Pressure Swing Permeation: Novel Process for Gas Separation by Membranes

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A novel process for gas separation, called pressure swing permeation, was investigated to elevate the relatively low permeate pressure by pressurization with high-pressure feed gas, thereby reducing or eliminating additional permeate compression costs where a pressurized permeate is required. This process uses two or more membrane modules and operates in a cyclic fashion, with each module repeatedly undergoing the sequential steps of feed admission and permeation, residual removal, permeate reception, permeate pressurization, and product withdrawal. The unsteady-state permeation associated with pressure swing permeation was studied parametrically, and a bench-scale unit compromising two hollow-fiber membrane modules in parallel was tested for H_2/N_2 separation to demonstrate the effectiveness of the process. The permeate product at a pressure as high as the feed pressure can be produced without using a compressor. This is impossible with traditional steady-state processes where a pressure differential across the membrane must be maintained. The pressure swing permeation is analogous to pressure swing adsorption and has the potential to be synergistically integrated with the pressure swing adsorption process for enhanced separation of gases.

Introduction

Permeation of gases through polymeric membranes is now an important component of many gas-separation applications. Membrane gas separation is a pressure-driven and rate-controlled process in which the separation is obtained as a result of the difference in the rate of transmission of different gas species through the membrane. The effectiveness of gas separation by a membrane is dependent not only on the selective permeability of the membrane but also on the difference in operating pressure of the gas on both sides of the membrane. In order for permeation to take place, the upstream (feed side) pressure should be higher than the downstream (permeate side) pressure. This can be accomplished in principle by either compressing the feed gas to an elevated pressure level or maintaining the permeate side at subatmospheric pressures, or a combination of both. The maximum reduction in permeate pressure achievable by using a vacuum pump is physically limited, however, and for comparable pressure ratios, operating a vacuum pump is normally more costly than operating a compressor. Therefore, to create the transmembrane driving force for permeation, feed-gas pressurization is most widely employed in practice, while keeping the permeate side at vacuum conditions is only used in a few specific applications such as the production of oxygen-enriched air. In the latter case, the feed air is readily available at atmospheric pressure and energy savings are achieved since only the permeate stream, instead of the entire feed stream, must be compressed to a desired product pressure. It is generally not considered worthwhile to use both a compressor and a vacuum pump in order to increase the transmembrane pressure differential for permeation.

Membrane gas separation processes are operated conventionally in a steady-state fashion. Both the feed pressure and the permeate pressure are maintained at constant levels, and the permeation rate and permeate concentration do not

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change with time, except in the initial start up period. The steady-state operation has the advantages of ease of startup and shut down, simplicity of pressure and flow controls, large throughput of permeation, and low maintenance requirements. However, there have been a few patent disclosures that suggest and demonstrate the benefits of operating membrane gas separations in an unsteady-state fashion for some applications. Ueda et al. (1990) proposed a cyclic process for air separation that comprises repetition of the steps of pressurization of feed and evacuation of permeate. In this process, the feed air is repeatedly pressurized and fed to the membrane unit for a short period of time. Before the air pressure on the feed side of the membrane reaches a steady value, the feed air flow is stopped. Whilst permeation is continuing, the permeate gas accumulates in the permeate side and its pressure increases. The permeate is then evacuated. The pressurization of feed and evacuation of permeate can be carried out by using the same pump, thereby avoiding the necessity of operating a compressor and a vacuum pump separately. The pressure difference across the membrane in this unsteady-state process was shown to be higher than in the conventional steady-state processes where either the feed gas is supplied continuously at an elevated pressure or the permeate is under constant evacuation.

LaPack and Dupuis (1994) described another unsteady-state process to improve permeation selectivity by operating the membrane permeation system dynamically. According to the solution-diffusion mechanism, the steady-state permeation responds to the permeability coefficient P, which, as a first approximation, can be considered to be equal to the product of solubility coefficient S and diffusion coefficient D. On the other hand, before the permeation reaches the steady state, the transient permeation rate, which can be described by Fick's second law equation for diffusion, responds to D and S more independently. The dynamic process of LaPack and Dupuis (1994) is primarily based on the differences in the diffusivities of different permeating components through the membrane. From the instant that the feed gas is admitted to the upstream side of the membrane and before the slow diffusing component reaches steady-state permeation, the rate of mass transport through the membrane varies with time. During this period of transient permeation, the faster diffusing gas component is enriched in the permeate side. In a continuous operation, the feed can be introduced intermittently at appropriate time intervals such that steady-state permeation is never reached. Alternatively, the difference in the desorption falloff rates due to the difference in the diffusivities can also be utilized to effect the separation, and the permeate collected will be a mixture enriched in the slower diffusing component.

Comparing the steady-state permeation and the transient permeation, it is clear that for a given membrane gas-separation system, only when the mobility selectivity, that is, the relative diffusion coefficient (D_i/D_j), is significantly greater than the corresponding permselectivity (P_i/P_j) of the membrane will a remarkable improvement in selectivity be attained by using the transient permeation process in preference to the steady-state process. It should be pointed out that the idea of using transient permeation for enhancing separation efficiency was proposed in the early 1970s by Paul (1971), and an experimental study was performed by Beckman et al. (1991) in the late 1980s using a relatively thick (147 μm) membrane. Higuchi and Nakagawa (1989) carried out a parametric study of the transient permeation process to show the improvement in selectivity over steady-state operation by pulsing the upstream pressure as suggested by Paul (1971). The productivity was shown to be much lower than what would be achieved by the steady-state permeation. Kao et al. (1991) proposed two process schemes to carry out the transient permeation for the cases where the membrane exhibited opposite diffusivity and solubility selectivities, depending on the mobilities and solubilities of the gas species to be separated, and the viability of the process was supported by the experimental results of He/CH_4 separation with a silicone rubber membrane. This is a typical system for which a transient process can be advantageously employed (Paul, 1971).

The effectiveness of separation by transient permeation obviously depends on the relative scale of the length of permeation on-line time and the time lag of the membrane-gas system. The time lag θ is a quantity characterizing the time elapsed for a transient permeation to reach steady state. For a simple gas-membrane system, $\theta = l^2/6D$, where l is the effective thickness of the membrane. With very few exceptions, the diffusivities of gases in most polymeric materials that are used to produce membranes are of the order of 10^{-8} cm^2/s (Stern, 1994; Paul and Yampol'skii, 1994). For most commercial gas-separation membranes, which are structurally asymmetric to enhance productivity, the effective thickness of the skin layer is typically in the range of 1,000–2,000 Å, and a thinner thickness (400–1,000 Å) is attainable in more finely tuned membranes (Koros and Chern, 1987; Koros and Fleming, 1993). Based on these data, the time lag for transient permeation of gases through an asymmetric membrane can be estimated to be of the order of 10^{-5} to 10^{-3} s. Since steady permeation through the membrane will be established after a period of about three times the time lag (Crank, 1975), it can easily be concluded that the dynamic permeation process will have to be run at a cycle frequency that is too fast to be acceptable for the hardware (that is, the flow-switching valves) if an asymmetric membrane is used. Consequently, the use of transient permeation for gas separation encounters a harsh reality; that it can be done in principle does not mean it can be done in practice, at least with currently available membranes.

Because of the nature of pressure-driven permeation, the permeate stream from the membrane system is collected at a pressure significantly lower than the feed-gas pressure, and recompression of permeate product is often required. In the present study, we present a novel unsteady-state permeation process for gas separation. The primary objective is to produce a permeate stream at a pressure that is as high as the feed pressure without using a compressor. The idea is to elevate the relatively low permeate pressure by periodically pressurizing, or ‘‘pushing,’’ the permeate with the high-pressure feed gas. This process distinguishes itself from all other dynamic permeation processes in that a permeate stream at a pressure as high as the feed pressure can be obtained, which is otherwise impossible with the conventional steady-state process as well as the aforementioned transient permeation processes. Furthermore, the process, called pressure swing permeation due to its cyclic nature, has the potential of being synergistically integrated with the pressure swing adsorption process, which is a complementary process for gas separation based on selective adsorption. In a hybrid membrane/adsorption process, the high efficiency of membrane technology for bulk separation is complemented by the high efficiency of adsorption separation for producing high purities. An integrated membrane/pressure swing adsorption process has been investigated (Feng et al., 1998). If the permeate product from the membrane unit can be obtained at a high pressure, the subsequent adsorption separation will be more efficient.

In this article, the unsteady-state permeation associated with the cyclic pressure swing permeation process was analyzed theoretically, and the separation of hydrogen from nitrogen was performed experimentally to demonstrate the effectiveness of the process. It was shown that the pressure swing permeation process is capable of producing hydrogen-enriched permeate product at a pressure as high as the feed pressure. This is a significant improvement, because neither permeate flow nor hydrogen enrichment can be accomplished in a conventional permeation process if the permeate pressure and the feed pressure are maintained at the same level.

Pressure Swing Permeation

Though the pressure swing permeation process can be run as a batch process, it is more efficient to operate the membrane system in a continuous fashion. In a continuous pressure swing permeation process, the membrane system, in a simple form, comprises two membrane modules (A and B) to perform a gas separation in a steady-state cyclic fashion. Each module contains two distinct void spaces separated by the membrane for the admission and removal of gas streams, respectively. After the high-pressure feed gas is introduced to membrane module A, permeation takes place, and the permeate from module A, which is at a relatively low pressure level as compared to the feed pressure, is received by module B. As the permeation in module A proceeds with time, the pressure of permeate collected in module B increases. Then the gas feeding to module A is stopped, and the permeate stored in module B is pressurized with the high-pressure feed gas, during which period the permeate product at a desired elevated pressure is displaced out of module B. In the meantime, the residue in module A is released. The two modules are arranged such that the void space in one module used for receiving the permeate from the other module will receive the feed gas when the two modules are switched to reverse their functions in terms of feed admission and permeate reception. Thus the membrane system is ready for the next cycle of operation. It should be mentioned that the membrane modules should be properly designed and the pressurization and displacement steps should be carried out in a sufficiently short period of time to prevent any breakthrough of feed gas into the permeate product. Hollow-fiber membranes are preferred because the lengthwise gas mixing in the membrane module is very limited. The two membrane modules can be synchronized, and each undergoes five basic operating steps in the following sequence:

1. Collection of the low-pressure permeate from the other module
2. Pressurization of the permeate by the high-pressure feed gas
3. Release of permeate product at an elevated pressure
4. Admission of feed to carry on permeation
5. Withdrawal of residue stream.

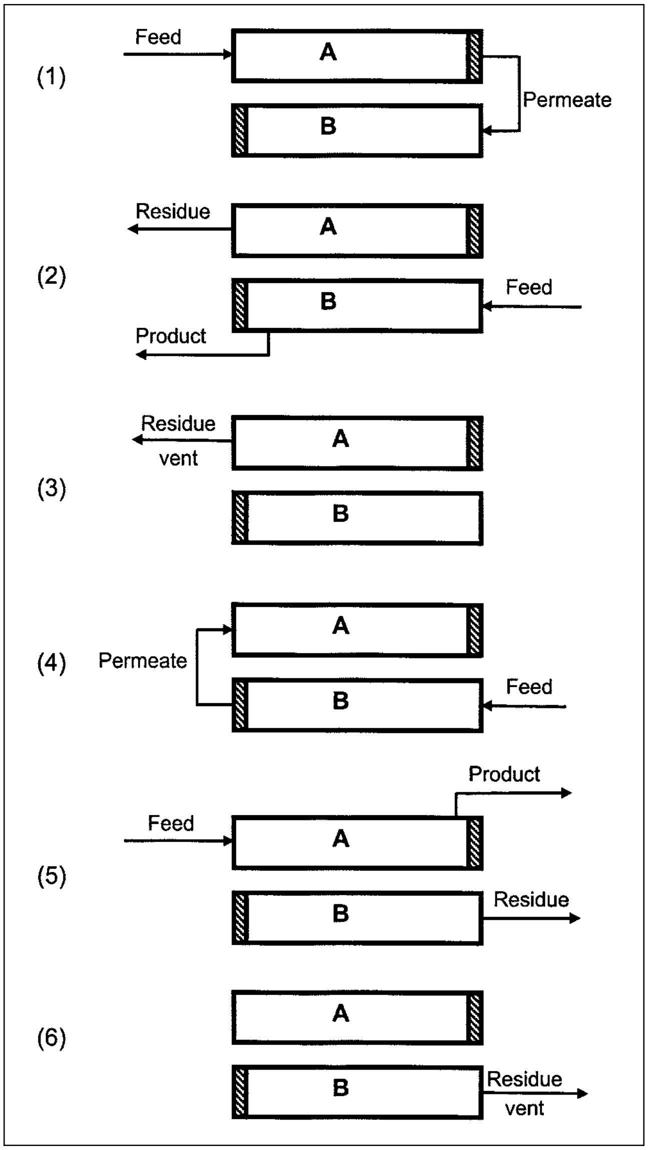


Figure 1. Cycle sequence of a two-permeator pressure swing permeation process.

Clearly, step 4 is responsible for the separation, and step 2 is responsible for producing a high-pressure permeate product. Engineering designs directed to minimizing back mixing of the gas during the pressurization step are necessary to ensure product purity.

Figure 1 represents the cycle sequence of a two-module pressure swing permeation process; a brief description of the cycle steps is shown in Table 1. Similar to the pressure swing adsorption process, operating the pressure swing permeation system at fast cycles can increase the product throughput in the pressure swing permeation. Further, multimodule arrangements can be used for large processing capacities with relatively steady and continuous flows of feed and purified product. Preferentially, the membrane modules used in the

Table 1. Cycle Steps in a Two-Module Pressure Swing Permeation Process

Step	Module A	Module B
1	Admission of feed gas and permeation	Reception of permeate from module A
2	Withdrawal of residue from module	Pressurization with feed gas and product release
3	Removal of residue remaining in gas line	Gas feeding stopped
4	Reception of permeate from module B	Admission of feed gas and permeation
5	Pressurization with feed gas and product release	Withdrawal of residue from module
6	Gas feeding stopped	Removal of residue remaining in gas line

pressure swing permeation process have the same design with the same permeation performance so that even cycle timings in the gas-flow controlling valves can be maintained. Note that the permeation step itself is an unsteady-state operation, but the pressure swing permeation process can be carried out in a steady-state cyclic fashion.

Analyses of Permeation Behavior

Consider the permeation system shown in Figure 2 that is relevant to the pressure swing permeation process. A binary gas mixture is admitted to the feed side of the membrane, and the permeate is collected in a receiving vessel, which would be another membrane module in the pressure swing permeation process. Let V_F and V_P be the volumes for admitting the feed and receiving the permeate, respectively. The permeation process is obviously an unsteady-state operation in that the permeation rate, the residue concentration, and the pressure and composition of the permeate vary with time. To formulate mathematical equations, the following assumptions are made:

1. The time lag of permeation due to transmission of gas molecules through the membrane is negligible. The permeate is thus assumed to be received in the reception vessel as soon as the permeation takes place.

2. The permselectivity of the membrane is independent of gas composition and pressure.

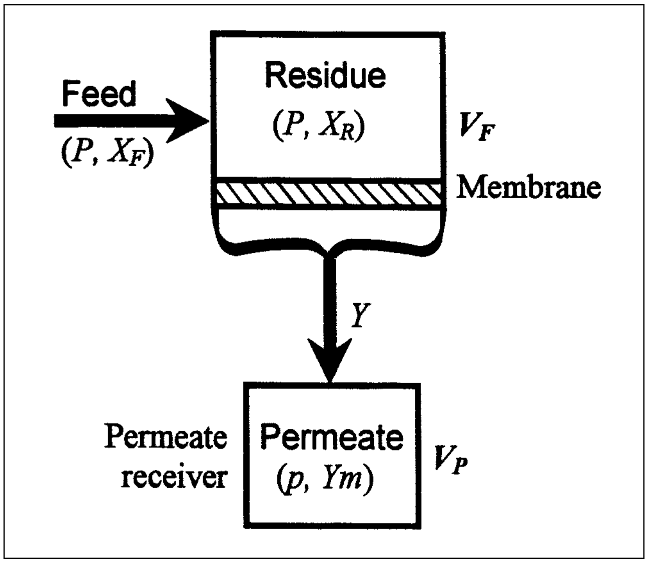


Figure 2. Permeation system with constant feed pressure and varying permeate pressure.

3. The membrane permeability during unsteady-state operation is the same as that at steady state.

4. There is no concentration polarization on the feed side, that is, the concentration on the membrane surface is the same as the bulk concentration of the feed.

5. On the permeate side, there is no back diffusion from the bulk permeate to the membrane surface.

6. During permeation, the feed gas is maintained at a constant pressure, and the pressure on the permeate side gradually increases with time due to the fixed volume of permeate gas.

Subject to the preceding assumptions, the permeation rate at a given instant can be written as

$$\frac{dQ_1}{dt} = J_1 A(PX - pY) \tag{1}$$

$$\frac{dQ_2}{dt} = J_2 A[P(1-X) - p(1-Y)], \tag{2}$$

where J is the membrane permeance, Q is the quantity of permeate, A is the membrane area, and P and p are feed pressure and permeate pressure, respectively. The subscripts 1 and 2 represent the fast and slow permeating components of the binary gas mixture, respectively, X is the feed concentration, and Y is the concentration of permeate on the membrane surface; both quantities are expressed in terms of the mol fraction of the fast permeating component. The local concentration of permeate leaving the membrane surface is determined by the relative permeation rates of the gas components. Thus, Y can be calculated by

$$Y = \left(\frac{dQ_1}{dt}\right) \Big/ \left(\frac{dQ_1}{dt} + \frac{dQ_2}{dt}\right). \tag{3}$$

The bulk concentration of permeate, Y_m, also expressed in terms of the mol fraction of the fast permeating gas, is determined by the relative amount of the gases accumulated in the receiving vessel, and is given by

$$Y_m = \frac{Q_1}{Q_1 + Q_2}. \tag{4}$$

Since the pressure on the feed side is kept constant and no residue is withdrawn from the permeator during permeation, the molar rate of gas fed to the permeator is equal to the molar rate of permeation. For the purpose of illustration of the unsteady-state permeation, let us assume complete mixing of feed gas in the membrane module to simplify the calculation. On the basis of a materials balance and assuming ideal gas behavior, the residue concentration X on the high-pressure side of the membrane is related to the concentration of the feed X_F by

$$X = \frac{(PV_F/RT)X_F + (Q_1+Q_2)X_F - Q_1}{PV_F/RT}. \tag{5}$$

The pressure change on the permeate side is related to the permeation rate by

$$\frac{dp}{dt} = \left(\frac{dQ_1}{dt} + \frac{dQ_2}{dt}\right)\frac{RT}{V_P}. \tag{6}$$

For the case of interest where one membrane module is used to receive the permeate from the other in the pressure swing permeation process, the volume of the permeator occupied by the feed gas V_F is preferentially equal to the volume of the permeate reception vessel V_P.

The preceding set of equations constitutes an initial-value problem. For given initial conditions, all the quantities p, X, Y, Q_1, Q_2, and Y_m at any instant can be determined by solving these equations. For the purpose of parametric analyses, the following numerical values of membrane properties and operating conditions were chosen in the calculations:

$$J_1 = 1\times10^{-4}\text{cm}^3(\text{STP})/(\text{cm}^2\cdot\text{s}\cdot\text{cm Hg})$$

$$J_1/J_2 = 60$$

$$P = 5{,}000 \text{ kPa}$$

$$X = 0.5$$

$$T = 298.15 \text{ K}.$$

For a special case with initial conditions of $Q_1 = Q_2 = 0$ and $p = 0$ at $t = 0$, the initial value of Y is determined by the relative permeation rate of the gas components by cross-flow permeation and can be approximated by substituting Eqs. 1 and 2 into Eq. 3 to yield

$$Y = \frac{(J_1/J_2)X_F}{1+(J_1/J_2-1)X_F} \quad \text{at } t=0. \tag{7}$$

The permeance ratio (J_1/J_2) represents the permeation selectivity of the membrane, and is sometimes referred to as the ideal separation factor. Equation 7 is very similar to the well-known equation relating the liquid and vapor phase compositions in distillation (Seader and Henley, 1998). Figure 3 shows the calculated results for an equal volume of $V_F = V_P$; for simplicity, the subscripts are dropped in the discussions that follow. It is shown that as permeation proceeds with time, the residue is depleted in the fast-permeating species, and the permeate pressure builds up. Therefore, the transmembrane driving force for permeation is gradually decreased. Consequently, the permeation rate in the initial period of time is fast and gradually slows down. Consider that the partial permeation rate of a gas component is proportional to its partial pressure difference across the membrane. As permeation continues, the reduction in the driving force for the fast gas permeation is more significant as compared to the slow permeating gas. Thus, the concentration of the fast permeating component in the permeate leaving the membrane surface is gradually decreasing, resulting in a reduction in the bulk permeate concentration of that component.

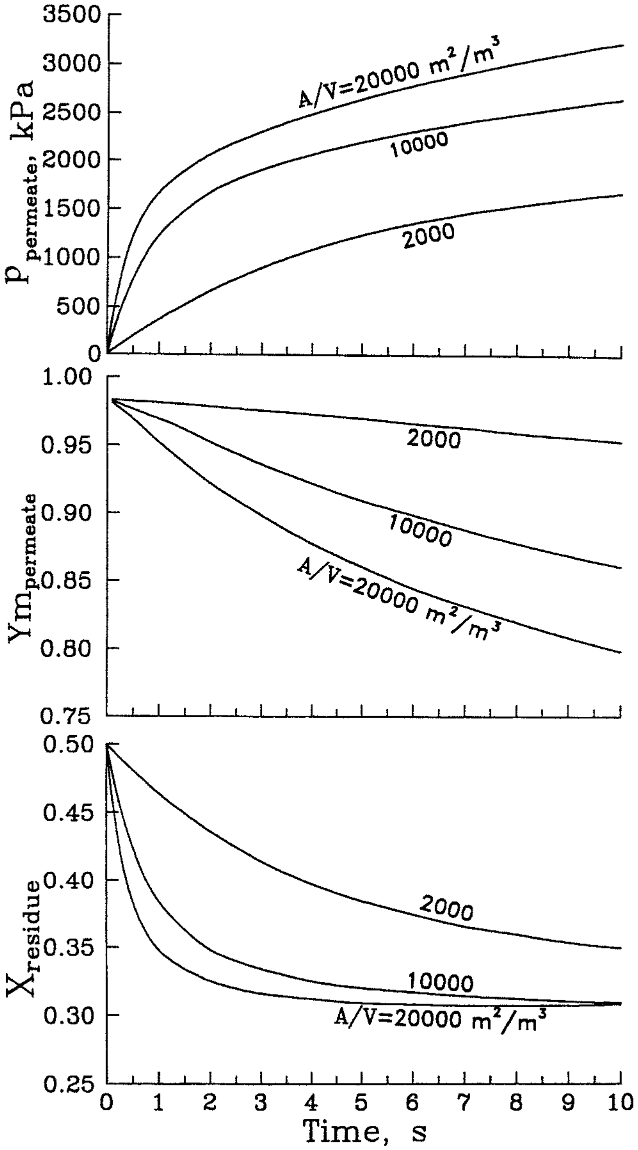


Figure 3. Calculated results of permeate pressure, permeate concentration and residue concentration as function of time.

Figure 3 also shows that the separation performance is influenced by the ratio of the membrane area A and the permeate receiving volume V. They are two independent physical parameters characterizing the design of the membrane module. It is shown that for the initial conditions just given, as long as the ratio A/V is maintained constant, variations in A and V do not affect the separation behavior. This can also be derived directly from the mathematical model because of the special initial conditions used, that is, at $t = 0$, $Q_1 = Q_2 = 0$ and $p = 0$. Therefore, the membrane area for permeation and the volume for permeate reception can be combined as a single operating variable to show their joint effects on the permeation performance. At a given instant, increasing the value of A/V leads to an increase in the permeate pressure and a decrease in the residue concentration. This is desired from the standpoint of gas separation. However, as the residue concentration decreases, so does the instant permeate concentration, leading to a reduction in the bulk permeate concentration. Fortunately, in the early period of permeation, the beneficial increase in permeate pressure and decrease in residue concentration outweigh the detrimental decrease in permeate concentration. As such, by operating the pressure swing permeation at a considerably fast cycle to keep the permeation time reasonably short, the advantage of operating the unsteady-state permeation will be retained. For hollow-fiber membrane modules, a ratio of A/V as high as 20,000 m^2/m^3 can readily be achievable with the state-of-the-art membrane technology (see Appendix). Referring to Figure 3, for the case under study a permeation step time on the scale of a few seconds to 10 s is preferentially desired. Such a time scale is technically achievable with the normal switching valves currently available, and the technical feasibility of running the pressure swing permeation is thus rationalized.

In pressure swing permeation, the residue stream can be withdrawn at a reduced pressure. This can be followed by further venting the residue that is still retained in the permeator to atmosphere or to vacuum. The preceding calculation is based on an initial condition of zero permeate pressure at $t = 0$, which corresponds to an extreme case of vacuum venting of residue. Deviation from the ideal condition will result in some reductions in the separation efficiency. In the following, the atmospheric venting of residue, which is of particular interest for practical applications, will be evaluated. It can be mentioned that it is now no longer adequate to group the membrane area A and the permeate receiving volume V as a single parameter to characterize their joint effects on the separation performance because of the amount of gas present on the permeate side before a permeation step starts. Consider the case of the pressure swing permeation where $A = 100$ m^2, $V = 0.005$ m^3, the atmospheric pressure $p_o = 101.3$ kPa, and the permeation step time = 5 s. Due to the cyclic nature of the process, the module used for receiving permeate from the other module still contains some residue gas after the residue venting step. Therefore, the initial conditions used to solve Eqs. 1 to 6 are dependent on the final concentration of residue when the permeation is stopped prior to the next permeation step. This residue concentration is in fact one of the parameters to be determined. Consequently, a trial-and-error method needs to be used. Basically, guess a value of the residue concentration X_R. The initial values at $t = 0$ can thus be estimated to be as follows

$$Q_1 = (PV/RT)X_R$$

$$Q_2 = (PV/RT)(1 - X_R)$$

$$Y = X_R$$

$$p = p_o$$

Then integrate Eqs. 1, 2, and 6 from $t = 0$ to $t = 5$ s, and compare the value of the final residue concentration so obtained to the one used to calculate the initial conditions. Repeat the procedure until convergence is achieved. As such, the pressure and concentration of permeate and the concentration of residue at the end of a permeation step are determined.

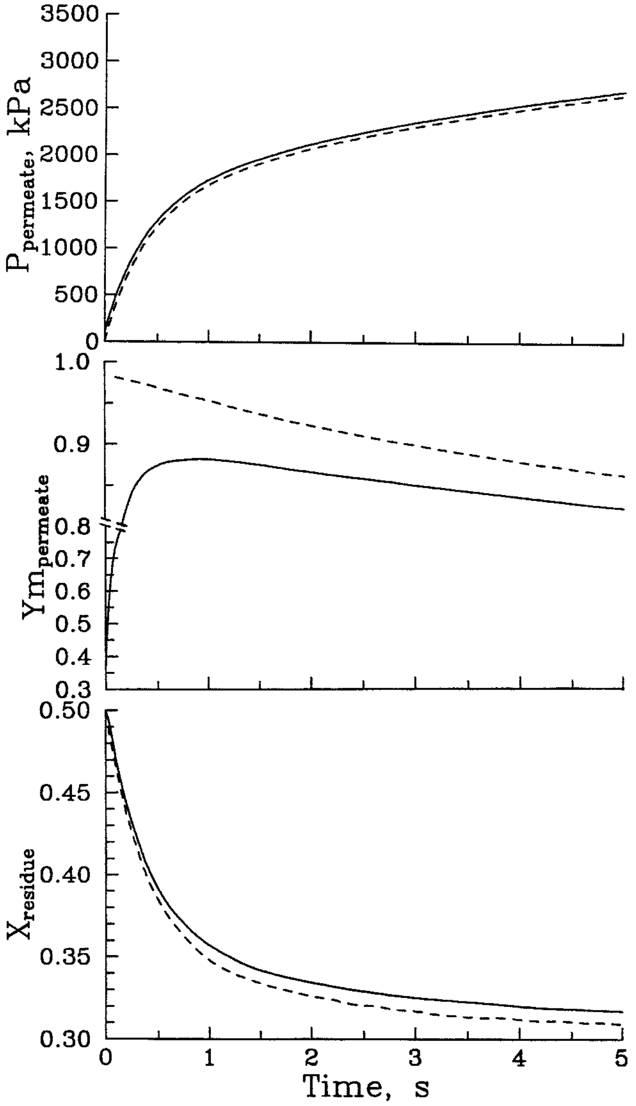


Figure 4. History of permeate pressure, permeate concentration and residue concentration during permeation.

Solid and dotted lines represent residue venting to the atmosphere and to vacuum, respectively. $A/V = 20,000$ m^2/m^3.

The calculated results are illustrated in Figure 4; for comparison, the results for residue venting to vacuum ($p = 0$ at $t = 0$) are also presented in the figure. It can be seen that the separation is less efficient with residue venting to the atmosphere than to vacuum. As shown in Figure 4, in contrast to the case of vacuum venting of residue where the concentration of permeate decreases monotonically with time, the permeate concentration initially increases and then decreases during permeation when the residue is vented to the atmosphere. This is due to two opposing effects. On the one hand, the space for receiving permeate in this permeation cycle is initially filled with the remaining residue product from the last cycle after residue venting. Thus, an accumulation of permeate, whose concentration is higher than the residue product, tends to increase the concentration of the faster permeating gas on the permeate side. On the other hand, as mentioned earlier, the concentration of the permeate leaving the membrane surface gradually decreases as permeation proceeds in time, which tends to reduce the bulk concentration of the faster permeating gas in the permeate. Two opposing effects result in the concentration of the faster permeating gas reaching a maximum concentration in the permeate before it subsequently declines. It can be expected that the lower the residue venting pressure is, the higher the magnitude of the maximum permeate concentration, and the faster the permeate concentration reaches its maximum. The vacuum venting ($p = 0$ at $t = 0$) case represents the upper limit of separation performance achievable with the unsteady-state permeation.

It must be pointed out that the preceding calculations, which are based on the assumption of complete mixing of feed gas (that is, there is no concentration gradient along the length of the membrane module), are for illustration purposes only. In practice, mixing of feed gas is limited, especially in a hollow fiber or spiral-wound membrane module. The results of Figures 3 and 4 thus represent a conservative scenario, and a better permeation performance is expected in practical applications.

Experimental Demonstration of Pressure Swing Permeation

A bench-scale pressure swing permeation unit comprising two hollow-fiber membrane modules is shown schematically in Figure 5. Hollow-fiber membranes developed at the Alberta Research Council were used in the study. The membrane had an asymmetric structure with a thin outer skin layer on a microporous support. The nominal outside diameter of the hollow-fiber membrane was 165 μm. The designs of the two membrane modules were essentially identical, and each module contained a bundle of 300 fibers housed in a 4.8-mm-ID stainless-steel tubing. Each end of the modules was potted with epoxy resins to form a fluid-tight tubesheet, resembling a shell and tube heat exchanger. The effective length of the fiber was 22.5 cm, and the membrane area in each module was 350 cm^2, corresponding to a membrane area packing density of approximately 8,600 m^2/m^3. At ambient temperature (23°C), the membrane exhibited a hydrogen permeance of about 1×10^{-4} cm^3(STP)/(cm$^2\cdot$s$\cdot$cm Hg), or 3.35×10^{-8} mol/(m$^2\cdot$s$\cdot$Pa) in SI units, and a hydrogen/nitrogen permeance ratio of about 55.

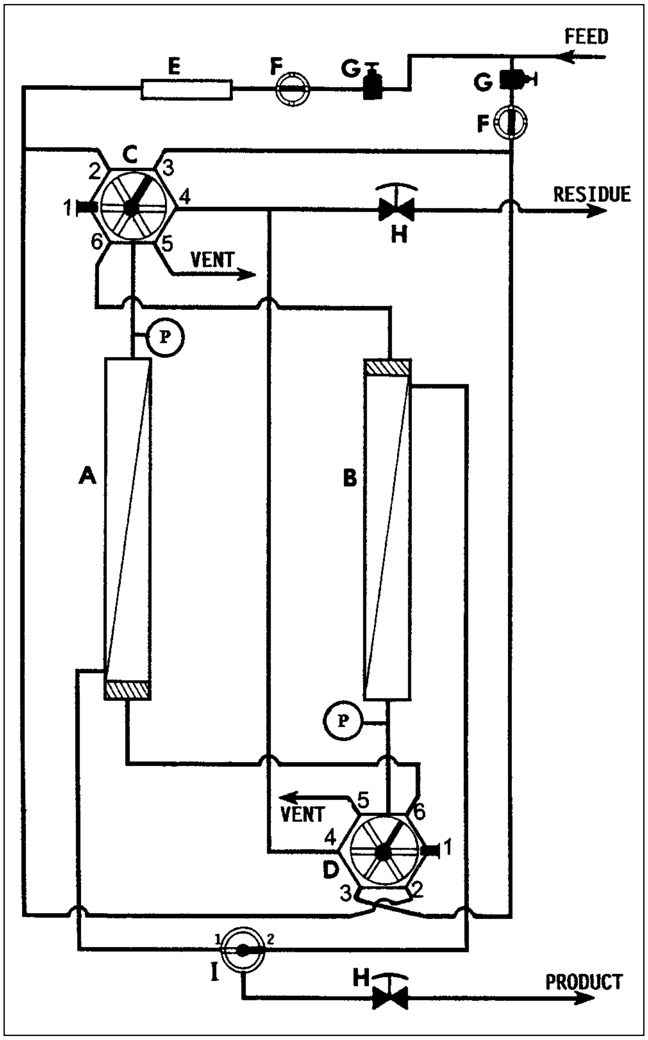


Figure 5. Experimental setup.

A and B: Membrane modules; C and D: 6-port sequential switching valves; E: storage vessel of "pushing" gas; F: on−off switching valve; G: pressure regulator; H: back-pressure regulator; I: 3-port switching valve; P: pressure transducer.

The test unit consisted of a pair of membrane modules (A and B) and a few switching valves (C, D, F, and I) for directing the flows of the gas streams. Both C and D were six-port sequential valves with the ports at position 1 being plugged. Valves F and I were the on−off and three-port switching valves, respectively. All of the switching valves were automated by timer-controlled actuators. The membrane units were arranged such that the feed gas was always introduced to the shell side of the membrane module that underwent permeation. During permeation, the residue outlet on the shell side of the module was closed, and the permeate produced on the bore side was received by the space on the shell side of the second module. The permeate was then "pushed" with a secondary feed gas to pressurize the permeate product. Obviously, the time for the pressurization step should be sufficiently short to prevent the "push gas" from breakthrough at the outlet of the permeate product. In this experiment, for easy control of the gas pushing, the "push gas" was stored in a storage vessel (E) before being released to a membrane module. The pressure of the "push gas" can be maintained independently of the operating permeation pressure, and the storage volume can be adjusted. Unless specified otherwise, the push gas pressure was set at about 300 kPa higher than the desired permeate product pressure, and the push gas storage volume was fixed at 6.4 mL. The pressures of both the residue and the permeate products released from the membrane unit can be controlled by back-pressure regulators (H). In the experiments, however, the residue stream was withdrawn at essentially local atmospheric pressure (which was 94 kPa absolute) by using a short piece of

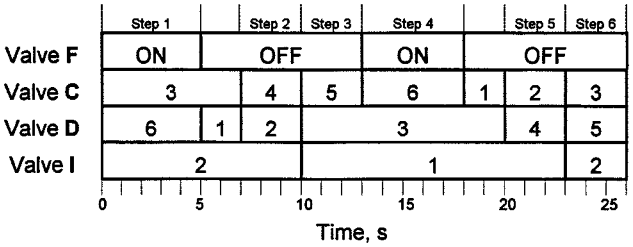


Figure 6. Cycle sequence chart showing the position of switching valves during pressure swing permeation.

capillary tubing to provide the necessary restriction to gas flow. The pressure changes in both modules during pressure swing permeation were monitored by pressure transducers.

Owing to the cyclic operation of the pressure swing permeation process, the flow rates and concentrations of both residue and permeate product also underwent a cyclic variation. To smooth out these variations, a surge tank with a substantially large volume was installed in the gas lines. As a result, the measured gas flow rate and concentration are time-averaged quantities. Figure 6 is a cycle-sequence chart that shows the distribution of time in each step and the corresponding positions of the switching valves. The cycle time for each membrane module was maintained at 13 s; the percentage permeation on-line time was 38.5%, and the permeate pressurization time was 23.1%. The pressure swing permeation system was tested for the separation of hydrogen from nitrogen, and the results are discussed below.

Table 2 illustrates the results of an experiment in which a permeate product containing 78.8 vol % hydrogen at a pressure of 1320 kPa was produced from a 1590 kPa feed gas containing 49.4 vol % H_2. A hydrogen recovery of 29% was achieved. The significance of the results is that the partial pressure of hydrogen in the permeate product is about 32% higher than its partial pressure in the feed. This can never be accomplished by using the conventional permeation process without recompression of the permeate, since a partial pressure differential across the membrane must always be maintained for the permeation and separation to occur. It should be mentioned that a distinction between the residue "product" and the residue "vent" streams is made here. After the residue was released from the membrane module at a specified pressure, the remaining residue in the membrane system needs to be vented before the feed gas is introduced to the membrane system for the next cycle of permeation operation. During the residue venting step, some of the permeate gas entrapped in the gas line that connected the two membrane modules was swept to the vented residue stream. Thus the concentration of fast permeating gas in the residue vent stream was higher than in the residue product, though the residue vent steam was in a very small amount. Reducing the holdup volume of the gas line or recycling the entrapped permeate back to the permeator will obviously improve the recovery.

Table 2. Pressure Swing Permeation Test for Hydrogen/Nitrogen Separation

	Pressure kPa Gauge	Concentration H_2 vol %	Flow Rate cm^3(STP)/min
Feed	1,590	49.4	386.6
Residue product	~ 94	41.3	300.0
Residue vent	94	71.4	16.6
Permeate	1,321	78.8	70.0

It is of interest to compare the performance of the pressure swing permeation with a conventional steady-state process. The separation performance that would be obtained with a conventional process under the same conditions of feed and pressures as in Table 2 was calculated for one of the membrane modules using Pan's model (1986) for the shell-side feed and countercurrent flow configuration. At a residue concentration of 42.9% H_2, which is equivalent to the overall residual concentration in Table 2, the permeate concentration and permeate flow rate are 54.9% H_2 and 0.28 cm^3(STP)/min, respectively. Both values are substantially lower than those shown in Table 2. Further, with the traditional permeation process, the maximum permeate hydrogen concentration that can be obtained at zero stage cut (that is, zero permeate flow) is calculated to be 58.3% H_2, which is significantly lower than that obtained with the pressure swing permeation process. Obviously, the results shown in Table 2 are otherwise impossible with the conventional process.

To illustrate the transient change of the gas pressure during the cyclic steady-state permeation process, the gas pressure in the membrane system was monitored continuously using on-line pressure transducers. Figure 7 shows the pressure change of the push gas and the permeate product. As expected, the pressure of the push gas dropped during permeate pressurization and eventually declined to the permeate product pressure. The push-gas pressure oscillated in a pulse-wave fashion, while the pressure of the permeate product was relatively constant. The pressure changes in the two membrane modules are presented in Figure 8, which shows the history that the two synchronized modules experienced. An intuitive depiction of the pressure change in a module is shown in Figure 9, which also shows the events during the process. In this figure, the pressures corresponding to BC and GH are the pressures of feed and permeate product, respectively, and the pressure at point F is the pressure of the permeate before being "pushed" to a higher level. It can be seen from Figure 8 that in this particular experiment, the permeate pressure was increased by about 130% due to the pres-

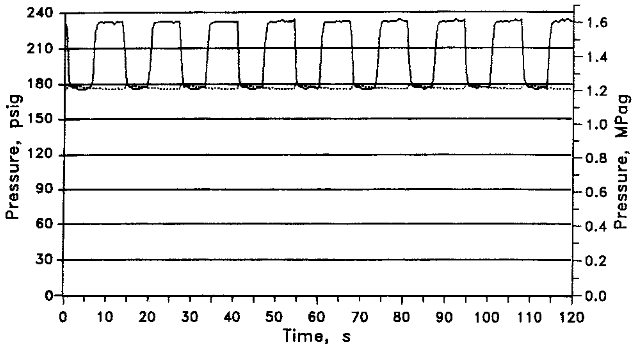


Figure 7. Pressure histories of "push" gas (solid line) and permeate product (dotted line).

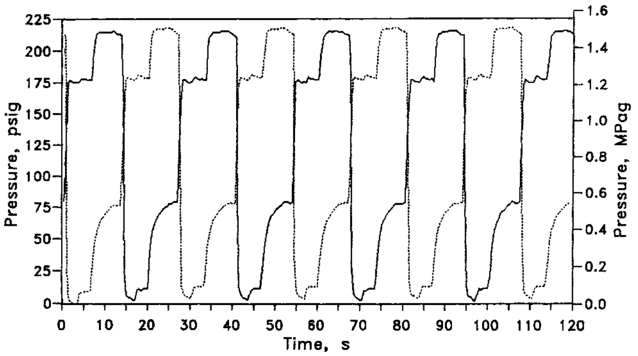


Figure 8. History of gas pressure in the two-module pressure swing permeation system.

The solid and dotted lines represent modules A and B, respectively.

surization step. The results imply that it is possible to synergistically integrate the pressure swing permeation with a pressure swing adsorption process for enhanced separation without using an interstage compressor.

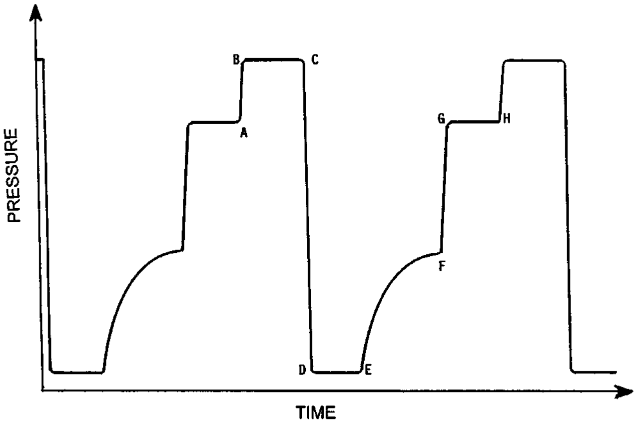
The gas-separation test was also carried out to produce permeate product at different pressures. This was done by adjusting the back-pressure regulator for permeate release at desired pressure levels. Typical results are summarized in Table 3, where the residue concentration was the overall concentration of the residue product and the residue vent. It is shown that the pressure swing process is even capable of producing hydrogen-enriched permeate gas at the feed pressure level. Examination of the data in Table 3 shows that:

1. An increase in the permeate product pressure tends to decrease the product purity and the product recovery.

2. At a given product pressure, the flow rate of the permeate product is usually lower when the product purity is higher.

3. The trade-off relationship between product purity and product recovery commonly observed in the conventional gas permeation process seems to not apply in the pressure swing permeation process.

It should be emphasized that the preceding performance data were just to illustrate the pressure swing permeation process, and the experiments were not conducted under optimized operating conditions. Because of the cyclic nature of the process, the permeation on-line time is only a fraction of the entire cycle time, and thus the feed throughput is normally lower than the conventional permeation process. Similar to the pressure swing adsorption process, the feed throughput of the pressure swing permeation process can be increased by increasing the cycle frequency or by using more sophisticated multimodule configurations.



A→B: Feeding of gas mixture into module
B→C: Permeation
C→E: Residue release
E→F: Reception of permeate produced from the other module
F→G: Elevation of permeate pressure by pressurization with feed
G→H: Release of permeate product

Figure 9. Pressure changes in the module.

Conclusions

A novel permeation process for gas separation, called pressure swing permeation process, was presented. This process uses two or more synchronized membrane modules that repeatedly and alternatively undergo the sequential steps of permeation, permeate reception, permeate pressurization, and product withdrawal. The pressure of permeate product is elevated by pressurization with the high-pressure feed gas, thereby reducing or eliminating permeate compression costs where a pressurized permeate is required. The pressurization step was carried out in a sufficiently short period of time to ensure the purity of the permeate product.

Pressure swing permeation is a cyclic membrane process. The unsteady-state permeation associated with the pressure swing permeation was analyzed parametrically to investigate the feasibility of the process, and a bench-scale unit comprising two hollow-fiber membrane modules was assembled and

Table 3. Pressure Swing Permeation Test for Hydrogen/Nitrogen Separation*

Permeate Stream			Residue Stream		Hydrogen Recovery in Permeate %
Pres. kPa	Conc. H_2 vol %	Flow Rate cm^3(STP)/min	Conc. H_2 vol %	Flow Rate cm^3(STP/min)	
2,163	76.0	97.0	40.0	274.5	40.2
2,163	77.1	80.3	40.4	247.2	38.3
1,473	79.0	112.6	38.2	297.6	43.9
1,473	80.3	76.6	40.3	260.1	37.1
784	81.4	125.1	37.1	325.4	45.7
784	82.5	94.6	38.2	279.5	42.2
94	89.0	169.8	33.2	415.1	52.3

*Feed pressure 2,163 kPa, residue pressure 94 kPa, feed concentration 49.4 vol % H_2.

tested for the separation of hydrogen from nitrogen to demonstrate the capability of the process. The experimental results showed that the permeate product at a pressure as high as the feed pressure can be produced without using a compressor. This is otherwise impossible with the traditional steady-state permeation processes if the pressures of the permeate and the feed are maintained at the same level. Due to its cyclic nature, the feed throughput of the process can be increased by using faster cycle frequencies and/or multimodule configurations. The pressure swing permeation process is analogous to the pressure swing adsorption and has the potential to be synergistically integrated with pressure swing adsorption, which is often used as a complementary technique to membrane permeation, to enhance the overall separation performance without needing an interstage compressor.

Notation

T = temperature, K
t = permeation time, s

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Appendix

Define
fiber inside diameter $= d_i$
fiber outside diameter $= d_o$
membrane area $= A$
module volume $= V_o$
packing factor based on fiber outside diameter $= \epsilon$.
Then
the volume taken by membrane $= \epsilon V_o$
the volume of fiber lumen $= (d_i/d_o)^2 \epsilon V_o$
the shell-side void volume $= (1-\epsilon)V_o$.

The shell-side void volume is the volume of feed chamber, V_F, for the permeation where gas is introduced to the shell side and permeate is produced from the lumen side. When one module is used to receive permeate gas from the other module with the same design, the volume for permeate reception, V_P, is

$$V_P = (d_i/d_o)^2 \epsilon V_o + (1-\epsilon)V_o.$$

The ratio (d_o/d_i) for hollow-fiber membranes normally ranges from 2.5 to 4, and the typical membrane packing factor is 0.4 ~ 0.5. Thus

$$V_P \approx (1-\epsilon)V_o = V_F.$$

This is the basis of assuming equal volumes of feed chamber and permeate receiver in the calculations. With the typical fiber dimensions, the membrane area per unit module volume, A/V_o, is 2,000–4,000 ft^2/ft^3 (Koros and Fleming, 1993). The quantity A/V_P can thus be estimated to be in the range of 3,000–8,000 ft^2/ft^3 or 10,000–26,000 m^2/m^3.

Manuscript received Aug. 2, 1999, and revision received Nov. 29, 1999.