



CHAPTER 2

PRESSURE SWING ADSORPTION SYSTEMS

Adsorption is a well known unit operation that operates batchwise for each column adsorber as there must be a regeneration step after each adsorption step. Thus cyclic operation is a term used in adsorption processes. One also hears terms such as heat cycles or pressure cycles referring to the use of heat to regenerate adsorption columns, or the use of a lowering in pressure to regenerate adsorption columns. Pressure swing adsorption (PSA) is a continuous cyclic process, where pressure is a major operating parameter and operation is conducted at ambient temperatures. PSA is used for the separation of gaseous mixtures with the adsorbent being regenerated by reducing the partial pressure of the adsorbed component. Partial pressure reduction can be accomplished rather rapidly by lowering the total pressure or using a purge gas. The pressure swing process operates between two different points on the same equilibrium isotherm as shown in figure 2.1 [6]

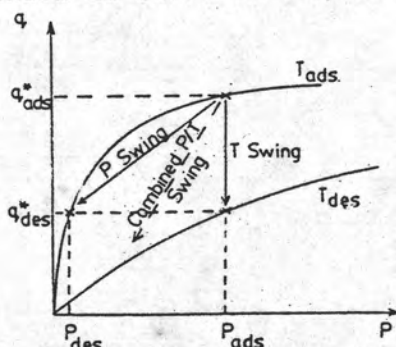


Figure 2.1 Isotherms showing pressure swing and thermal swing operation for an adsorption process.[6]

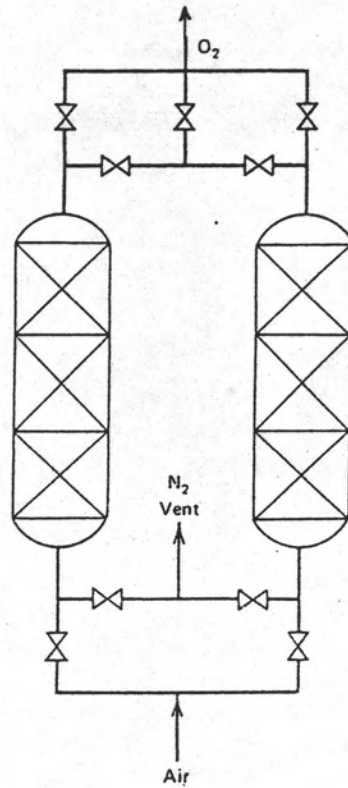


Figure 2.2 The basic two bed pressure swing adsorption system [6].

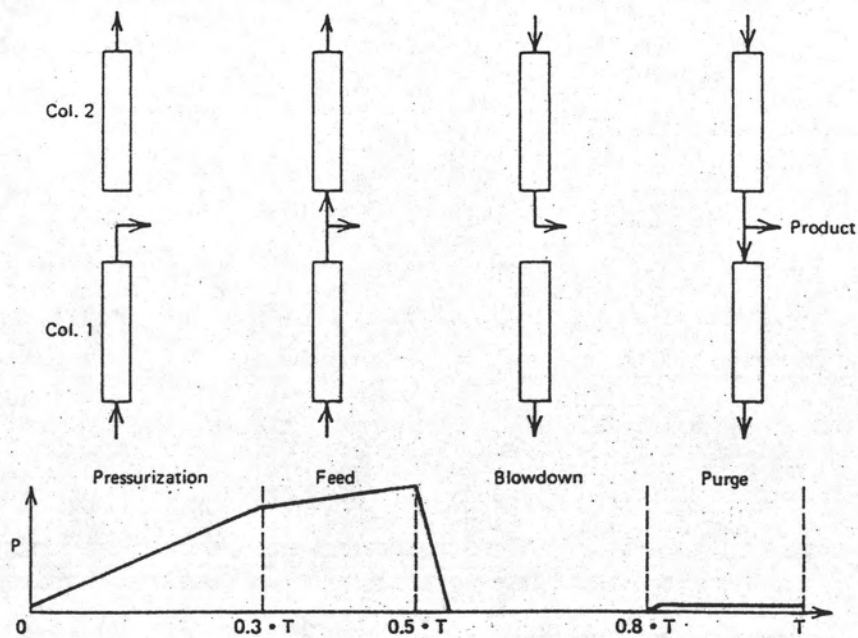


Figure 2.3 The sequence of steps in the basic PSA cycle [6].

2.1 Historical perspective of pressure swing adsorption processes

Several years after nitrogen, as a result of its higher quadrupole moment, was found to be preferentially adsorbed over oxygen on zeolites by Barrer, the successful development of synthetic zeolites stimulated the search for a method to separate air by adsorption in the 1950's and 1960's [4].

The original pressure swing adsorption system was the "heatless drier" developed by Skarstrom for air drying with the original patent fielded in 1958. The Skarstrom cycle uses two adsorption columns which are alternatively pressurized and depressurized sequentially through a program. The basic system is shown schematically in figure 2.2 and the sequence of the cycles is indicated in figure 2.3. At the end of the adsorption step, the first bed is depressurized to atmospheric pressure, at the same time a compressed feed mixture is switched to the second bed for the repressurization cycle. The adsorption step then proceeds at the feed pressure. A fraction of the purified effluent from the second bed is passed through the first bed, countercurrent to the feed direction, to purge the bed at atmospheric pressure. After the purge, the unit is ready for the next cycle [4].

The Skarstrom cycle has been widely used for air drying. For oxygen production from air, however, the oxygen recovery was too low and hence the energy requirement too high for the system to be economical [4]. The Skarstrom process was probably the first process to make use of pressure swing adsorption. The PSA concept spread

rapidly and developed into a major technology used for air drying, hydrogen purification, etc. In traditional PSA processes the number of columns used may range from one to twelve with varying arrangements of the streams between columns and varying sequences. A brief historical account of PSA commercialization is given in table 2.1.

Table 2.1 Historical account of PSA commercialization [4]

Year	PSA Commercial development highlights.
1960	Skarstrom cycle and Guerin-Domine cycle
1960	Drying of air and other gases
1961	n-Paraffin removal
1966	Hydrogen purification
1970	Oxygen production from air
1976	Nitrogen from air using molecular-sieve carbon
1977	Nitrogen(and oxygen)from air by "vacuum -swing adsorption" using zeolite
1977	"Poly bed" systems for large-scale hydrogen production
1980	Single-bed PSA for medical oxygen
1983	Nitrogen from air by zeolite

2.2 Use of pressure swing adsorption [7]

There are currently four major areas in which PSA is used

1. Air drying
2. Hydrogen recovery
3. Air separation
4. Exotic separations

1. Air drying

This is the oldest use of PSA and probably the most widely studied. Competing methods for the removal of water from ambient air are compressor/chiller systems, which are less energy efficient than PSA, or thermal swing adsorbers (where regeneration is achieved by heating and purging at constant pressure) which have the disadvantage that their thermal inertia necessitates long time cycles and therefore low throughputs per unit bed volume.

2. Hydrogen recovery applications

In commercial terms hydrogen recovery systems form the highest number of applications for PSA systems. Since 1966 Union Carbide alone built over 40 major hydrogen recovery units. Hydrogen is an expensive feedstock and recovery systems have attracted much attention. The processes competing with PSA are either based on palladium diffusion or are cryogenic processes. In contrast to these, PSA has proved itself to have higher reliability and more flexibility.

It generally requires less maintenance and can produce hydrogen of very high purity. PSA technology has recently been applied most successful to hydrogen recovery from purge gas streams in an ammonia synthesis loop purge resulting in up to 10% reductions in feedstocks/fuel costs.

3. Air separations

PSA can be used to produce either oxygen or nitrogen from air in low volume requirements. Low volume requirements ($< 200 \text{ N m}^3/\text{hr}$) of oxygen include :

1. Biological treatment of municipal and industrial wastewater.
2. Feed to ozone generators for wastewater treatment.
3. Oxygen for rivers and reservoirs, especially for fish farming.
4. Bleaching of chemical pulp and treatment of black liquor in the paper industry.
5. Nonferrous metal smelting.
6. Medical applications, domiciliary O_2 generators, etc.
7. Chemical oxidation processes.
8. Enriched O_2 combustion atmosphere to enhance fuel economy .

Nitrogen applications center around inert gas requirement ; inert flushing gas for petroleum tanks, plant flushing prior to start-up, etc. For low volume applications, PSA has the following

specific advantages over cryogenic methods and/or road tanker delivery systems :

1. fast and simple start-up and shut-down ;
2. simple, reliable and maintenance-free operation ;
3. low operating costs ;
4. low capital costs, especially as special materials of construction are not required ;
5. highly flexible production capability minimizes storage capacity and/or allows efficient operation even with large demand fluctuations;
6. being frequently skid-mounted, construction and installation costs are minimized .

4. Other separations

1. Gaseous isotope separations in the nuclear reprocessing industry.
2. Helium recovery from blast furnace gases.
3. Hydrocarbon separations, e.g. paraffins from aromatic hydrocarbons.

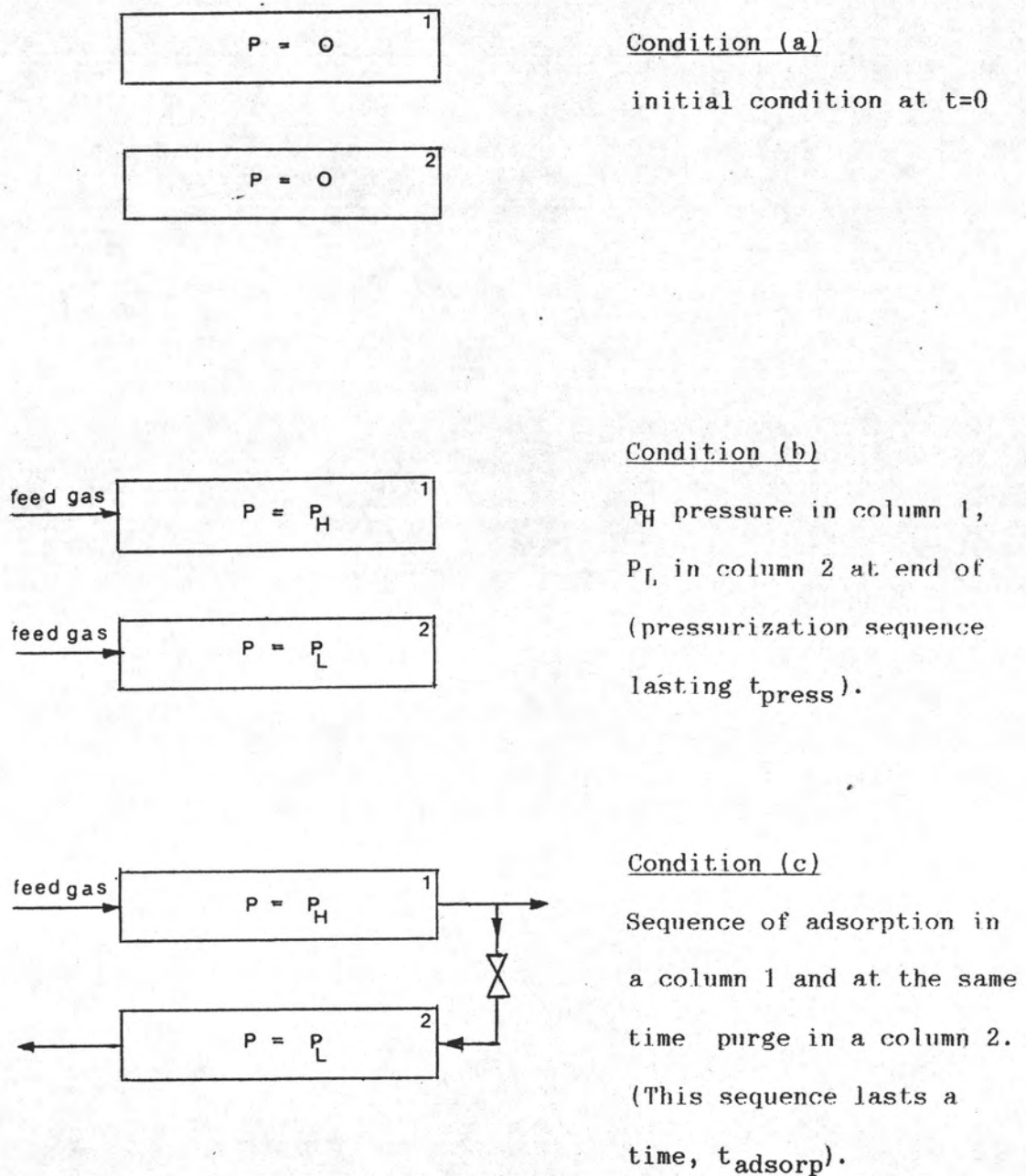
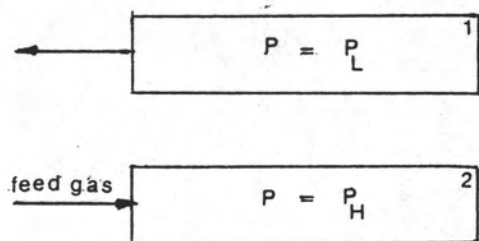
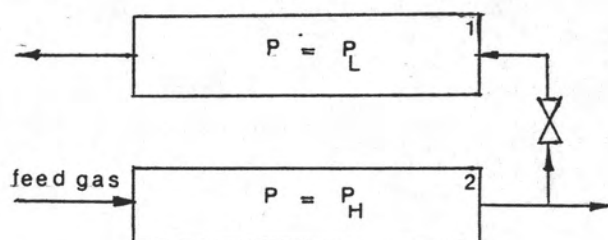


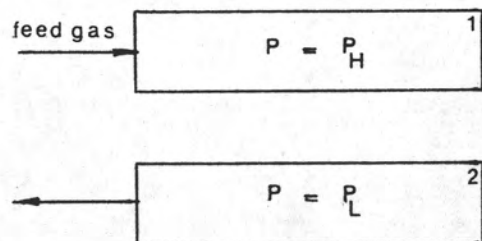
Figure 2.4 PSA adsorption-desorption sequence for a two columns system (we assume a gas A / gas B mixture with A being the more strongly adsorbed gas, and B the purified product).

Condition (d)

Sequence of blowdown for column 1 and pressurization for column 2. (This sequence will last a time, t_{press}).

Condition (e)

Sequence of adsorption in column and at the same time purge in column 1. (This step lasts a time, t_{adsorp}).

Condition (f)

Sequence of blowdown for column 2 and pressurization for column 1 (This sequence will last a time, t_{press}).

Figure 2.4 PSA adsorption-desorption sequence for a two columns system (we assume a gas A / gas B mixture with A being the more strongly adsorbed gas, and B the purified product)(cont.)

2.3 PSA cyclic operation

Pressure swing adsorption processes use varying numbers of columns, which may range from one to twelve, but the most widely used is the two column system [4]. Let us look at a basic two column PSA cycle operation.

2.3.1 Sequence for a two column pressure swing adsorption system

The steps in a PSA cycle are

- I. Pressurization.
- II. Adsorption.
- III. Blowdown.
- IV. Purge.

First of all we have two adsorption columns packed with the selected adsorbent. We start from zero gauge pressure in both columns (condition (a) in fig. 2.4). The first step is now to pressurize both columns to pressure P_H and P_L using feed gas which we assume takes a minimal time, t_{pres} , i.e. 1 seconds (condition (b) in fig. 2.4). The second step consists in allowing feed gas to adsorb in column 1 at a pressure P_H while at the same time allowing the purified product from column 1 which consists for example of purified gas B (gas A is assumed to be preferentially adsorbed) to act as purge gas in column 2 (condition (c)), this step will last for a time t_{adsorp} . The third step (condition (d)) involves a blowdown step for column 1 down to pressure P_L and a pressurization of column 2 with

feed gas up to pressure P_H , this step lasting a time t_{press} i.e., 1 second. The fourth step (condition (e)) is similar to step c with the columns switched, again for a time t_{adsorp} . Step five (condition (f)) is similar to step d with the columns switched.

The next step is now to proceed directly with step c and from there on the PSA sequence will operate from sequence c to sequence d, to sequence e and to sequence f, then back to c, and so on.

2.4 Operation of a single column PSA system.

Separation can also be made using a single column according to a patent deposited in 1980. As mentioned in chapter 1, for the production of oxygen from air zeolite adsorbent may be used in the column. Typical adsorption isotherms for nitrogen and oxygen on a 5A zeolite are shown in figure 2.5 and show that pure nitrogen is more strongly adsorbed than oxygen at both temperatures shown [4].

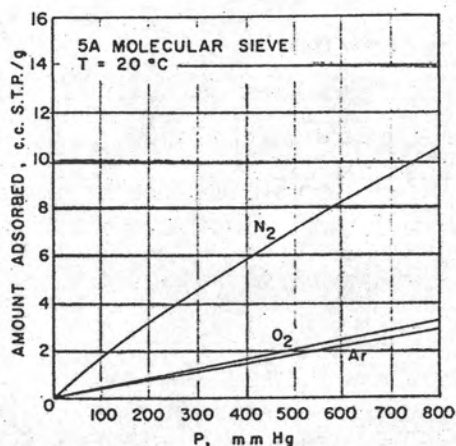


Figure 2.5 Isotherm on 5A zeolite [4].

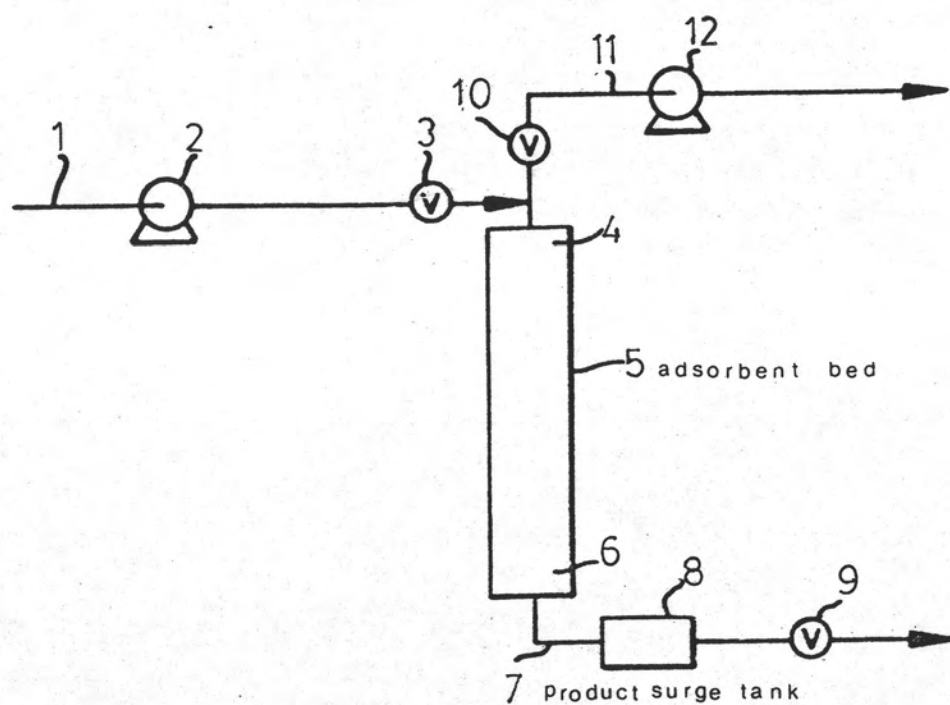


Figure 2.6 Diagram of the single column PSA system (from the patent 4,194,892 [4]).

The mentioned patent [1] uses adsorbents such as made up of single material such as a crystalline zeolite molecular sieves or activated carbons, or it may comprise multiple layers or mixtures of different adsorbents for selective removal of particular components from the feed gas. As shown in figure 2.6 the feed gas contains at least two components and is introduced through conduit(1) and pressurized if necessary by compressor (2)(if necessary followed by a feed surge tank) before introduction through valve(3) into the first end (4) of the adsorbed bed (5). An enriched product gas is discharged from the back end of the adsorbent bed(6) into conduit(7). A product surge tank (8) may be provided in conduit (7) upstream of valve (9). This is the so called "feed gas introduction period". During this period the one component depleted gas is discharged from the single bed and the other is desorbed .

Following the feed gas introduction period feed valve (3) is closed and exhaust valve (10) in conduit (11) joining the front end (4) is opened. During the exhaust period the one component depleted gas within the adsorbent bed (5) flows in the reverse direction towards the front end inlet (4). This gas sweeps the one component depleted gas towards the front end after the pressure of such gas has been reduced i.e, the pressure differential between the gas in the bed during the feed gas introduction period and the exhaust pressure. Flow reversal occurs in the adsorbent bed while product is being continuously removed from the back end, and the flow reversal zone moves quickly from the front to the back end during exhaust. It may be desirable to provided pump(12)in exhaust conduit(11) to accelerate the reverse flow of product gas purging unwanted adsorbed component.

Although not essential, rapid pressure swing adsorption (RPSA) systems often employ a front end flow suspension time after feed gas introduction period by valve (3) and valve (9) although discharge of product gas is continuous during this period through the back end (6).

The mathematical simulation to be made in this study will attempt at quantitatively explaining the operation of a single column pressure swing adsorption process for oxygen enrichment described in patent [1]. The sketch of the apparatus is shown in figure 2.6. The range of the system geometry and the operating conditions are presented in table 2.2.

TABLE 2.2 System geometry and operating condition of Jones et al's 1980 patent.

<u>SYSTEM GEOMETRY.</u>	
Bed I.D. range	up to 3 inches
Bed length range	up to 96 inches
Adsorbent particle size range	40-80 mesh
(5A molecular sieve zeolite)	0.175-0.35 m.m.
<u>OPERATING CONDITIONS.</u>	
Input feed gas pressure range	8-60 psig
Feed gas introduction period	0.25-1.5 seconds
(Adsorption time range)	
Time delay (optional)	< 10 times adsorption time
(pressure equalization step)	< half of blowdown time
Reverse outward flow	3-6 seconds (but at least
(Blowdown time range)	2 times adsorption time)
Total cycle time	< 30 seconds

The authors of the patent presented four cases as follows.

CASE 1 : The first claim of the patent is that it can produce a product gas comprising 75-95% oxygen through maximum adsorbent productivity with a penalty of less than maximum product recovery. The feed gas may be varied from 20-60 psig using crystalline zeolite molecular sieves of at least 5 angstroms apparent pore size and between 40-80 mesh with a bed length of 15-30 inches . The feed gas introduction period is 0.1-1 seconds, the period of flow suspension is less than 2 seconds and also less than five times the feed gas introduction period. The reverse outward flow period is 1-6 seconds but more than 3 times and less than 40 times the feed gas introduction period and terminates at atmospheric pressure. For case 1 3-20 pounds of oxygen per day are produced per pound of crystalline zeolite molecular sieve adsorbent, and 10-25 % of the oxygen in the feed air is recovered in the product gas. In case 1 the product oxygen pressure varies cyclically within the range of about 0.01 to 8 psig.

CASE 2 : The second claim of the patent is to achieve maximum recovery of product oxygen at some loss of adsorbent productivity. The feed air is also supplied at 20-60 psig for a feed gas introduction period of 0.3-1 second to an adsorbent bed comprising the same adsorbent in case 1, and particle size are between 40- 80 mesh with bed length of 3-5 feet. The duration of the flow suspension step is between five and ten times the feed gas introduction period but less than five seconds, and the reverse outward flow period is 8-20 seconds and terminates at atmospheric pressure. By this case

25-40 % oxygen in the feed air is recovered in the product gas. The product gas is provided with purity in the range of 85-95% oxygen corresponding to oxygen enrichment in the range of 21 to 72. The adsorbent productivity is up to about 3 pounds of contained oxygen per day per pound of crystalline zeolite molecular sieve adsorbent and product oxygen is discharged at 0.01-5 psig.

CASE 3 : The third claim of this patent is to provide a system for producing oxygen product gas suitable for human breathing from air feed gas of about 8-15 psig and with compact portable equipment which can be used in the home by persons requiring an immediately available source of oxygen. This system is also called a medical oxygen system. The adsorbent particles (the same adsorbent materials) have sizes between 40-80 mesh and bed length of 15-30 inches. The feed introduction period is 0.25-1.5 seconds. The flow suspension period is between one-half and three times the feed gas introduction period but less than 1.5 seconds and the second period of reverse outward flow is between two and one-half and twelve times the feed gas introduction period and also between 3 and 6 seconds and terminates at atmospheric pressure. In this case the oxygen recovery is 10- 20 % and the product purity is 85-95 % oxygen corresponding to oxygen enrichment in the range of 21 to 72. Up to 1.5 lbs of contained oxygen is produced per pound of crystalline zeolite molecular sieve per day and the product oxygen is discharged at about 0.5-4 psig.

CASE 4 : The last case is similar to the medical oxygen (breathing) portable system, but especially suited for supplying relatively large quantities of 85-95 % oxygen for industrial gas,

e.g. 0.5-20 tons per day of contained oxygen. This so called tonnage oxygen system receives air feed gas at 8-15 psig, discharges oxygen product at 1-4 psig and employs the same adsorbent in a 40-80 mesh particle size range and bed length of 5-30 inches. The feed gas introduction period and the flow suspension period are each 0.75-2.0 seconds, and the second period of reverse outward flow is between two and eight times the feed gas introduction period and also between 3-6 seconds, terminating at atmospheric pressure. In this case 10-20% oxygen in the feed air is recovered in the product and up to 1.5 lbs of contained oxygen is produced per pounds of adsorbent per day.

It is seen from case 1 that product purity is of the order of 75-95% and cases 2, 3 and 4 have product purities of 85-95% oxygen. Product purity is therefore fairly equivalent in each case. For case 2 a high product recovery of 25-40% is achieved with a bed length of 3-5 feet whereas in case 1 a product recovery of 10-25 % oxygen and 10-20% oxygen for cases 3 and 4 the bed lengths are 15-30 inches. Feed gas pressures in cases 1 and 2 are high and in the range of 20-60 psig and 8-15 psig in cases 3 and 4. Therefore in case 2 we have a long bed, a high pressure feed gas and recovery ; case 1 has a short bed, a high pressure feed gas and a moderate recovery ; case 3 and 4 have short beds, moderate feed gas pressure and moderate recoveries.

This simulation will be based on case 2 for which high feed air pressure is used and reasonable product purity is obtained, and where long beds are used.