygen recovery in increased.

Hirooka and Miyoshi (14) introduced two new concepts for three-bed oxygen processes. First, one or two pressure equalizations between the beds which have finished feed-production and vacuum purge steps. The product end of the bed providing the pressure equalization gas is connected with the product or the feed end of the bed receiving the pressure equalization gas. Second, while the bed is receiving pressure equalization gas from the product end, it is also repressurized by air from the feed end. The entire cycle depicted in Fig. 2 has the following steps:

1. Feed → product
2. Cocurrent depressurization (CoC DP) to provide first pressure equalization (PE1) gas

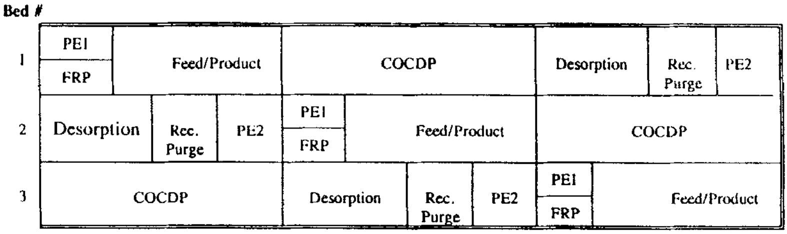


FIG. 2 Cycle chart for the oxygen VSA process in UK Patent GB 2,154,895B (14), COCDP = cocurrent depressurization, PE = pressure equalization, FRP = feed repressurization, Rec. Purge = receive purge.

3. Cocurrent depressurization to provide purge gas
4. Cocurrent depressurization to provide second pressure equalization (PE2) gas
5. Desorption by countercurrent evacuation (CCC EVAC)
6. Vacuum purge by gas from Step 3 (Rec. Purge)
7. Second pressure equalization (PE2) by gas from Step 4
8. Simultaneous first pressure equalization (PE1) by gas from Step 2 and feed repressurization (FRP)

Examples in the patent using NaX zeolite adsorbent quote 716 kg of adsorbent requirement per TPDc oxygen at 93%, and 890 kg of adsorbent per TPDc oxygen at 95% product purity for the one-pressure equalization option. For the two-pressure equalization option, 1041 kg of adsorbent per TPDc oxygen at 95% oxygen product purity is quoted. Surprisingly, the recovery for the two-pressure equalization option is also lower. This patent clearly demonstrated the feasibility of pressure equalizations in a vacuum swing adsorption process and demonstrated the superiority of one-pressure equalization over two-pressure equalization for these processes.

Haruna et al. (15) extended the concept of pressure equalization to a three-bed process to emphasize that the time of pressure equalization should be shortened so that the quantity of nitrogen transferred from one bed to the other is minimized. They accomplish this by simultaneously evacuating the bed from the feed end while the same bed is being used to provide pressure equalization gas to the other evacuated bed. By using a CaA adsorbent they decreased the adsorbent requirement from 1068 kg per TPDc to 758 kg per TPDc oxygen at 93% by emphasizing the concept of simultaneous cocurrent depressurization and countercurrent evacuation. Oxygen recovery also increased from 41 to 47%.

Largee and Leavitt (16) outlined a two-bed oxygen VSA process which included some of the features such as vacuum product purge and pressure equalization steps developed for the three-bed processes. This patent application marked the beginning of competitive cycle development for an efficient two-bed oxygen VSA process. Prior to this, the three-bed processes were considered to be the "state of art" in oxygen VSA. The outlined process had discontinuous feed blower and vacuum train operation. It also used only feed air for repressurization.

Haruna et al. (17) outlined a more efficient two-bed process for oxygen production. The process cycle chart as shown in Fig. 3 consists of the following steps:

1. Feed → product
2. Cocurrent depressurization (CoC DP) to provide purge gas
3. Simultaneous cocurrent depressurization (CoC DP) to provide pressure equalization (PE) gas and countercurrent evacuation (CCC EVAC)
4. Desorption by countercurrent evacuation (CCC EVAC)
5. Countercurrent purge by product from the storage vessel (Prod. Purge)
6. Countercurrent purge by the cocurrent depressurized gas in Step 2 (Rec. Purge)
7. Simultaneous product repressurization with the product gas from the storage vessel (Prod. RP), and pressure equalization with the gas from the cocurrent depressurization gas in Step 3 (F/PE)
8. Simultaneous product repressurization with the product gas from storage vessel, and repressurization by feed air (FRP)

Clearly, many of the features developed for the three-bed cycles have been integrated in the two-bed process. The main advantage of these pro-

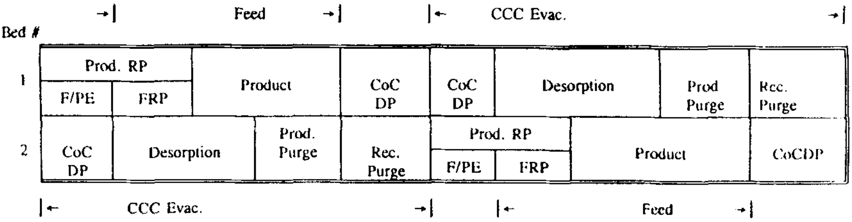


FIG. 3 Cycle chart for the oxygen VSA process in US Patent 4,917,710 (17). Prod. RP = product repressurization, COCDP = cocurrent depressurization, CCC Evac. = countercurrent evacuation, Prod. Purge = product purge, Rec. Purge = receive purge, F/PE = pressure equalization by providing the gas to the feed end, FRP = feed repressurization.

cesses over the prior three-bed processes is the use of two beds, therefore, by turning over the beds faster, higher adsorbent productivity is realized. Haruna et al. (17) reported only 346 kg of CaA adsorbent requirement per TPDc at 93.3% oxygen production. In addition, product repressurization along with product and provide purges are carried out. However, the feed blower operates discontinuously.

The problem of discontinuous feed blower was resolved by Reiss (18). The cycle shown in Fig. 4 consists of the following steps:

1. Feed → product
2. Simultaneous cocurrent depressurization (CoC DP) and countercurrent evacuation (CCC Evac.)
3. Countercurrent evacuation (CCC Evac.)
4. Simultaneous pressure equalization by CoC DP gas from Step 2 and feed repressurization (FRP)
5. Simultaneous feed and product repressurization (F/PRP)

As an option, countercurrent evacuation in Step 2 is replaced by a feed step, and the corresponding feed repressurization in Step 4 is replaced by countercurrent evacuation. The preferred option produces 93% oxygen using 349 kg CaA adsorbent per TPDc oxygen.

Many two-bed oxygen VSA patents followed with some minor variation in the above-mentioned cycles. Two significant ones are US Patent 5,122,164 issued to Hirooka et al. on June 16, 1992 (19) and US Patent 5,223,004 issued to Eteve et al. on June 29, 1993 (20).

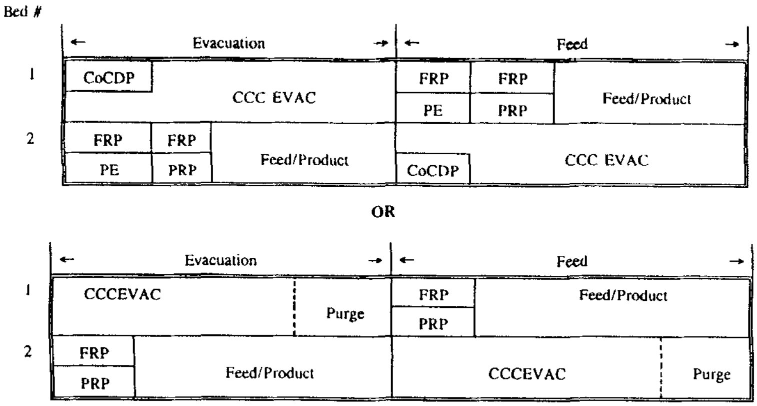


FIG. 4 Cycle chart for the oxygen VSA processes in US Patent 5,015,271 (18). COCDP = cocurrent depressurization, CCC Evac. = countercurrent evacuation, FRP = feed repressurization, PE = pressure equalization, PRP = product repressurization.

Kumar et al. (21) introduced the concept of ambient air repressurization in two- and three-bed oxygen VSA processes. By properly balancing the amount of ambient air and product used for repressurization, oxygen recovery of ~63% is claimed. This recovery is based upon the air fed through the blower. Since ambient air used in repressurization does not require compression, this concept reduces power consumption.

The trends in oxygen VSA have been to simplify the process scheme, reduce power, reduce capital, and increase the production range. The above discussion clearly demonstrates the attempts at simplifying the process scheme and reducing power. As the process scheme is simplified, capital is also reduced. However, another method to reduce capital is by decreasing the cycle time. All oxygen VSA processes consist of two primary steps: production and regeneration. The total time it takes one bed to finish its production and regeneration steps and return to the starting production step is termed the cycle time. As the cycle time reduces, the adsorbent is cycled more frequently and therefore the adsorbent is in the production mode more often, increasing the total production per day, and therefore, increasing production from the same plant or reducing capital cost for the same production. However, in oxygen VSA, since regeneration is carried out by evacuation and regeneration time also decreases with cycle time, pressure drop during the evacuation step increases with the decreasing cycle time. This in turn results in increasing specific power consumption as cycle time decreases. To counteract the increase in power consumption, one has to reduce the adsorbent bed length in oxygen VSAs. At present, the bed lengths are usually between 6 to 8 feet and the corresponding cycle time is between 60 to 90 seconds. Efforts to further reduce the cycle time are restricted by the minimum time required to open and close valves in the system. This is usually around 5 seconds, and the minimum occurs during the pressure equalization step. Processes with even shorter cycles have been mentioned in the literature (22).

Production capacities from oxygen VSAs are also limited by the size of the vacuum train. The largest vacuum trains are typically capable of producing 80–100 TPDc oxygen depending upon the adsorbent used. Therefore, to increase production, one approach is to install multiple trains of VSA units. Another, and more efficient approach is to install multiple vacuum trains in a properly integrated multibed system.

One such example was illustrated by Engler et al. (23). The inventors suggested the use of two different types of vacuum pumps, one volumetric and the other centrifugal, each in its preferred range of pressure operation to minimize power consumption. The process utilizes five beds to increase production from a "single" train. Hay (24) extended the same idea to a three-bed system.

Kumar et al. (25) outlined a four-bed system integrated with two vacuum trains. The cycle in this process, Fig. 5, is integrated such that any one bed is on "extended" evacuation, thereby reducing power consumption for similar production or increasing production for similar power consumption. The illustrated examples compare the performance of this four-bed process against a comparable three-bed process. At similar specific power (~9.5 kW/TPDc) this process shows ~55% more production by using only ~33% more adsorbent. At similar production (~73–80 TPDc), the four-bed cycle consumes about 10% less specific power.

Still another limitation in oxygen VSAs is caused by fluidization considerations. Diameter of adsorption vessels is calculated based upon maximum allowable velocity for fluidization. Therefore, vessel diameter has to increase as the plant capacity increases. However, transportation considerations and cost and availability of vessel heads limit the maximum vessel diameter to about 5 m. To further increase the production, horizontal or crossflow beds are used. As compared against the vertical beds (Fig. 6a), horizontal (Fig. 6b) and crossflow (Fig. 6c) beds flow the feed gas parallel to the bed diameter. In both of these configurations the area of cross-section along which the feed gas flows first increases and then decreases in the direction of flow. This causes an increase in the fluid velocity along the curved wall after the central plane of the bed. This in turn results in early fluidization at the top layer of the horizontal bed near the curved wall (small circles in Fig. 6b). Therefore, the feed velocity through the horizontal vessels has to be lower than allowed for vertical vessels. However, plant capacity can be increased without any limits simply be extending the vessel length.

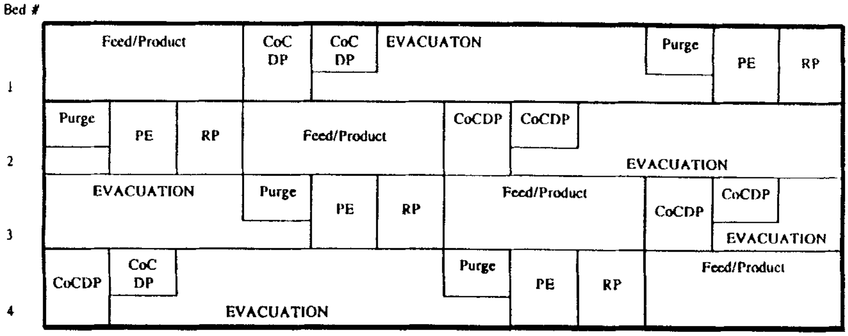
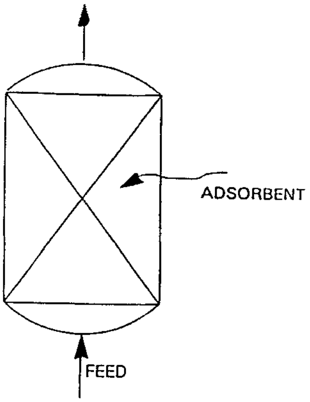
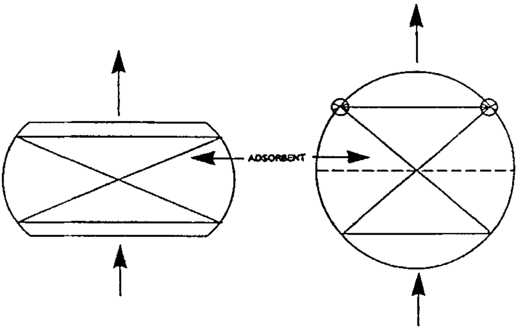


FIG. 5 Cycle chart for the oxygen VSA process in US Patent 5,330,561 (25). COCDP = cocurrent depressurization, PE = pressure equalization, RP = repressurization.

(a) Vertical Vessel



(b) Horizontal Vessel



(c) Cross-flow Vessel

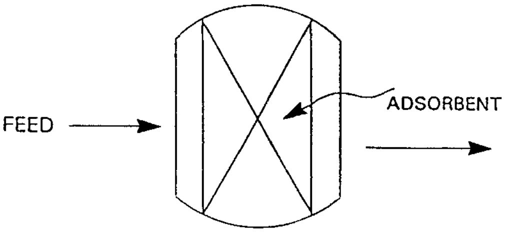


FIG. 6 Various vessel geometries for oxygen VSA processes.

The crossflow vessel, in addition, has the disadvantage that a gas by-pass along the top vessel header may occur due to adsorbent settling. Hay and Vigor (26) outlined a mechanism to continuously fill the top layer of the bed and avoid the gas by-pass.

Still another method to increase production from an oxygen VSA process while avoiding the fluidization concerns is to employ multiple decks of beds in a single vertical vessel (27, 28).

COLD SPOTS

A unique problem with adsorptive separation processes for producing oxygen from air is the formation of cold spots in the bed. Temperature at the inlet end of the bed, especially at the interphase of the two different adsorbent layers, cools down to very low levels (up to ~-70°F). This phenomenon adversely affects the performance of these processes. This effect is even more challenging since it is observed only in adiabatic beds and therefore always missed in small diameter lab columns. This usually results in optimistic plant designs and failure in the field. Collins (29) first mentioned this effect for an oxygen pressure swing adsorption process. The suggested solution for cold spots was to heat the feed air. Later, Collins (30) also suggested another solution for the same problem by employing vertical, metal-conducting plates from the bed support. These plates transferred heat from the "hot" sections of the bed to the cold spots, thus reducing the temperature depressions and improving the process performance. Similar concepts were later outlined by Haruna and Shiozawa (31), Gardner and Garett (32), and Toppel (33). Armond (34) also suggested the installation of a heater at the cold spot location inside the adsorbent beds. Leavitt (35) employs two thermal regenerators inside the adsorbent bed to take advantage of the cold spots and stabilize the axial temperature in the bed at a uniform but lower level.

The primary reason for the cold spots is the difference between adsorption characteristics, loading and heat of adsorption, of the different layers of adsorbents used in the bed. Generally an adsorbent with lower nitrogen and oxygen capacities and heats of adsorption is employed at the feed end of the bed to remove water, and one with higher capacities and heats of adsorption is employed at the product end of the bed for main separation. This difference in adsorption characteristics causes the formation of cold spots. The larger the difference, the lower the temperature drop in the cold spot. Even though it can never be eliminated, a proper combination of adsorbents reduces the severity of cold spots.

Cold spots can also occur in single layered adsorbent beds since nitrogen and oxygen loadings on the adsorbent at the feed end are reduced to almost zero due to water loading at the front end of the bed.

CONCLUSION

In the last 25 years, oxygen VSA has been transformed from a lab curiosity to a formidable industrial process. This has been possible by evolving more efficient and simpler cycles as well as developing higher efficiency adsorbents. To move this technology to the next stage would require increasing the range of its application by innovative process designs, and developing higher capacity and efficiency vacuum pumps. Of course, new discoveries in adsorbent area will have a major impact on this technology. Adsorbents, such as oxygen selective materials (36–38), may change the landscape of this technology forever.

NOTATION

b_0, d_0	dual site Langmuir parameters for the first and second sites
m_1, m_2	monolayer capacities on the first and second sites of dual site Langmuir model
n	solid phase loading
Δn	difference in solid phase loading between initial and final conditions of the evacuation step
P	pressure
q_1, q_2	heat of adsorption for the first and second sites
R	gas constant
S	selectivity
T	temperature
Y	gas phase mole fraction
ρb	packed bed density
ϵ	external bed voidage

Subscript

i	N_2, O_2

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