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GAS PURIFICATION BY PRESSURE SWING ADSORPTION

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INTRODUCTION

The first reference to a pressure swing adsorption (PSA) cycle seems to have appeared as a patent in Germany in 1942, and was later published under the name "Sorbogen" process[1], for removing water and CO_2 from air. Further developments were made toward the end of the 50's by Guerin de Montgareuil and Domine[2] in France and by Skarstrom[3-5] in the U.S., as an alternative to thermal regeneration in adsorption processes, under the names of "isothermal adsorption" and "heatless adsorption" respectively. PSA saw important industrial developments[6,7] at the end of the 60's and the beginning of the 70's. During the same period, detailed scientific studies were published[8,9]. The main applications were then air drying, enrichment of air in oxygen, and hydrogen purification. In recent years, PSA has raised renewed interest, related to new needs in gas separations on one hand, and to a better knowledge of the basic processes involved on the other hand. A great variety of operating schemes have resulted, comprising sometimes a large number of columns and complex flow-sheeting.

The aim of the present review is to present a comprehensive, flow-sheet oriented review of PSA processes, emphasizing general principles and offering possibly new concep-

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tual tools for comparison, analysis and evaluation of these processes. The processes considered here are restricted to those where the separation is based on decreasing the pressure and usually purging at low pressure with the pure gas produced by the process. Processes which also require temperature variations or the use of a separate purge gas or desorbent will not be covered. Theoretical developments and description of specific applications are kept to a minimum, and the reader is referred to further literature on these topics.

BASIC PRINCIPLES

Thermodynamic considerations

Pressure swing adsorption being a nearly isothermal adsorption process is governed largely by the adsorption isotherms. Figure 1 shows examples of adsorption isotherms in two different forms. At a given temperature, the amount adsorbed q is a unique function of partial pressure (Fig. 1a); the "pressure-swing" is basically a partial pressure change ΔP, which modifies the amount adsorbed Δq, here in a non-linear way, from point A to point B. However, the partial pressure change may result from a change in total pressure ΔP, or from a change in composition Δx of the mixture treated, or from both simultaneously. These three types of changes are actually encountered in PSA, and may be visualized in Figure 1b, which contains the same information as Figure 1a, but has mole fraction x as variable and total pressure P as a parameter. The path AB_1 corresponds to desorption at constant total pressure, by dilution of the gas with non-adsorbed component (say, helium) resulting in a decreasing x. Path AB_2 corresponds to desorption by lowering the total pressure: the component desorbed from the adsorbent enriches the gas phase, and thus x increases. A combination of these two basic processes is conceivable and may lead to paths intermediate between AB_1 and AB_2.

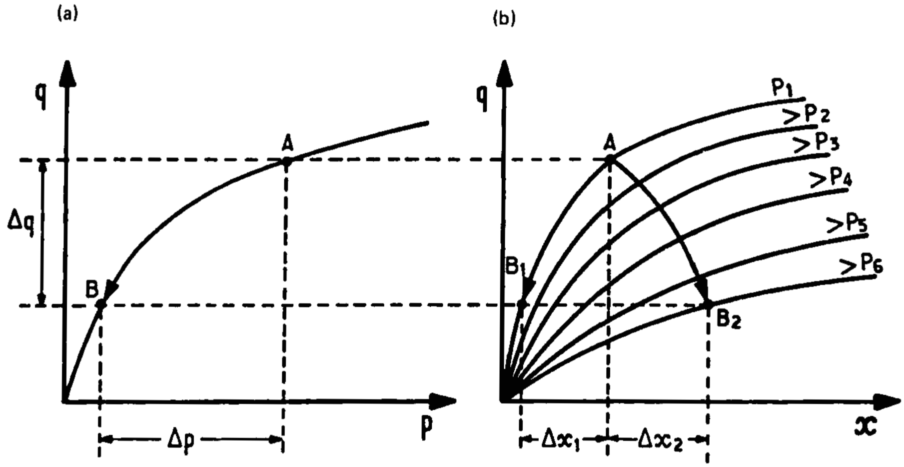

FIGURE 1

Representations of gas adsorption isotherms.

1a: As a function of partial pressure of the adsorbed component.

1b: As a function of mole fraction of adsorbed component, with total pressure as parameter.

From a classical thermodynamic point of view, PSA is in principle a straightforward process: the free enthalpy increase required by the separation of the components is simply obtained by forcing a pressure, and thus an enthalpy change. These changes are calculable analytically, for instance under the ideal gas assumption, thus allowing evaluation of the thermodynamic efficiency of a PSA process. Note that in other adsorption processes, the "source" of free enthalpy can be temperature changes or the dilution of a solvent or efluent. By contrast, pressure-swing adsorption works without addition of heat or of a foreign efluent.

Strangely, little attention has been paid to these aspects since the early work of Guerin de Montgareuil and Domine[10] and Brunel[11]. Their results show in particular that linear isotherms are more favorable to approach a reversible operation than non-linear ones.

Of course, the usual non-idealities encountered in adsorption processes make PSA an irreversible operation (mass transfer resistances, friction, heat effects, turbulent mixing, etc...). But in many schemes, some intermediate states in the cycle are practically equilibrium states between the adsorbent and the gas, and therefore "equilibrium models" (see below) have been able to give useful conceptual and semi-quantitative information.

The standard operating cycle

Figure 2 illustrates the four steps of a relatively simple but frequently used cycle, as applied to a single column. This cycle may be considered as a sort of standard case. We shall examine later on more complex cycles, involving several columns. Let us discuss briefly the standard cycle on the example of the purification of a non-adsorbed gas, helium, from an adsorbed minor impurity such as nitrogen. The adsorbent for that purpose may be active carbon or 5A molecular sieves.

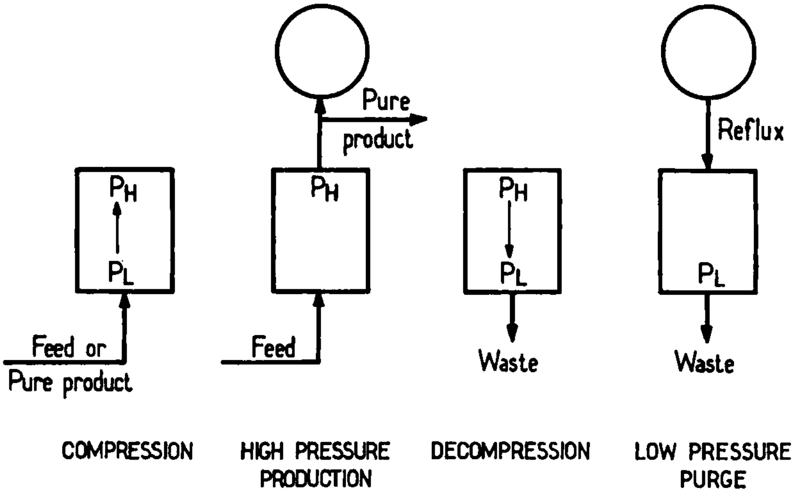

FIGURE 2

A standard pressure-swing operating cycle.

— Compression step:

The column being free of nitrogen and at low pressure P_L, feed mixture or pure helium is introduced at high pressure at one column end, the other end being closed. The pressure then rises from P_L to P_H. If mixture is fed, nitrogen is adsorbed in the first adsorbent layers, and a concentration front of nitrogen builds up and propagates in the column.

— High pressure production step:

The column remaining at high pressure P_H, feeding is continued with mixture, while the opposite end of the column is opened and pure helium exits as high pressure product. Part of that product is stored in a reservoir. This operation is continued until the nitrogen front starts breaking through at the product end.

— Decompression step:

At nitrogen breakthrough, feed and production are interrupted, and with one end closed, the column is emptied down to pressure P_L through the other end, usually in the direction opposite to the feed. Nitrogen is thus desorbed, and a "waste" enriched in nitrogen is obtained (cf. path AB_2 in Fig. 1).

— Low pressure purge:

The remaining nitrogen is purged out, or eluted, by pure helium stored in the second step, the column remaining at P_L. Desorption occurs through lowering of the partial pressure of nitrogen (path AB_1 on Figure 1).

The notion of reflux and the analogy with distillation and parametric pumping

The purge step may be characterized as a reflux step in the sense that, as in distillation, a fraction of the high enthalpy product (step 2) is "refluxed" countercurrently at a low enthalpy (step 4). The ratio of the mass or molar reflux flow to the production flow is the reflux ratio. Just as in distillation, the higher the reflux ratio, the purer the helium product (owing to a better regeneration of the adsorbent), but the lower the net production and the higher the unit operating cost. There is a minimum reflux ratio below which pure helium may not be produced, and similarly there is a minimum reflux for any specified purity of the product. An approximate rule valid when the adsorption isotherm is linear, is that the minimum reflux ratio for a pure product (no impurity breakthrough) is such that the volume of purge is equal to the volume of feed, which is roughly equivalent to a molar reflux ratio $r_M = P_L/P_H$.

In contrast with distillation, this minimum reflux is not an unattainable abstraction, since the adsorption column does behave practically as a cascade with an infinite number of stages, and can produce a pure product. In the operating scheme of Fig. 2, there is reflux only at one end of the column. The column thus behaves as a stripping section alone, not as a complete fractionation system. If one wanted to produce pure nitrogen, one would have to provide an enriching section with "reboiling" (or reflux at high pressure) of pure nitrogen! Note also that we defined the reflux ratio in terms of molar or mass flow, not volumes. The actual volume of gas refluxed at P_L may be considerable, and is usually larger than the volume of product measured at P_H.

PSA being an adsorption process using modulation of a thermodynamic variable and reflux instead of an efluent, can be considered as an antecedent of "parametric pumping" [12]. We refer the readers to the most recent reviews on this topic[13,14]. The relationship between the two processes seems to have escaped most workers until recently, probably because temperature was the only variable largely used in parametric pumping studies. Let us emphasize however two main differences between thermal adsorption parametric pumping, which one may also call temperature swing adsorption, and PSA. In the latter, the pressure changes are obtained by adding or subtracting matter to the system; in the former, the temperature changes may be effected by direct heat transfer, thus independently of the material balance. It results that equilibrium shifts comparable to that of Fig. 1 are easily calculable in thermal parametric pumping once the isotherms are known, whereas they require complete resolution of the material balances in PSA. Therefore, there is no direct equivalence of the solutions of even the simplest models of the two processes. In spite of this difference, the theoretical approaches are very close and use the same mathematical tools, as will be seen in the theory section. The second major difference is that in PSA reflux is done after expansion of the gas. This allows one to use a high volumetric reflux ratio while the molar (or mass) reflux ratio is small. Expansion is not possible in liquid parametric pumping systems and much higher molar reflux ratios must be used. It might be possible to combine pressure and temperature changes in a combined cycle gas system to obtain the advantages of isotherm shift due to temperature, pressure, and inert, and a low reflux ratio because of expansion of the reflux gas.

THE PSA LITERATURE

Publications on PSA are essentially patents, reports of plant operation, and experimental laboratory or pilot plant results, with relatively few theoretical articles, as compared to many other unit operations. In Tables I, II and III we present some non-exhaustive collections of references, arranged in a comprehensive way.

ADSORBENTS AND OPERATING CONDITIONS

The adsorbents used in PSA processes belong to the classical families of carbons, zeolites, alumina and silica. The latter are relatively infrequent in the PSA cycle itself, but silica gel often serves for drying in pretreatment units. Both types A and X zeolites are used. Their interest is their selectivity and especially the possibility of total exclusion of some components, which can then easily be recovered very pure. Their disadvantages are their high affinity for water or other polar molecules, which makes drying a prerequisite for certain applications, and their cost. Conventional active carbons usually have little

TABLE I

Applications of pressue swing adsorption

Typical references (not exhaustive)
See also Table II for patents

Hydrogen purification and recovery

from CO_2:	Shendalman and Mitchell[8]; Raghuraman US Pat. 3,703,068, 3,986,849 (Union Carbide); 4,171,206 (Air Products) Europ. Pat. 008 512 (1980; Air Prod.); 060,199 (1982; Union Carbide)
from N_2:	Raghuraman and Tiemann[70]; Lazslo et al [71]; Ger. Offen. 2, 153, 807 and 3, 032, 799 (Union Carbide)
from CH_4:	Domine and Hay[7]; Wang and Yang[72]
from H_2S:	Bandermann and Harder[73]
from $NH_3 + N_2$:	Eluard and Simonet[74]; Lancelin et al.[42] Japan Pat. 8,012,295 (1980); Germ. Pat. 3,032,789 (1982)
from hydrocarbons:	Alexis[41]; US Pat. 4,171,207; Belg. Pat. 858, 762 (1978)
Various:	Stewart and Heck[75]; Eluard and Simonet[74]; Katira and Stewart[76]; Lancelin et al.[42]; Corr et al.[77]; Werner and Schlichtharle[78]; Sanwal[79]; Heck[80]; Myiairi[81]; Anon[82-84]; Cassidy[85]; Wagemans and DenBoer[86]

Nitrogen and/or oxygen and/or rare gases from air

Domine and Hay[7]; Lee and Stahl[40]; Lee[29]; Smith and Armond[87]; Collins and Gareis[88]; Szanya et al.[89]; Flores-Fernandez and Kenney[32]; Kitagawa and Yuki[90-92]; Shen et al[94]; Armond[93]; Takebayashi and Morishita.[95]

Helium purification or recovery

Domine and Hay[7]; Mitchell and Shendalman[9]; Bird and Granville[96]; Cheng and Hill[97].

Air drying and purification

Skarstrom[3-6]; King[53]; Ausikaitis[98]; Harms et al. [99]

Others

N_2/CH_4:	Turnock and Kadlec[25]; Kowler and Kadlec[36]; Doshi et al.[17].
N_2/ethylene:	Jones and Keller[38]
Kr/air or N_2:	Kawazoe and Kawai[100]; Ayers et al.[66]
H_2 isotopes:	Weaver and Hamrin[101]; Wong and Hill[34].
CO/Ar:	Domine and Hay.[7]
Ne/N_2:	Domine and Hay.[7]
O_3/O_2:	Lassmann and Benkmann[102].
Various:	Lambert[103]; argon, nitrogen and protective gases

TABLE II

Typical[x] patents of main companies

x (This list is by no means exhaustive)

PSA patents are most often retrieved under the following international codes:

B 01 D 53/nn or C 01 B 13/nn or C 01 B 3/nn, where B01 refers to chemical and physiochemical processes and apparatuses, D to separation of gases, liquid or solids, and 53/nn to separation of gases and solvent recovery; nn is most often 00 (general) or 04 (fixed bed adsorption).

Esso Patents				
Skarstrom C.W.	U.S.P.	2,944,627	(1960)	- separations
Skarstrom C.W.	U.S.P.	3,082,166	(1963)	- drying
Skarstrom C.W.	U.S.P.	3,101,261	(1963)	- hydrogen purification
Skarstrom C.W.	U.S.P.	3,102,013	(1963)	
Skarstrom et al.	U.S.P.	3,142,547	(1964)	- pressure equalization
Skarstrom and Phillips	U.S.P.	3,212,236	(1965)	
Skarstrom et al.	U.S.P.	3,237,379	(1966)	- various separation
Skarstrom et al.	U.S.P.	3,282,647	(1966)	
Marsh W.D.	U.S.P.	3,142,547	(1964)	- (see Fig. 13)
Berlin N.H.	U.S.P.	3,280,536	(1966)	- (see Fig. 12)
Exxon Patents				
Waghorne et al.	U.S.P.	4,319,892	(1982)	magnetic moving beds
Hatch et al.	U.S.P.	4,319,893	(1982)	
Anon	E.P.	0,045,210	(1982)	- heat storage zone in bed

(continued)

Table II (continued)

<u>Union Carbide Patents</u>				
Batta L.B.	U.S.P.	3,564,816	(1971)	
Batta L.B.	U.S.P.	3,636,679	(1972)	- (see Fig. 16)
Batta L.B.	U.S.P.	3,717,974	(1973)	- separ. of air
Wagner J.L.	U.S.P.	3,703,068	(1972)	- H_2/CO_2
Wagner J.L.	U.S.P.	3,430,418	(1969)	- (See Figs. 18 & 19)
Fuderer and Rudelstorfer	U.S.P.	3,986,849	(1976)	- $H_2/N_2,CO_2$ mixed beds
Eares and Long	U.S.P.	4,194,891	(1980)	- oxygen
Keller G.	U.S.P.	4,354,859	(1982)	- (See Fig. 20)
	E.P.	013,680	(1979)	- oxygen; rapid cycle
	E.P.	060,199	(1982)	- H_2/CO_2; 2 feed system
	E.P.	064,267	(1982)	- non-isothermal
	E.P.	067,740	(1982)	-Two-step recompression
	E.P.	071,964	(1982)	- see Keller
Mc Combs	Ger. Offen	2,153,807	(1973)	- H_2/N_2
Fuderer	Ger. Offen.	3,032,799	(1982)	- $H_2,N_2/CO,CO_2,CH_4$
<u>L'Air Liquide Patents</u>				
Guerin de Montgareuil	Fr. Pat.	1,223,261	(1957)	
and Domine	Fr. Pat.	1,317,918	(1961)	
	Fr. Pat.	1,552,064	(1967)	
Guerin de Montgareuil et al.	U.S.P.	3,242,645	(1966)	
Domine and Hay	Fr. Pat.	1,602,353	(1968)	H_2

(continued)

Table II (continued)

Domine and Hay	Fr. Pat.	1,587,758	(1968)	H_2
Domine and Hay	U.S.P.	3,638,398	(1972)	H_2
Domine et al.	U.S.P.	3,619,984	(1972)	
Eluard	Fr. Pat.	1,601,126	(1968)	- O_2
Simonet and Lesur	Fr. Pat.	2,070,387	(1969)	- H_2
Simonet and Lesur	U.S.P.	3,702,525	(1972)	
Simonet and Pivard	Fr. Pat.	2,135,386	(1971)	
Hay	Fr. Pat.	2,270,927	(1974)	
Hay	Fr. Pat.	2,270,928	(1974)	
Hay	Fr. Pat.	2,363,362	(1976)	

Air Products and Chemicals Patents

Cormier and McAuley	U.S.P.	3,967,464	(1974)	- air drying
Sircar S.	U.S.P.	4,077,779	(1978)	- binary gas
Sircar S.	U.S.P.	4,171,206	(1979)	- multicomponent, unsymmetric
Sircar S.	U.S.P.	4,171,207	(1979)	configuration
	E.P.	0,008,512	(1980)	- 2 adsorbents
	E.P.	0,008,882	(1980)	- multicomponent
	E.P.	0,016,558	(1980)	- use of vacuum
	E.P.	0,042,159	(1981)	- oxygen recovery

British Oxygen Co. Patents

Jeyasekaran et al.	Brit. P.	2,003,742	(1979)	- O_2/air
Grahan	Brit. P.	2,018,153	(1979)	- O_2/air
Smith	Ger. Offen.	3,007,427	(1980)	- oxygen; 2 adsorbents
Armond	Brit. P.	2,073,043	(1981)	- N_2; carbon sieves
Armond and Smith	Brit. P.	2,086,258	(1982)	- N_2

(continued)

Table II (continued)

<u>Linde A.G. Patents</u>				
Benkmann	Ger. Offen.	2,840,357	(1980)	- hydrogen
Lassmann and Benkmann	Ger. Offen.	2,854,060	(1980)	- ozone
Baldus	Ger. Offen.	2,906,057	(1980)	- ejector used
Benkmann	Ger. Offen.	2,916,585	(1980)	- O_2/CO_2
Benkmann	Ger. Offen.	2,930,782	(1981)	
Leitgeb	Ger. Offen.	3,030,081	(1980)	
	E.P.	0,009,217	(1980)	- unsymmetric configuration
	E.P.	0,011,872	(1980)	- multicolumn "failure proof" system
	E.P.	0,072,496	(1983)	- 2 adsorbents
<u>Hitachi Patents</u>				
Mori	Jpn. Kokai	80 27 034	(1980)	- air
Anon	Jpn. Kokai	80 61 915	(1980)	- heat storage
Anon	Jpn. Kokai	80 97 221	(1980)	- temperature swing
Anon	Jpn. Kokai	80 152 517	(1980)	- two adsorbents
Anon	Jpn. Kokai	80 152 518	(1980)	- oxygen
Otani et al.	Ger. Offen.	3,045,451	(1981)	- two adsorbents
Anon	Jpn. Kokai	82 07 802	(1982)	- oxygen
Anon	Jpn. Kokai	82 24 615	(1982)	- heat recuperation
Anon	Jpn. Kokai	82 21 936	(1982)	- hydrogen
<u>Japan Oxygen Co Patents</u>				
Okada	Jpn. Kokai	78 37 583	(1978)	Energy recuperation
Okada and Wakaizumi	Jpn. Kokai	78 37 584		

(continued)

Table II (continued)

Katsuki and Wakaizumi	Jpn. Kokai	78 39 993	(1978)	- O_2/O_3
Anon	Jpn. Kokai	81 63 804	(1981)	- air
Petrolcarbon Devel. Patents				
Bird G.	U.S.P.	3,944,400	(1976)	- helium purific.
Bird G.	Brit. Pat.	1,444,231	(1978)	- helium purific.
Toray Ind. Patent				
Miwateru et al.	Jpn Kokai	77 99 973	(1977)	- air
Inoue and Miwa	Ger. Offen.	3,045,978	(1981)	- high pressure reflux
Bendix Patents				
Gardner	E.P.	0,026,694	(1981)	- oxygen
Pall Corp. Patents				
Anon	E.P.	0,019,879	(1980)	- bed heating by microwaves
Berbwerksverb. Patents				
Anon	E.P.	0,049,782	(1980)	- two desorption steps
Anon	E.P.	0,066,869	(1982)	- pretreatment columns
Anon	E.P.	0,066,868	(1982)	- two-step decompression and purge
Calgon Corp. Patents				
Anon	E.P.	0,055,669	(1982)	Carbon sieves; pressurization with breakthrough gas
Anon	E.P.	0,055,961	(1982)	

TABLE III

Reviews on (or including) pressure-swing adsorption

Domine and Hay[7]	(1968)	(Engl)	PSA
Lee and Stahl[40]	(1973)	(Engl)	PSA
Skarstrom[8]	(1973)	(Engl)	PSA
Kenny and Kirkby[39]	(in press)	(Engl)	PSA
Suzuki[104]	(1979)	(Japan)	PSA
Czaplinski and Mrozek[105]	(1980)	(Pol)	PSA
Cassidy and Holmes[106]	(1984)	(Engl)	PSA
Richter et al.[107]	(1984)	(Ger)	PSA
Wankat[18]	(1981)	(Engl)	Cyclic Separation processes
Ray[108]	(1983)	(Engl)	Zeolite Separation of gases
Gawronski[109]	(1979)	(Pol)	Cyclic separation process
Landolt and Kerr[110]	(1973)	(Engl)	Zeolite Separation of gases
Mersmann et al.,[111]	(1984)	(Engl)	Adsorptive Gas Separation
Keller[112]	(1983)	(Engl)	Adsorptive Gas Separation
Ruthven[19]	(1984)	(Engl)	PSA and Adsorption in general
Chen and Yang[113]	(1984)	(Engl)	Cyclic Gas Separations

selectivity. For example, oxygen is much less adsorbed than nitrogen on zeolites but as much on active carbon. However, in recent years, carbon molecular sieves have been developed by Bergbau - Forschung GmbH[15], which exhibit a wide difference in the rate of adsorption in favor of oxygen, allowing a process for producing pure nitrogen[16]. When several adsorbents can be used, process economics control which is chosen[17].

The low pressure P_L of the cycle is most often slightly above atmospheric pressure. However, some processes use vacuum purge, which allows the suppression of reflux, and therefore entails a larger recovery. The disadvantage of using vacuum is the investment for a vacuum pump, and the relatively long times required to reach a very low pressure in large columns. This in turns lengthens the cycle time and diminishes the overall throughput.

The choice of the high pressure P_H will depend on the purity and the recovery desired, on the pressure at which the gas is available, and on the pressure at which the pure product is to be used. Some processes work up to 50 bars (hydrogen purification), while for air drying, the high pressure seldom exceeds 5 to 8 bars.

Increasing P_H/P_L increases the volume of gas available for reflux, for a given molar reflux ratio, and thus increases purity; alternatively, a smaller molar reflux ratio may be used, for the same volume of reflux, thus increasing recovery. There is a minimum value of the pressure ratio related to the minimum reflux mentioned earlier: to obtain a reflux volume (purge) equal to the feed volume, the pressure ratio must be larger than the reciprocal of the non-adsorbed component mole fraction: $P_H/P_L > 1/x_{He}$. Skarstom[6] noted that the volumetric purge to feed ratio must be greater than 1.0 and recommended from 1.1 to 1.5.

Although most processes work around ambient temperature, or at the temperature of the feed gas, the working temperature should be considered as an important decision parameter. Temperature affects the equilibrium capacity of the adsorbent, the shape of the adsorption isotherm, the selectivity between different components, and the adsorption kinetics. For example, the choice of a relatively high working temperature may make the adsorption of a particular component relatively negligible, and therefore facilitate its recovery as a pure product. Concerning the adsorbed components, if the isotherms are more nearly linear in the operating range, desorption will be facilitated, the kinetics improved, and the operation as a whole may be less irreversible with respect to mass transfer. Generally lower reflux ratios will result. On the other hand, the effective capacity of the column will be smaller, that is, less feed will be treated per cycle, and this is not necessarily compensated by shorter cycle times, because the durations of the compression and decompression steps are not significantly affected.

The only cycles operating at very low temperature (that of liquid air for example) are those for separating rare gases, such as Ne and Helium[7]. Some processes involving the adsorption of gases such as N_2, O_2, Ar, Kr may be advantageously operated below ambient[18]. Figure 3 shows the adsorption isobars (760 mm Hg) of various gases on Linde molecular sieves[7].

Flow velocities in the isobaric steps are those generally used in gas adsorption, that is comprised between 0.01 and 0.5 m s^{-1}. The choice of velocity will be mainly determined

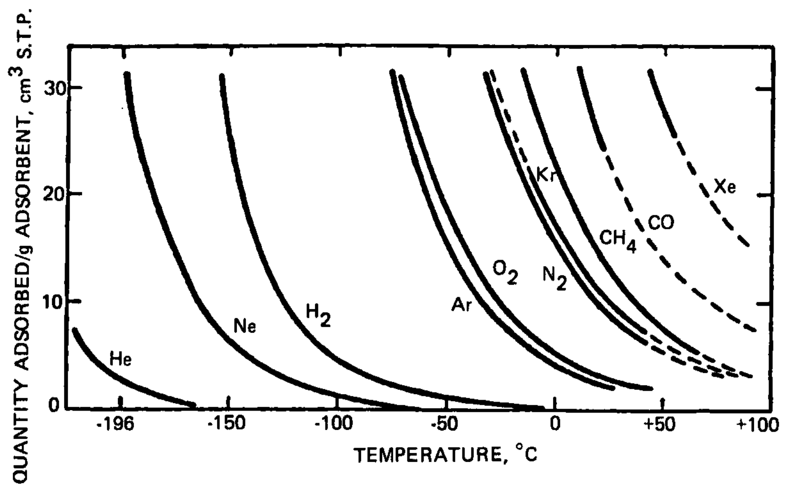

FIGURE 3

Adsorption isobars (760 mm Hg) on molecular sieve Linde 5A[7].

by the pressure drop admissible, itself a function of the granulometry of the adsorbent. The velocity will also depend on the concentration of adsorbable components (the lower that concentration, the higher the allowable velocity) and on the transfer kinetics, characterized for example by a characteristic mass transfer time between gas and solid. As a general rule, the average residence time of the gas in the bed should be significantly larger than the characteristic transfer time, for sharp adsorption fronts to be obtained. For example, for kinetics governed by internal diffusion in the crystallites of a molecular sieves adsorbent, the characteristic time is given by the ratio d^2/D, where d is the aveage crystallite size and D the diffusion coefficient. Taking as orders of magnitudes respectively 10 μm and 10^{-6} cm^2s^{-1}, we find a characteristic time of one second. In an adsorbent bed 0.5 m thick, the flow velocity should therefore be smaller than 0.5 m s^{-1} in order to avoid internal diffusion control. An exception to this rule is the case already mentioned of the nitrogen/oxygen separation on carbon molecular sieves, which is based on a difference of adsorption kinetics[16].

A review on diffusion in zeolites is found in Ruthven[19] and a detailed discussion of kinetic phenomena in PSA is found in Kotsis and Argyelan[20,21] and Argyelan and Kotsis[22].

PSA THEORIES

The focus of this paper is on PSA processes. Obviously, theories are very important in developing new processes. In this section we will very briefly review PSA theories and give the interested reader references for future study.

The most common theories for qualitative understanding of PSA are forms of the equilibrium theory. These theories assume that gas and solid are locally in equilibrium. This assumption will only be valid when mass transfer rates are very high; however, this assumption greatly simplifies the analysis. In addition, equilibrium theories often assume:

negligible dispersion, isothermality, constant velocity, negligible pressure drop, ideal gas and linear equilibrium. Some of these assumptions can be relaxed (see Table 4). What is left after all these assumptions have been made is the contribution of equilibrium to separation. During the time a solute molecule is adsorbed, its velocity is zero. When it is not adsorbed, the molecule will move at the interstitial gas velocity v. During the isobaric periods, the observed solute velocity is then

$$U_{solute,i} = (\text{fraction of time solute is adsorbed})\ v \tag{1}$$

For an ideal gas and linear equilibria[8,23]

$$U_{solute,i} = \frac{v}{1 + \frac{1-\epsilon}{\epsilon} k_i} \tag{2}$$

where the equilibrium expression is

$$n_i = k_i C_i = \frac{k_i P}{R\ T} y_i \tag{3}$$

The average movement of the solute (the characteristics) can be determined for the isobaric periods by plotting a line of slope $U_{solute,i}$ on a graph of axial distance z versus time t.

During the periods when pressure varies (blowdown, pressure equalizations and repressurization), the mole fractions before and after the period are related by[23],

$$\frac{y_{i,after}}{y_{i,before}} = \left[\frac{P_{after}}{P_{before}}\right]^{\beta_i - 1} \tag{4}$$

where

$$\beta_i = \frac{\epsilon + (1-\epsilon) k_{inert}}{\epsilon + (1-\epsilon) k_i} \tag{5}$$

The characteristic positions shift during the pressure change by an amount

$$\frac{z_{after}}{z_{before}} = \left[\frac{P_{after}}{P_{before}}\right]^{-\beta_i} \tag{6}$$

where z must be measured from the closed end of the column.

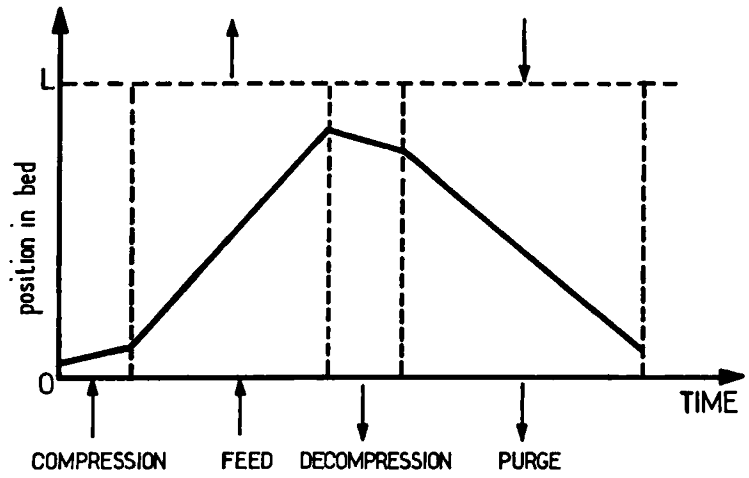

FIGURE 4

Characteristic diagram for pressure-swing cycle of Fig. 2, under linear local equilibrium assumption. The heavy line shows the position of the adsorption front.

The graphical local equilibrium solution for this simplest case (none of the assumptions have been relaxed) is shown in Figure 4 for the simple Skarstrom type of cycle (Figure 2). More detailed applications of the local equilibrium model are listed in Table IV.

For quantitative understanding of PSA, mass transfer effects must be included in the theory. Kinetic models are listed in Table V. These models all require a numerical solution. Alternatives also shown in this table are equilibrium-staged models, where kinetics and dispersion are lumped in the HETP value.

As can be seen from the assumptions made, much work remains to be done before we can predict the behavior of competitive, non-linear multicomponent systems in non-isothermal operation.

Although a complete theory has not been published, considerable information can be gleaned from the published theories and experimental results. The purity of the high

TABLE IV
Local Equilibrium Model Solutions for PSA

Process Applied To	Assumptions[x]	Sample Calculations (SC) or Comparison with experiment (E)	Ref.
Simple Skarstrom type System (Figure 2)	Carrier does not adsorb. Instantaneous blowdown and repressurization	CO_2 removal from He on silica gel (E)	8
Simple Skarstrom type system (Figure 2)	Entire bed is in equilibrium (Mass balance theory). Carrier does not adsorb.	D_2 from H_2 on Pd deposited on alumina (E)	101
Simple Skarstrom type system (Figure 2)	Carrier does not adsorb.	HT from H_2 on vanadium hydride (E)	33
Simple Skarstrom type system (Figure 2)	Carrier can adsorb.	Arbitrary β_1 value (SC)	23
Simple Skarstrom system (Figure 2)	Carrier can adsorb Variable flow rate due to sorption effect. Numerical solution required.	Arbitary parameter values (SC)	28
Multicomponent PSA system	Non-interacting solutes. Carrier can adsorb.	Ethylene and acetylene from N_2 on activated carbon (SC)	62
1 or 2 column system No separate purge step	Carrier strongly adsorbs.	Arbitrary parameter values (SC)	31
1 or 2 column system No separate purge step	Linear and non-Linear isotherms Variable flow rate due to sorption effect. Numerical solution required.	O_2 and N_2 in air on 5A mole sieve (E)	32
Two pairs of columns with different adsorbent	Non-interacting solutes. Carrier can adsorb.	Arbitrary parameter values (SC)	44,61

(continued)

Table IV (continued)

1 and 2 column systems. Both with purge steps. Start-up and transient calculations.	Carrier can adsorb.	O_2 and N_2 from air on 5A molecular sieve (SC)	114
1 column, Continuous product withdrawal, very rapid cycles	Pressure fluctuations in column included. Numerical solution required.	CH_4 and N_2 on 5A molecular sieve (E)	35

x Unless otherwise stated the following assumptions were made: local equilibrium, negligible dispersion, isothermal, constant velocity, negligible pressure drop, ideal gas, and linear equilibrium.

TABLE V

PSA Theories Including Mass Transfer or Staged Models

Process	Model and Assumptions^x	Sample Calculations (SC) or Comparison with experiment (E)	Ref.
2 column Skarstrom type system (Figure 2)	Lumped parameter mass transfer. Finite difference solution for constant pressure portions. During blowdown and repressurization composition is either frozen or at equilibrium	CO_2 removal from helium on silica gel (E)	9
2 column Skarstrom type system	Lumped parameter mass transfer. Assume thermal equilibrium but not isothermal. Arrhenius temperature dependance. Crank-Nicholson integration	Drying air using Activated alumina (SC)	24
		Drying air using silica gel (E)	26
2 column Skarstrom type system (Figure 2)	Lumped parameter mass transfer Orthogonal collocation and finite difference calculations	CO_2 from He on silica gel (SC)	19 115
2 column system with pressure equalization step	Numerical integration	Drying air with Mobil Sorbead R(E)	25

(continued)

Table V (continued)

1 or 2 column systems	Well-stirred equilibrium cell model		116
1 column system	Well-stirred equilbrium cell model	CH_4 from He on activated carbon (E)	97
1 column, 3 step system. Regenerate with vacuum	Explicit finite difference (equilibrium cell model). Case 1. Δp and v from Darcy's law. Case 2. Const. v and $\Delta p = 0$	Unspecified (E)	30
1 column, continuous product withdrawal. Very rapid cycles	Equilibrium staged model Use Darcy's law	CH_4 and N_2 on 5A molecular sieves (E)	36
1 column, continuous product withdrawal. Very rapid cycles	Well mixed cells. Nonlinear isotherms; variable velocities. (Results only - no details)	O_2 and N_2 on 5A molecular sieve (E)	32
Study of depressurization step	Ideal back mix and ideal plug flow. Langmuir kinetics	Removal of CH_4, CO CO_2, N_2 from H_2 on carbon sieve (E)	117

x Unless otherwise stated the following assumptions are made: negligible dispersion, isothermal, constant velocity, negligible pressure drop, ideal gas and linear equilibrium.

pressure product can be increased by increasing the volumetric purge to feed ratio, γ. To achieve high purity the local equilibrium models predict $\gamma = 1.0$ is sufficient. In practice $\gamma > 1.0$ is required. Unfortunately, increasing γ decreases the concentration of the waste product and lowers the recovery of desired product. Isothermal models predict more separation than adiabatic models,[24] but in practice operation is closer to adiabatic than isothermal. Temperature variations in the range of 2 °[26] and 4 ° C have been observed for drying air. Cycles should be short enough that neither mass nor thermal breakthrough occurs. The faster the cycles the less temperature variation will be observed. An optinum temperature of operation will exist[17,27]. At lower temperatures adsorption is easier, but purging becomes more difficult. Repressurization should be done with pure product gas, not feed gas.[28] This works as a sort of reflux and will produce more product. Pressure equalization steps help produce more product. The higher the pressure ratio the more pressure equalization steps can be profitably employed.

PSA CONFIGURATIONS

Since modern PSA processes sometimes involve many columns and/or complex cycles, a common framework for their description is helpful in the analysis of these processes. In the present section, we describe some typical fixed-bed configurations within such a framework. By "configuration", we mean the flow-sheet and the operating sequence of the set of columns. Besides the operating conditions (temperature, pressures, flow-rates, nature of gases) the configurations differ by

1. The minimum number of columns (and possibly reservoirs) necessary for the configuration to work.
2. The number and nature of distinct steps undergone by each column.
3. The phase shift between columns for each step.
4. The coupling between columns.
5. The relative flow directions.

In the following, only the minimum number of columns, labelled A, B, C etc. is represented; clearly each configuration can also work (and most often does) with several independent such sets, operated in parallel but out of phase, and leading to a quasi-continuous production. Each step, (labelled 1, 2, 3 etc.) is shown once. We therefore have a compact representation of the configuration. To appreciate this, the reader should compare the compact representation of the 4-column, 8-step Wagner configuration (Fig. 18) with its full representation (Fig. 19) showing each column at each step.

Surge tanks are often included in these configurations, to allow continuous withdrawal of products. These tanks are not represented unless they play an essential role in the process (for recycle or purge). The format used for the presentation is the following:

Name of configuration and figure number

a. References

b. Main characteristics of configuration

c. Steps of the cycle

d. Comments and examples of applications.

In the figures, M designates the feed mixture, P a pressurized product flux, B a blowdown or low pressure product flux, V a flux resulting from evacuation, R a reject resulting from reflux purge. The steps are numbered 1, 2, 3..; the first compression step after the lower pressure has been attained is usually labelled number 1. The full representation (Fig. 19 for example) is obtained by operating circular permutations on the steps.

Single Column Configurations With Vacuum Regeneration

Bayer-Mahler configuration (Figure 5)

a. Chem. Eng., *77*, 54-55 (1970); Inform. Chimie, *13*, 49-54 (1971), Lee[29] See also Szolcsanyi et al[30] for the study of a similar configuration

b. - 1 column; 3 steps of equal duration

- No isobaric step

- Vacuum regeneration

c. 1 : Compression with feed mixture M

2 : Decompression and production P

3 : End of decompression and vacuum regeneration

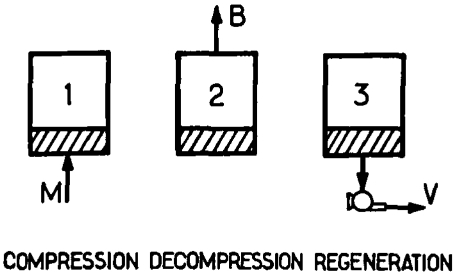

FIGURE 5

Bayer-Mahler single column, 3-step configuration.

d. - Applied to production of oxygen rich gas from air

- Proposed with 3-beds working 1/3 cycle phase shift

- A dryer column is included (represented by hatched zone in Figure 5) and undergoes

the same cycle.

<u>Comex configuration</u> (Figure 6)

a. Fr. Pat.[18]

b. - 1 column, 1 reservoir, 5 unequal steps

- Recycle of part of the decompression product

- Vacuum regeneration

c. 1 : Compression with feed from reservoir

2 : Isobaric production

3 : Decompression into reservoir

4 : Decompression to atmosphere (waste)

5 : Vacuum regeneration

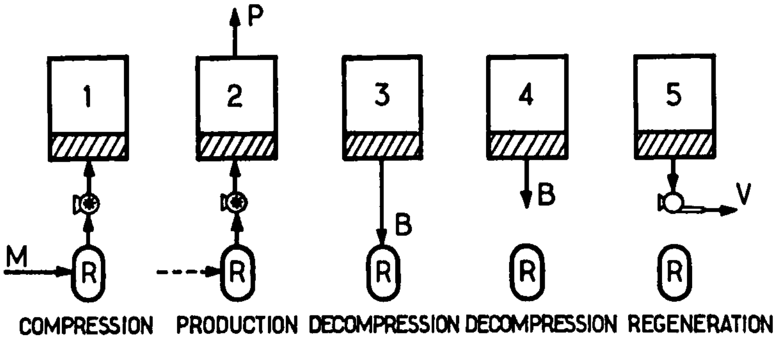

FIGURE 6

Comex single column, 5-step configuration.

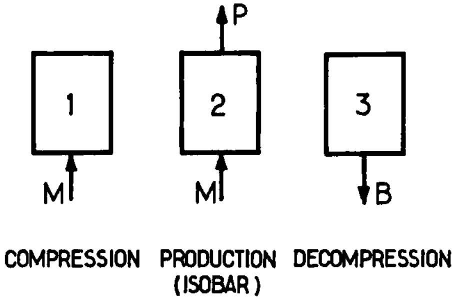

FIGURE 7

Basmadjian single column, 3-step configuration.

d. - Applied to purification of helium from nitrogen for diving gases

- Works on active carbon (oxygen removal also) or zeolite (nitrogen removal only), below ambient temperature (- 10 ° C)
- A dryer column is included (hatched zone) and undergoes the same cycle
- Proposed with 2 or 3 phase-shifted beds.

Single Column Configurations Without Vacuum Regeneration Nor Purge

Basmadjian configuration (Figure 7)

a. Hill[31], Flores-Fernandez and Kenney[32], D. Basmadjian and L. Pogorski, U.S. Pat. 3,279,153 (Oct. 1966)

b. - 1 column, 3 steps

- No purge

- No vacuum regeneration

c. 1 : Compression with feed

2 : Isobaric production

3 : Decompression (blowdown)

d. - Experimental results on N_2/O_2 separation

- Configuration adapted to recovery of a weakly adsorbed minor component, because of each desorption.

<u>Wong and Hill configuration</u> (Figure 8)

a. Wong and Hill[33,34]

b. - 1 column, 4 steps

- No purge, no vacuum

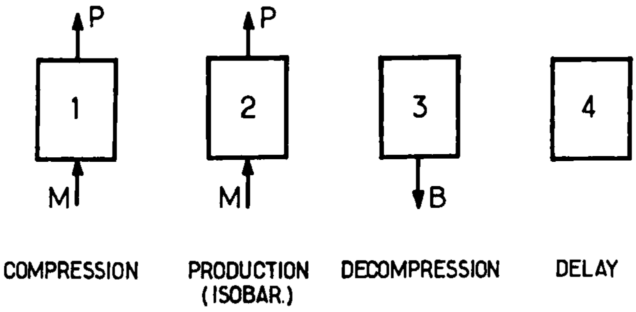

FIGURE 8

Wong and Hill single column, 4-step configuration.

c. 1 : Compression with feed and product withdrawal (very rapid)

2 : Isobaric production

3 : Fast decompression

4 : Delay for slow desorption

d. - Compression and decompression are very rapid (a few seconds)

- Similar to previous case

- Surge tank on the product line allowing continuous product flux.

Single Column Configurations With Pressure Gradients

Kadlec configuration (Figure 9)

a. Turnock and Kadlec,[35] Kowler and Kadlec.[36]

b. 1 column, 2 steps

Rapid cycle

No isobaric step; no purge, no vacuum

A pressure gradient exists and moves in bed

c. 1 : Compression with mixture and product withdrawal

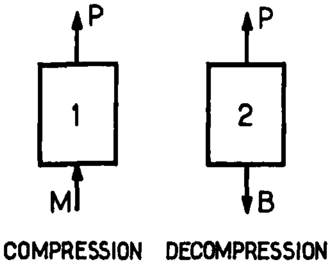

FIGURE 9

Kadlec single column, pressure gradient configuration.

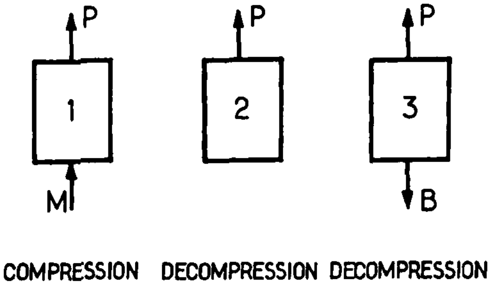

FIGURE 10

Keller and Jones' pressure-swing parametric pumping.

2 : Bi-directional decompression while withdraw product and waste

d. - Laboratory scale experiments for nitrogen-methane (30% nitrogen) on 5A molecular sieve around ambient temperature

- The two steps are approximately of equal duration
- Cycle time is from 2.5 to 20 seconds
- Surge tanks on feed and product lines
- Small adsorbent particles (around 50 μ)

<u>Union-Carbide pressure-swing parametric pumping</u> (Figure 10)

a. Keller and Jones,[37] Jones and Keller,[38] US Pat. 4,194,891 and 892 (1980), Chem. Eng., *71* (Nov. 30, 1981)

b. 1 column, 3 steps

Rapid cycle

No isobaric step, no purge, no vacuum

A pressure wave is created in the column

c. 1 : Compression with mixture <u>and</u> product withdrawal

2 : One directional decompression while product is withdrawn

3 : Bi-directional decompression while withdraw product and waste

d. - $P_m > P_P > P_B$

- Provides an additional operating parameter with respect to previous case
- First two steps are short (0.5 to 3 seconds); third step is 5 to 20 sec.
- A surge tank on the product line
- Adsorbent grains of small size to allow pressure wave to build up.

Symmetric Two Column Configurations

(The two columns undergo the same cycle)

Esso-Skarstrom configuration (Figure 11)

a. Skarstrom, US Pat. 2,944,627 (1960), Skarstrom[6], Chan et al [23] Kenney and Kirkby[39]

b. 2 columns, with a half cycle phase shift

4 steps of similar duration

Countercurrent purge step

c. 1 : Compression with mixture (or pure product P)

2 : Isobaric production

3 : Decompression

4 : Low pressure countercurrent purge with product

d. - The operating cycle of each column is identical to the "standard" cycle of Figure 2

- The other states of the two-bed system are obtained by circular permutation on the step number (column A goes to step 2, while column 3 goes to step 1, etc ...)

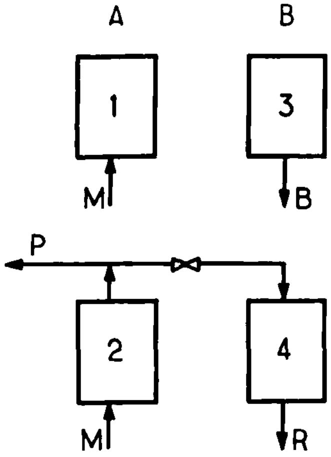

FIGURE 11

Esso-Skarstrom 2-column, 4-step configuration.

- The withdrawal of pure gas in step 2 and of gas for purge may be simultaneous or successive
- Figure 10 could also represent 4 distinct columns with 1/4 cycle phase shift

Esso-Berlin configuration (Figure 12)

a. Berlin N.H., US. Pat. 3,280,536 (1966), Lee and Stahl.[40]

b. 2 columns, symmetrical, 1/2 cycle phase shift

6 equal steps

Pressure equalization (steps 1 and 4)

c. 1 : Compression by blowdown of other column (pressure equalization)

2 : Compression by mixture

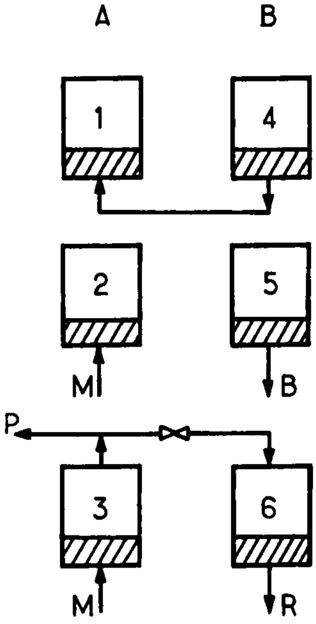

FIGURE 12

Esso-Berlin 2-column, 6-step configuration (also Chemical Design configuration).

3 : Isobaric production

4 : Decompression into other column (pressure equalization)

5 : Decompression

6 : Low pressure purge with product (countercurrent with respect to feed)

d. - Steps 2, 3, 5, 6 are equivalent to Skarstrom's cycle

- Pressure equalization saves blowdown gas and compression work, and improves recovery of pure product
- Exit and entrance ends of columns in pressure equalization are optional
- Figure 11 could also represent a 4 column or a 6 column system

Chemical Design configuration (Cf. Figure 12)

a. Alexis[41]

b. Configuration identical to that of Berlin, but a small guard column is added, packed with a different adsorbent (represented by hatched area on Fig. 12). The guard column undergoes the same cycle as the main column. It may serve as dryer or in hydrogen purification, as a scavenger for heavy hydrocarbons, the lighter ones being adsorbed on the main column.

Esso-Marsh configuration (Figure 13)

a. Marsh W.D., US P. 3,142,547 (1964), Lee and Stahl[40]

b. 2 columns with half cycle phase shift

1 reservoir to store blowdown product

10 steps of equal duration (3 of which are identical)

Countercurrent two-step purge using the stored blowdown

c. 1 : Compression with product of other column

2,3,4 : Isobaric production (presented as 3 distinct steps to preserve symmetry)

5 : Isobaric production used to purge other column

6 : Isobaric production used to compress other column

7 : Decompression into reservoir, preferentially through production end

8 : Decompression to waste, preferentially through feed end

9 : Low pressure purge by gas stored in reservoir

10: Low pressure purge by product of other column

d. This configuration improves the Berlin configuration in several respects;

- Compression is done with high pressure product instead of blowdown or mixture

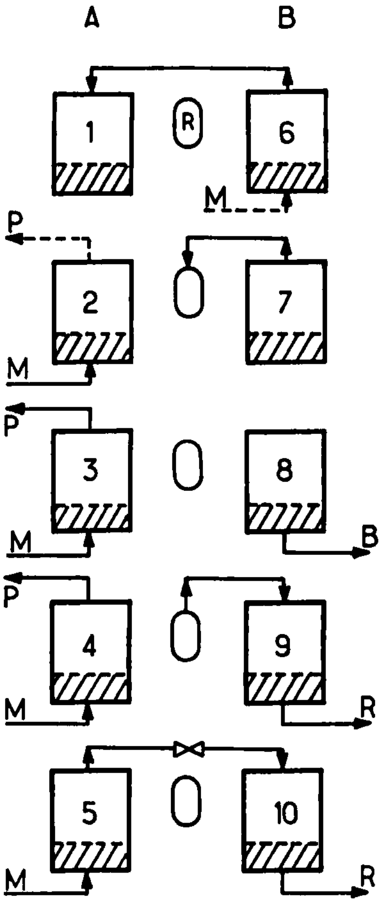

FIGURE 13

Esso-Marsh and Grace, 2-column, 10-step configuration (dotted lines are in Esso-Marsh only).

(note that there is no pressure equalization step);

- This high pressure product need not be pure; thus, breakthrough is allowed in step 6, implying a full use of the bed capacity
- Blowdown is used as a first purge (step 9), thus reducing the need for pure product purge in step 10

The use of the storage resevoir allows decoupling of the columns during steps 2, 3, 4 of one, and 7, 8, 9 of the other column, and therefore a better optimization of flow rates and cuts in these steps.

Clearly, the Marsh configuration may be operated with any number of pairs of columns. If the pairs are suitably phase shifted, a reservoir may be common to two pairs.

Used for oxygen production from air.

Grace configuration (Cf. Figure 13)

a. Lee and Stahl[40]

b. The Grace configuration differs little from the Marsh configuration.

The three differences are

- Use of a small guard bed (a dryer, for hydrogen purification on zeolites; represented by hatched zone on Fig. 13)
- Steps 1 and 6 are a pressure equalization step, as in the Berlin configuration; thus, no feed is introducted in step 6
- As a consequence, step 2 is a continuation of the compression: no product is withdrawn.

A Dissymetric Two-Column Configuration

L'Air Liquide configuration (Figure 14)

a. Guerin de Montgareuil and Domine,[10] Fr. Pat. 1 223 261 (1957), US Pat. 3,155,468 (1964), and 3,242,645 (1966); Domine and Hay[7]

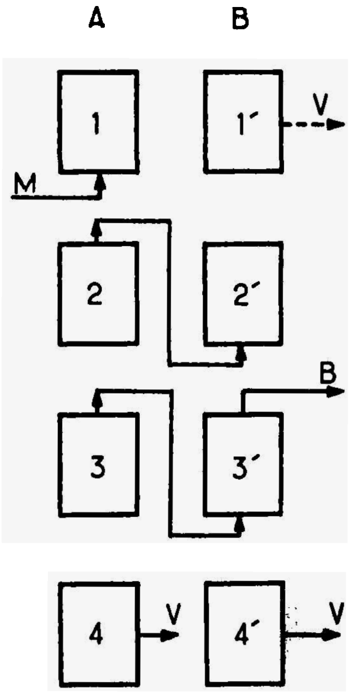

FIGURE 14

L'Air Liquide 2-column dissymetric configuration.

b. 2 columns, 4 steps

Vacuum regeneration through middle of bed

Decompression of the two beds in series

Column B is always second in line

c. 1 : Compression with mixture; 1' : delay or end regeneration

2,2' : Pressure equalization of the two beds

3,3' : Decompression of the two beds in series

4,4' : Vacuum regeneration in parallel

d. - Typical step duration for oxygen from air process are:

1 : 35 s; 2 : 10 s; 3 : 15 s; 4 : 60 s

- See discussion in 3-column section

Three-Column Symmetric Configurations

Nippon-Steel configuration (Figure 15)

a. Tamura T., Fr. Pat. 1 502 458 (1967), Lee and Stahl[40]

b. 3 columns, 3 steps, 1/3 cycle phase shift

Vacuum regeneration

Compression with product

c. 1 : Compression with product

2 : Isobaric production

3 : Countercurrent blowdown and vacuum

d. - Pretreatment column (dryer) undergoes same cycle

- Proposed for oxygen-rich air generation

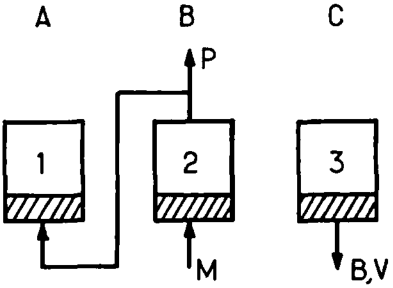

FIGURE 15

Nippon-Steel 3-column, 3-step configuration.

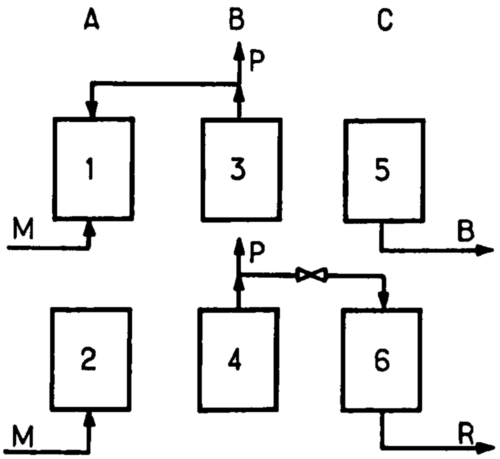

FIGURE 16

Union-Carbide-Batta 3 column, 6-step configuration.

Union Carbide - Batta configuration (Figure 16)

a. Batta L.B., US Pat. 3,636,679 (1972), Lee and Stahl[40]

b. 3 columns with 1/3 cycle phase shift

6 steps of equal duration

No isobaric high pressure step; compression simultaneously from both ends

c. 1 : Compression from both ends simultaneously, with feed mixture at one end, and blowdown product at the other

2 : End of compression with mixture

3,4 : Decompression and production: recompress one column, then purge the other

5 : End of decompression, countercurrent

6 : Purge by decompression product

d. Proposed for hydrogen purification

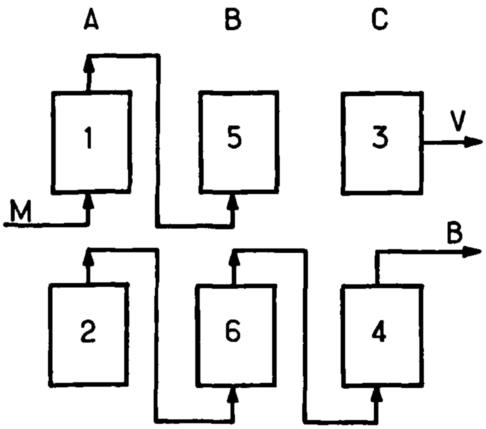

FIGURE 17

L'Air Liquide 3 column, 6-step configuration.

<u>L'Air-Liquide configurations</u> (Figure 17)

a. Guerin de Montgareuil and Domine,[10] Fr. Pat. 1 223 261 (1957), US Pat. 3,155,468 (1964), US Pat. 3 242 645 (1966); Domine and Hay[7]

b. 3 columns or more

Typically 6 steps, for 3 columns

Vacuum regeneration through middle of bed

Compression and/or decompression through several beds in series

c. 1 : Compression by feed mixture

2 : Decompression through the other beds

3 : End of decompression and vacuum through middle of bed

4 : Refill through decompression product of two other beds, and production

5 : Compression by high pressure product of other column

6 : Decompression in second position

d. This configuration is seen to be quite different from Esso and Union Carbide processes, and constitutes a family in itself. Besides using an exhaust line located near the middle of the bed rather than at an end, it is characterized by the decompression through a series of columns. The last of the series being newly regenerated, this prevents breakthrough and allows the blowdown to be collected as a pure product. Contrary to the other configurations, this pure product is obtained at low pressure. Note that there is no isobaric step, no reflux, and that the flow occurs always in the same direction. In a complete cycle, any column undergoes twice compression (steps 1 and 5) and decompression (steps 2 and 6). L'Air Liquide designate their configurations by a set of numbers: N is the number of columns "in association" compressed in series (here, 2) N' the number of columns into which the compressed columns are decompressed (here, 1), P the number of columns simultaneously regenerated (here, 1) and $P' = N+N' - P$ the number of relay columns that are switched from the decompression to recompression without being regenerated (here, 2, columns B and C go from steps 6 and 4 to steps 1 and 5 respectively).

The general designation is "Association N–N', relay P'" so that Figure 17 will "association 2-1, relay 2." This particular configuration is symmetric, that is all columns undergo the same series of steps. Unsymmetric configurations have been used, analogous to that of Figure 13, and resulting from non-circular permutations of columns.

These configurations have been tested and results presented[7] for the following separations: N_2/H_2, CH_4/H_2, CO/Ar, Ne/N_2+He and O_2/air.

A Four Column Configuration

Union-Carbide - Wagner configuration (Figures 18 and 19)

a. Wagner, J.L., US Pat. 3,430,418 (1969), Lee and Stahl,[40] Lancelin et al,[42]

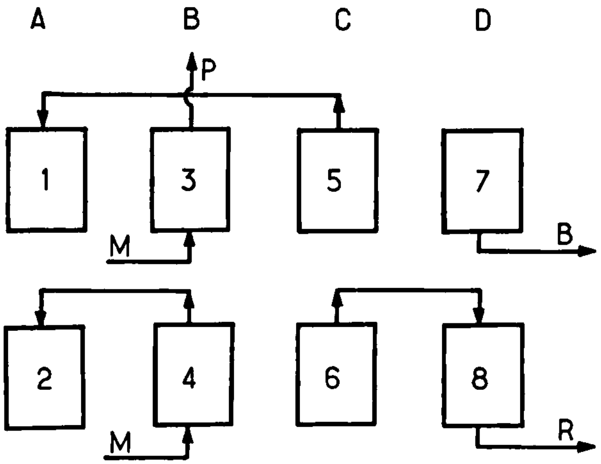

FIGURE 18

Union Carbide-Wagner 4 column, 8-step configuration.

b. 4 columns, with 1/4 cycle phase shift

Symmetric configuration

c. 1 : Compression by pressure equalization

2 : End compression by high pressure pure product

3 : Isobaric high pressure production

4 : Production used to compress a column in step 2

5 : Start decompression into a second column (pressure equalization)

6 : Continue decompression into a third column to purge it

7 : End decompression to atmosphere

8 : Purge by decompression product

d. This configuration is characterized by efficient compression and decompression schemes: the compression is done in two steps and with gases of different composition, countercurrent to the production step; decompression is effected in three steps,

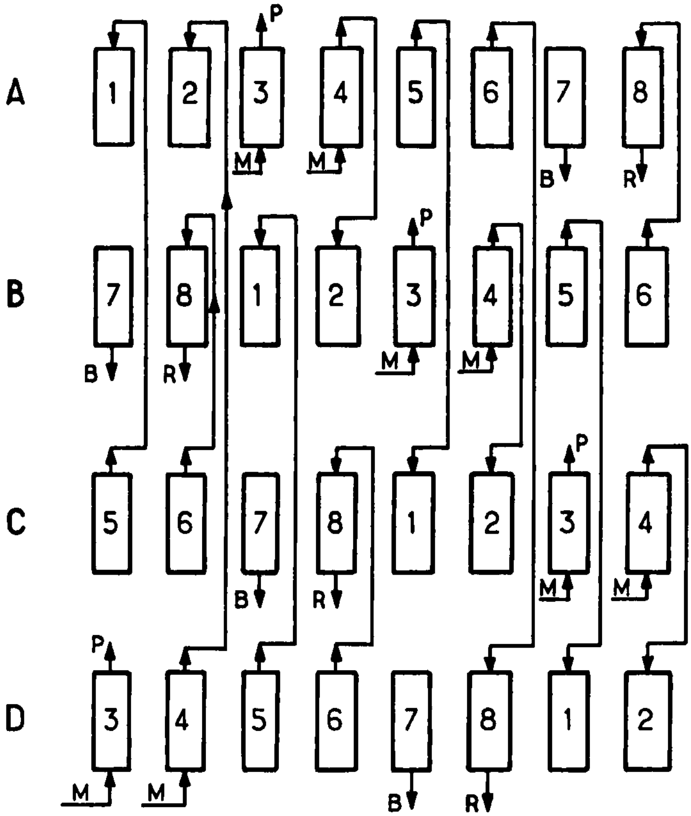

FIGURE 19

Union Carbide-Wagner configuration. Full representation: each column is shown at each step.

the blowdown being directed successively to two different columns. Note for example that the effluents of a given column are directed successively in 5 different directions during the cycle (steps 3 to 7): pure product, columns 1, 2, 3, and waste.

Fig. 19 shows a full representation of the operating cycle.

DISCUSSION OF THE CONFIGURATIONS

What reasons justify the use of more and more complex configurations? To understand this evolution, one should remember that the first applications of PSA concerned air drying and production of oxygen-enriched air. In both these cases, the raw material is practically free and the purity required is not high. In addition, for certain applications, small units are required (medical applications and laboratory air drying). Thus simple configurations yielding low recovery and purity were used. With hydrogen purification, more complex cycles were developed aiming at three objectives:

- increasing recovery of the useful product
- increasing product purity
- approach quasi-continuous production.

Let us examine how some of the configurations approach these goals on the example of nitrogen removal from helium.

Blowdown policies

A configuration like Bayer-Mahler (Fig. 5) will produce pure helium only with a poor recovery, because the blowdown will rapidly contain nitrogen and must therefore be rejected. This type of configuration is adapted to the production of a gas weakly enriched in helium. Many configurations have an isobaric high pressure step during which a nitrogen adsorption front moves through the column (see Comex, and Hill, Figs. 6 and 8 for single columns): pure helium is produced until this front breaks through. These configurations are therefore well adapted to the production of very pure helium, or in the general case, of pure non-adsorbed or weakly adsorbed component. The existence of an isobaric step improves the performances over the Bayer-Mahler configuration, but requires more elaborate flow and pressure controls.

The Comex flow sheet (Figure 6) illustrates a means of increasing recovery, by recycling part of the blowdown. This requires recompression of this blowdown and seems interesting only inasmuch as the pressure ratio is high, in which case, the loss during blowdown may be high. More generally, the recuperation of part of the blowdown is an objective of several configurations. Several means are employed for that purpose

- Store part of the blowdown in a reservoir for use in a later step (Comex, Marsh, Figs. 6 and 13).
- Direct the blowdown flux directly into another column to recompress it (Berlin, Alexis, Fig. 12; Wagner Fig. 18; Grace, Fig. 13, L'Air Liquide, Fig. 14).
- Use the blowdown as low pressure purge (Batta, Fig. 16; Wagner, Fig. 18)
- Split the blowdown into several fluxes; for example in the Batta and Wagner configurations (Figs. 16, 18) blowdown is used to recompress a column, to purge another one, and only the end of blowdown constitutes the waste.

Reflux policies

We have mentioned that reflux, that is the use of part of the product at low pressure to purge the column, allows cycles to work without a vacuum pump. The Esso-Skarstrom configuration shows the simplest way to effect reflux, usually countercurrent to the adsorption step. The role of reflux is to lower the partial pressure of nitrogen over the adsorbent. Therefore, if complete regeneration is sought, pure helium must be refluxed, and this of course diminishes the recovery. To overcome this, besides using vacuum regeneration, various techniques are used:

- Start the purge with impure blowdown gas (see above, Batta and Wagner, Marsh, Grace)
- Purge with impure production gas, from the end of the production step (Marsh, Fig. 13, Steps 5-10).
- Use partial countercurrent purge; the reflux ratio is such that not all the nitrogen is

removed, and only the end of the bed receiving the reflux is perfectly regenerated; this end then becomes the production end, and therefore still allows a pure product to be obtained, at the cost of a somewhat lower effective capacity of the bed. All schemes using reflux work on this principle.

Compression policies

The simplest configurations (Fig. 5 to 11) all use a single compression step with the feed mixture. More elaborate schemes use the following devices:

- Compress with flows of increasing impurity concentration, for example start with first blowdown and end compression with feed mixture (Berlin, Fig. 12; Marsh, Fig. 13). This minimizes the overall distance travelled by the adsorption front during compression, and retards breakthrough.
- Compress simultaneously several column in series (L'Air Liquide, Fig. 16); The impurity is adsorbed in the first column, and the following columns are thus compressed with pure helium.
- Compress with relatively pure gas, for example first blowdown and end of isobaric production flux (Wagner, Fig. 18; Nippon Steel, Fig. 15).
- Compress with pure gas on the production end and with impure gas or feed mixture on the inlet end; the Batta configuration (Fig. 16) realizes these two steps simultaneously.

The philosophy of elaborate compression policies is to avoid introducing impurities at the end of the column which will be the outlet end in the subsequent production step. This result can of course be achieved by using pure product for recompression, but this is detrimental for the productivity. Compression is therefore often combined with blowdown recycle. The simplest such method is the so called "pressure-equalization", in which a high pressure column is directly connected to a low pressure one. This can be observed in Berlin-Alexis (Fig. 12), March (Fig. 13), L'Air Liquide (Fig. 14), Wagner (Fig. 18).

Breakthrough policies

The issue is whether breakthrough of the adsorption front is allowed at the end of the high pressure adsorption and production steps. This of course depends on the purity required and on the destination of the effluent. Stopping the operation just short of breakthrough requires either an on-line concentration sensor placed on the outlet lines and controlling the cycle, or very reproducible cycles. This is rather constraining, and the usual configurations are designed to allow at least partial breakthrough without harm. This is not a problem when purity requirements are low, as is most often the case with the simplest configurations, (Bayer-Mahler, Kadlec) and specially those whose product is a blowdown.

The more elaborate configurations use various recycling schemes of the impure effluent to other columns. For example, L'Air Liquide configurations (Fig. 14 and 17) use several columns in series, so that the first is brought to full saturation, and the breakthrough front is trapped in the second, which is subsequently switched to first position. The Nippon-Steel and Wagner configurations (Fig. 15 and 18 respectively) use the last effluent of the production period to recompress another column. The Berlin (Fig. 12), Marsh and Grace (Fig. 13), Batta (Fig. 15) configurations use that effluent for low-pressure purge.

Clearly, many other combinations of policies than those presented may be imagined, and may be optimal for particular sets of constraints and objectives. To illustrate further the extending field of PSA, we review in the following section some recent developments, which are mostly outside the framework of description used above.

RECENT DEVELOPMENTS

The double-piston Keller-Kuo system[43]

Fig. 20 illustrates the principle of this process. A single column with center feed is used, each of its end connected to a piston. The two pistons are acted with the same period, but with a phase shift and different amplitudes. The amplitude of the piston displacements adjusts the reflux ratio at each end (ratio of the amount pumped back into the column to the amount withdrawn as product through valves V). The phase angle allows decoupling of the pressure variations and the direction of flow in each part of the

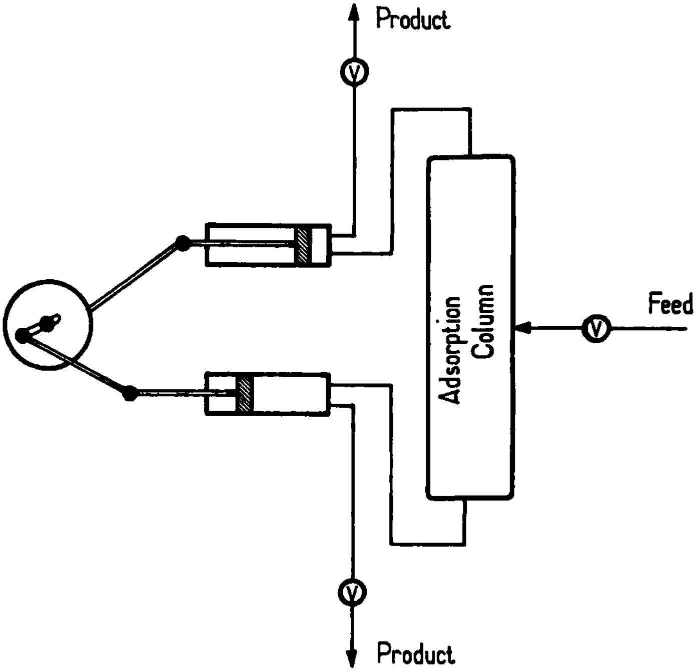

FIGURE 20

The double piston Keller-Kuo system.

column (on either side of the feed), and therefore allows one to optimize these two variables. Note that a similar, but less optimal effect is obtained in conventional configurations when compression and blowdown are effected in several steps, with different fluxes and in different flow directions.

An essential characteristic of this design is the existence of reflux at both ends of the column, whereas none of the configurations shown above have a high pressure reflux, which would require additional compressions (see also section below). This feature allows it to produce two pure products from a binary mixture. Note also the analogy with parametric pumping and with distillation.

High-pressure refluxing

Repressurization of waste gas and either recycling or refluxing this gas has been suggested. Alexis[41] shows an optional recycle of the waste stream. Wankat and Tondeur[44] suggested using compressors to send the waste gas from one PSA unit to another PSA in their parallel two-adsorbent scheme. Inoue and Miwa[45] and Miwa and Inoue[46] developed a method which desorbed nitrogen under vacuum and then compressed part of this stream for reflux. The remainder of the desorbed nitrogen was the desired product. A zeolite molecular sieve was used.

Recuperation of compression energy

An alternative or perhaps supplement to pressure equalization between columns is to send the compressed gas to an adiabatic expansion apparatus where some of the mechanical energy can be recovered.[47,48] The low temperature gas obtained can be used for cooling.

Control of heat waves in PSA

Skarstrom[4,6] called the PSA process heatless adsorption since a separate heat source is not required. The heat generated during the adsorption steps is temporarily stored in the column and is then available for the desorption steps.

This requires that thermal breakthrough not occur during the cycle. If this is a problem, a non-adsorptive heat-storing material can be mixed in with the adsorbent to slow down the thermal wave.[49] If desired one can also combine temperature and pressure changes[50,51], although this may be awkward because of different inherent cycle periods for pressure and temperature swings. A solution to this problems may be to incorporate microwave adsorbing material in the bed.[52]

Use of two adsorbents

Two adsorbents can be usefully employed in PSA systems. Alexis[41] employed guard beds containing a weak adsorbent in front of the normal adsorbent beds in a hydrogen purification scheme. The guard beds adsorbed the heavier hydrocarbons to protect the regular beds which adsorbed methane and ethane. The beds were desorbed in series. A PSA system with coconut charcoal was used to remove hydrocarbons from compressed air and 5A zeolite molecular sieves to obtain a slight increase in oxygen content.[53] The use of a desiccant layer is standard in packaged PSA systems for production of oxygen using a zeolite molecular sieve and for nitrogen production using an adsorbent carbon.[54,55] The desiccant removes water so that it does not interfere with the adsorption of the gas being removed. The use of layers of activated carbon and zeolite in the calcium form has been used for purifying hydrogen containing CO_2, CO, N_2 and CH_4 impurities.[56] Layers of zeolite and activated Al_2O_3 have been used for removal of CO_2 and H_2O from air.[57,58] See also Figs. 5, 6, 12, 13 and 15 of the present paper.

A different use of two adsorbents in PSA is to fractionate a mixture into several products. Sircar[59,60] used the two adsorbents in series in complex cycles. In one case[59] the cycle includes a feed (adsorption) step, two rinse or purification steps, two or three pressure equalization steps, a depressurization or blowdown step, two purge steps, an evacuation to vacuum step, and two pressurization steps. This method[59] was applied to a system with a non-adsorbed or weakly adsorbed carrier, a secondary key component, and an impurity. Pure carrier and pure secondary key component which was most strongly adsorbed, were produced while the impurity was removed in a waste stream containing all three components. The system was applied to purification of hydrogen and carbon dioxide from a hydrocarbon reformer plant. The waste gas included methane, carbon monoxide and nitrogen impurities. The two adsorbents were activated carbon and 5A molecular sieve. The second cycle[60] had a similar purpose except the dilute impurities were most strongly adsorbed. This system was applied to hydrogen and methane recovery and removal of C_2+ from the effluent gas of a hydrodesulfurization plant. The two adsorbents were activated carbon and coke.

Two alternate fractionation schemes were studied by Wankat and Tondeur.[44] A series scheme where all solutes were fractionated from each other was developed. The solutes were each recovered in a mixture containing the non-adsorbed carrier gas. A parallel scheme could separate binary mixtures into pure products with no waste stream. Extra compressors were required for the parallel scheme. No experimental results were presented. Knaebel[61] presented a slightly different parallel scheme.

Alternate methods for doing multicomponent PSA fractionation were developed by Nataraj and Wankat.[62] These schemes used a single adsorbent and recovered the solutes diluted in the non-adsorbed carrier gas. A system without flow reversal was similar to chromatography and would be useful when the distribution coefficients of the solutes were similar. A system with flow reversal was closer to classical PSA and would be useful when the distribution coefficients of the solutes were very different. Experimental work is now in progress.

Moving-bed PSA

Exxon has developed a magnetically stabilized fluidized bed system which is capable of moving solids in rigid plug flow countercurrent to a gas stream.[63] This method has been applied to develop a continuous moving bed adsorber for hydrogen recovery using both pressure and temperature swings.[64,65] The adsorption and desorption steps are done in separate beds. A moving carbon bed has been proposed for concentrating Kr 85 from air.[66]

Coupling PSA with other separation methods

Pressure swing adsorption can be coupled with other separation processes. For example, cryogenic hydrogen recovery systems typically have high recoveries (96 to 98 %) but the hydrogen purity is low (90 %). PSA systems produce high purity (> 99 %) but recovery is low (70 to 90 %). Combining cyrogenic and PSA systems can give both high recovery and high purity.[67,68] If the hydrogen concentration in the feed is high, the PSA system should be first while if the feed concentration is low the cold box should be first. As a second example, PSA and gas permeation can be coupled to improve hydrogen recovery.[69] The feed gas is sent to a PSA unit where high purity H_2 is produced. The purge gas stream is sent to the permeation unit. The gas which passes through the membrane is concentrated in H_2 and is recycled to the PSA unit while the non-permeated gas is sent to waste. This method will increase hydrogen recovery.

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