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

Recent Advances in Molecular Sieve Unit Design for Air Separation Plants

D. R. Acharya[a]; R. Jain[a]
[a] THE BOC GROUP TECHNICAL CENTER, MURRAY HILL, NEW JERSEY

To cite this Article Acharya, D. R. and Jain, R.(1995) 'Recent Advances in Molecular Sieve Unit Design for Air Separation Plants', Separation Science and Technology, 30: 18, 3489 — 3507
To link to this Article: DOI: 10.1080/01496399508015131
URL: http://dx.doi.org/10.1080/01496399508015131

SEPARATION SCIENCE AND TECHNOLOGY, 30(18), pp. 3489–3507, 1995

Recent Advances in Molecular Sieve Unit Design for Air Separation Plants

D. R. ACHARYA* and R. JAIN
THE BOC GROUP TECHNICAL CENTER
MURRAY HILL, NEW JERSEY

ABSTRACT

For various reasons interest in adsorption-based prepurification units has continued to increase in air separation industries. This has led to significant development efforts in this area with the objective of generating optimized designs rather than simply workable designs. Emphasis has been placed on the ability to optimize for both energy and capital cost. This paper presents the background to the design of these units. It shows how an extensive program of practical measurements made on a purpose-built large-scale test rig followed by detailed theoretical work to ensure correct interpretation of the information gathered has made it possible to understand this temperature swing adsorption process and at the same time to develop robust and confident designs.

INTRODUCTION

Air purification prior to its low temperature liquefaction or processing is an important step in the technology of cryogenic air separation. The purification involves the removal of minor impurities such as water vapor, carbon dioxide, and potentially dangerous hydrocarbons. Historically, the air separation industry has employed various methods of removing these impurities from air. These processes have been reviewed by Ward et al. (1), Rhode (2), Petit (3) and more recently by Kerry (4) and von Gemmingen (5) in detail.

* To whom correspondence should be addressed. Permanent address: BOC Process Plants, Guildford, UK.

Reversing heat exchangers (RHE) were the most common method of impurity removal and heat exchange until the early 1980s. The multicomponent adsorption processes [PPU (prepurification unit) or FEP (front end purification)] were then considered to be more capital and power intensive. However, with the advances in adsorption technologies and with growing demand for nitrogen, the adsorption-based processes began to appear more attractive as they offered several additional advantages over the RHE system. For example, in addition to CO_2 and water removal, hydrocarbon impurities such as acetylene and ethylene could also be removed by adequately sizing the adsorber. This increased the process safety and eliminated the need for low temperature adsorbers. Use of adsorption systems also makes the plant more stable since adsorption bed changeover occurs less frequently than RHE changeover. In general, the ability of adsorption systems to efficiently and economically remove impurities made them a favored process option for air pre-purification.

As mentioned before, PPUs are based on adsorptive removal of impurities. The process relies on the properties of certain adsorbents to preferentially adsorb one or more components of a gas mixture, combined with the characteristic that the adsorption capacity increases with higher operating pressures and lower operating temperatures. In this case the adsorbent material, zeolite molecular sieve, has a higher adsorption capacity for carbon dioxide and water vapor. This capacity is limited, and once saturation is reached the sieve must be regenerated, which is typically achieved by lowering the bed pressure and providing heat. Thus, full continuous operation can only be achieved with a minimum of two vessels with one adsorbing while the other is being regenerated. Although a two vertical vessel arrangement is the most widely used, three and four vertical or horizontal vessel arrangements must be considered for large air separation plants (about 700 MTPD oxygen plants and over).

A usual operating procedure is to employ a packed bed of adsorbents within a vessel. The two typical arrangements of the PPU, vertical and horizontal beds, are shown in Fig. 1. In all cases the adsorption bed will undergo the same general steps:

Pressurization
Adsorption
Depressurization
Regeneration

The manner in which these steps are carried out will vary depending on the design. For example, the adsorption is typically carried out in upflow direction as shown in Fig. 1. However, when the feed air flow is large, a downward direction may also be adopted. The regeneration is usually

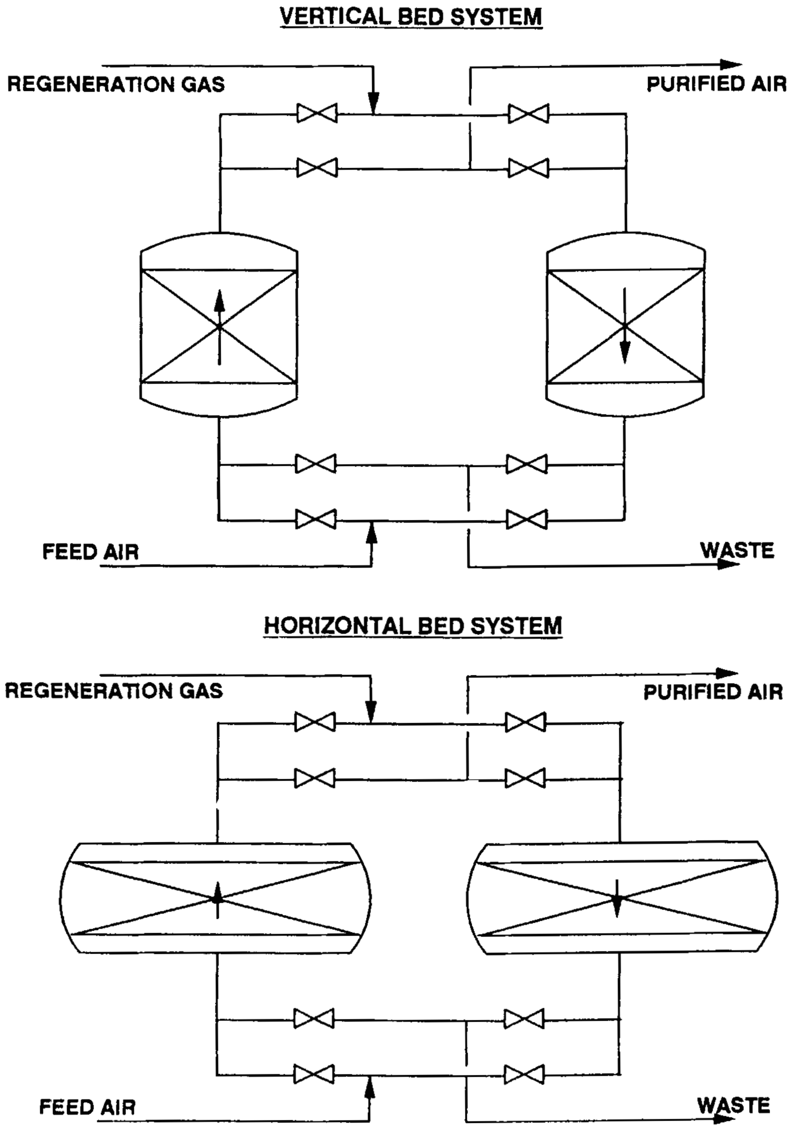

FIG. 1 PPU arrangements.

TABLE 1
Parameters Involved in PPU Optimization

Adsorbent	Manufacturer/grade/shape
	Particle size
	Aging effects
Adsorption	Pressure/temperature
	Flow direction
	Flow velocity
	Layered beds
	Adsorption time
	Flow distribution
Regeneration	Temperature
	Flow
	Heating and cooling times
	Static heat
	Flow distribution
Vessel	Number of beds
	Orientation/geometry
	Insulation

countercurrent to adsorption regardless of the direction. The other two steps, pressurization and depressurization, can also be carried out in either an upward or a downward direction.

The PPUs are generally designed using the mass transfer zone or LUB concept. These methods have been described by Lukchis (6) and Barrow (7) among others. Although the LUB concept is very simple to use, the design and optimization of a PPU for a given air separation plant is fairly complex as there are at least 17 parameters which need to be considered (listed in Table 1).

While some of the parameters listed in the table will be fixed for a particular application, there still remain a large number of parameters about which sufficient information must be available for an optimum choice to be made. The primary aim of this paper is to discuss the progress made in understanding and optimizing this process with particular reference to thermal swing air purification.

PROGRESS IN OPTIMIZATION

The removal of water and carbon dioxide from air by means of reversing exchangers is a very elegant method as it achieves two steps in one, i.e. cooling and impurity removal. In the early days of PPU development, PPU's were considered to be more expensive both in terms of power and capital when compared to reversing heat exchangers. Thus, to be able to claim parity of capital cost and power consumption with the reversing plant has been a goal of PPU design and a major driving force in PPU development efforts over the years.

In order to minimize the PPU plant capital cost, every aspect of the PPU design and operation was scrutinized, and the areas which promised significant potential for cost reduction were identified. These areas are summarized in Table 2. The significant development in each of these areas is described below.

Power Saving

Dual Layer Beds

In the first generation of PPUs, molecular sieve was usually employed to remove both CO_2 and moisture. Regeneration of water from molecular sieve requires higher energy, and at the same time molecular sieves are susceptible to hydrothermal degradation. This problem was addressed by employing dual layer beds involving a layer of activated alumina to adsorb moisture and a second layer of molecular sieve to remove CO_2. Since activated alumina does not remove CO_2 to any significant extent, such designs can be modeled as two section designs.

Dual layer beds have become increasingly popular in PPU application. Unlike molecular sieve, alumina releases adsorbed water more readily, thus regeneration temperature and therefore power requirements are lower than for all molecular sieve bed. Activated alumina is also less expensive and a more resilient material than molecular sieve, which brings

TABLE 2
Focus Areas in PPU Optimization

Focus area	Route
Power saving	Dual layer beds Low temperature regeneration Minimize pressure drop
Product recovery	Low flow regeneration
Capital saving	Ambient adsorption Adsorption onto a hot bed Short cycles Shallow beds

the adsorbent cost down and increases the useful service life of the adsorbent.

Figure 2 gives a schematic of single and dual layer beds.

Low Temperature Regeneration

Greater than 50% power savings can be achieved by a low regeneration temperature design. This design point also brought PPU and RHE plants closer in terms of power and capital. The reduction in regeneration power is achieved by a "partial regeneration" technique. The technique allows a quantity of permanent residual moisture to remain on the adsorbent bed during its operating life. A small amount of bed capacity is, therefore, sacrificed for a significant reduction in regeneration power.

Carefully measured data are required to understand operation with a permanent deposit of moisture. Sequential testing involving alternate adsorption and regeneration steps under closely controlled conditions is required to establish the extra length of bed required and to demonstrate that steady-state conditions are reached, i.e., that there was no gradual creeping of the water zone.

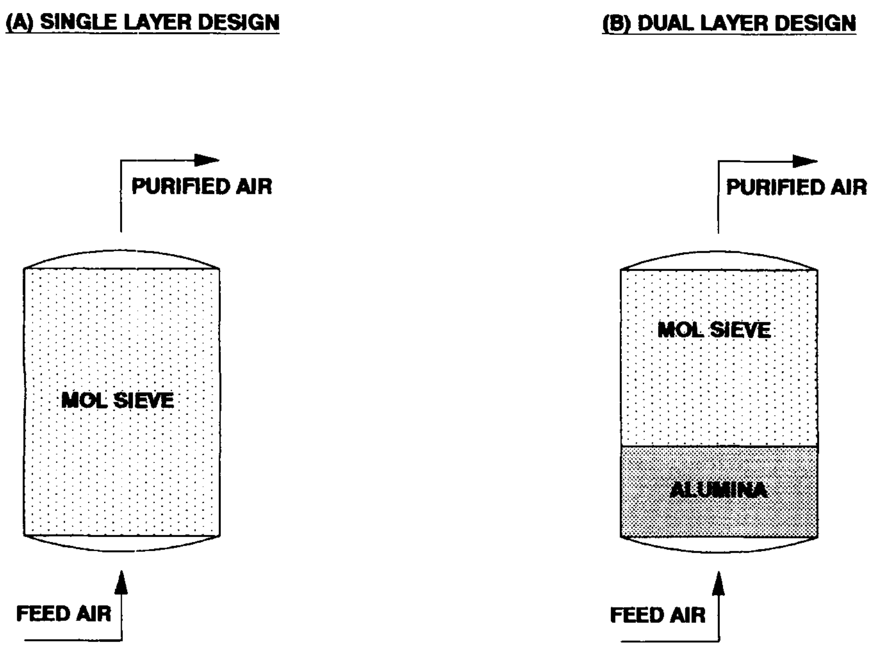

FIG. 2 Single and dual layer beds.

This design is extremely effective when the regeneration gas is preheated by the waste heat from the main air compressor.

Minimize Pressure Drop

Any maldistribution of the flow reduces the performance of a PPU. This is because part of the adsorbent is subjected to excessive air flow and as a result gets overloaded with the impurity. And since regeneration takes place in the reverse direction, the pattern of maldistribution may be different. The overloaded adsorbent may receive inadequate regeneration. Thus, in terms of design, the existence of maldistribution means that increased bed depth must be provided. However, as the bed height increases, the bed pressure drop increases too, and since the reduction of bed pressure drop is part of the strategy of PPU optimization, it implies that bed height must be reduced. Therefore, the smaller the bed pressure drop, the better must be the gas distribution arrangements at the bed inlet and outlet.

Product Recovery

Product recovery can be enhanced by conducting regeneration at low flow and moderate or high temperature. This mode of regeneration is also known as thermopulse regeneration. Little or no difference in regeneration power can be expected for this mode of regeneration compared to low temperature regeneration. There is more potential for nitrogen product as less regeneration gas is required. It should be noted, however, that where power costs are high and the capital cost of air compressor heat recovery (waste heat) can be justified, a low regeneration temperature will give the greater power saving.

Capital Saving

Ambient Temperature Adsorption

The term ambient temperature has been applied to a PPU that has no precooling prior to adsorption except a water-cooled aftercooler. The temperature to the PPU would be dependent on the cooling water temperature which would, in turn, depend on the ambient conditions. The main feature of this type of PPU is that these are designed to operate at variable feed temperatures. The obvious advantage is the capital and maintenance cost savings in eliminating the precooling equipment.

Traditionally, the lowest achievable temperature is considered to be the best temperature for adsorption because it reduces the water content of air and increases the capacity of the molecular sieve for carbon dioxide.

In practical terms, a temperature of 5°C is the realistic minimum if freezing of moisture is to be avoided. However, the achievement of a temperature as low as 5°C requires the provision of chilling equipment, adding both capital and running costs and at the same time making the PPU circuit more complex as shown in Fig. 3. It is therefore attractive to carry out adsorption at higher temperatures.

A higher water loading and lower adsorbent CO_2 occurs in ambient temperature adsorption, and hence a shorter adsorption cycle is required to minimize capital costs. Higher regeneration power are implied. Figure 4 qualitatively describes the effect of warmer adsorption temperature on adsorption and regeneration conditions. A number of strategies have been developed to make regeneration more effective.

Adsorption onto a Hot Bed

During the adsorption step, a temperature front advances through the bed ahead of the mass transfer zones, and this brings the bed rapidly to a temperature closer to the feed stream temperature. This means that if the bed is initially free of water and carbon dioxide, then its initial temperature has no effect on the course of the adsorption step. The main advantage of this is that the cooling step at the end of the heating step can be omitted altogether if desired, as discussed by Basmadjian (8). The heating time can be extended in this case and a relatively short cooling time can be used. The need to cool down the bed to the adsorption temperature no longer exists, and the bed may be brought on-line regardless of its temperature.

The advantage of being able to eliminate the cooling step would be more effective bed regeneration in a given regeneration time. For example, more moisture can be desorbed in a given time or a given amount of water can be removed using a smaller regeneration flow. This is extremely important as it could offset the effect of adsorbing at higher temperatures. However, hot bed adsorption will certainly generate a steep heat bump on bed changeover (see Fig. 5), and this must be prevented from entering the cold box. This situation can be avoided by providing a water-cooled aftercooler to maintain a constant temperature to the cold box. The aftercooler can be bypassed once the heat bump has passed and the temperature of the PPU outlet air has returned to its normal value.

It is important to note that regeneration in PPUs is never complete, and residual moisture always remains on the bed. Any design which aims to adsorb onto a hot bed must allow for this factor.

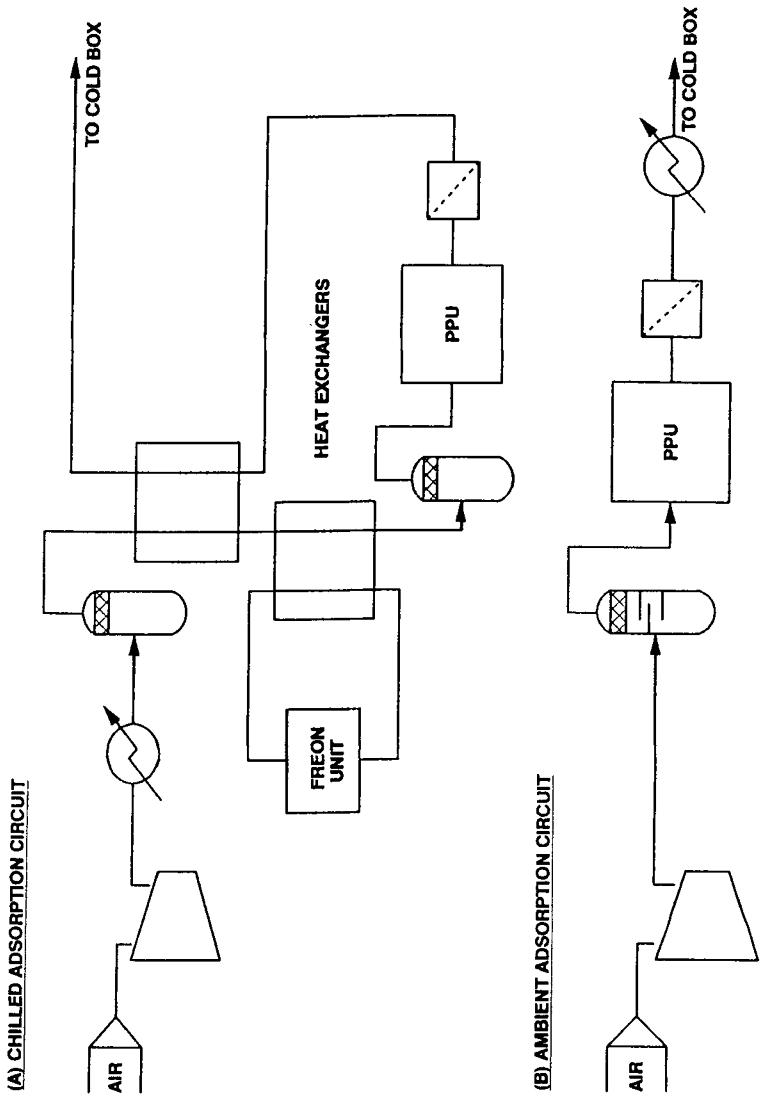

FIG. 3 Comparison of chilled adsorption with ambient.

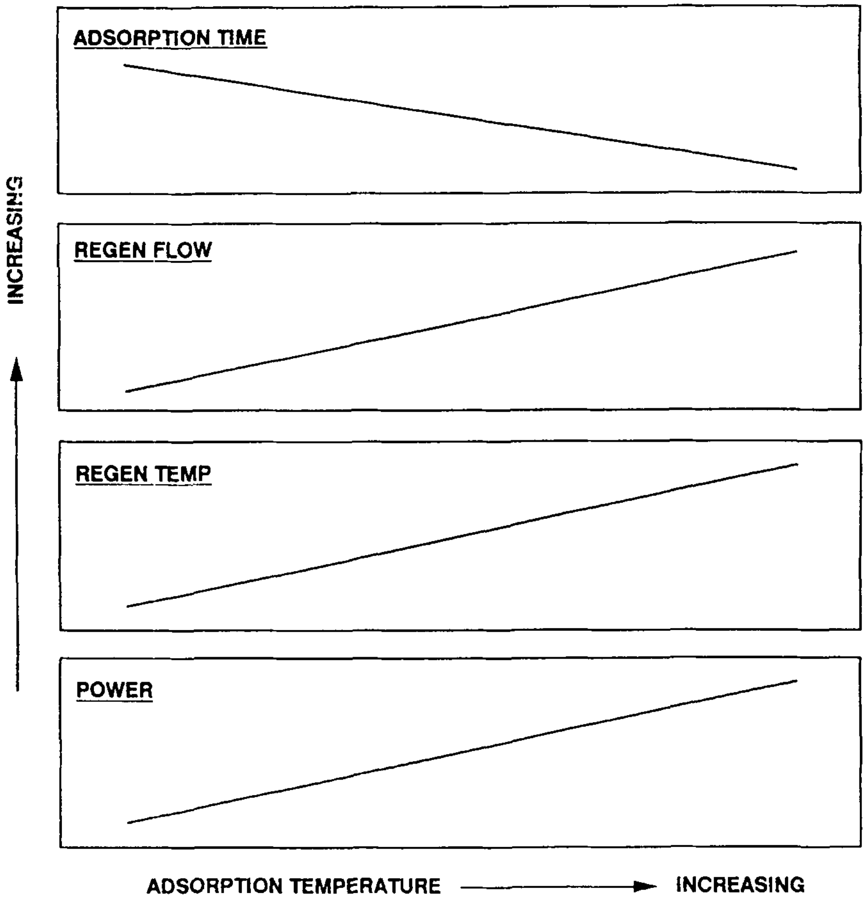

FIG. 4 Effect of adsorption temperature.

Short Adsorption Cycles

One of the areas of significant interest in terms of PPU optimization is in the direction of short adsorption times. Shorter cycle means less adsorbent and therefore smaller vessels. Shortening of the cycle time is therefore an integral part of optimizing PPU design—particularly for large air separation units. However, short adsorption time also requires that other sources of inefficiencies are eliminated. For example, better flow distribution, rapid pressurization and depressurization, quicker transport of heat to the bed, etc. factors need to be carefully considered. The penalty of

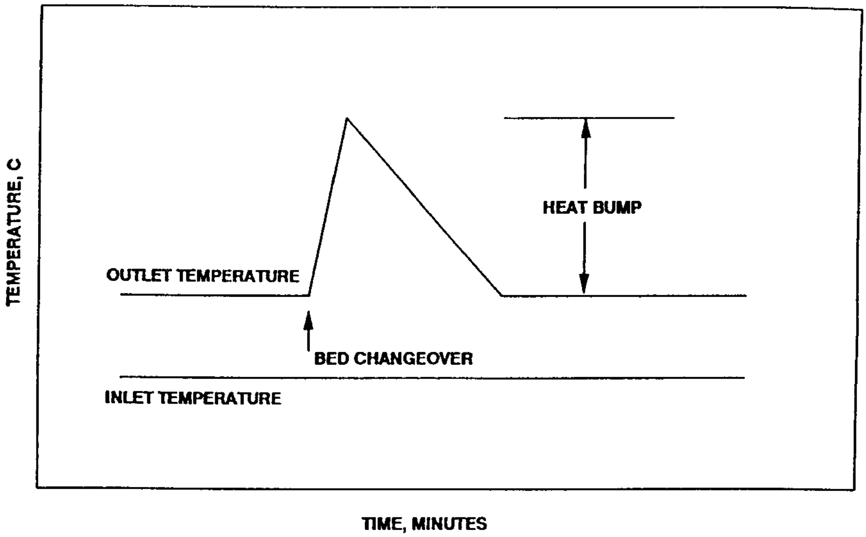

FIG. 5 Heat bump profile.

using short cycle is the increased power consumption and also increased pressure drop in the regeneration circuit. This is usually a trade-off which must be evaluated for a given design.

MODELING

The simultaneous adsorption of water vapor and carbon dioxide on molecular sieves, and their subsequent regeneration, has always been known to be a complex subject. In contrast to single component adsorption, the analysis of multicomponent adsorption is difficult and often uncertain. The possible competitive and interactive nature of the mass transfer processes make it further complicated. For such a situation there are basically two types of alternative treatments, ranging from the fully theoretical to the fully empirical. The former would require a detailed mathematical representation and accurate basic data (equilibrium capacities, diffusion rates, etc.) over the whole area of interest, while the latter, on the other hand, would involve a much more simplified mathematical representation sufficient to correlate the results of practical measurements. A largely empirical approach based on several correlations is usually adopted in designing these units. The correlations used in the design method are normally developed by making sufficient practical measurements of each appropriate variable to enable what is to be a curve-fitting operation.

Significant progress has been made on the theoretical aspects in the recent past. A review of papers published shows that adsorption has been extensively modeled, though regeneration still continues to be neglected. This is perhaps because the complexity of the regeneration processes has been underestimated. For example, the two major areas which are still not fully understood are the influence of carbon dioxide desorption on water desorption and the complexity and significance of incomplete desorption of water. The available information is not sufficiently comprehensive to enable true optimization of a design.

A fully theoretical treatment would take its basic data from laboratory tests. The advantages of using a theoretical model that has been thoroughly tested with experimental data are obvious. For example, one advantage of this is that it could obviously cover a range of adsorption and regeneration operating conditions, which an experimental testing unit cannot do. The need for expensive experimental rigs and field testing is minimized. Additionally, problems of scale-up can also be handled easily by the model. On the other hand, it is not clear that a fully theoretical treatment is feasible even if a mathematical representation of the process is possible. For example, it might be prohibitively expensive to use it. The pragmatic approach would be to combine the development of a mathematical model with laboratory derived data so as to produce accurate predictions with the level of complexity of the model to be adjusted with the acceptable matching of experimental results.

Mathematical modeling can be of great assistance in providing a framework on which the practical measurements can be superimposed. Provided the model is soundly based, it can benefit in the following ways:

1. It can enable a maximum of information from a minimum of measurements.
2. It can extend the applicability beyond the area in which the measurements were made.
3. It can enable optimum operating conditions to be located by calculation rather than by practical testing.
4. It can determine the characteristics of a new adsorbent from a minimum of testing.
5. It can enable maldistribution to be studied and avoided. This information is critical when horizontal adsorbers are required.

An initial classification of the published work groups the models into three types, i.e., simulators, CFD based, and integrated. These are described below.

Simulators

This is an area which has received the most attention, and a wide variety of approaches can be found in the literature; see, for example, Munstermann (9). In general, the simulator type of models can be divided into those assuming equilibrium and those where nonequilibrium conditions prevail. Equilibrium in this context implies that the amount adsorbed is given directly from the bulk gas concentration with no complications from intervening mass transfer restrictions. Such a model could well be termed a homogeneous model since its derivation is based on a cross section of the bed with no distinction between particulate material and fluid. Conversely, nonequilibrium models allow for the possibility of mass transfer resistances either strongly or combined, and are therefore capable of wider development which allows for the presence of both particulate and fluid phases and may also involve a detailed structure for the particles. Such models could therefore be described as heterogeneous. An intermediate type of model assumes that the effluent concentration profile is independent of the bed length, and this type of model is therefore known as the constant pattern model. The assumption that the effluent concentration is independent of bed length reduces the material balance equation to a simple form because the derivative of concentration with respect to the bed length vanishes. However, a mass transfer step of some kind is involved, and therefore such models cannot be described as equilibrium or homogeneous models. Because of the constant pattern assumption, these models are different from nonequilibrium models which involve neither equilibrium nor constant pattern assumptions.

A detailed classification may be made using these three broad divisions. The structure of such a classification is given in Fig. 6 which also shows the various subdivisions.

CFD Models

Computational fluid dynamics (CFD) is the term given to the technique of numerically solving the equations of motion (continuity and Navier–Stokes) together with relevant models to predict fluid flow and associated phenomena. The advent of the fast, large memory computers has made CFD into a tool which is now accessible to a wide audience. Although CFD is still regarded by many as a research tool, it is now used on a day-to-day basis in a variety of situations. The gas distribution in packed beds has been recently investigated by Parsons and Porter (10) and Porter et al. (11).

CFD modeling in PPU applications has become an important and useful tool. Many PPU designs involve vessels with shallow beds where the

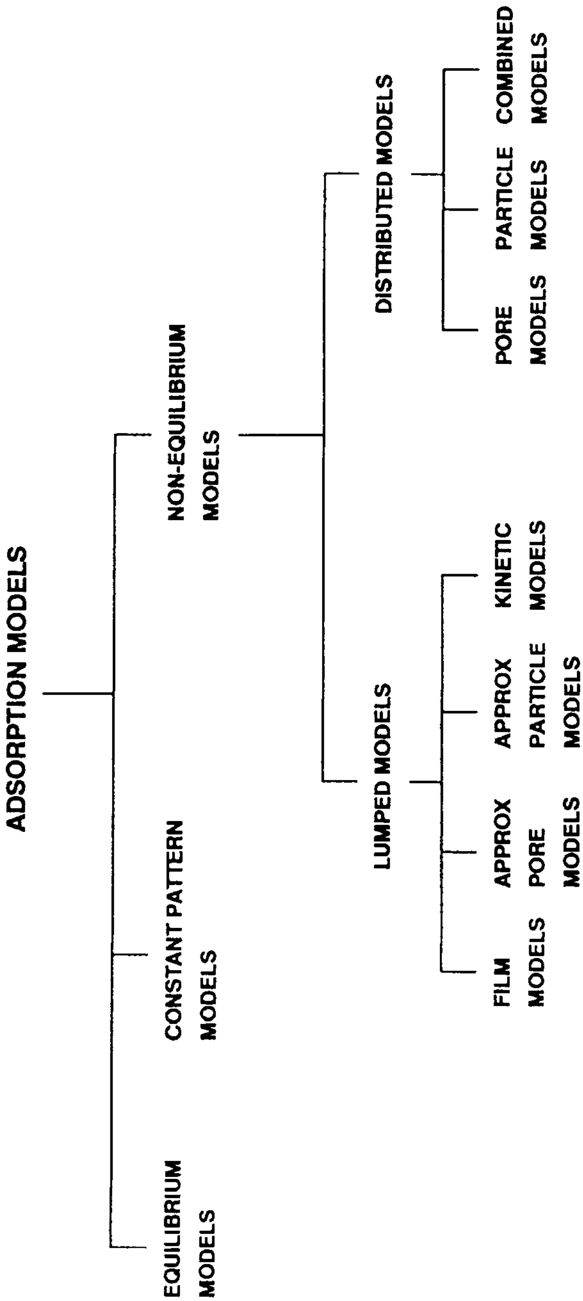

FIG. 6 Classification of adsorption models.

packed depth is less than the bed diameter. However, gas maldistribution can occur in shallow beds, which leads to expensive performance failure. The consideration of uniform gas flow distribution in shallow vertical and horizontal vessels is therefore important as optimized designs generally include short cycle times and shallow beds.

An excellent example of the CFD model applied to PPU is the work reported by Kler and Lavin (12). The authors developed a model based on PHOENICS, a general purpose commercially available CFD package, to simulate flow distribution in vertical adsorber vessels. The model results were tested against experimental data using transient temperature profiles during heating.

A typical flow distribution in a horizontal vessel obtained using a CFD model is shown in Fig. 7a for the inlet and outlet nozzle area and in Fig. 7b for the bed itself.

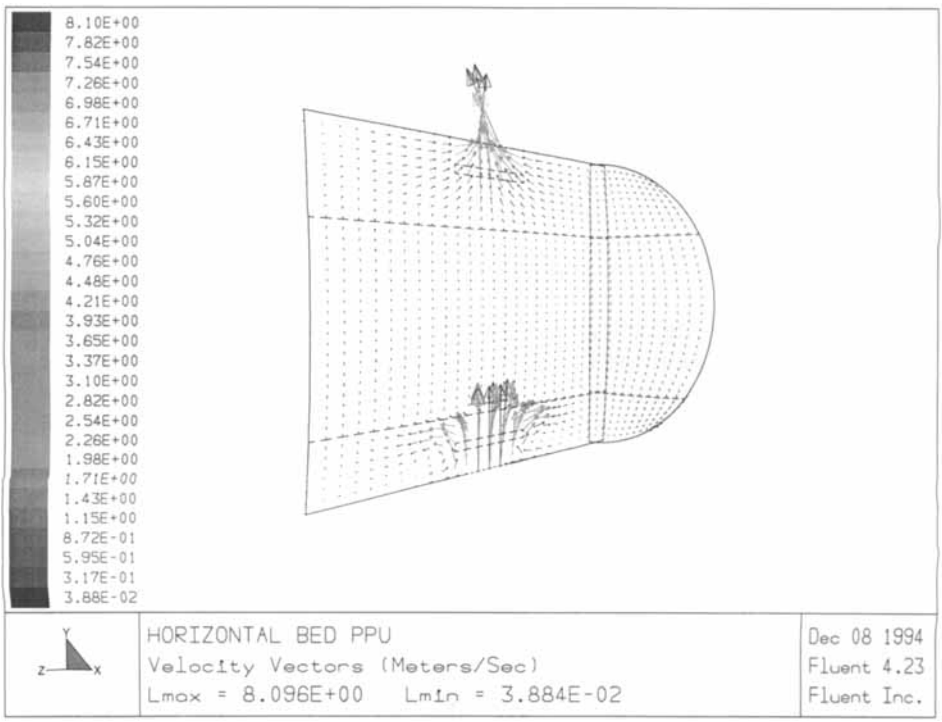

FIG. 7a Velocity distribution in a horizontal adsorber: Inlet and outlet nozzle area.

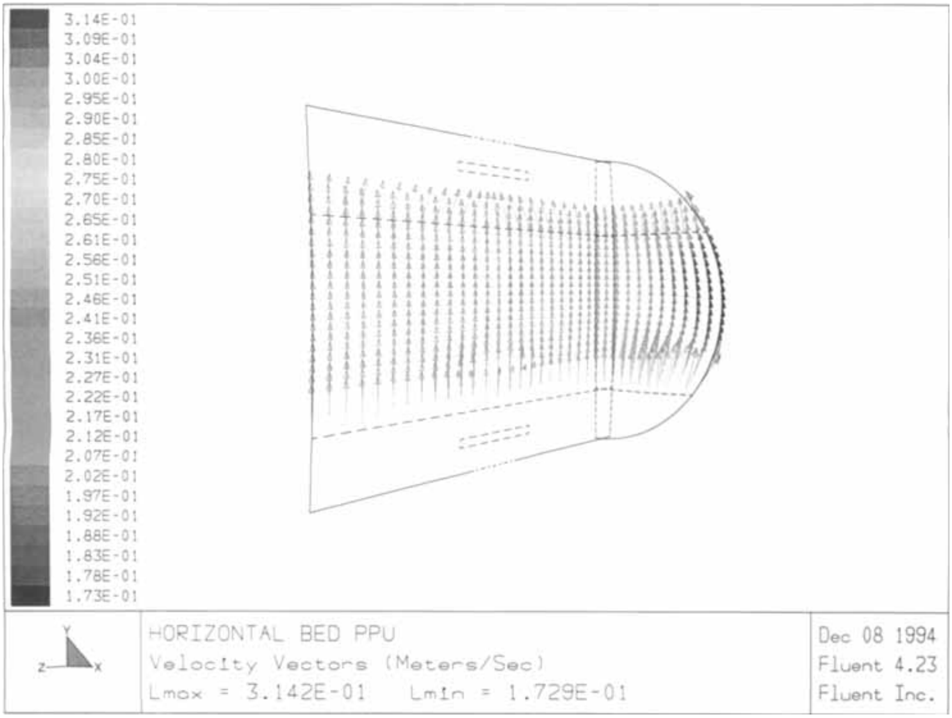

FIG. 7b Velocity distribution in a horizontal adsorber: In the adsorbent bed.

Integrated Models

Integrated models reflect the most recent trends in adsorption modeling. These model exploit the equation-solving capabilities of a CFD package by introducing known and established principles of adsorption in terms of user-defined subroutines. Keeton and Tierney (13) reported results of one such study using the proprietary CFD code ASTEC.

SPECIALTY PPU

Adsorption and Catalysis

Nitrogen of ever-higher purity is needed by the electronics industry for the manufacture of chips with ever-increasing line densities. The reactive impurities in nitrogen, CO and H_2, have to be removed to extremely low levels. Recent specifications have called for less than 1 ppb CO and less than 5 ppb H_2 in the product nitrogen. Conventionally, these impurities have been removed by heating the feed air to 150–200°C and then passing it over a catalyst bed for the oxidation of impurities. Because of the use of inexpensive catalysts, heaters, and pressure drop due to the use of gas to gas heat exchangers, this approach is fairly expensive. More recently, however, catalyst-adsorption-type purifiers have been proposed and discussed by Murakami and Nomura (14) and Jain (15).

A recent proprietary BOC development (PreAir Process) utilizes catalysts active at the PPU operating temperature in the PPU bed itself to oxidize CO and H_2. The reaction products are subsequently removed by adsorption. The bed configuration is shown in Fig. 8.

Pressure Swing PPU

Pressure swing or PSA PPU is another recent proprietary development of The BOC Group (16). In this process, both adsorption and regeneration

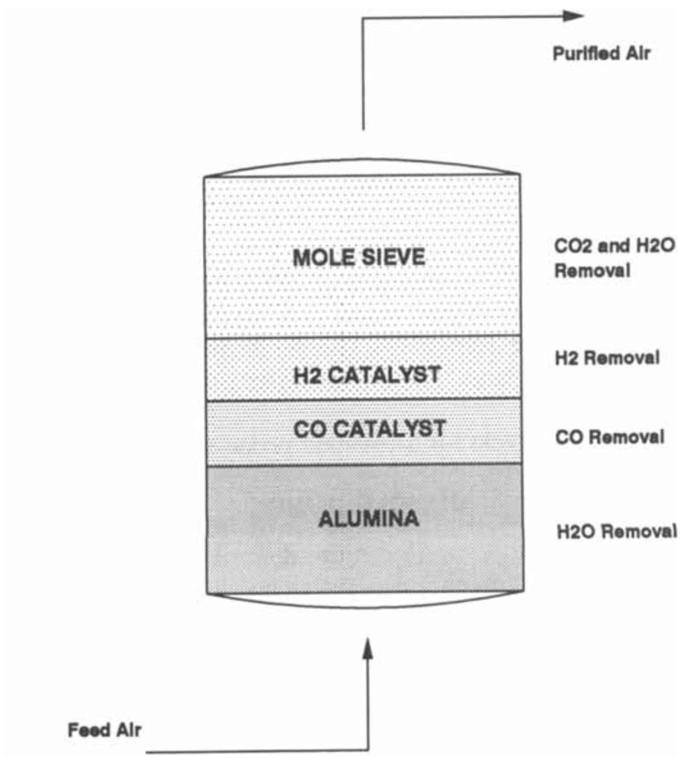

FIG. 8 PPU with catalyst layers.

TABLE 3
Typical PSA PPU Cycle[a]

Bed A	Bed B	Time (seconds)
Backfill with product from Bed B	Produce, backfill Bed A	60
Produce	Vent to atmosphere	30
Produce	Purge with waste gas	510
Produce, backfill Bed B	Backfill with product from Bed A	60
Venture to atmosphere	Produce	30
Purge with waste gas	Produce	510

[a] Total cycle is 20 minutes or 1200 seconds.

take place at ambient temperature (20–45°C). Since no cooling of the feed gas and heating of the regeneration gas are required, the power and capital cost associated with a Freon unit and a regeneration heater are eliminated. Also, unlike thermal swing PPU, the pressure swing process is relatively insensitive to the feed temperature, with less than a 25% change in capacity over a temperature range of 20–45°C. The adsorption time in PSA PPU is considerably shorter than a temperature swing adsorption (TSA) system (10–20 minutes compared to 4–8 hours for TSA PPU). This leads to more frequent bed depressurizations and repressurizations. The air lost during bed depressurization has to be made up by compressing additional air, and this is the only power consumption in a PSA PPU. PSA PPU typically require 30–40% of the waste gas (based on feed) for bed repressurization, which is higher than the TSA PPU. This limits the applicability of PSA PPU to plants that have large amounts of waste gas available for regeneration.

A typical PSA PPU cycle for a two-bed process is shown in Table 3.

CONCLUSIONS

To make success of PPU optimization, it was necessary to be able to select the appropriate combination of design parameters for any particular application. This required more extensive study of some areas which traditionally received only brief attention. The result is that the technology is now firmly based on exacting development data specifically derived to permit scale-up. Additionally, the technology refines the optimization process of PPUs for both power and capital cost by combining experimental results with the information generated using validated mathematical models.

ACKNOWLEDGMENTS

The authors wish to thank the management of The BOC Group for permitting this work to be published. Thanks are also due to N. Lemcoff for providing CFD information.

REFERENCES

1. D. E. Ward, D. O. Briscoe, and D. T. Linnett, "Purification of Cryogenic Gases," in *Gas Purification Processes for Air Pollution Control*, 2nd ed. (G. Nonhebl, Ed.), Newnes-Butterworth, London, 1972.
2. W. Rhode, "20 Years of Molecular Sieves in Air Separation," *Linde Rep. Sci. Technol.*, *40*, 48–51 (1985).
3. P. Petit, *Recent Developments in the Field of Front-end Purification Units in Air Separation Plants*, ACHEMA, Frankfurt, West Germany, June 1985.
4. F. G. Kerry, "Front-ends for Air Separation Plants—The Cold Facts," *Chem. Eng. Prog.*, pp. 48–54, (August 1991).
5. U. von Gemmingen, "Design of Adsorptive Dryers in Air Separation Plants," *Linde Rep. Sci. Technol.*, *54*, 8–12 (1994).
6. G. M. Lukchis, "Adsorption Systems. Part I: Design by Mass Transfer Zone Concept," *Chem. Eng.*, pp. 111–116 (June 11, 1973); "Part II: Equipment Design," *Chem. Eng.*, pp. 83–87 (July 9, 1973); "Part III: Adsorbent Regeneration," *Chem. Eng.*, pp. 83–90 (August 6, 1973).
7. J. A. Barrow, "Proper Design Saves Energy," *Hydrocarbon Process.*, pp. 117–120 (January 1983).
8. D. Basmadjian, "On the Possibility of Omitting the Cooling Step in Thermal Gas Adsorption Cycles," *Can. J. Chem. Eng.*, *53*, 234–238 (1975).
9. U. Munstermann, A. Mersmann, and J. Schadl, "Non-isothermal Multicomponent Adsorption and Desorption of CO_2 and H_2O on Molecular Sieve," *Ger. Chem. Eng.*, *6*, 1–8 (1983).
10. I. M. Parsons and K. E. Porter, "Gas Flow Patterns in Packed Beds: A Computational Fluid Dynamics Model for Wholly Packed Domains," *Gas Sep. Purif.*, *6*, 221–227 (1992).
11. K. E. Porter, Q. H. Ali, A. O. Hassan, and A. F. Aryan, "Gas Distribution in Shallow Packed Beds," *Ind. Eng. Chem. Res.*, *32*, 2408–2417 (1993).
12. S. C. Kler and J. T. Lavin, "Computer Simulation of Gas Distribution in Large Shallow Packed Adsorbers," *Gas Sep. Purif.*, *1*, 55–61 (1987).
13. J. A. Keaton and M. J. Tierney, *Simulation of an Industrial Adsorber-Regenerator Unit*, AEA-InTec-1796, January 1994.
14. M. Murakami and M. Nomura, "Catalyst-Adsorption Type Purifiers for Ultra-pure Gas Supply," *Gas Sep. Purif.*, *2*, 95–102 (1988).
15. R. Jain, "Low Temperature Purification of Gases," US Patent 5,110,569 (May 5, 1992).
16. R. Jain, "Process for Pre-Purification of Air for Air Separation," US Patent 5,156,657 (October 20, 1992).

Received by editor February 21, 1995
Revised April 17, 1995