



Assessment of air separation technologies for the recovery of oxygen for use in hypersonic flight
by Nathan Jeremiah Binau

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Various methods of air separation to recover large quantities of oxygen for use in hypersonic flight were investigated in this review. The specific separation processes that were considered included silver membranes, mixed conducting membranes, polymeric membranes, facilitated transport membranes, reversible chemical reactions, solid state adsorption, vapor-liquid equilibrium, and magnetic fields.

Despite the numerous commercial air separation technologies that exist, it was found that the volume and weight of the established, land-based air separation-systems prohibit their use in hypersonic flight.

The most promising hypersonic air separation method appears to be a vapor-liquid equilibrium system designed to operate on the principle of differential condensation and differential vaporization. The equipment to carryout the combined differential processes would require extensive engineering to make the system practical for hypersonic air separation.

One device in which differential condensation and differential vaporization may occur is a vortex tube. The vortex tube has been shown to separate high purity oxygen from air, but the oxygen recoveries were extremely low. Before the vortex tube could be useful in hypersonic air separation, its performance must be improved and a compression system must be developed to supply the tube with air at the required pressure level. If future experimental work could overcome these obstacles, the vortex tube has the potential to be successful in hypersonic air separation.

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Nathan Jeremiah Binau

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APPROVAL

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Nathan Jeremiah Binau

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Various methods of air separation to recover large quantities of oxygen for use in hypersonic flight were investigated in this review. The specific separation processes that were considered included silver membranes, mixed conducting membranes, polymeric membranes, facilitated transport membranes, reversible chemical reactions, solid state adsorption, vapor-liquid equilibrium, and magnetic fields.

Despite the numerous commercial air separation technologies that exist, it was found that the volume and weight of the established, land-based air separation systems prohibit their use in hypersonic flight.

The most promising hypersonic air separation method appears to be a vapor-liquid equilibrium system designed to operate on the principle of differential condensation and differential vaporization. The equipment to carry out the combined differential processes would require extensive engineering to make the system practical for hypersonic air separation.

One device in which differential condensation and differential vaporization may occur is a vortex tube. The vortex tube has been shown to separate high purity oxygen from air, but the oxygen recoveries were extremely low. Before the vortex tube could be useful in hypersonic air separation, its performance must be improved and a compression system must be developed to supply the tube with air at the required pressure level. If future experimental work could overcome these obstacles, the vortex tube has the potential to be successful in hypersonic air separation.

CHAPTER 1

INTRODUCTION

Traditional propulsion systems for hypersonic flight utilize onboard supplies of liquid hydrogen and oxygen for fuel. The liquid oxygen is obtained from a land-based air separation facility such as a cryogenic distillation plant. In order to eliminate the need for onboard oxygen storage on takeoff, it is desirable to develop a launch vehicle that is not only capable of takeoff using airbreathing engines but is also able to collect, separate, and store oxygen for later use in flight.

The goal of the current project is to screen available air separation technologies for possible use in hypersonic flight. Based on this objective, four main tasks were developed for the successful completion of the project. These tasks are as follows:

- 1) Define the technology requirements and performance evaluation criteria;
- 2) Identify feasible candidate technologies for detailed evaluation;
- 3) Evaluate the potential performance of the feasible technologies; and
- 4) Prepare a report on the findings.

Project task 1 was completed on August 14, 1996 in a project kickoff meeting involving representatives from NASA, MSE Technologies, and Montana State University. The following list of project requirements was developed in this meeting:

- 1) The feed rate to the separation system must be 100 pounds per second;
- 2) The purity of the oxygen product must be at least 90% (molar) and the oxygen recovery must be at least 50% (molar);
- 3) The mass of the system divided by the inlet air mass flowrate cannot exceed 10 lbs/(lbs/s) (1,000 pounds) and the volume of the system divided by the inlet air mass flowrate cannot exceed $0.5 \text{ ft}^3/(\text{lbs/s})$ (50 ft^3);
- 4) The feed air will be supplied dry and carbon dioxide free at a pressure of 10 psia and a temperature of 100 K. If different feed conditions are required, the process must deal with impurities (such as carbon dioxide and water) in the feed stream;
- 5) The minimum pressure of the oxygen product is 8 psia; and
- 6) Liquid hydrogen at 25 R and 20 psia is available for use as a refrigerant.

Project tasks 2, 3, and 4 are addressed in the subsequent chapters of this review. The format of these chapters will include a discussion on the theory of the separation technology, an evaluation of the technology's applicability to air separation in hypersonic flight, and a recommendation as to whether or not the technology should be included in further research or laboratory testing.

In the evaluation of all the separation technologies included in this review, the composition of the feed air was assumed to be 79% nitrogen and 21% oxygen. The actual composition (volume) of dry air at sea level is 78.08% nitrogen, 20.95% oxygen, and 0.93% argon with the remaining balance containing carbon dioxide, helium, krypton, and other rare gases (Lide 1993, 14-12). Although the 79% nitrogen and 21% oxygen feed air composition is reasonable for an initial screening of separation technologies, the actual composition must be considered in any calculation requiring extremely accurate results.

CHAPTER 2

SILVER MEMBRANES

Summary of the Technology

Many researchers have verified that the permeation of gases through dense metal membranes can be modeled with a solution to Fick's Law. This relationship, which is known as Sieverts law (Eichenauer and Müller 1962, 324), is given as:

$$\frac{M_i}{A} = \frac{q_i}{l} (P_{i,h}^{0.5} - P_{i,l}^{0.5}) \quad (2.1)$$

In this equation, M_i is the permeation rate of the species of interest through the membrane, A is the membrane area, q_i is the permeability of the gas species through the membrane, l is the membrane thickness, and $P_{i,h}$ and $P_{i,l}$ are the partial pressures of the permeating species on the high and low pressure sides of the membrane (Hwang and Kammermeyer 1975, 92). This relationship is very similar to the governing equation for the diffusion of gases through polymeric membranes, the only difference being that the permeation rate through metals is governed by the difference in the square root of the permeating species' partial pressure instead of the partial pressure itself.

It is widely known that elemental silver is nearly 100% selective for the permeability of oxygen over nitrogen (Mullhaupt 1967, 1). The permeability of atomic oxygen through metallic silver is given by the product of oxygen's diffusivity and solubility

which is a strong function of temperature (Gryaznov, Gul'yanova, and Kanizius 1973, 1517). Equations 2.2 and 2.3 have been developed to describe the diffusivity and solubility of atomic oxygen in solid silver over the temperature range of 750 to 950 °C (Ramanarayanan and Rapp 1972, 3239).

$$D_o(Ag) = 0.0049 \cdot e^{\frac{-11600}{RT}} \text{ (cm}^2\text{/s)} \quad (2.2)$$

$$N_o^s(Ag) = 7.2 \cdot e^{\frac{-11500}{RT}} \text{ (at. pct.)} \quad (2.3)$$

Using these equations, the diffusivity of oxygen in silver at 900 °C is calculated to be 3.38×10^{-5} cm²/s and the solubility of oxygen in silver is equal to 0.052 mole percent. The oxygen permeability through silver is therefore equal to 1.91×10^{-5} cm³-cm/cm²-s-atm^{0.5}. Similar calculations were made using data contained in other references and the results are shown in Table 1.

Table 1. Comparison of various literature values of the permeability of oxygen through silver at 900 °C.

Reference	Oxygen Permeability (cm ³ -cm/cm ² -s-atm ^{0.5})
Ramanarayanan and Rapp 1972, 3239	1.9×10^{-5}
Hwang and Kammermeyer 1975, 94	1.0×10^{-5}
Ramanarayanan and Rapp 1972, 3245	1.5×10^{-5}

Equation 2.1 indicates that the permeation rate of oxygen through silver is a linear function of the film thickness. Consequently, it is desirable to use a very thin film in the design of silver membranes. Since thin silver films are very delicate, a composite membrane must be used in which silver is deposited on a porous inorganic support

capable of withstanding high temperatures and pressures. Porous alumina is a commonly used support material (Hsieh 1996, 149).

Use of Silver Membranes in Hypersonic Air Separation

As was previously stated, the rate that oxygen permeates through silver is a strong function of temperature. The higher the membrane's temperature, the greater the rate of oxygen permeation. Equation 2.1 shows that the permeation rate will also be governed by the pressure of both the feed and product streams. Since the outlet stream from the feed gas conditioning unit will have both a low pressure (10 psia) and low temperature (100 K), it would be necessary to compress and heat the air prior to introduction into a silver membrane.

A convenient way to obtain compressed air at a high temperature would be to utilize the stagnation pressure that could be generated if the inlet air was brought to rest isentropically. The equation that can be used to estimate the stagnation pressure of a supersonic gas stream is presented as equation 2.4 (McCabe, Smith, and Harriott 1993, 151).

$$p_s = p_o \left(1 + \frac{\gamma - 1}{2} N_{Ma,o}^2 \right)^{\frac{1}{1-\gamma}} \quad (2.4)$$

In this equation, p_s is the stagnation pressure, p_o is the pressure in the undisturbed fluid, γ is the ratio of specific heat capacities, and $N_{Ma,o}$ is the Mach number of the approaching fluid. Since the stagnation process was assumed to be isentropic, it is by definition adiabatic. Because adiabatic processes have no heat transfer, the temperature of the gas

will dramatically increase during the stagnation process. The temperature of the gas after compression can be predicted by equation 2.5 (McCabe, Smith, and Harriot 1993, 151).

$$T_s = T_o \left(1 + \frac{\gamma - 1}{2} N_{Ma,o}^2 \right) \quad (2.5)$$

In equation 2.5, T_s is the stagnation temperature and T_o is the temperature in the undisturbed fluid. When the ratio of the specific heat capacities is assumed to be constant and published atmospheric temperature and pressure data as a function of altitude (Lide 1993, 14-13 to 14-14) are used to describe the pressure and temperature of the undisturbed fluid, equations 2.4 and 2.5 can be used to compute the stagnation pressure and temperature of a supersonic gas stream as a function of Mach number. The results of the calculations are shown in Figures 1 and 2.

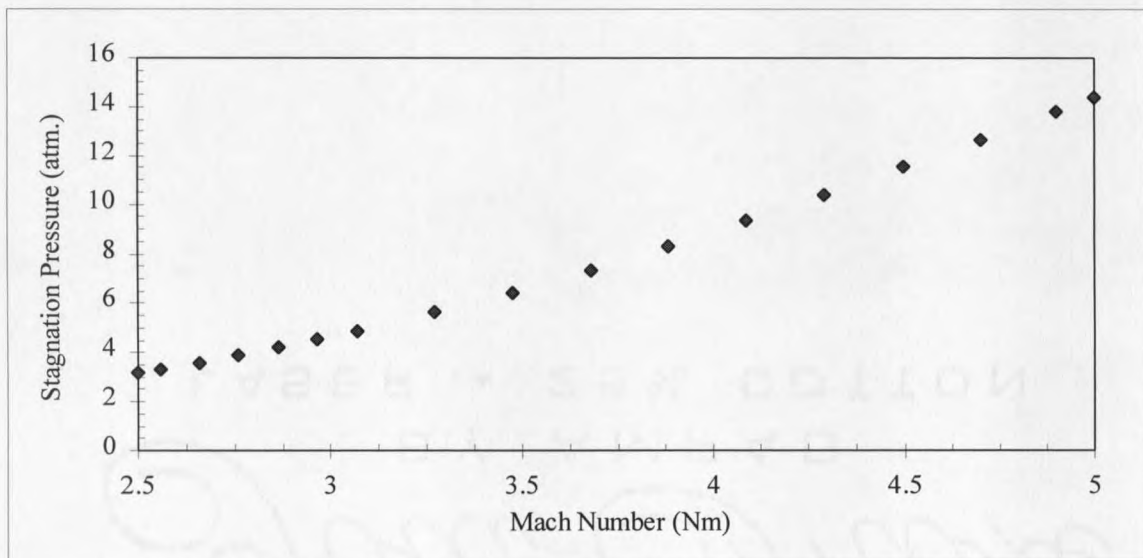


Figure 1. Stagnation pressure as a function of Mach number in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

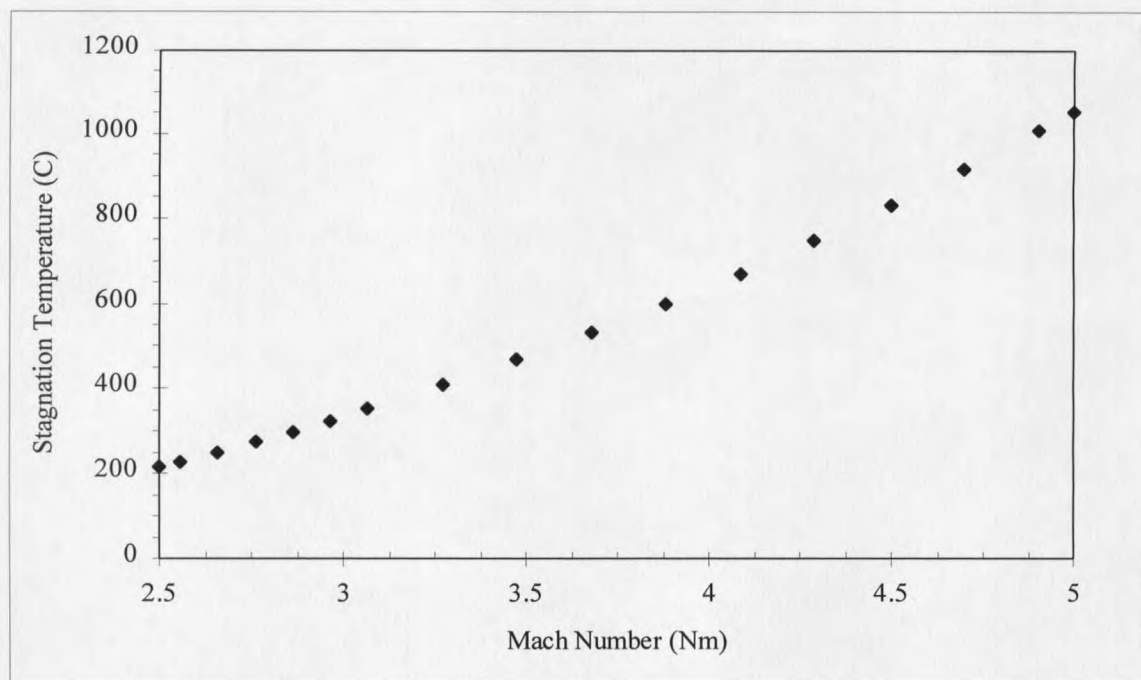


Figure 2. Stagnation temperature as a function of Mach number in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

The data contained in these plots shows that the expected stagnation pressure will range from approximately 3.2 to 14.4 atmospheres and the stagnation temperature will range from approximately 210 to 1050 °C in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

Calculation of the Required Membrane Area

In order to calculate the membrane area required to recover 50% of the oxygen from an inlet air stream of 100 lbs/s, the following assumptions were made regarding the operating conditions of the membrane module.

- 1) The membrane has a silver film thickness of 0.5 μm ;

- 2) The permeability of oxygen through the silver film is accurately described by the product of oxygen diffusivity and solubility predicted by equations 2.2 and 2.3, respectively;
- 3) There is no pressure drop in the feed or product streams and no mixing occurs in the feed stream; and
- 4) Oxygen diffusion through the porous media on which the silver is supported is very fast compared to the rate in which oxygen diffuses through the silver.

The required membrane area was calculated using a modified version of equation 2.1 which relates the incremental oxygen permeation rate to an incremental membrane area. This equation, which originally was derived for polymeric membranes (Saltonstall 1987, 186), was modified to reflect the permeation process through metallic membranes. After modification, the equation (given as equation 2.6) was incorporated into a MATLAB[®] program which calculates the membrane area as a function of the amount of feed gas that has permeated the membrane. Since equation 2.6 is an ordinary differential equation (ODE), it can be easily solved with MATLAB's[®] ODE 45 integrator. A copy of the program has been included as Appendix A.

$$\frac{dM_i}{dA} = \frac{q_i}{l} (p_{i,h}^{0.5} - p_{i,l}^{0.5}) \quad (2.6)$$

Using this program, a study was completed in which the required membrane area was calculated as a function of the feed pressure, product pressure, and membrane operating temperature. The results of this study have been summarized in Figures 3 through 5.

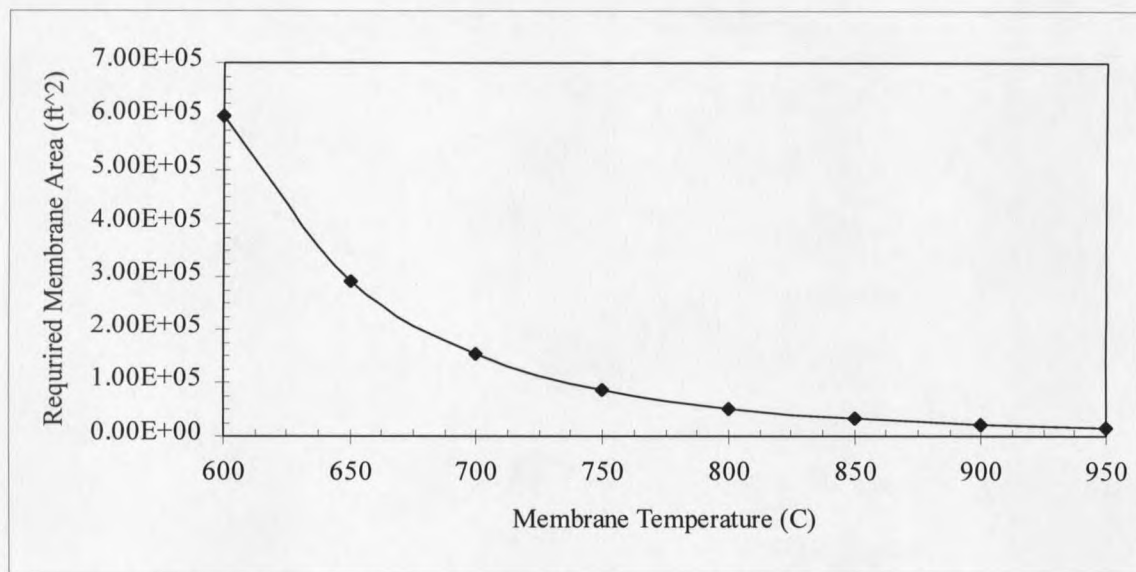


Figure 3. Required silver membrane area as a function of feed temperature (feed rate=100 lbs/s, oxygen recovery=50%, feed and product pressures of 10 atm. and 8 psia, and silver film thickness of 0.5 μm).

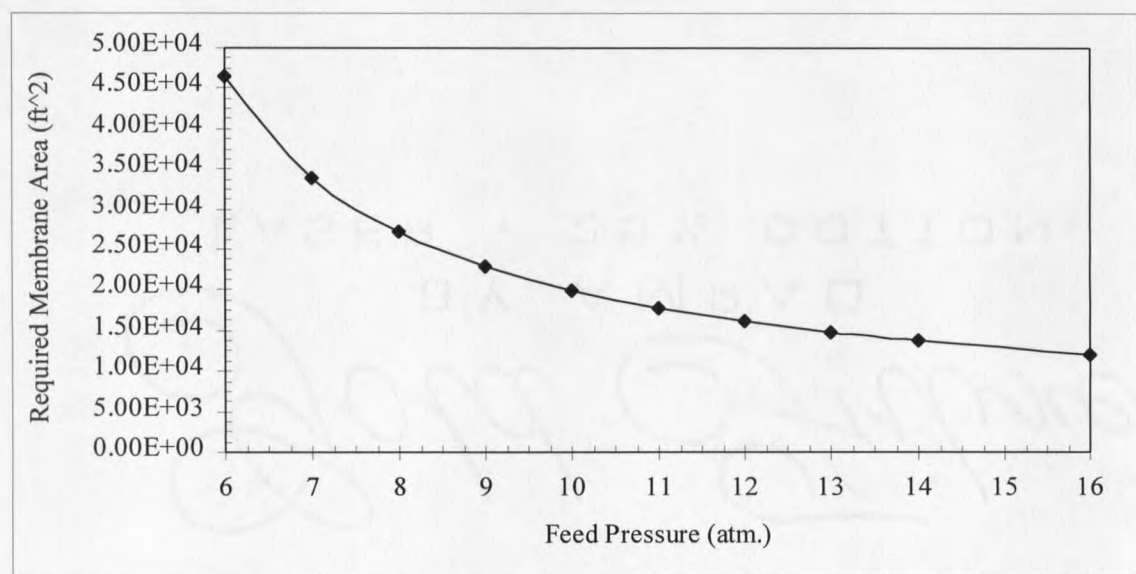


Figure 4. Required silver membrane area as a function of feed pressure (feed rate=100 lbs/s, oxygen recovery=50%, feed temperature of 900 °C, product pressure of 8 psia, and silver film thickness of 0.5 μm).

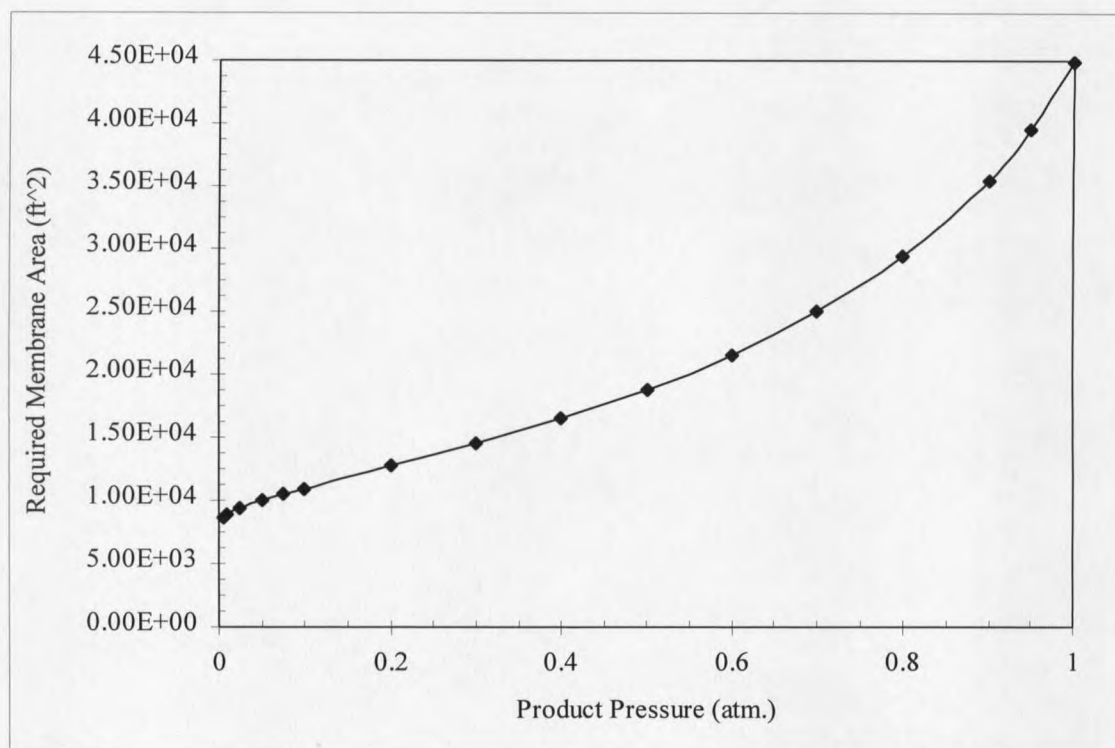


Figure 5. Required silver membrane area as a function of product pressure (feed rate=100 lbs/s, oxygen recovery=50%, feed pressure of 10 atm., feed temperature of 900 °C, and silver film thickness of 0.5 μm).

Inspection of Figures 3 and 4 indicates that both the membrane operating temperature and the feed pressure are extremely important in keeping the required membrane area at a reasonable value. In fact, as shown in Figure 3, decreasing the operating temperature from 900 to 800 °C requires that the membrane area increase from 20,000 ft² to over 50,000 ft². Figure 5 shows that at low product pressures the membrane area can be significantly reduced over the membrane area required at higher pressures. The practicality of reducing the product pressure to very low levels is questionable since the combination of high temperature and low pressure will cause the volumetric flowrate of the product stream to be enormous. Consequently, in the further evaluation of silver

membranes, product pressures less than 8 psia (the project's lower pressure limit) will not be considered.

If the separation process would occur as the vehicle was accelerating, the operation of a silver membrane system would become overly complicated because the temperature and the pressure of the feedstream would be constantly changing. Considering that silver has a melting point of 961 °C (Lide 1993, 4-95), and that the stagnation temperature at speeds very close to Mach 5 will exceed 1000 °C, the system design would have to include provisions for removing heat to keep the silver from melting. Furthermore, Figure 3 shows that at low temperatures, the required membrane area would be much too high to be practical in hypersonic air separation. As a result, heat would need to be added to the inlet stream for a majority of the separation period since the stagnation temperature at low Mach numbers is much less than the membrane's optimum operating temperature. As shown in Figure 4, the performance of the silver membrane increases as the feed pressure increases. Operating the membrane at the highest possible pressure will maximize the oxygen permeation rate which will in turn reduce the overall size and weight of the membrane module. Based on these reasons, the separation of oxygen with silver membranes would be best accomplished at a constant speed slightly less than Mach 5.0. As an example, when traveling at Mach 4.7 at an elevation of approximately 75,000 feet, the stagnation pressure of 12.6 atmospheres results in a stagnation temperature of 915 °C. Assuming a membrane thickness of 0.5 μm and a product pressure of 8 psia, the required area of a membrane module designed to recover 50% of the oxygen from an inlet air stream of 100 lbs/s while operating at 915 °C and 12.6 atmospheres would be 13,520 ft^2 .

Estimation of the Membrane Module Weight and Volume

Data from a major supplier of ceramic materials (Goodfellow) indicates that the density of porous alumina is approximately 2.55 g/cm^3 . As a starting point to estimate the weight and volume of the silver membrane module, it was assumed that thin silver films are able to be deposited on porous alumina tubes with an outside diameter (OD) of 8 mm, an inside diameter (ID) of 5 mm, and a length of 1524 mm (5 feet). With these dimensions, each of the tubes would have an available surface area of 0.4123 ft^2 . Since the silver module requires $13,520 \text{ ft}^2$ of active surface area, the module would need approximately 32,790 tubes. Since each of the tubes weighs 0.2626 pounds (neglecting the weight of the silver on the tube since its mass is very small compared to the mass of the tube itself), the weight of all the tubes combined would be approximately 8,600 pounds.

The volume of the module can be estimated by computing the surface area to volume ratio of the ceramic support and multiplying this value by a packing efficiency, which in this case was assumed to be 50%. When this procedure is applied to the example membrane module cited in the preceding paragraph, the packing factor is calculated to be approximately $75 \text{ ft}^2/\text{ft}^3$ which is within the range of packing factors available commercially for ceramic membranes (Hsieh 1996, 161). When the required membrane surface area of $13,520 \text{ ft}^2$ is divided by the packing factor of $75 \text{ ft}^2/\text{ft}^3$, the membrane module volume is calculated to be approximately 180 ft^3 .

Discussion

In order for silver membranes to be practical in hypersonic air separation, the membrane system should not only operate at temperatures near silver's melting point, but also with high feed pressures. In order to simplify the design and optimize the membrane's performance, the separation process should occur at speeds slightly less than Mach 5.0 with a high enough elevation so that the stagnation pressure would not cause problems with the mechanical stability of the membrane. Operation of the separation system while the vehicle is accelerating would complicate the module design and would result in a separation performance that would be below the system's potential.

The ability to deposit defect free, ultrathin silver films is very important in the fabrication of a silver membrane system. Although the deposition of ultrathin metallic films with a thickness in the range of 0.5 μm has been demonstrated in past research (Maréchal and Quesnel 1994, 1693 and Jayaraman et al. 1995, 89), no test data could be found which indicates that defect free silver films have been achieved in a large scale air separation device. If defect free thin films are difficult to obtain, the oxygen content of the product will decrease since nitrogen will permeate through the defects that are present in the membrane.

In order to reduce the weight of the membrane to the specified project limit of 1,000 pounds, it would be necessary to either reduce the wall thickness on the ceramic support or utilize a support media with a much lower density than porous alumina. When tubes with a reduced wall thickness (OD of 4 mm, ID of 2 mm) are used in the weight calculation, the mass of the module would be reduced to 5,300 pounds. Because the

reduction in wall thickness would likely require that the overall size of the tube be reduced to maintain the mechanical stability, the vapor velocities inside the tube could become too high to be practical. As an example, the average vapor velocity at the tube exit for the tubes illustrated above would have an unrealistic value of 470 feet per second. Clearly, the only way reduction of the support wall thickness would be practical is if the inside diameter of the tube would remain relatively large.

As indicated by equation 2.1, any reduction of the silver film thickness would also result in the reduction of the required membrane area, which would in turn reduce the weight of the membrane module. However, the practicality of reducing the thickness of the film must be weighed against increasing the defect concentration that occurs as the film thickness is reduced.

In order to reduce the volume of the membrane module to less than 50 ft³, either the packing factor of the module must be increased from the assumed value of 75 ft²/ft³ or the thickness of the silver film must be reduced. Although the packing factor of the module could significantly increase if hollow ceramic fibers were used as the porous support for the silver film (Hsieh and Bhave 1991, 90); this technology is not currently available in commercial membranes modules (Hsieh 1996, 155). As has been shown, if a support with a high surface area to volume ratio were used in the module design, the oxygen velocity inside the tubes would become too high to be practical. High velocities in small tubes and fibers would cause large pressure drops that could significantly degrade the performance of the membrane module.

Regardless of whether the porous support takes the form of tubes or hollow fibers, it is imperative that the material have an oxygen permeability that is significantly greater than the permeability of oxygen through the silver film. Design of a porous support that meets this criteria could be challenging due to the very high oxygen permeabilities through silver at high temperatures. If the need for a highly permeable support requires a large pore size in the support material, defect free films could be difficult to obtain (Jayaraman et al. 1995, 89).

A final area of concern dealing with the use of silver membranes lies in the stability of the silver film. Silver films are known to be very unstable when subjected to high temperature gas streams containing oxygen. Although incorporation of alloys such as gold and copper have been found to improve the stability of thick silver films (Mullhaupt 1967, 2), the stability of ultrathin films plated on porous supports was not found in research on the topic. Furthermore, unless the feed gas conditioning unit is capable of removing carbon dioxide and water at the stagnation temperature and pressure, it would be important that the silver film would not degrade when exposed to the impurities that would be present in the feed gas. No information on the stability of silver films when exposed to carbon dioxide and water was found in the literature that deals with oxygen permeation through silver membranes.

A potential advantage of utilizing a high temperature process such as silver membranes is that despite having to cool the oxygen from extremely high temperatures, the required cooling load is actually less than the energy needed to condense the entire feed stream, even when the feed is much cooler than the stagnation temperature. The

reduction in the cooling load is the result of only having to condense the oxygen that is recovered as product instead of liquefying the entire feed stream, the majority of which is nitrogen. In addition, the amount of hydrogen that is required to condense the oxygen product is significantly less than the quantity needed to condense the entire feed stream. The large reduction in hydrogen is the result of being able to warm the refrigerant to a much higher temperature which allows for the transfer of more energy per pound of hydrogen. As an example, assuming that the liquid hydrogen coolant is able to be warmed to within 15 degrees of the high temperature oxygen product, approximately 50 pounds of hydrogen per minute would be required to condense the oxygen product compared to approximately 1,000 pounds per minute to condense the entire feed stream from a temperature of 100 K. This reduction in cooling load could result in the reduction of the size and weight of other pieces of equipment such as heat exchangers.

Conclusions

Air separation with silver membranes is an interesting technology since the product obtained from the membrane module would theoretically be pure oxygen. The high purity product would enable the separation to be made in a single stage without the need for recycle streams. Product recycle generally requires recompression which not only requires the expenditure of a large amount of energy, but also increases the overall size of the separation system.

While air separation using silver membranes can be considered technically feasible, significant engineering and bench scale testing would be required to fabricate a stable

silver membrane module that could meet the current project's weight and volume requirements while maintaining reasonable vapor velocities inside the membrane tubes.

Although the use of silver membranes for oxygen permeation has been researched in the past, little research activity has been published since the late 1980's. Furthermore, no documentation could be found of any commercial air separation facility using silver membranes to produce oxygen. Considering that the current technology results in a membrane module that significantly exceeds the current project's weight and volume limits, it would appear that the use of silver membranes would not be feasible in hypersonic air separation unless significant improvements are made to the current technology.

CHAPTER 3

MIXED CONDUCTING MEMBRANES

Summary of the Technology

It is widely known that inorganic electrolytes are able to selectively conduct oxygen ions, especially at elevated temperatures (Lin, Wang, and Han 1994, 786). The oxygen ion transport is accomplished because of vacancies in the electrolyte's crystalline structure. Oxygen ions move from vacancy to vacancy across the membrane driven either by a difference in chemical potential (oxygen partial pressure) or from an applied voltage source (Wright and Copeland 1990, 33). Since the permeation of oxygen through thick electrolytes is slow, it is desirable to utilize thin films to increase the rate of oxygen permeation. Because thin electrolyte films are not self-supporting, the desirable configuration involves plating the electrolyte as a thin film on a porous ceramic support (Ziehfrend and Maier 1996, 2721-2722).

Although it is possible for the electrolyte to be designed so that it will pump oxygen from an area of low oxygen pressure to an area of higher pressure, the energy requirement of this process is substantial (Wright and Copeland 1990, 59). Considering that the current project does not have access to large quantities of electricity, an electrically driven system will not be considered in this review.

In order for the electrolyte to function as a pressure driven separator, it must be able to conduct both oxygen ions and electrons. Oxygen ion conductors commonly have fluorite or perovskite crystalline structures. These structures are important because they allow for the displacement of atoms having positive oxidation states with atoms having lower oxidation states. When an atom with a lower oxidation state is introduced into the crystalline structure, the electrolyte must lose an oxygen atom thereby creating a vacancy in the crystal. Once a sufficient concentration of vacancies is present, oxygen ions are able to travel through the material by moving from vacancy to vacancy. Because the oxygen transport through the electrolyte is in the form of ions, the electrolyte must also be able to cycle electrons across the membrane to maintain charge neutrality. Examples of materials that are capable of both ion and electron conduction (commonly known as mixed conductors) include $\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{3-x}$ and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (Wright and Copeland 1990, 33-38).

The transport of oxygen through mixed conducting membranes is a rather complicated process. Equation 3.1 has been used to describe the permeation of oxygen through thick electrolytes and was developed according to the Wagner theory of electrochemical transport (Lin, Wang, and Han 1994, 787).

$$J_{O_2} = \frac{\alpha T}{l} \int_{p_{O_2,low}}^{p_{O_2,high}} \sigma_n d(\ln p_{O_2}^*) \quad (3.1)$$

Inspection of this equation shows several important aspects about the transport of oxygen through electrolytic membranes. First, the rate of oxygen permeation is dependent on the membrane temperature. Second, the flux of oxygen through the membrane is inversely

proportional to the membrane's thickness. Finally, the driving force for oxygen permeation through the membrane is the result of the difference between the natural logarithms of the oxygen partial pressures on the high and low pressure sides of the membrane.

Additional research into oxygen transport through mixed conducting membranes has indicated that equation 3.1 does not adequately describe the permeation process in every situation. The main function of equation 3.1 is to describe the flux of oxygen through thick electrolytic membranes in which the bulk diffusion of oxygen is the rate limiting step in the transport process. As mixed conducting membranes continue to evolve, other parts of the permeation process (such as the dissociation of molecular oxygen into ions) will become more important in determining the rate of oxygen transport through the membrane. If increases in the oxygen diffusion rate are large enough such that the diffusion process is no longer the rate limiting step, the fundamental basis of equation 3.1 will no longer be valid. In such cases, new equations that include the surface dissociation and recombination of oxygen molecules must be utilized. In order to rigorously determine the oxygen flux through the membrane, one must solve a set of nonlinear equations that describe the transport process. Data for the rate parameters involved in different parts of the permeation process would be required to obtain a numerical solution to the problem (Lin, Wang, and Han 1994, 787-790).

In an initial screening to assess the feasibility of using mixed conducting membranes for hypersonic air separation, it is convenient to consider cases where a rate limiting step is present in the transport process. In these cases, a single equation can be used to

describe the oxygen permeation rate through the membrane. As has been previously discussed, equation 3.1 applies when thick membranes are used in the membrane design and bulk diffusion is the rate limiting step in the transport process. In this case, oxygen permeation will be governed by the difference in the natural logarithms of the oxygen partial pressures on the high and low pressure sides of the membrane. In the case of the rate limiting step being the surface dissociation of oxygen into ions, the rate of permeation has been shown to depend on the difference of the square roots of the oxygen partial pressure on the high and low pressure side of the membrane. A second model that has been proposed to describe oxygen permeation in the case of oxygen diffusion as the rate controlling step includes the difference of the oxygen partial pressures each raised to the 0.25 power (Lin, Wang, and Han 1994, 791-792).

Use of Mixed Conducting Membranes in Hypersonic Air Separation

As was discussed in the previous section, the oxygen permeation rate through mixed conducting membranes is a function of both pressure and temperature. Similar to silver membranes, the performance of mixed conducting membranes increases as the temperature and pressure increase. As a result, mixed conducting membranes should not only operate at very high temperatures, but also operate with high feed pressures. In order to simplify the design and optimize the membrane's performance, the separation process should occur near Mach 5.0 at a high enough elevation so that the stagnation pressure would not cause problems with the mechanical stability of the membrane.

Operation of the membrane while the vehicle is accelerating would complicate the design and would result in a separation performance that is below the system's potential.

Calculation of the Required Membrane Area

In order to obtain the data necessary to calculate the required membrane area, the literature was searched to find oxygen permeation rates through mixed conducting membranes at conditions similar to those that would be encountered in hypersonic air separation. A partial listing of the published values are presented in Table 2.

Table 2. A sample of the oxygen fluxes through mixed conducting membranes.

Reference	Membrane Material	Oxygen Flux (lbs/ft ² -s)	Mem. Temp. (K)	Mem. Thick. (cm)	P _{O₂} feed (atm)	P _{O₂} prod. (atm)
Itoh et al. 1994, 245	La _{0.4} Sr _{0.6} CoO ₃	1.5x10 ⁻⁵	1021	0.08	n/a	n/a
Lin et al. 1992, 224	YSZ	3.6x10 ⁻⁶	1273	10 ⁻⁵	0.03	10 ⁻⁵
Elshof, Bouwmeester, and Verweij 1995, 104	La _{0.6} Sr _{0.4} FeO _{3.5}	2.9x10 ⁻⁵	1273	0.05	n/a	0.02
Shen et al. 1994, 12	SrCo _{0.8} Fe _{0.2} O _{3.5}	1.5x10 ⁻⁴	1273	0.009	0.21	10 ⁻⁶
Balagopal et al. 1995, 15	Bi _{1.5} Y _{0.5} O _{3-z} -Ag	1.2x10 ⁻⁴	1123	0.025	n/a	n/a
Balachandran et al. 1995, 75	La _{0.2} Sr _{0.8} Fe _{0.6} Co _{0.4} O _x	1.5x10 ⁻⁵	n/a	n/a	n/a	n/a
Clark, Losey, and Sutor 1992, 203	YSZ	8.9x10 ⁻⁵	n/a	0.0125	0.21	1
Carolan et al. 1993, 10	La _{0.2} Ba _{0.8} Co _{0.8} Fe _{0.2} O _{2.6}	6.8x10 ⁻⁵	1107	<0.2	n/a	n/a
Carolan et al. 1993, 11	Pr _{0.2} Ba _{0.8} Co _{0.8} Fe _{0.2} O _{2.6}	9.3x10 ⁻⁵	1104	<0.2	n/a	n/a
Carolan and Dyer 1996, 13	La _{0.2} Ba _{0.8} Co _{0.8} Fe _{0.2} O _{3-z}	9.2x10 ⁻⁴	1123	7x10 ⁻⁴	0.21	0.001
Thorogood et al. 1993, S-3	La _{0.2} Ba _{0.8} Co _{0.8} Fe _{0.2} O _{3-z}	2.6x10 ⁻⁴	1123	0.021	n/a	n/a
Thorogood et al. 1993, 24	La _{0.2} Ba _{0.8} Co _{0.8} Fe _{0.2} O _{3-z}	5.5x10 ⁻⁴	n/a	0.025	14.6	1.1
Mazanec et al. 1994, 39	La _{0.2} Sr _{0.8} CoO _x	1.4x10 ⁻³	1373	n/a	n/a	n/a

The most interesting membranes contained in Table 2 are the $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-z}$ membranes being developed by Air Products and Chemicals. Details of the membranes have been disclosed in U. S. Patents 5,534,471 and 5,240,480. In an attempt to gain more information on the current status of the membranes, Dr. Paul Dyer of Air Products was contacted on February 21, 1997. Dr. Dyer stated that since the membranes are still in the developmental stage, no information other than what was disclosed in the patents was able to be released at the current time. As a point of interest, most of the data presented in patents 5,534,471 and 5,240,480 is the result of computer simulations of the oxygen permeation process based on Air Products' internal models. Examination of the two patents has shown that the highest oxygen flux that appears to have been actually measured was 2.6×10^{-4} lbs/ft²-s (Thorogood et al. 1993, S-3). It is also interesting to note that in U. S. Patent 5,306,411, the Standard Oil Company disclosed oxygen fluxes of similar membranes that were comparable to Air Products' simulations. These fluxes were not actually measured but were calculated using material balances on the changes of the fuel stream composition as it was oxidized by the oxygen that permeated the membrane (Mazanec et al. 1994, 37 and 39).

U. S. Patent 5,534,471 describes the use of a four layer composite membrane for the separation of oxygen from air. The operating conditions proposed by Air Products included a membrane temperature of 850 °C, a feed pressure of 1 atm., and a product pressure of 0.001 atm. At these conditions, Air Products calculated an oxygen flux of 18.8 cm³/cm²-min (Carolan and Dyer 1996, 13), which is equivalent to 9.2×10^{-4} lbs/ft²-s.

As was discussed in Chapter 2, the combination of the extremely low pressure and high temperature of the oxygen product would cause the actual vapor volume obtained from the membrane at these operating conditions to be immense. Consequently, in further evaluation of mixed conducting membranes, product pressures less than 8 psia (the project's lower pressure limit) will not be considered.

In an attempt to alleviate the problem associated with the large vapor volume, the membrane must be redesigned to utilize a higher product pressure. Such a system is described in U. S. Patent 5,240,480. The first layer of the membrane would be thin (10 μm) and composed of porous $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-z}$ (mean pore size of approximately 0.2 μm). The second layer would be a thin (5 μm) dense film made of $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-z}$. The third layer would be identical to the first layer. The fourth and final layer would be a thick (1.975 mm) porous layer of an inert support material such as alumina or stabilized zirconia. The operating conditions proposed by Air Products included a feed pressure of 14.6 atm. and a product pressure of 1.1 atm. Based on these conditions, Air Products calculated an oxygen flux of 11.2 $\text{cm}^3/\text{cm}^2\text{-min}$ (Thorogood et al. 1993, 24), which is equivalent to 5.5×10^{-4} $\text{lbs}/\text{ft}^2\text{-s}$.

In order to calculate the membrane area required to separate oxygen from air using mixed conducting membranes, one must be able to calculate the change in oxygen flux across the membrane as the feed air is depleted in oxygen. As was previously discussed, if a rate limiting step is present in the permeation process, the change in flux would be related to either the difference in the natural logarithms of the oxygen partial pressures on

the high and low pressure sides of the membrane or the difference in the oxygen partial pressures, each raised to either the 0.5 or 0.25 power. Inspection of the data presented in Air Products' patent indicates that none of the rate limiting cases apply when comparing oxygen fluxes for simulations made on the multi-layer membranes with different feed and product pressures. For example, U. S. Patent 5,240,480 states that the oxygen flux through the membrane was $20.8 \text{ cm}^3/\text{cm}^2\text{-min}$ when operating with an oxygen partial pressure in the feed of 3 psia and a product pressure of 0.015 psia. When the same membrane's operating conditions are changed such that the oxygen partial pressure in the feed is 45 psia and its product pressure is 16.6 psia, the calculated flux decreased to $11.2 \text{ cm}^3/\text{cm}^2\text{-min}$ (Thorogood et al. 1993, 24). If the relationship between the flux and the difference in the natural logarithms of partial pressures was valid, the predicted flux should have decreased to $3.9 \text{ cm}^3/\text{cm}^2\text{-min}$. If the relationship between the oxygen flux and the difference in the partial pressures, each raised to either the 0.5 or 0.25 power was valid, the flux should have either increased to $34.1 \text{ cm}^3/\text{cm}^2\text{-min}$ or decreased to $12.3 \text{ cm}^3/\text{cm}^2\text{-min}$. Since these fluxes are different from the flux that Air Products reported in their patent disclosure, it appears that the model Air Products used to calculate the flux does not contain any of the rate limiting assumptions previously discussed. In fact, inspection of the patent indicates that the relationships used to model the permeation process are very detailed and include equations based on bulk diffusion and surface reaction kinetics (Thorogood et al. 1993, 13-16). Since the model used several linked equations, the effect of partial pressure changes on the calculated oxygen flux is not easily determined.

In order to obtain a rough estimate of the required membrane area and to simplify the calculations, it was assumed that the permeation rate of oxygen through mixed conducting membranes is not a function of oxygen partial pressure. Although this assumption will give a membrane area that is smaller than would actually be required, it is a starting point from which an initial assessment of the technology can be made. Applying this assumption to a membrane with an oxygen flux of $11.2 \text{ cm}^3/\text{cm}^2\text{-min}$, the minimum membrane area required to recover 50% of the oxygen from an inlet air stream of 100 lbs/s is $21,400 \text{ ft}^2$.

Estimation of the Membrane Module Weight and Volume

The procedure used to estimate the weight of a mixed conducting membrane module is similar to the procedure used in Chapter 2 to determine the weight of a silver membrane module. Data from a major supplier of ceramic materials (Goodfellow) indicates that the density of porous alumina is approximately 2.55 g/cm^3 . As a starting point, it was assumed that the tubes used in the fabrication of the mixed conducting membrane module would have an outside diameter (OD) of 8 mm, an inside diameter (ID) of 4 mm, and a length of 1524 mm (5 feet). With these dimensions, each of the tubes would have a surface area of 0.4123 ft^2 . Since the mixed conducting membrane module requires $21,400 \text{ ft}^2$ of active surface area, the module would require approximately 51,900 tubes. Assuming that the membrane is fabricated according to the example membrane presented by Air Products with the additional assumption that the density of the dense $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-z}$ electrolyte is approximately 6 g/cm^3 , each

of the tubes would weigh 0.3305 pounds. With these assumptions, the weight of the module would be approximately 17,200 pounds.

The procedure used to estimate the volume of a mixed conducting membrane module is identical to the procedure described in Chapter 2 for silver membranes. Since the two membranes were assumed to have the same OD, the packing factor for the mixed conducting membrane module will have the same value as was calculated for the silver membrane module. Application of the $75 \text{ ft}^2/\text{ft}^3$ packing factor to the required membrane area of $21,400 \text{ ft}^2$ gives a membrane module volume of approximately 290 ft^3 .

Comparison of Silver Membranes and Mixed Conducting Membranes

Mixed conducting membranes have two distinct advantages over silver membranes. First, while the current literature does not indicate ongoing research into silver membranes, mixed conducting membranes are currently being researched extensively by major corporations (Air Products & Chemicals and Praxair) and research institutions (Gas Research Institute). By examining recent patent activity on electrolytic membranes, it appears that Praxair is focusing on membranes operating with a supplied potential difference (Prasad and Gottzmann 1996, 3) while Air Products is focusing on mixed conducting membranes driven by differences in the oxygen partial pressure across the membrane. Air Products has recently patented a design for a complete system that incorporates mixed conducting membranes as the tool to separate oxygen from air (Kang et al. 1996, 3). Second, the mixed conducting membranes being developed by Air Products do not require the removal of carbon dioxide or water from the inlet air prior to

entering the membrane module (Carolan et al. 1993, 2). This property is very important since it would allow for the elimination of the carbon dioxide and water removal system that may be required for silver membranes.

Since mixed conducting membranes and silver membranes are very similar to each other, it is interesting to compare the oxygen permeation rates that can be achieved with the two membranes. As was previously stated, Air Products reported an oxygen flux of $11.2 \text{ cm}^3/\text{cm}^2\text{-min}$ when a mixed conducting membrane was operated with a feed and product pressure of 14.6 atm. and 1.1 atm., respectively and a dense film thickness of $5 \text{ }\mu\text{m}$. Although the membrane's operating temperature was never explicitly stated, it is assumed that it was $850 \text{ }^\circ\text{C}$. At these same conditions, the oxygen flux through a silver membrane would be $1.0 \text{ cm}^3/\text{cm}^2\text{-min}$, which is an order of magnitude lower than the mixed conducting membrane. However, when the silver membrane is used at the more efficient operating conditions of $900 \text{ }^\circ\text{C}$ and a film thickness of $0.5 \text{ }\mu\text{m}$, the oxygen flux increases to $15.8 \text{ cm}^3/\text{cm}^2\text{-min}$. Although there is little doubt that decreasing the thickness and increasing the operating temperature of the mixed conducting membrane could also improve its performance, the improvement in the flux that would be realized is difficult to predict due to the complex nature of the oxygen transport process through the membrane. As has been previously discussed, decreasing the membrane thickness would not improve the oxygen flux if other steps in the transport process become rate limiting.

Based on the data presented above, it would appear that unless improvements are made in the mixed conducting membranes, they would require a slightly larger permeation area than silver membranes. The exception to this statement would be if the

oxygen permeation rate through the mixed conducting membrane was increased to levels comparable to the flux of oxygen through silver and if the mixed conducting membranes could be designed so that they were less sensitive to decreases in the oxygen partial pressure in the feed stream which occur as oxygen permeates the membrane. Figure 6 shows the differences in the slope of the driving force multiplier as a function of three specific models used to describe how the change in oxygen partial pressure would affect the oxygen permeation rate in mixed conducting membranes. The faster the pressure multiplier decreases from the value at which the initial oxygen flux was reported, the more sensitive the membrane is to decreases in the oxygen partial pressure in the feed stream. In practical terms, decreasing the pressure multiplier causes the oxygen flux to decrease which increases the membrane area required for the specified production rate.

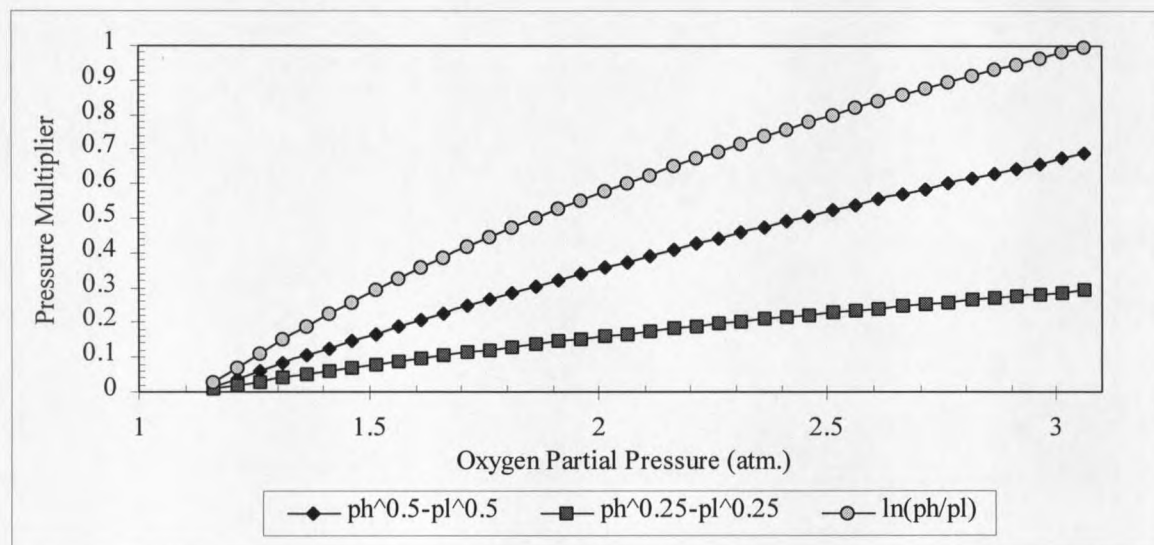


Figure 6. Slope of the pressure multiplier as a function of three specific models used to describe how the change in oxygen partial pressure would affect the oxygen permeation rate in mixed conducting membranes (initial partial pressure of oxygen in the feed of 45 psia and a product pressure of 16.6 psia).

Since the permeation of oxygen through silver membranes is known to depend on the difference in the square roots of the oxygen partial pressures, the required membrane area for mixed conducting membranes could be less than silver membranes if the pressure multiplier curve's slope is smaller and the initial permeation rate of oxygen through the membranes are comparable to each other.

Discussion

In order for mixed conducting membranes to be practical in hypersonic air separation, the membrane system should not only operate at high temperatures but also with high feed pressures. In order to simplify the design and optimize the membrane's performance, the separation process should occur at speeds near Mach 5.0 with a high enough elevation so that the stagnation pressure would not cause problems with the mechanical stability of the membrane. Operation of the separation system while the vehicle is accelerating would complicate the module design and would result in separation performance that would be below the system's potential.

To reduce the module weight to the project limit of 1,000 pounds, two methods could be utilized. First, it would be necessary to either reduce the wall thickness on the ceramic support or utilize a support with a much lower density than alumina. Second, it would also be desirable to decrease the thickness of each of the active layers of the membrane to the minimum level necessary to ensure the deposition of a defect free film. Thin film deposition is an area of continuing research, and current research suggests that films with desirable properties and thickness of less than 1 μm are attainable (Ziehgroud and Maier

1996, 2721). However, reduction of the film thickness to the level in which the rate of diffusion through the membrane is faster than the rate in which molecular oxygen dissociates into ions is pointless since the rate of oxygen dissociation would control the oxygen permeation rate for the entire system. Regardless of which method is chosen to reduce the weight of the module, the final membrane must have mechanical properties that would allow it to withstand large pressure differentials and high operating temperatures.

To reduce the volume of the membrane module to less than 50 ft³, either the packing factor of the membrane module must be increased from the assumed value of 75 ft²/ft³ or the thickness of the membrane must be reduced. Similar to silver membranes, if a support with a high surface area to volume ratio were used in the module design, the oxygen velocity inside the tubes could become too high to be practical. High velocities in small tubes and fibers would cause large pressure drops that could significantly degrade the performance of the membrane module.

As with silver membranes, it is imperative that the support material have an oxygen permeability that is significantly greater than the permeability of oxygen through the mixed conducting membrane. Design of a porous support that meets this criteria could be challenging due to the high oxygen permeabilities through electrolytes at high temperatures.

Conclusions

The advantages of air separation with mixed conducting membranes are the same as for silver membranes. These include the production of high purity oxygen in a single separation stage and a cooling load that requires the removal of less energy than is needed to condense the entire feed stream from temperatures much lower than the stagnation temperature. Mixed conducting membranes have an additional advantage over silver membranes of proven stability when exposed to carbon dioxide and water vapor which would eliminate the need for a feed gas conditioning unit.

While air separation using mixed conducting membranes can be considered technically feasible, significant improvements to the membranes that are currently available would be required in order to fabricate a membrane module that could meet the current project's weight and volume requirements. However, as this technology continues to evolve, it could prove to be useful in future air separation applications.

CHAPTER 4

POLYMERIC MEMBRANES

Summary of the Technology

Polymeric membranes have been used for many years to separate gas streams. The first commercial oxygen enrichment membrane system was introduced by the Oxygen Enrichment Company in 1977 (Prasad, Notaro, and Thompson 1994, 226). As the technology of membrane systems has progressed, the number of commercial membrane suppliers has grown to include several large companies (Scott 1995, 854). The main use of polymeric membranes in air separation has been in applications that require a relatively small amount of oxygen-enriched air (OEA) such as health care, copper smelting, and fermentation. Polymeric membranes have not been used commercially in large scale applications due to high compression costs which make their use economically unattractive (Prasad, Notaro, and Thompson 1994, 226). In fact, a study that was completed roughly a decade ago concluded that the production of 90% OEA was not remotely feasible with the membrane technology that was currently available (Matson et al. 1986, 89-90).

Polymeric membranes are generally considered to be made up of two major classes of membranes: rubbery and glassy. Rubbery membranes are used at temperatures above

their glass transition temperature and are therefore soft and pliable. These membranes contain deformable molecular voids through which gases of varying size can easily adsorb and diffuse. Glassy polymeric membranes are operated at temperatures below their glass transition temperature and are therefore rigid. These membranes contain fixed molecular voids which allow small gas molecules to diffuse much more easily than large molecules (Wright and Copeland 1990, 27-29). As a result, glassy membranes are typically more selective but less permeable than rubbery membranes (Robeson 1991, 174).

Theory of Polymeric Membrane Separations

The mechanism for polymeric membrane separations is best explained by a thermodynamic analysis of the separation process. From basic thermodynamic principles (with the assumption that perfect gas relationships hold), the chemical potential of a species in a gaseous mixture is given as:

$$\hat{\mu}_i = \mu_i^\circ + RT \ln p_i \quad (4.1)$$

When two gases are separated by a solid phase, such as a polymeric membrane, the difference in the chemical potential on opposing sides of the membrane is given by:

$$\hat{\mu}_i^p - \hat{\mu}_i^f = RT \ln \frac{p_i^p}{p_i^f} \quad (4.2)$$

In order for the separation process to be spontaneous, the change in chemical potential between the feed and the product must be negative which means that the natural logarithm of the partial pressure ratio must also be negative. Practically, this means that

the partial pressure of the permeating species in the feed stream must be greater than its partial pressure in the product stream (Zolandz and Fleming 1992, 22-23).

The flux of the species of interest through the membrane is described by an integrated form of Fick's law:

$$J_i = D_i \frac{C_{i,f} - C_{i,p}}{l} \quad (4.3)$$

Assuming that Henry's law is valid for predicting the concentration of the dissolved species in the polymer, the governing equation becomes:

$$J_i = \frac{D_i S_i (p_{i,f} - p_{i,p})}{l} \quad (4.4)$$

In equation 4.4, J_i is the flux of the species of interest through the membrane, D_i is the diffusivity of the species through the polymer, S_i is the solubility of the species in the polymer, $p_{i,f}$ is the partial pressure of species in the feed stream, $p_{i,p}$ is the partial pressure of the species in the product stream, and l is the membrane thickness (McCabe, Smith, and Harriot 1993, 841). Since the diffusivity and the solubility of the species must be determined experimentally, the values of the two constants are usually grouped together and given the name permeability with the symbol P_i . Inspection of equation 4.4 shows that the flux of a gas species through the membrane is a function of the diffusivity and solubility of the permeating species, the partial pressure difference across the membrane, and is inversely proportional to the membrane's thickness. Consequently, it is desirable to operate gas separating membranes with a large difference between the feed and product pressures with as thin a membrane as possible. Since thin polymeric films are very

delicate, a composite membrane must be used in which polymer is deposited on a porous backing which provides mechanical support (Zolandz and Fleming 1992, 56).

The selectivity of a membrane is a means of measuring a specific membrane's effectiveness for separating a given set of gaseous species. When considering polymeric membranes, the selectivity can be measured by the local separation factor and is defined by the ratio of the pure gas permeabilities (Stern and Walawender 1969, 157).

$$\alpha^*_{ij} = \frac{P_i}{P_j} \quad (4.5)$$

In the nitrogen/oxygen binary system, oxygen is the faster permeating gas species, so membranes with an α^* greater than 1 will give a product stream that is enriched in oxygen and a residue stream that is enriched in nitrogen.

Modeling Polymeric Membrane Modules

The three distinct local flow patterns that exist between the product and residue streams in membrane modules are cocurrent, countercurrent, and crossflow. In cocurrent and countercurrent flow, the composition of the product at a given point along the membrane consists of the gas that has just permeated the membrane combined with the gas that has previously permeated the membrane. Consequently, the product composition is related to the feed side composition by a set of coupled ordinary differential equations. For membranes that operate in crossflow, the permeated gas composition is only a function of the feed gas composition at a given point along the membrane since no mixing is present in the product stream (Zolandz and Fleming 1992, 62). These three

flow patterns have been extensively modeled in the past, and the results indicate that countercurrent flow gives the best separation, followed by crossflow, and finally cocurrent flow (Walawender and Stern 1972, 571-573). Since the crossflow model is the most likely flow pattern that exists in thin membranes backed by thick porous supports (Zolanz and Fleming 1992, 62), it will be used as the basis for all calculations that will be made in the current analysis of hypersonic air separation with polymeric membranes. It is important to note that the crossflow pattern only describes the microscopic flow of gas through the membrane. It does not imply that other flow patterns do not exist in the membrane module as a whole. Figure 7 shows a simplified schematic of a membrane that is operating with crossflow gas permeation.

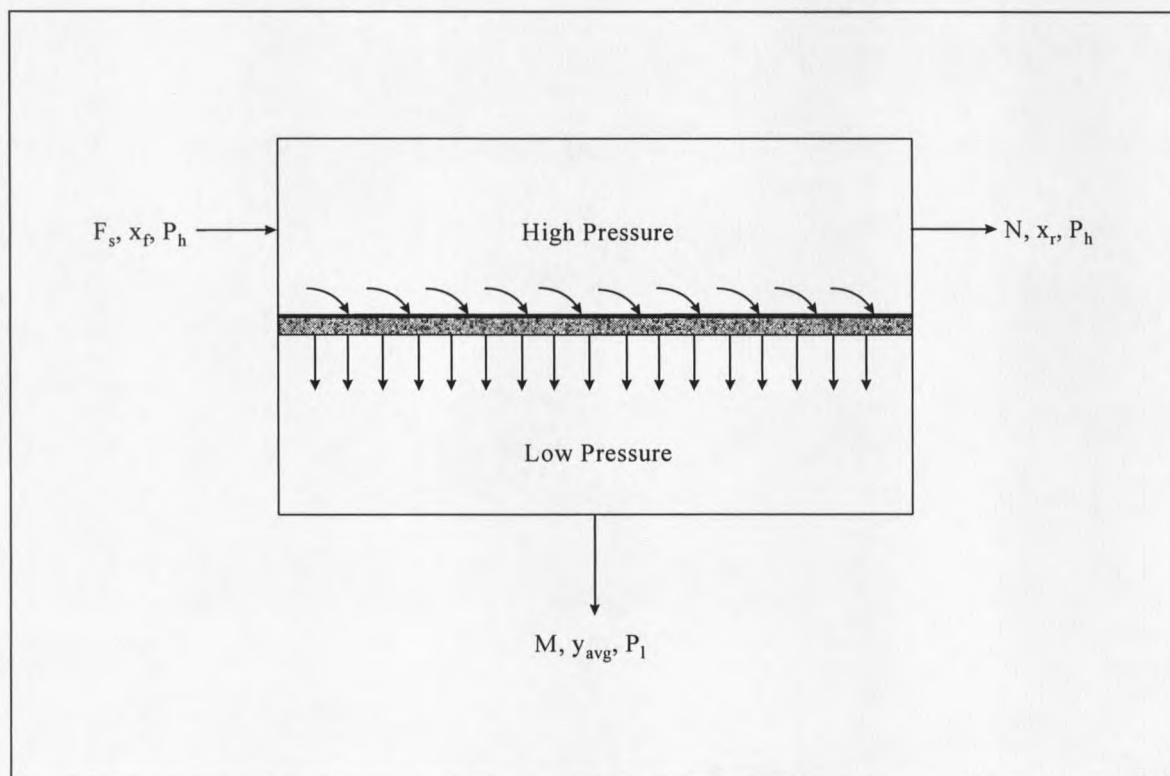


Figure 7. Schematic of a membrane operating with crossflow gas permeation.

Using equations 4.4 and 4.5 combined with material balances, it is possible to derive an analytically exact set of equations that completely characterize the gas stream compositions in a membrane module that is operating with crossflow permeation (Saltonstall 1987, 185-189). Since the derivation of the equations is quite lengthy, only the results will be presented here. Utilizing a slightly different notation than Saltonstall used in his derivation, the equations for crossflow permeation are given as:

$$y_i^2 - y_i(1 + r(\beta - 1) + rx_i) + \beta rx_i = 0 \quad (4.6)$$

$$1 - \frac{\beta - y_{i,r}}{\beta - y_{i,f}} \cdot \left(\frac{1 - y_{i,r}}{1 - y_{i,f}} \right)^a \cdot \left(\frac{y_{i,r}}{y_{i,f}} \right)^b = \theta \quad (4.7)$$

$$\frac{x_{i,f} - x_{i,r}}{\theta} + x_{i,r} = y_{i,avg} \quad (4.8)$$

$$\frac{F_s \theta (\beta - y_{i,avg})}{P_i \frac{P_f}{l} (r - 1) (\beta - 1)} = A \quad (4.9)$$

In these equations, y_i and x_i are the mole fractions of the species of interest at any point along the membrane in the permeated and feed streams, respectively, $y_{i,r}$ and $y_{i,f}$ are the mole fractions of the species in the permeated gas stream at the outlet and entrance of the membrane module, respectively, $x_{i,f}$ and $x_{i,r}$ are the mole fractions of the species in the feed stream at the entrance and outlet of the membrane module, respectively, θ (stage cut) is the fraction of the feed stream that permeates the membrane, $y_{i,avg}$ is the pooled average mole fraction of the species in the product stream, F_s is the volumetric flowrate (at standard conditions) of feed stream, P_i/l is the permeance of the species through the membrane, and P_i is the absolute pressure on the product (low pressure) side of the

membrane. Equations 4.10 - 4.13 are used to describe the remaining constants that appear in equations 4.6 - 4.9.

$$r = \frac{P_h}{P_l} \quad (4.10)$$

$$\beta = \frac{\alpha^*}{\alpha^* - 1} \quad (4.11)$$

$$a = \frac{1 - \beta \cdot r}{r - 1} \quad (4.12)$$

$$b = \frac{\beta \cdot r}{r - 1} - 1 \quad (4.13)$$

Use of Polymeric Membranes in Hypersonic Air Separation

Polymeric membranes can be used in many different module configurations depending on the purity and recovery required for the specific application. In the sections that follow, several of the common membrane arrangements will be considered for potential use in hypersonic air separation.

Single Stage Membrane Module

A single stage membrane module is the simplest means of obtaining OEA with a membrane. In assessing the performance of a single stage membrane module, it is desirable to determine three key parameters: 1) the purity of the oxygen product, 2) the fraction of the oxygen contained in the feed recovered as OEA, and 3) the membrane area required to produce the specified quantity of product.

Using equations 4.6 - 4.8, it is possible to calculate the oxygen content of the product stream as a function of the membrane module's stage cut. After the purity of the product has been determined, the oxygen recovery can be calculated by a mass balance around the membrane module. Finally, the membrane area required for the separation can be calculated by equation 4.9. Figures 8 and 9 show the results of these calculations for a hypothetical air separation membrane module operating at conditions commonly used in gas phase membrane separations.

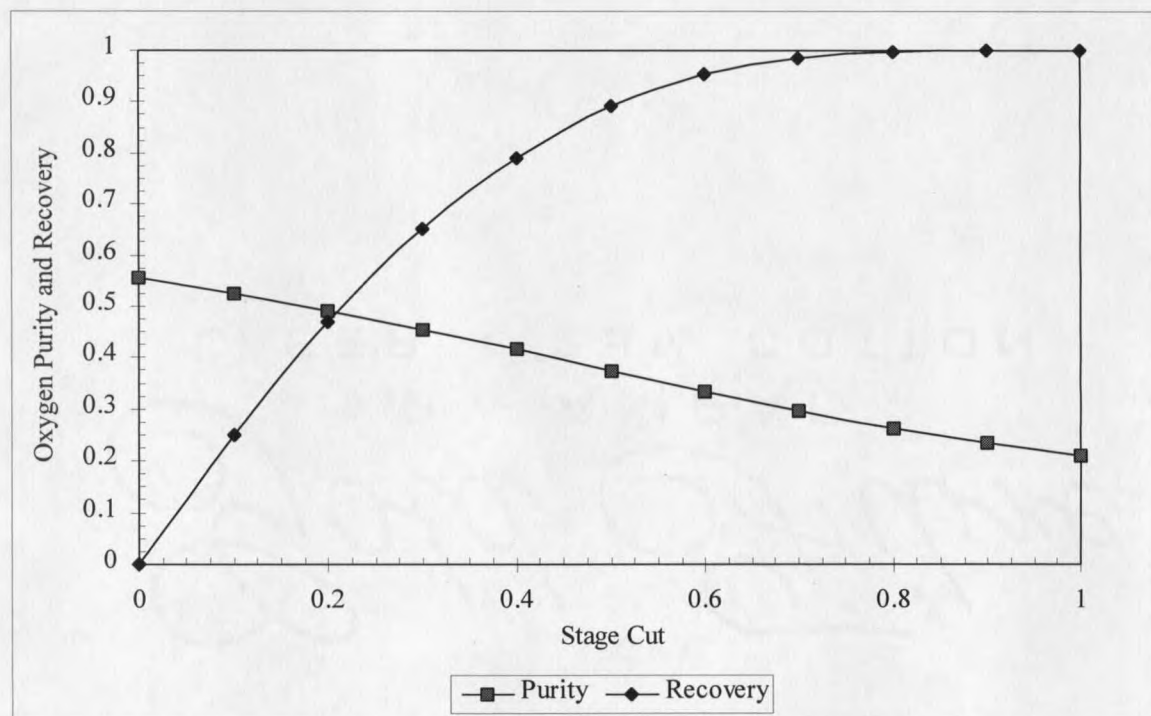


Figure 8. Oxygen purity and recovery as a function of stage cut (feed rate=100 lbs/s, $\alpha^* = 6$, feed and product pressure of 10 atm. and 1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

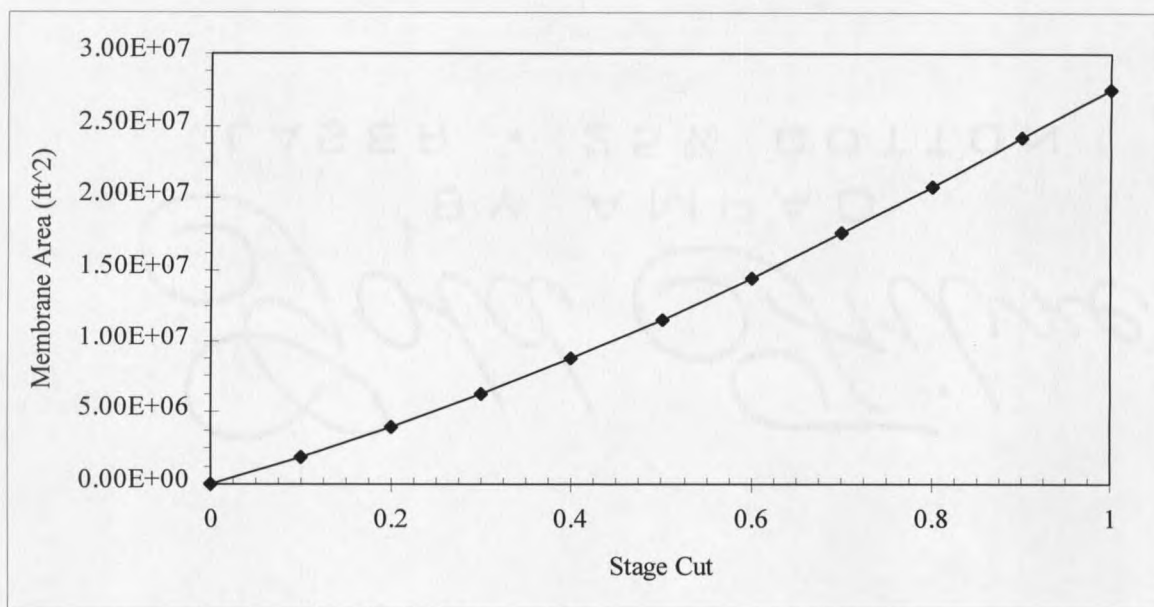


Figure 9. Required membrane area as a function of stage cut (feed rate=100 lbs/s, $\alpha^*=6$, feed and product pressure of 10 atm. and 1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

Figures 8 and 9 show several important aspects of gas phase membrane separations. First, for a membrane with a separation factor of 6 operating with a feed to product pressure ratio of 10, the maximum possible product purity of 55% oxygen occurs as the stage cut approaches zero. Second, as the stage cut increases, the oxygen recovery increases, but the product purity decreases. Finally, the required membrane area increases as the stage cut increases since the higher stage cut requires that more gas permeates the membrane.

To investigate how other variables such as feed and product pressure and membrane selectivity affect the oxygen purity and recovery and the membrane area, a parametric study was made in which each of these variables was changed from the base case values used in Figures 8 and 9. Results of this study are presented in Figures 10 - 15.

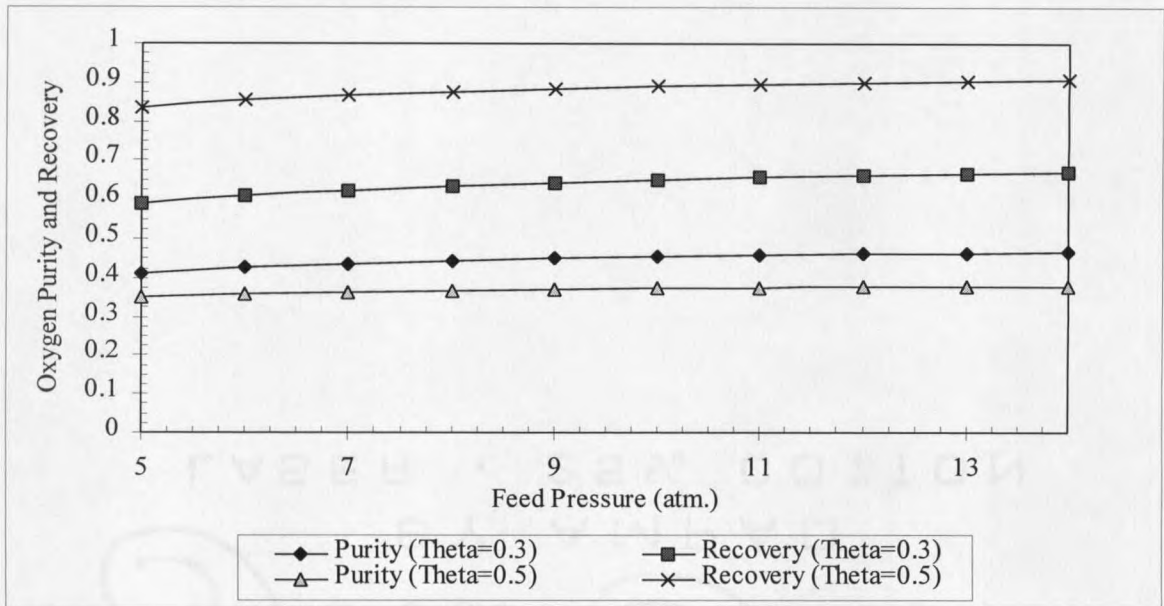


Figure 10. Oxygen purity and recovery as a function of stage cut and feed pressure (feed rate=100 lbs/s, $\alpha^*=6$, product pressure=1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

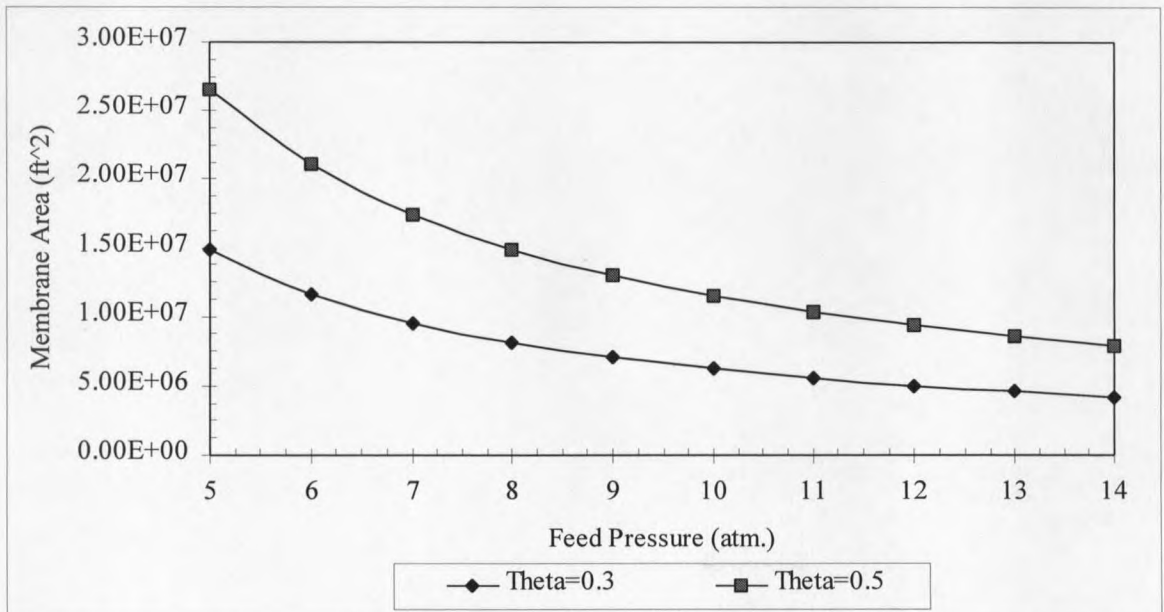


Figure 11. Required membrane area as a function of stage cut and feed pressure (feed rate=100 lbs/s, $\alpha^*=6$, product pressure=1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

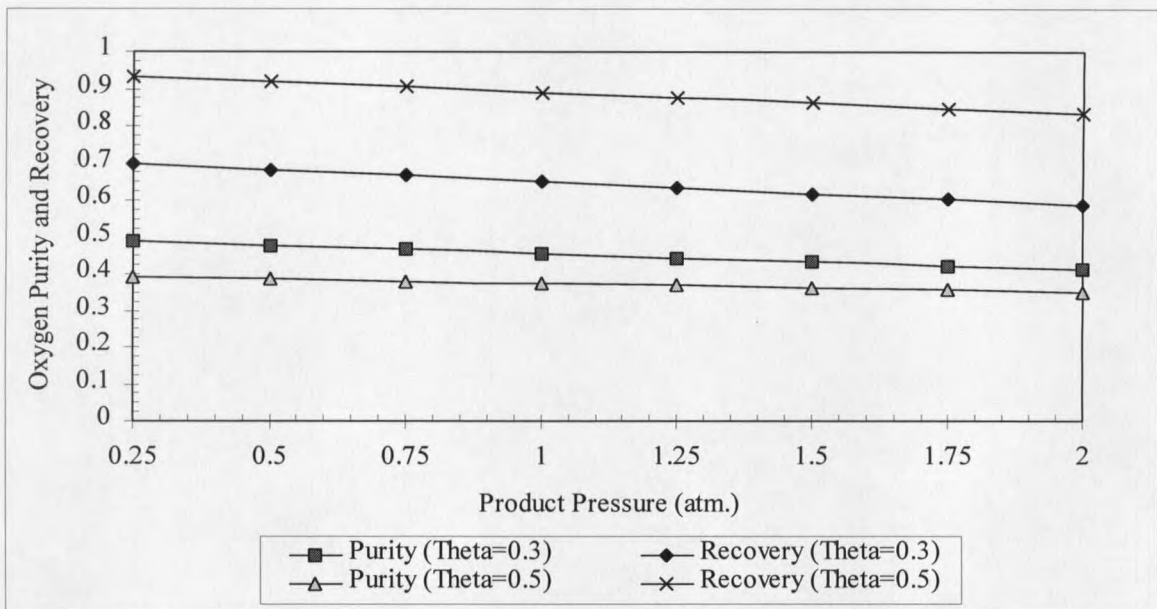


Figure 12. Oxygen purity and recovery as a function of product pressure and stage cut (feed rate=100 lbs/s, $\alpha^*=6$, feed pressure=10 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

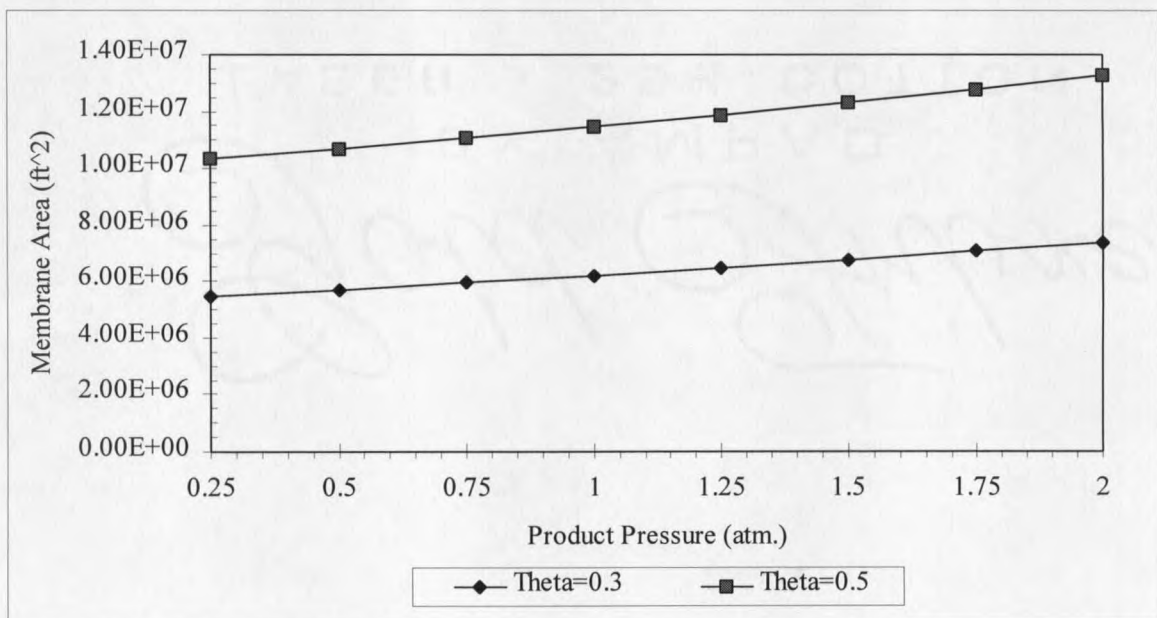


Figure 13. Required membrane area as a function of product pressure and stage cut (feed rate=100 lbs/s, $\alpha^*=6$, feed pressure=10 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

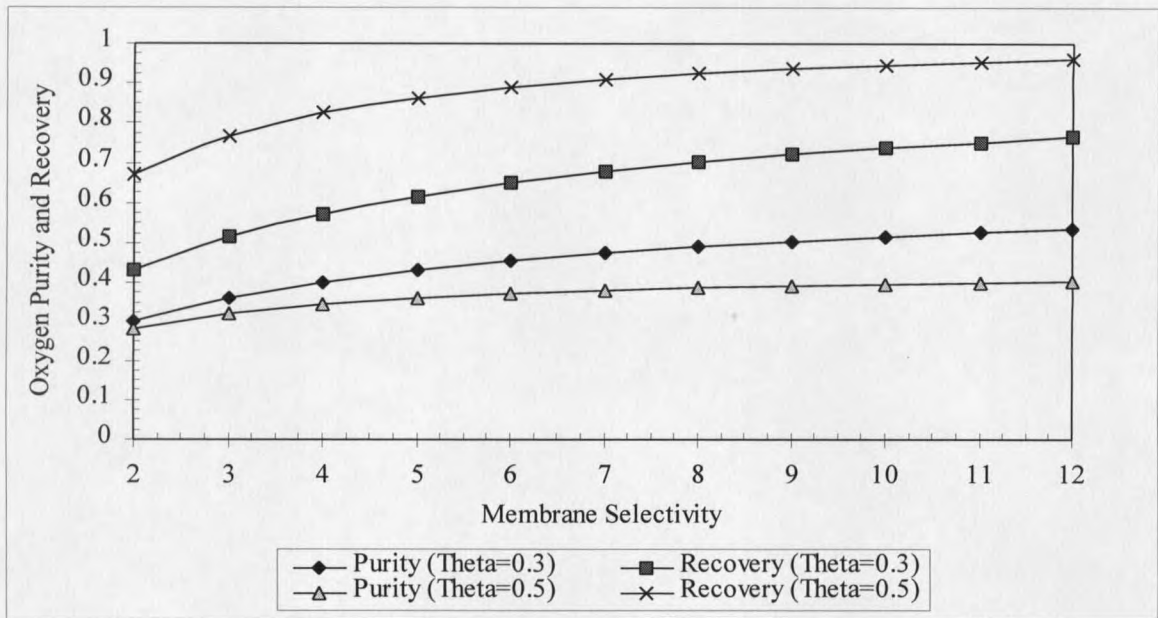


Figure 14. Oxygen purity and recovery as a function of membrane selectivity and stage cut (feed rate=100 lbs/s, feed and product pressures of 10 atm. and 1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

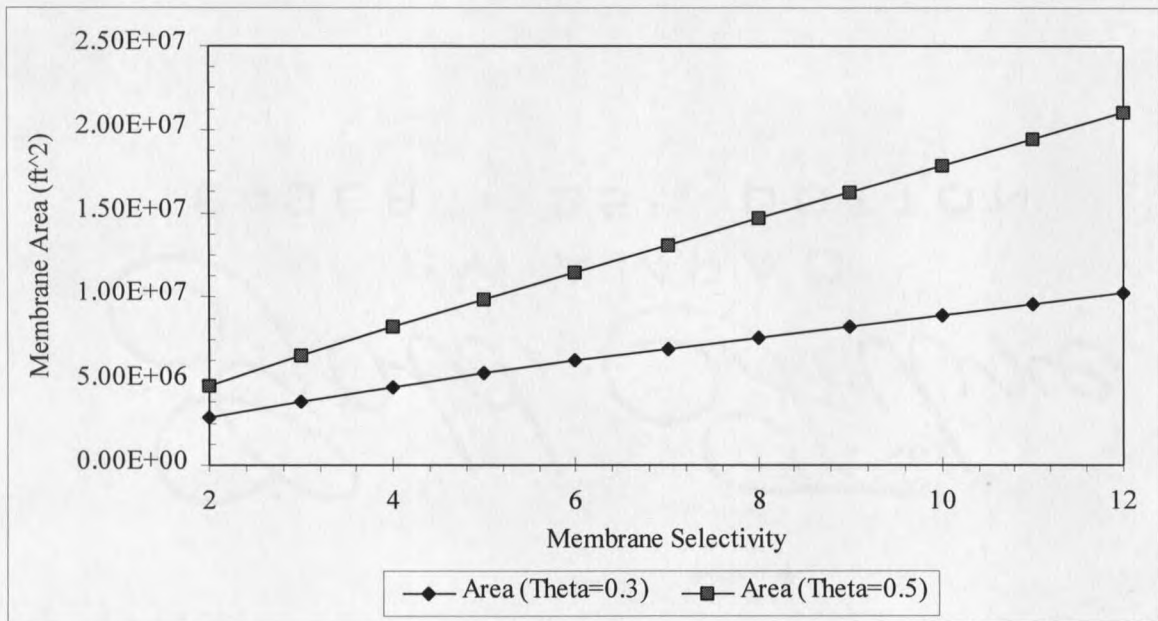


Figure 15. Required membrane area as a function of membrane selectivity and stage cut (feed rate=100 lbs/s, feed and product pressures of 10 atm. and 1 atm., and oxygen permeance= 2.49×10^{-5} ft³/ft²-s-atm.).

Figure 10 shows that increasing the feed pressure slightly increases both the product purity and oxygen recovery while Figure 11 indicates that increasing the feed pressure significantly decreases the required membrane area. Figure 12 shows that increasing the product pressure decreases both the product purity and oxygen recovery, while Figure 13 indicates that increasing the product pressure will increase the membrane area required for the separation. Finally, Figures 14 and 15 show that increasing the membrane selectivity will significantly increase the product purity, oxygen recovery, and the required membrane area.

The results of this study clearly show that in order to obtain OEA with the required oxygen content of 90% in a single stage membrane module, a membrane with a selectivity of significantly greater than 12 would need to be utilized. In fact, depending on the chosen operating conditions, the membrane could require a separation factor of nearly 60 to meet the product purity and recovery specifications. Since such a membrane has not yet been developed, a single stage membrane separation process does not appear to be a viable separation technique for hypersonic applications.

Simple Enriching Membrane Cascade

One method to increase the oxygen content of the product stream obtained from a single stage membrane module is to connect the stages in series as shown in Figure 16. As this figure shows, an enriching membrane cascade requires compression before each stage in the series. Since the cascade does not reprocess the residue from the membrane

stages, a significant portion of the oxygen is thrown away, resulting in a low oxygen recovery.

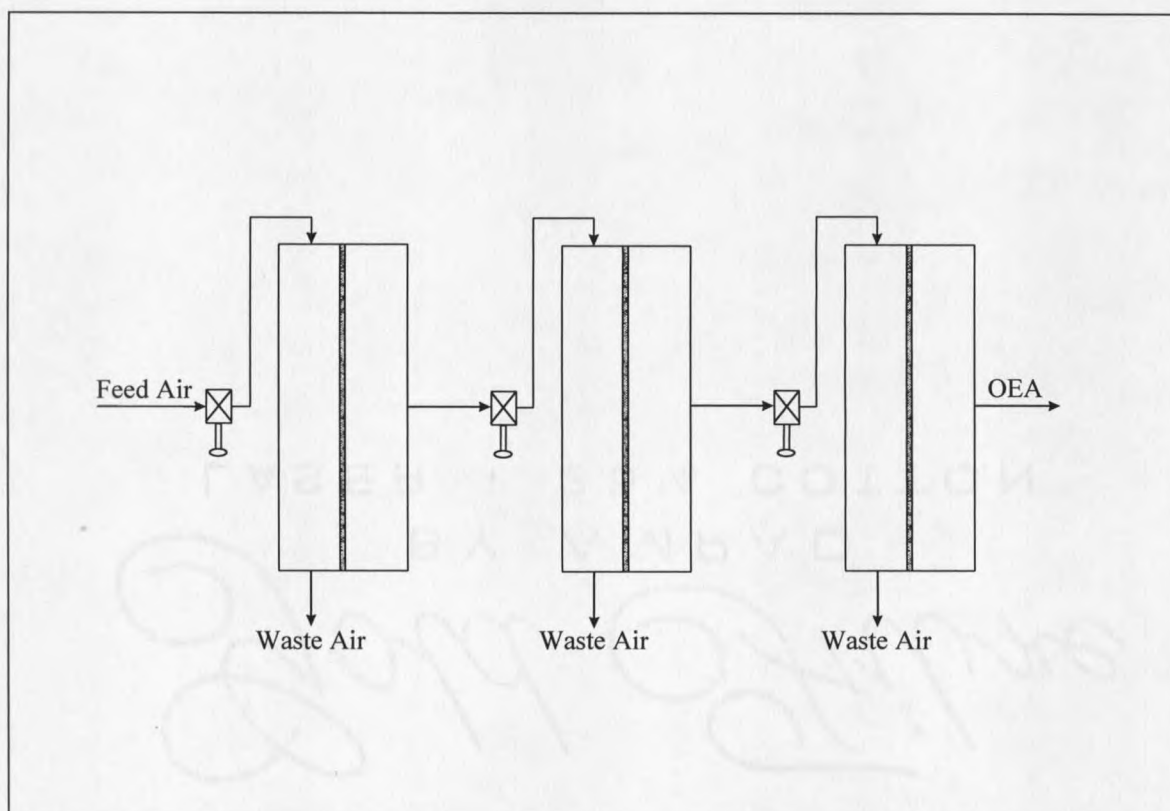


Figure 16. A simple enriching membrane cascade for the production of oxygen-enriched air.

To illustrate the typical performance possible with an enriching membrane cascade, assume that the membrane cascade shown in Figure 16 is operated with a feed pressure of 10 atm., a product pressure of 1 atm., a stage cut of 0.3, and a membrane separation factor of 6. With these operating parameters, OEA with a purity of 93.5% could be obtained in the final product stream. The downfall to this system is that only 12% of the oxygen in the feed stream is recovered as product.

The oxygen recovery of the cascade could be increased by increasing the stage cut on each of the membrane stages. For example, if each module's stage cut was increased from 0.3 to 0.6, the oxygen recovery would increase to 56%; however, an additional separation stage would be required to produce OEA with a purity of greater than 90%.

Countercurrent Recycle Membrane Cascades

As was shown in the previous section, if a sufficient number of membrane modules are used and the stage cut for each of the modules is large enough, it would be possible to produce OEA that meets the project's specifications in a simple enriching cascade. Unfortunately, as was shown in Figure 9 on page 41, the significant increase in the required membrane area as the membrane module's stage cut is increased would make an enriching membrane cascade impractical in hypersonic air separation.

A better way to produce product with the required purity and oxygen recovery is to incorporate product recycle in the system design. Some of the common types of membrane modules that utilize product recycle include the one unit recycle (OUR) module, the two unit series (TUS) module, the continuous membrane column (CMC), the countercurrent recycle cascade (CRC) with constant recycle ratio (CRR), and the no-mix countercurrent recycle cascade (NMCRC). Theoretical studies on the efficiencies of each of these systems in membrane separations has been carried out in the past and the results show that the OUR module is least efficient, followed by the CMC and the TUS designs. The CRC with constant recycle ratio and the NMCRC have significantly higher efficiencies than the other cascade types (McCandless 1996, 742).

A schematic of a CRC is shown in Figure 17. The cascade can be divided into two sections that differ in their operational purpose. The portion of the cascade from the top stage down to and including the feed stage is known as the enriching section. The portion of the cascade below the feed location to the bottom stage is the stripping section. The function of the enriching section is to make product with the required purity. In contrast, the purpose of the stripping section is to remove the desired component from the bottoms product so that the recovery specifications are met. The flow of material from the next higher stage ($i+1$) to the stage of interest (stage i) is known as recycle. The recycle ratio (RR) is defined as the quantity of material leaving stage $i+1$ to stage i divided by the product rate leaving the top of the cascade (Benedict, Pigford, and Levi 1981, 651-655).

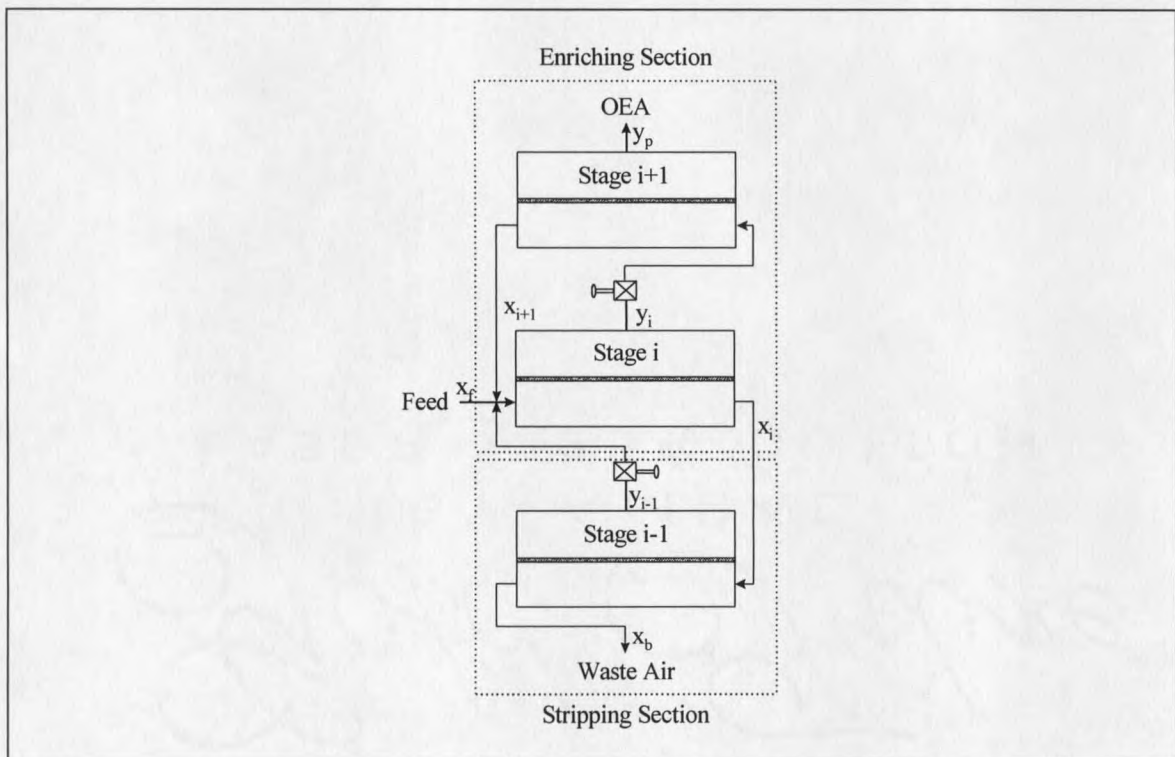


Figure 17. A three stage countercurrent recycle membrane cascade designed to produce oxygen-enriched air.

The theory of CRC separations has been described in detail in past publications and will not be repeated here; however, several of the key points will be summarized in the text that follows. The role of product recycle in a CRC can be seen by inspection of equation 4.14 which arises from a material balance in the enriching section of the cascade.

$$y_i - x_{i+1} = \frac{y_p - y_i}{RR} \quad (4.14)$$

The larger the recycle ratio, the smaller the difference between y_i and x_{i+1} . As the recycle ratio approaches infinity, the difference between y_i and x_{i+1} approaches zero and the number of stages required to make the specified separation reaches a minimum. As the recycle ratio in the cascade decreases, the difference in composition between corresponding streams on adjacent stages (e.g. y_i and y_{i+1}) also decreases. When the composition difference reaches zero, the minimum reflux ratio has been established. A cascade that is operating at its minimum reflux ratio requires an infinite number of stages to make a specified separation. Equation 4.15 shows that the minimum recycle ratio depends on both the stage composition and the stage separation factor. Consequently, the minimum recycle ratio increases as the stage composition departs from the specified product and bottom compositions (Benedict, Pigford, and Levi 1981, 655-658).

$$RR_{\min} = \frac{(y_p - y_i)[y_i + \alpha(1 - y_i)]}{(\alpha - 1)y_i(1 - y_i)} \quad (4.15)$$

At this point, the distinction must be made between the stage separation factor (α) and the local separation factor (α^*). Taking air as a binary mixture between nitrogen and oxygen, the stage separation factor can be defined in the usual manner.

$$\alpha_{ij} = \frac{y_i(1-x_i)}{x_i(1-y_i)} \quad (4.16)$$

The local and stage separation factors are related to each other through equation 4.17 (Stern and Walawender 1969, 157).

$$\alpha_{ij} = \alpha_{ij}^* \left(\frac{(1-x_i)/(1-y_i)}{(1-x_i)/(1-y_i) + 1/r(\alpha_{ij}^* - 1)} \right) \quad (4.17)$$

Consequently, it can be seen that the stage separation factor depends on the local separation factor, the pressure ratio, and the stage composition. As the pressure ratio becomes very large, $\alpha = \alpha^*$. The stage separation factor gives the degree of separation that occurs within a given stage in a CRC. For a membrane cascade that is operating with crossflow permeation, the stage separation factor is not constant and can exceed the value of the local separation factor.

A cascade that utilizes the same recycle ratio in every stage is known as a constant recycle ratio cascade. Two inherent characteristics of this type of cascade are: 1) the interstage flow throughout the cascade is constant; and 2) at the bottom and top portions of the cascade, the difference between the actual recycle ratio and the stage minimum recycle ratio is greater than it is at the feed point. The second characteristic suggests that a cascade designed with reduced reflux ratios in the intervals between the feed point and product ends of the cascade could be made to reduce equipment size in these areas.

Cascades of this type are known as tapered cascades. One example of a tapered cascade which minimizes the cascade's interstage flow is an ideal cascade. An ideal cascade operates with the following two constraints: 1) the heads separation factor (defined by equation 4.18) is constant for all stages, and 2) all feed streams to a given stage have the same composition (Benedict, Pigford, and Levi 1981, 648 and 657-658). Ideal cascades are attractive in the design of a membrane cascade for hypersonic air separation since both the membrane area and compressor duty would be smaller than if the cascade was designed with a constant reflux ratio.

$$\beta_i = \frac{y_i(1-x_{i,f})}{x_{i,f}(1-y_i)} \quad (4.18)$$

In order to design a countercurrent recycle membrane cascade to produce OEA for hypersonic flight, it is desirable to utilize a membrane that represents the state of the art in current membrane technology. It has been shown in the past that a linear relationship exists between the logarithm of permeability and the logarithm of selectivity in membrane separations (Robeson 1991, 180). Data analysis indicates that in the oxygen/nitrogen system, this relationship can be described by equation 4.19.

$$P_{O_2}(\text{barrers}) = 389,224 \alpha_{O_2/N_2}^{-5.8} \quad (4.19)$$

Equation 4.19 gives the permeability of a membrane as a function of its local separation factor (α^*). This equation is dimensional with the membrane permeability given in the commonly used units of barrers, where 1 barrer is equal to $1 \times 10^{-10} \text{ cm}^3\text{-cm/cm}^2\text{-s-cm Hg}$. Equation 4.19 predicts an upper limit of membrane permeability as a function of its

selectivity which, as of the publication date of Robeson's study, had not been verifiably exceeded by any polymeric membrane (Robeson 1991, 174).

Using equation 4.19 as a guide for predicting the upper limit of polymeric membrane performance, several CRC designs were made to determine if a membrane cascade could be designed that would meet the current project's weight and volume requirements. The membranes used in these designs included a membrane with a selectivity of 6 with a permeability of 10 barrers and a membrane with a selectivity of 12 with a permeability of 0.1 barrers. In both cases the membrane was assumed to have a film thickness of 1 μm grafted to a thick porous support. For operational simplicity and optimum cascade performance, the feed pressure to the membrane cascade was assumed to be 14.4 atm. which represents the stagnation pressure that could be obtained at Mach 5.0 at an elevation of 80,000 feet. The cascade calculations were made using equations 4.6 - 4.13 and appropriate material balances which were incorporated into Mathcad[®] worksheets. Copies of the worksheets for the CRC and the NMCRC designs are included as Appendix B. The results of the study are shown in Table 3 on the following page.

Inspection of the data contained in Table 3 shows the limitations of air separation using a membrane cascade. Even at the project's minimum requirements of 90% OEA with 50% oxygen recovery, the lowest compressor duty (defined as the amount of recycle requiring recompression) would be 21,050 scfm (assuming that the feed gas has already been compressed to the stagnation pressure as described in Chapter 2). When it is assumed that the recycle streams are compressed with a polytropic compression cycle, over 7,800 theoretical horsepower would be required to bring the low pressure recycle

streams back to the inlet pressure of the cascade. The required membrane area for this cascade would be 5.22×10^8 ft² which is too high to be practical in hypersonic air separation. In comparison, the system with the lowest required membrane area would require compressors capable of providing 15,400 theoretical horsepower to the recycle streams. As a point of interest, Runs 18 - 21 indicate that a properly designed NMCRC, which approximates an ideal cascade (McCandless 1996, 755), requires less membrane area and compressor duty than a CRR cascade.

Table 3. Summary of the performance of various countercurrent recycle membrane cascades for the separation of oxygen from air.

Run	Cascade Type	# of Stages	α^*	RR	P ₁ (atm)	P _h /P ₁	O ₂ Purity	O ₂ Recovery	Membrane Area (ft ²)	Comp. Duty (scfm)
1	CRR	3	12	0.21	14.4	26.45	90%	50%	5.22×10^8	21,050
2	CRR	3	12	0.48	14.4	26.45	95%	50%	5.50×10^8	24,390
3	CRR	3	6	2.11	14.4	14.40	90%	50%	8.88×10^6	54,170
4	CRR	3	6	1.67	14.4	26.45	90%	50%	7.37×10^6	46,510
5	CRR	3	6	2.31	14.4	14.40	90%	75%	1.51×10^7	86,740
6	CRR	3	6	1.83	14.4	26.45	90%	75%	1.25×10^7	73,970
7	CRR	3	6	3.26	14.4	14.40	90%	90%	2.47×10^7	133,790
8	CRR	3	6	2.53	14.4	26.46	90%	90%	1.98×10^7	110,730
9	CRR	4	6	0.69	14.4	14.40	90%	50%	7.39×10^6	44,160
10	CRR	4	6	0.59	14.4	26.45	90%	50%	6.60×10^6	41,560
11	CRR	4	6	0.72	14.4	26.45	90%	75%	1.15×10^7	67,330
12	CRR	4	6	0.87	14.4	26.45	95%	50%	6.74×10^6	46,400
13	CRR	4	6	1.03	14.4	26.45	95%	75%	1.18×10^7	75,520
14	CRR	4	6	1.02	14.4	26.45	90%	90%	1.76×10^7	94,970
15	CRR	4	6	1.42	14.4	26.45	95%	90%	1.83×10^7	108,190
16	CRR	5	6	0.79	14.4	26.45	95%	75%	1.37×10^7	88,540
17	CRR	5	6	1.08	14.4	26.45	95%	90%	2.09×10^7	123,590
18	NMCRC	4	6	n/a	14.4	26.45	90%	84.34%	1.36×10^7	74,780
19	CRR	4	6	0.85	14.4	26.45	90%	84.34%	1.46×10^7	81,690
20	NMCRC	5	6	n/a	14.4	26.45	97%	87.2%	1.66×10^7	104,400
21	CRR	5	6	1.08	14.4	26.45	97%	87.2%	1.83×10^7	117,180

In order to develop a membrane cascade that would approach the project's weight and volume limits, it would be desirable to use a membrane with both a high selectivity and a high oxygen permeability in the cascade design. A literature search was conducted to see if a membrane with these properties has been developed since the publication date of Robeson's study on membrane permeability and selectivity. The most promising membrane identified in this search was poly[1-(trimethylsilyl)-1-propyne] (PTMSP). PTMSP membranes are reported to be the most permeable polymer that would be suitable for gas separations (Vigo et al. 1996, 349). In fact, oxygen permeates this membrane 1,000 times faster than the hypothetical membrane with a α^* of 6 that was used to generate the data presented in Table 3 (Srinivasan, Auvil, and Burban 1994, 73). Studies have shown that the high oxygen permeability is the result of very fast gas diffusion caused by the large void volume in the polymer structure (Nagai and Nakagawa 1995, 261). However, PTMSP membranes are not flawless. Two of the major drawbacks to their use include a low oxygen/nitrogen separation factor (Srinivasan, Auvil, and Burban 1994, 73), and decreasing gas permeability as the membrane ages (Vigo et al. 1996, 350).

Several researchers have found ways to increase the oxygen/nitrogen separation factor while maintaining the desirable property of high oxygen permeability. These methods include plasma polymerization (Lin, Chen, and Xu 1994, 81), fluorination (Chen, Griesser, and Mau 1993, 99), and UV-irradiation (Hsu et al. 1993, 1). Application of any one of these techniques gives a membrane with a separation factor around 5 with an oxygen permeance ranging from 4.7×10^5 to 1.0×10^6 barrers/cm. Using equation 4.19, it

can be shown that the modified PTMSP membranes significantly exceed the upper limit of permeability as a function of the membrane separation factor.

Although the significant increase in the oxygen permeability would reduce the membrane area from the values reported in Table 3, the compressor duty would increase since the membranes have a separation factor that is slightly lower than the value used in the study to prepare Table 3. It is the size of the recycle compressors that may limit the practicality of the PTMSP membrane cascade. As an example, if a modified PTMSP membrane was used in a cascade with the operating conditions shown in Run 10 of Table 3, the required membrane area would be reduced to 7.07×10^5 ft². Unfortunately, the recycle streams used in the cascade would require approximately 19,400 theoretical horsepower for recompression back to the feed stream pressure. Past personal experience with gas compressors indicates that traditional land-based compressors capable of delivering this much energy to a process stream would greatly exceed the project's weight and volume limitations.

Researchers at Air Products and Chemicals have observed an additional improvement to PTMSP's oxygen selectivity at cryogenic temperatures. When UV modified PTMSP membranes were used at temperatures of approximately -100 °C, the membrane's separation factor increased from 4.7 to 12, while the oxygen permeance only decreased from 1.0×10^6 to 9.3×10^4 barrers/cm (Hsu et al. 1993, 1). A membrane with a selectivity of 12 is very attractive for air separation since it would allow for the production of 90% oxygen in only three membrane stages. As an example, if the modified PTMSP membrane was used in a cryogenic cascade with the operating conditions shown in Run

10 of Table 3, the required membrane area would be 5.61×10^6 ft². The recycle streams in the cascade would require approximately 4,600 theoretical horsepower for recompression back to the feed stream pressure. Although the compressor duty has been substantially reduced over the previous non-cryogenic cascade designs, the size of the compressors may still be too large to be utilized in hypersonic air separation.

Integration of Membranes with Other Air Separation Technologies

The previous section has shown that a membrane cascade which meets the current project's weight and volume limitations cannot be designed unless improvements are made to the PTMSP membranes described in the literature. Instead of trying to produce oxygen-enriched air that would meet the project's specifications entirely in a membrane cascade, it may be feasible to use a single stage membrane module as a preconcentrator for another separation device in hypersonic air separation. The PTMSP membrane previously discussed is especially attractive for this application because of its high oxygen selectivity and permeability at cryogenic operating conditions. Using equations 4.6 - 4.13 and appropriate material balances, the purity of the OEA, the oxygen recovery, and the required membrane area as a function of stage cut and feed pressure were calculated for a PTMSP membrane operating at cryogenic conditions. The results of the calculations are shown in Figures 18 and 19.

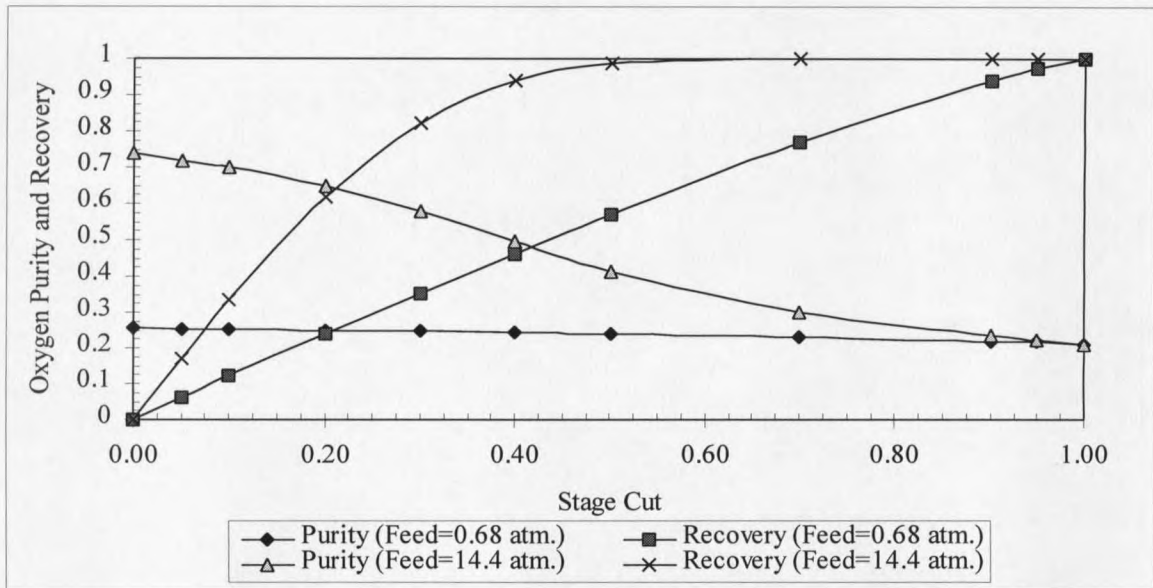


Figure 18. Oxygen purity and recovery as a function of stage cut and feed pressure for a PTMSP membrane operating at $-100\text{ }^{\circ}\text{C}$ (feed rate=100 lbs/s, $\alpha^* = 12$, product pressure=8 psia, and oxygen permeance= $2.32 \times 10^{-5}\text{ ft}^3/\text{ft}^2\text{-s-atm.}$).

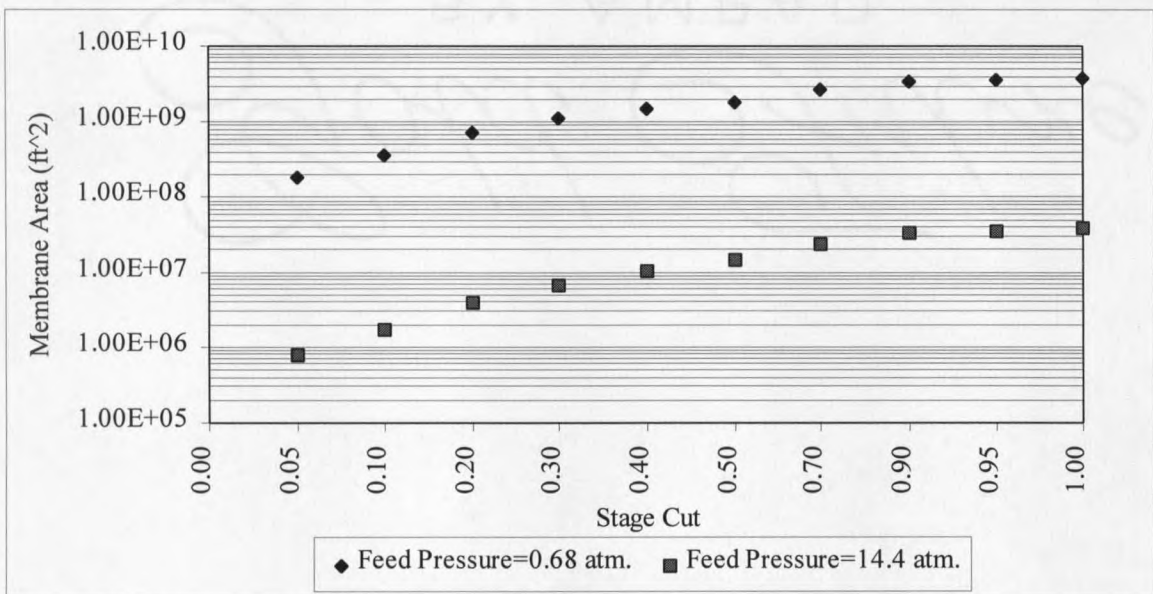


Figure 19. Required membrane area as a function of stage cut and feed pressure for a PTMSP membrane operating at $-100\text{ }^{\circ}\text{C}$ (feed rate=100 lbs/s, $\alpha^* = 12$, product pressure of 8 psia, and oxygen permeance= $2.32 \times 10^{-5}\text{ ft}^3/\text{ft}^2\text{-s-atm.}$).

Inspection of the data contained in Figure 19 shows that the required membrane area is too high to be practical when the feed to the module is taken at 0.68 atmospheres (the outlet pressure from the feed gas conditioning unit). The membrane area requirements are significantly reduced when the feed pressure is increased to 14.4 atm. A feed pressure of 14.4 atm. represents the expected stagnation pressure that could be obtained at Mach 5.0 at an elevation of 80,000 feet. For operational simplicity and optimum module performance, a feed pressure of 14.4 atm. will be used in the following analysis of single stage membrane modules. With these operating conditions and a stage cut of 0.3, Figure 18 indicates that the cryogenic PTMSP module is capable of producing OEA containing 58% oxygen with 82% oxygen recovery. Although the required membrane area of 6.58×10^6 ft² is nearly the same as the area required by the three stage cascade designed to produce 90% OEA with 50% oxygen recovery, the single stage module does not require the use of a compressor if the feed gas has been compressed to the stagnation pressure.

As an alternative to using the single stage PTMSP membrane module at cryogenic temperatures, it may be possible to use the membrane at operating temperatures near 20 °C. Operating the membrane at this condition would increase the oxygen permeability and thereby decrease the required membrane area. As a trade off to the increase in permeability, the membrane's separation factor would decrease from 12 to 4.7. Using equations 4.6 - 4.13 and appropriate material balances, the purity of the OEA, the oxygen recovery, and the required membrane area as a function of stage cut and feed pressure were calculated for a PTMSP membrane operating at 20 °C. The results of the calculations are shown in Figures 20 and 21.

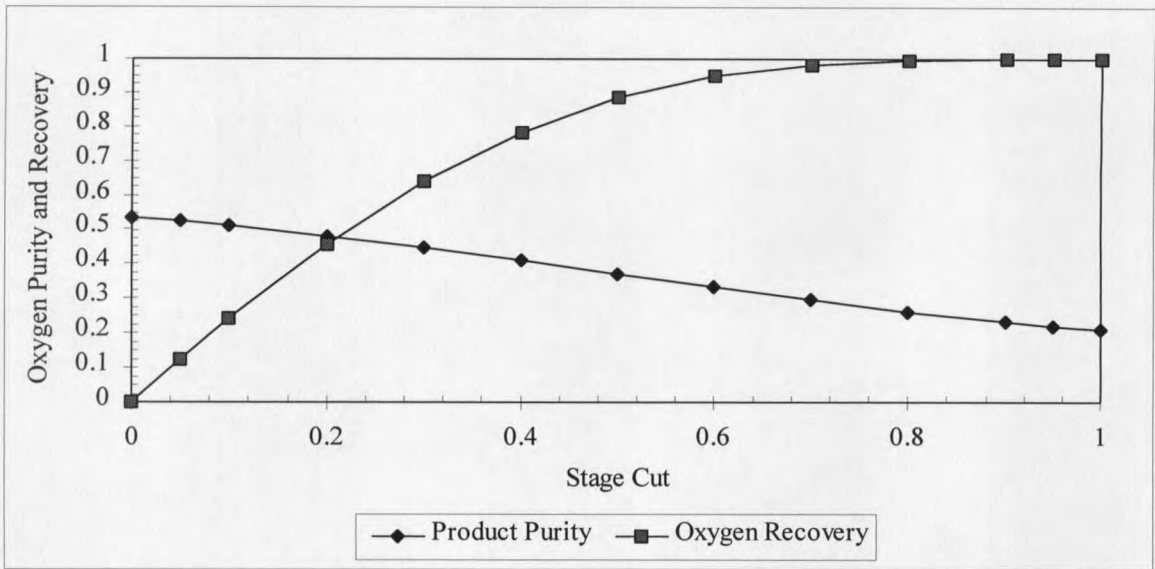


Figure 20. Oxygen purity and recovery as a function of stage cut for a PTMSP membrane operating at 20 °C (feed rate=100 lbs/s, $\alpha^*=4.7$, feed and product pressures of 14.4 atm. and 8 psia, and oxygen permeance= 2.49×10^{-4} ft³/ft²-s-atm.).

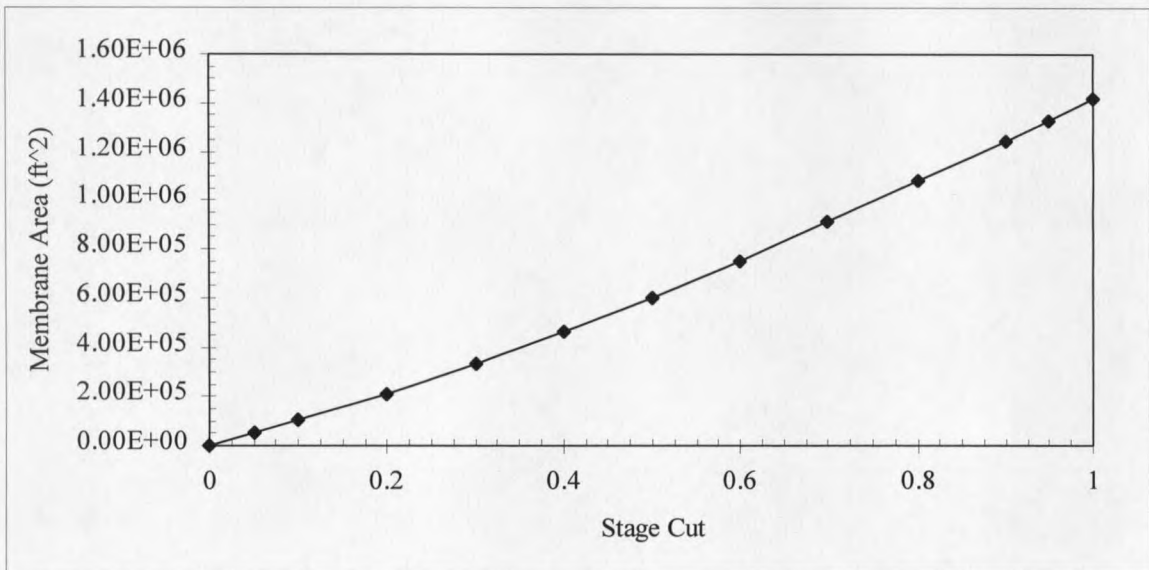


Figure 21. Required membrane area as a function of stage cut for a PTMSP membrane operating at 20 °C (feed rate=100 lbs/s, $\alpha^*=4.7$, feed and product pressures of 14.4 atm. and 8 psia, and oxygen permeance= 2.49×10^{-4} ft³/ft²-s-atm.).

As can be seen from inspection of Figure 20, the decrease in the membrane's separation factor causes a significant decrease in the oxygen purity and recovery in the product stream. As expected, Figure 21 shows that the required membrane area is reduced by more than a factor of ten over the operation at cryogenic conditions due to an increase in the oxygen permeability through the membrane. Figure 20 and 21 show that with a stage cut of 0.4, the module is capable of producing OEA containing 41% oxygen with 78% oxygen recovery with a required membrane area of $4.59 \times 10^5 \text{ ft}^2$.

To reduce the membrane area further, it would be necessary to decrease the membrane thickness from the value used by Air Products in their study on PTMSP membranes. Untreated PTMSP films with a thickness of less than $1 \mu\text{m}$ have been discussed in previous research (Asakawa et al. 1989, 118), but no data on ultrathin treated films could be located in the literature.

Design of a Single Stage Membrane Module for Hypersonic Air Separation. To meet the tight volume limitations in hypersonic air separation, polymeric membrane modules must utilize very high membrane packing factors. Published packing factors range from $45 \text{ ft}^2/\text{ft}^3$ for a tube-in-shell arrangement to over $9,000 \text{ ft}^2/\text{ft}^3$ for hollow fibers (Hsieh 1996, 161). However, it may not be desirable to use the upper end of packing factors for hollow fibers, since it requires the use of very small diameter fibers which have the potential for causing large pressure drops in the product as it travels through the fiber bore (Koros 1995, 69).

As a first attempt to estimate the volume of a PTMSP membrane module, it was assumed that the membrane packing factor was 4,000 ft²/ft³. This factor was based on a hollow-fiber configuration with a fiber outside diameter (OD) of 150 μm and a 50% packing efficiency in the module (Koros 1995, 69 and 78). When this packing factor is applied to a module with a required membrane surface area of 4.59x10⁵ ft², the module volume would be 115 ft³.

As previously mentioned, an area of concern with the use of hollow fibers is the pressure drop in the product stream as it travels through the fiber bore. To determine if pressure drop would be a concern in the PTMSP module, it was assumed that the fibers mentioned above have an inside diameter (ID) of 100 μm and a length of 5 feet. Since each of the fibers would have a surface area of 7.73x10⁻³ ft², a total of 5.938x10⁷ fibers would be needed to provide the necessary gas permeation area of 4.59x10⁵ ft². Since each fiber has an available flow area of 8.454x10⁻⁸ ft², the total area available for product flow would be approximately 5.0 ft². Based on these assumptions, coupled with a product permeation rate of 982 actual cubic feet per second, the velocity of the OEA in the fiber bore at the module outlet would be approximately 196 ft/s. The Hagen-Poiseuille equation can be used to predict the pressure drop on the tube side of the hollow fibers (Zolandz and Fleming 1992, 69).

$$\frac{dP_t}{dz} = \frac{-8\mu\bar{V}}{g_c r_i^2} \quad (4.20)$$

In this equation, P_t is the pressure inside the fiber, z is the length along the fiber, μ is the dynamic viscosity of the oxygen-enriched product, \bar{V} is the average gas velocity in the

fiber, r_i is the radius of the fiber, and g_c is the gravity proportionality constant. Using equation 4.20, the pressure drop at the fiber outlet is calculated to be 13.1 psi/in. Clearly, this pressure drop would not be acceptable since the pressure of the product stream was assumed to be only 8 psia.

In order to reduce the pressure drop of the gas as it flows inside the fiber, a membrane with a larger area for gas flow must be utilized. Unfortunately, membranes with large flow areas do not have high packing factors and their use would cause the volume of the module to increase dramatically. As an example, assume that increasing the OD and ID of the hollow fibers to 1,000 μm and 700 μm , respectively produces a hollow-fiber membrane that is mechanically stable. With these new fiber dimensions, the increase in the area available for product flow would decrease the velocity at the fiber outlet to 26.6 ft/s. Applying equation 4.20, the pressure drop at the fiber exit would be reduced to 0.04 psi/in. Unfortunately, the increase in the diameter of the fiber would cause the membrane packing factor to decrease to approximately 600 ft^2/ft^3 which would cause the required membrane volume to increase to approximately 765 ft^3 . Clearly, this volume is much too high to be used in hypersonic applications.

A second area of concern in the design of a membrane module for hypersonic applications would be the development of a porous support as backing for the thin polymer membrane. Past studies have shown that the design of the support material is at least as important as the preparation of the selective layer itself (Pinnau et al. 1988, 87). Since the preceding paragraph has shown that the only way to obtain reasonable product velocities was to use large diameter fibers, the design of the support material would be

critical since the fibers would likely require relatively thick walls to maintain mechanical stability. The permeation rate of the product through the porous support must be large enough such that it does not pose a resistance to the flux of product through the polymer. If such a support could not be developed, the overall performance of the membrane module would decrease from the levels presented in the preceding sections.

Discussion

The operational simplicity and low densities of polymeric membranes make their use attractive in hypersonic air separation. Unfortunately, the preceding study has shown that the performance of currently available polymeric membranes limits their utility in all aspects of air separation for hypersonic flight. When membranes with a high oxygen permeability are incorporated into membrane recycle cascades, the compression requirement is too large to allow the use of traditional land-based compressors. On the contrary, membranes that have high separation factors require a permeation area that is too large for practical application in hypersonic flight. Furthermore, when small diameter hollow-fiber membranes are used to reduce the volume of a single stage membrane module, the high vapor velocity would cause excessive pressure drops in the product stream. To reduce the pressure drop, fibers with a larger diameter must be used; however, the associated decrease in the membrane packing factor would cause the volume of the module to greatly exceed the project's limit. Although the vapor velocities could be reduced if a less permeable membrane was used in the module design, the

required membrane area would increase which would also cause the project's volume limit to be significantly exceeded.

Conclusions

While land-based air separation using polymeric membranes is a demonstrated technology, the current project's volume limitations prohibits their use in hypersonic flight. Consequently, it appears that the only way polymeric membranes could be used in this application is if substantial improvements were made to the technology that has been demonstrated to date.

CHAPTER 5

FACILITATED TRANSPORT MEMBRANES

Summary of the Technology

As was discussed in Chapter 4, polymeric membranes are the most common type of membrane used in commercial gas separations. However, a second type of membrane that could be used in the separation of oxygen from air is liquid membranes. As the name implies, the pore space of liquid membranes contains fluid which is beneficial in the separation process since diffusion in liquids is approximately two orders of magnitude faster than it is in polymers. Despite the high rates of diffusion, typical gas permeation rates through liquid membranes are approximately the same as through polymeric membranes due to the increased thickness of the membrane (Way and Noble 1992, 834). Since liquid membranes are inherently more complex than polymeric membranes, the only way they would be an attractive separation tool would be if their selectivity would exceed the values commonly found in polymeric membranes.

In the 1980's, a research study was undertaken to determine if a liquid membrane could be designed that would outperform the already established polymeric membranes. The membranes used in the study utilized solution-diffusion, which is identical to the transport mechanism that occurs in polymeric membranes. This study showed that

although the liquid membranes that were tested had very high oxygen permeabilities, they did not have a high enough separation factor to be economically competitive with existing oxygen separation technologies (Baker, Roman, and Lonsdale 1987, 26-27).

In order to improve the selectivity of liquid membranes, the fluid phase must contain a dissolved compound (known as a carrier) that will selectively and reversibly bind one of the species which is desired to be separated. This process is typically known as facilitated transport. When the fluid phase contains carrier compounds, the net flux of a given species across the membrane is the sum of the transport due to solution-diffusion and the diffusion of the species chemically bound to the carrier. Very high purity product is able to be obtained with facilitated transport membranes since the selectivity of the carrier is designed to be very high for one of the species being separated. Despite the high theoretical separation factors, the actual product purity obtained with facilitated transport membranes can be much lower when the feed pressure is increased. For example, at low feed pressures, the flux of a given species across the membrane by solution-diffusion is low which means that the membrane's selectivity will be very high since facilitated transport is the dominant transport mechanism. Conversely, at high feed pressures, the membrane selectivity will deteriorate since the carrier present in the membrane is easily saturated with solute molecules. Saturation of the carrier allows an increased percentage of the overall transport of a given species to occur through solution-diffusion which is much less selective than facilitated transport (Way and Noble 1992, 834).

Liquid membranes that utilize facilitated transport can be broken down into two major classes. The first class, known as immobilized liquid membranes, consist of a porous solid phase impregnated with a liquid solution which contains the dissolved carrier. The liquid is held in the membrane's pore space by capillary forces. Immobilized liquid membranes are known to be unstable due to solvent losses from the membrane and irreversible oxidation of the carrier compound. The second type of facilitated transport membranes is known as fixed carrier membranes. These membranes utilize a solid phase in which the carrier is physically attached to the polymer chains. Fixed carrier membranes are considered to be much more stable than immobilized liquid membranes (Way and Noble 1992, 834-835).

Use of Facilitated Transport Membranes in Hypersonic Air Separation

Air separation using liquid facilitated transport membranes has been studied since 1960. The first generation of facilitated transport membranes consisted of aqueous solutions of hemoglobin. The researchers studying these membranes noted a large increase in oxygen flux when the membranes were in use but concluded that their utility in an air separation system was limited since the hemoglobin that was used was very unstable when it was taken outside of the body. Subsequent studies that utilized synthetic oxygen carriers resulted in both low oxygen permeabilities and selectivities. It was also noted that the useful life of the oxygen carriers was relatively short (Johnson et al. 1987, 33).

Since the early 1980's several different types of facilitated transport membranes have been studied. In the following sections, a number of the more interesting membranes will be reviewed for potential use in hypersonic air separation.

Liquid Membranes Containing Cobalt Complexes

In the 1980's, Bend Research was involved in a project sponsored by the Department of Energy (DOE) to develop a facilitated transport membrane system to produce oxygen-enriched air. In the course of their study, the researchers identified three characteristics that an oxygen carrier must possess to be considered for use in a facilitated transport membrane:

- 1) The carrier must rapidly and reversibly bind oxygen at moderate temperatures and pressures;
- 2) The carrier must be soluble in a suitable liquid solvent; and
- 3) The carrier must be resistant to irreversible oxidation.

Using these criteria, 18 compounds were identified for potential use as oxygen carriers. Oxygen sorption and permeation experiments indicated that the cobalt complex $\text{Co}(\text{3-MeOsaltnen})$ dissolved in a suitable solvent such as γ -butyrolactone (BLO) produced the best overall results (Johnson et al. 1987, 33-43).

To test the performance of the carrier/solvent pair, the carrier was impregnated in a porous regenerated cellulose membrane supported by porous polytetrafluoroethylene (PTFE). The typical performance obtained with this membrane included an oxygen permeability of 260 barrers with a selectivity of 26. The oxygen flux through the

membrane was reported to be between 2 - 3 scf/ft²-day when the feed and product pressures were 1 atm. and 0.03 atm., respectively. The membrane was reported to be stable for several days when synthetic air was used as the feed, but was very unstable when the feed air contained carbon dioxide and water vapor (Johnson et al. 1987, 52-62).

In a subsequent paper, Bend Research proposed a complete air separation using spiral wound liquid membranes containing Co(3-MeOsaltmen) dissolved in BLO. Oxygen-enriched air was to be produced with a purity of 85% by weight with an oxygen recovery of 61% by weight. The feed pressure to the module was designed to be 1 atmosphere with the product being withdrawn at 0.05 atmospheres. For a system designed with a feed rate of 1.81 lbs/s and an oxygen flux of 2.7 scf/ft²-day through the membrane, the authors reported a required membrane area of 75,000 ft². Using equations presented in the paper, the required membrane area to produce oxygen at a rate of 11.65 lbs/s would be 4.19×10^6 ft² (Matson and Lonsdale 1987, 70-75). Although the authors presented an additional system based on improvements in the flux of oxygen through the membrane, this case was not considered in the current review of facilitated transport membranes since no documentation was provided to determine if the assumed improvements were technically feasible.

Estimation of the Membrane Module Weight and Volume. A majority of the weight in a liquid membrane would be the liquid contained in the membrane's pores. To estimate the weight of Bend Research's cobalt complex membrane, it is convenient to assume that a hollow-fiber configuration would be used in the fabrication of the

membrane system. The fibers used in the module were assumed to have an outside diameter (OD) of 1,000 μm , an inside diameter (ID) of 700 μm , and a length of 5 feet. In addition, it was assumed that the liquid filled portion of the membrane has a thickness of 4 μm , the membrane has a porosity of 80%, and the liquid in the membrane's pore space has a specific gravity of 1.1 (the specific gravity of the BLO solvent). With these assumptions, the weight of the liquid contained in a cobalt complex membrane module with a surface area of $4.19 \times 10^6 \text{ ft}^2$ is estimated to be 3,000 pounds.

To estimate the volume of a cobalt complex liquid membrane, a packing factor of 275 ft^2/ft^3 was assumed for the spiral wound membrane modules (Hsieh 1996, 161). With this packing factor, the volume of Bend Research's liquid membrane system would be approximately 15,000 ft^3 .

Discussion. Several areas of concern were noted when this membrane system was reviewed for potential application in hypersonic air separation. First, the system volume would greatly exceed the current project limit of 50 ft^3 . The extremely high volume requirement of 15,000 ft^3 is the result of specifying the use of a spiral wound membrane in the system design. These membranes have very low packing factors compared to other membrane configurations such as hollow-fiber membranes. If hollow-fiber membranes could be used in place of the spiral wound modules, the required volume could be substantially reduced. However, as was shown in Chapter 4, the use of extremely small diameter hollow fibers have the potential to cause large pressure drops in the product stream. Consequently, the fibers would have to be sized to give the highest possible

packing factor while maintaining a reasonable product pressure drop. Second, the liquid in the membrane would likely cause the weight of the membrane module to exceed the current project's limit of 1,000 pounds. Finally, the stability of the membrane would need to be proven, especially since Bend Research's membrane was shown to be unstable when exposed to carbon dioxide and water vapor.

Liquid Membranes Containing Molten Salts

A different type of facilitated transport membrane that has been investigated in the past used molten salts as the oxygen carrier. The molten salt membrane consisted of a stainless steel wire mesh which supported the liquid salt solution. When liquid lithium nitrate salt was used in the membrane at a temperature of 429 °C, a maximum oxygen permeability of slightly over 2,000 barrers with a selectivity of 170 was obtained (Pez and Carlin 1992, 24). Although the molten salt membrane has an oxygen permeability that is nearly an order of magnitude higher than Bend Research's cobalt complex membrane, its thickness was 50 times greater. Consequently, the oxygen flux through the salt membrane would be lower than the membrane containing the cobalt complex.

In the patent disclosure on the molten salt membranes, the authors stated that the membrane could be composed of thinner material cast on a porous ceramic support (Pez and Carlin 1986, 5-6). If this arrangement would prove to be feasible, the thickness of the salt membrane could be reduced to levels which would make the oxygen flux equal or exceed the flux through the cobalt containing membrane. However, since no

experimental evidence was presented to substantiate the claim of the composite membrane, it will not be considered in the current analysis of the molten salt system.

Discussion. Several shortcomings of the molten salt membrane were found when the system was considered for potential application in hypersonic air separation. First, since the density of molten salts is greater than the density of the BLO solvent used in Bend Research's membrane, it would appear that the weight of a molten salt membrane module would exceed the value estimated for the cobalt complex membrane. As was shown in the previous section, the weight of the cobalt complex membrane would significantly exceed the current project's limit. Second, because the flux of oxygen through the molten salt appears to be comparable to the flux of oxygen through the cobalt complex membrane, the volume of the molten salt membrane module would likely be similar to the value estimated for the cobalt complex membrane. As was shown in the previous section, the volume of the cobalt complex membrane would significantly exceed the current project's limit. Finally, as will be discussed in Chapter 6, since molten salts are known to be very corrosive, the stability of the membrane system would need to be proven.

Liquid Membranes Containing Hemoglobin

One of the more novel approaches to air separation with liquid facilitated transport membranes that was found in the literature review involved the use of bovine hemoglobin impregnated in the pores of a cellulose membrane. Tests of the membrane's performance found that the permeability of oxygen decreased from 600 barrers at an oxygen partial

pressure less than 2 cm of Hg to less than 100 barrers at an oxygen partial pressure of 20 cm of Hg (Chen, Nishide, and Tsuchida 1996, 258).

An explanation as to why the permeability of oxygen decreased with increasing pressure can be found by considering the mechanism for oxygen permeation in facilitated transport membranes. As has been previously stated, the net flux of oxygen across facilitated transport membranes is the sum of the transport due to solution-diffusion and the transport due to interaction with the carrier present in the membrane. This relationship, known as dual mode permeation, can be expressed mathematically by equation 5.1.

$$P_{O_2} = kD_{O_2} + \frac{[C]_0 KD_c}{1 + Kp_{O_2}} \quad (5.1)$$

In this relationship, P_{O_2} is the permeability of oxygen through the membrane, k is the solubility of oxygen in the liquid, D_{O_2} is the diffusivity of oxygen through the liquid, C_0 is the initial concentration of the carrier, K is the equilibrium constant for the reversible oxidation of the carrier, D_c is the diffusivity of the oxidized carrier through the liquid, and p_{O_2} is the partial pressure of oxygen on the feed side of the membrane. Inspection of this equation shows that the permeability of oxygen will decrease as the partial pressure of oxygen on the feed side of the membrane increases (Chen, Nishide, and Tsuchida 1996, 256-259).

The preceding paragraph has shown that facilitated transport membranes are most effective when operating at low feed pressures. As the pressure on the feed side of the membrane increases, the permeability of oxygen will decrease which also causes the

membrane's overall separation factor to decrease since the permeability of nitrogen is unaffected by the increase in feed pressure. This characteristic is very different from polymeric membranes in which both the permeability and selectivity of the membrane are considered to be independent of pressure. Consequently, it can be seen that increasing the feed pressure in facilitated transport membranes gives the counterproductive result of a decrease in the product purity. In order to obtain high product purities with facilitated transport membranes, the feed pressure must be kept low which eliminates the benefit of increased permeation rates which are possible at higher operating pressures.

Fixed Carrier Facilitated Transport Membranes

As has been previously mentioned, fixed carrier membranes have the advantage of increased stability compared to liquid membranes. A literature search was conducted to see if any fixed carrier membranes have been developed with the properties necessary for application in hypersonic air separation. In the literature review, fixed carrier membranes were not considered unless their performance would equal or exceed the performance of the polymeric membranes that were studied in Chapter 4. Although one article was found that identified several membranes with selectivities comparable to the previously considered polymeric membranes (Choi, Park, and Lee 1995, 2374), none of the membranes had an oxygen permeability that exceeded the value used in the study of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes in Chapter 4. Consequently, these membranes are not useful in hypersonic air separation since the volume of the membrane module would substantially exceed the current project's limits.

A further review of the literature revealed a patent in which a cobalt complex was successfully incorporated into a highly porous glass membrane. The test results of the membrane included a separation factor of 7 and an oxygen permeance of 4.1×10^5 barrers/cm (Tsuchida et al. 1995, 6). Although this membrane has interesting properties, the fact that its permeability is lower than the PTMSP membrane used in the polymeric membrane study makes it unusable in hypersonic air separation.

In a 1986 patent, a membrane with an oxygen selectivity of over 1,000 and an oxygen permeance of up to 50,000 barrers/cm was claimed to have been synthesized by German researchers. The validity of the data contained in their patent has not yet been proven (Way and Nobel 1992, 847) and no mention of their findings could be located in a review of the current literature. Since the claim has not been substantiated, this membrane will not be considered in the current analysis of facilitated transport membranes.

Conclusions

Facilitated transport membranes have been shown to be capable of producing oxygen-enriched air in a laboratory setting. However, in general these membranes are unstable, have high weights, occupy a large volume per unit surface area, and have decreasing performance with increasing feed pressures. Furthermore, to the author's knowledge, they have not been utilized in a large scale, commercial air separation system. For these reasons, it appears that the use of facilitated transport membranes in hypersonic air separation would not be feasible.

CHAPTER 6

REVERSIBLE CHEMICAL REACTIONS

Summary of the Technology

The facilitated transport membranes described in Chapter 5 are a specific example of a process that utilizes a reversible chemical reaction to separate oxygen from air. In chemical air separation processes, oxygen is selectively removed from air by reacting it with a carrier that is present in either the solid or liquid phase. After the reaction has occurred, the temperature and/or the pressure of the oxidized carrier is altered, allowing the reacted oxygen to be released and recovered as product. Since the carrier is usually completely selective for oxygen, the purity of the product is generally very high (Erickson 1983, 14). In the following sections, several of the more promising chemical air separation methods will be reviewed in detail to determine if any could be useful in hypersonic air separation.

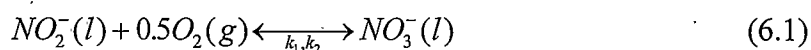
Molten Salts

In the 1980's, Air Products and Chemicals received several patents for an air separation system using the reversible oxidation of alkali metal salts. The principle of operation of the salt system involved contacting a molten nitrite and nitrate salt with air at

a temperature and pressure such that the oxygen would react with the salt solution. The oxidized salt is then passed to a flash vessel where the temperature is increased and/or the pressure is decreased to liberate the oxygen that has been absorbed (Weimer 1987, 4). Simulations indicate that a product with an oxygen purity of greater than 99% and an oxygen recovery of 98% are capable of being produced by the molten salt process (Erickson 1988, 5). The specific salts used in the molten salt system were a mixture of sodium and potassium nitrate and nitrite catalyzed by sodium peroxide (Dunbobbin and Brown 1987, II-2)

Reaction Thermodynamics and Kinetics of the Nitrite/Nitrate Salt System

The reaction between the nitrite ion and oxygen can be described by the overall stoichiometric equation given as equation 6.1.



Since the heat of the reaction for the oxidation of nitrite is -24.5 kcal/mole (Freeman 1956, 1491), the oxidation of the salt should be carried out at the minimum temperature necessary to give an adequate rate of reaction. Studies of the volume of oxygen absorbed as a function of time indicate that at low temperatures (600 °C), the equilibrium oxygen uptake is approximately 0.2 grams of oxygen per gram of sodium nitrite. Unfortunately, the rate of uptake is very slow at this temperature as it takes approximately 40 minutes to reach 50% of the equilibrium conversion. At higher temperatures, the rate of oxidation is considerably faster but, as expected, the amount of oxygen that is absorbed is much lower. The rate of decomposition of nitrate to nitrite is much faster than the oxidation

reaction. With the decomposition occurring in argon at 750 °C, it takes less than 5 minutes to reach 50% of the equilibrium conversion. At temperatures above 750 °C, experimental data suggests that the nitrite ion further decomposes to nitrogen dioxide, oxygen, and nitrogen (Freeman 1956, 1488-1490). Similar trends in the absorption/desorption thermodynamics and kinetics of potassium nitrite/nitrate have also been shown to exist, although the rate of oxygen desorption appears to be slower than in the sodium nitrite/nitrate system (Bartholomew 1966, 3444).

Use of Molten Salts in Hypersonic Air Separation

As previously mentioned, Air Products and Chemicals thoroughly investigated an air separation system using sodium and potassium nitrite/nitrate salts. A pilot plant that used the MOLTOXTM technology (Air Products' trademark for the molten salt air separation process) was built and operated between 1985 and 1986. The plant successfully produced 99+% pure oxygen at a recovery of 98+%. Operation of the plant showed that corrosion, especially in the high temperature oxygen desorber, was an area of concern (Dunbobbin and Brown 1987, I-2 to I-8).

Volume and Weight of a MOLTOXTM System. Since the oxidation and reduction kinetics of the nitrite/nitrate salt system indicate that the reaction between oxygen and the salt is relatively slow, one would expect that the volume and weight of the MOLTOXTM system would be substantial. To verify this hypothesis, data was extracted from the report on the MOLTOXTM pilot plant operation. The plant operational data showed that the oxygen absorber, which was designed for an inlet air flowrate of 1,200 scfh, had a

diameter of 6 inches and a height of 25.5 feet (Dunbobbin and Brown 1987, IV-4 and IV-7). Making the assumption that this piece of equipment can be approximated by a cylinder, the volume of the absorber was calculated to be 5 ft³. The combination of the absorber volume alone and the inlet air flowrate equates to a specific volume (defined as the volume of the separator divided by the mass flowrate of the inlet air) of 185 ft³/(lbs/s) which is several orders of magnitude above the current project's limit of 0.5 ft³/(lbs/s).

The weight of the fluid contained in the absorber and desorber would be a significant contribution to the overall weight of the MOLTOXTM system. Data contained in the description of the pilot plant indicated that the residence time in the oxygen desorber ranged from 1 - 2.5 minutes and the pump rate of the molten salt averaged 1.6 gpm (Dunbobbin and Brown 1987, IV 7). Assuming a salt density of 100 lbs/ft³ (Erickson 1983, 24), the weight of the salt in the desorber alone would be approximately 40 pounds. The combination of the mass of the salt in the desorber and the inlet air flowrate equates to a specific mass (defined as the mass of the separator divided by the mass flowrate of the inlet air) of approximately 1,500 lbs/(lbs/s) which is several orders of magnitude above the current project's limit of 10 lbs/(lbs/s).

Improvements to the MOLTOXTM System. After operating the MOLTOXTM pilot plant, Air Products patented several improvements to the process, two of which are relevant to the current project. The first relevant patent dealt with adding recycle streams to the absorption column. The goal of the new design was to improve the recovery of oxygen and reduce the volume of salt that was required to produce the necessary quantity

of oxygen product. The patent indicates that the new configuration could reduce the salt throughput by up to 40% over the previous system design (Weimer 1987, 5). Since the preceding section has shown that a 100 lbs/s MOLTOXTM system would likely exceed the current project's volume and weight requirement by a substantial amount, it is unlikely that a 40% reduction in salt throughput would result in a system with the necessary size and weight for use in hypersonic air separation.

The second published improvement of interest to the MOLTOXTM process involved the utilization of a new catalyst for use in the absorber and desorber reaction vessels. The patent in which the information on the catalyst was disclosed indicates that the new catalyst would not only enhance the activity of the oxygen acceptors in the salt solution, but also would reduce corrosion in the system. Furthermore, the patent indicates that the new catalyst would not be susceptible to poisoning by nitrogen oxide, carbon dioxide, and water and would not be vaporized as easily as the catalyst used in the previous design. Data presented in the patent indicates that the new catalyst would increase the activity of the oxygen salt by a factor of 12 when the salt is exposed to the normally damaging nitrogen oxides, carbon dioxide and water vapor (Carlin and Dunbobbin 1989, 5 and 8). Although the increased catalyst activity represents a significant improvement to the MOLTOXTM process, it is unlikely that even a factor of 12 reduction in the weight and volume of the equipment would result in a system with the necessary properties for use in hypersonic air separation.

Conclusions. Molten salts have been shown to be capable of producing high purity oxygen-enriched air with high oxygen recoveries in land-based pilot plant tests. However, the slow reaction kinetics and the high density of the salt solution would make the volume and weight of a molten salt system significantly exceed the current project's limits. Before molten salts could have utility in hypersonic air separation, significant improvements would have to be made in the rates of the oxidation and reduction reactions. Faster reaction rates would lead to reductions in the required vessel residence times which would reduce both the weight and the volume of the molten salt system.

Solid Metallic Oxides

The use of metallic oxides to recover oxygen from air dates back to the mid-1800's with the invention of the barium oxide-peroxide system known as the Brin Process (Tarman and Massey 1974, 1). Since then, materials used or proposed for metallic oxide air separation systems include copper (Gorin 1947, 1), calcium and magnesium (Tarman and Massey 1974, 1), manganese (Parker 1964, 3), strontium (Mullhaupt and Stern 1971, 1), sodium, potassium and manganese (Turner 1978, 2), and praseodymium and cerium (Mullhaupt 1976, 2).

The process for air separation with metallic oxides is very similar to the molten salt process described in the preceding section. The reduced oxide is contacted with air (usually dry and CO₂ free) at a high temperature for oxidation. After reacting with oxygen, the material is heated and/or reduced in pressure to liberate the reacted oxygen. The main difference between the two processes is that the metallic oxides are generally

used in a single bed with changing operating conditions while the molten salts are pumped to different vessels continuously operating at the same conditions.

Thermodynamics of Metallic Oxide Air Separation Systems

With basic thermodynamic principles (Kyle 1992, 336-361), it is possible to predict the temperature at which equilibrium will be established between oxygen and the metallic oxide. In order to find this equilibrium point, the reaction's equilibrium constant as a function of temperature must be known.

The change in the Gibbs free energy of a reaction is related to the reaction equilibrium constant (K) by the expression given in equation 6.2.

$$\Delta G^\circ = -RT \ln K \quad (6.2)$$

Since the change in Gibbs free energy of a reaction at any temperature is generally available from tabular data, the value of the equilibrium constant can be found by direct application of equation 6.2. The reaction equilibrium constant is also defined by the relationship given by equation 6.3.

$$K = \prod \hat{a}_i^{v_i} \quad (6.3)$$

In this equation, a_i is the activity of the species of interest and v_i is the stoichiometric coefficient of the species (negative for reactants and positive for products). Using the reversible oxidation of strontium oxide to strontium peroxide (equation 6.4) as an example reaction, the equilibrium constant is given by the relationship shown in equation 6.5.



$$K = \frac{\hat{a}_{\text{SrO}_2}}{\hat{a}_{\text{O}_2}^{0.5} \hat{a}_{\text{SrO}}} \quad (6.5)$$

Since the activity of a pure, condensed phase can be taken as unity, the activity of oxygen in equation 6.5 is equal to the inverse of the equilibrium constant squared. Because air separation with metallic oxides generally takes place at high temperatures and low to moderate pressures, the activity of oxygen can be approximated by its partial pressure. For the example reaction, the partial pressure of oxygen in equilibrium with SrO_2 can be taken as the inverse of the equilibrium constant squared. If the actual oxygen partial pressure that is present at a given reaction temperature is greater than the equilibrium partial pressure, the lower oxide (SrO) is not thermodynamically stable and the only phase present at equilibrium would be the fully oxidized compound (SrO_2). Conversely, if the actual partial pressure of oxygen is less than the equilibrium value, the lower oxide (SrO) would be the only species present at equilibrium. Using published thermodynamic data (Weast 1976, D-45 to D-50), the equilibrium oxygen pressure as a function of reaction temperature was calculated for the oxidation of several metallic oxide systems. The results of these calculations are presented in Figure 22.

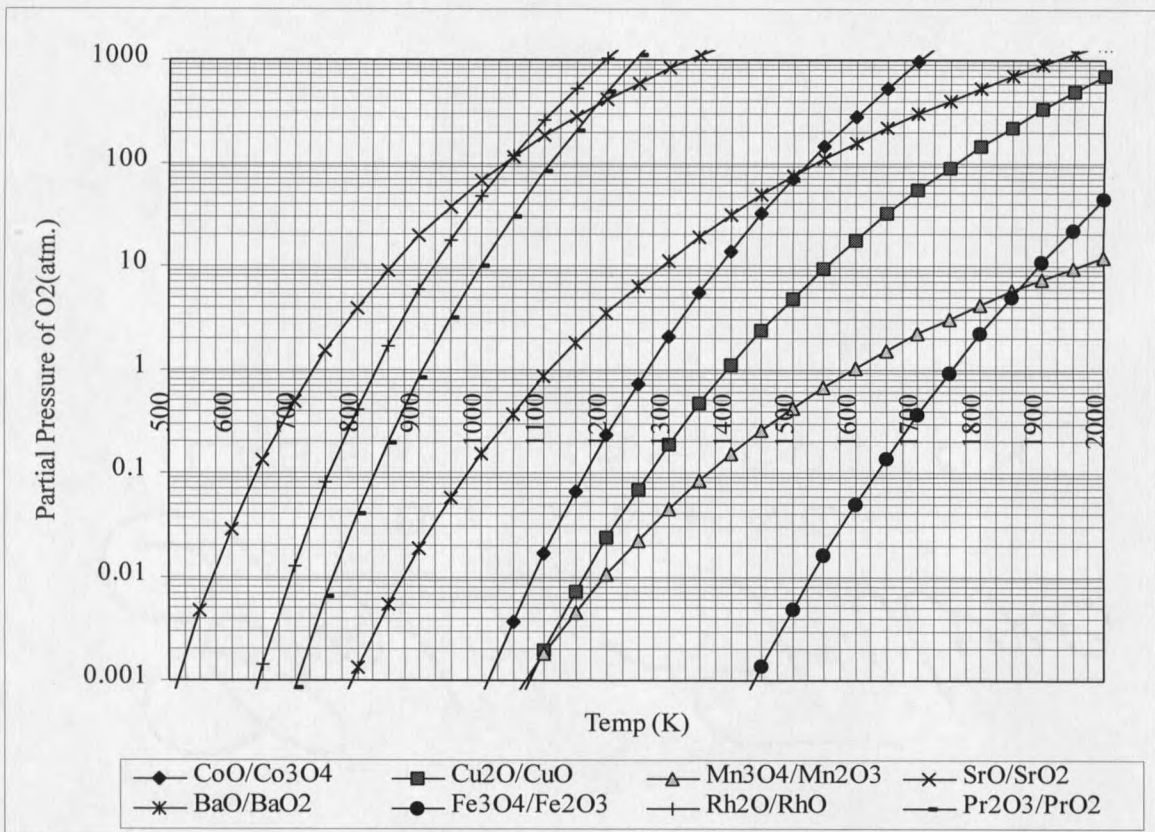


Figure 22. Relationship between the equilibrium partial pressure of oxygen and the reaction temperature in the oxidation of several metallic oxide systems.

Use of Metallic Oxides for Hypersonic Air Separation

In the 1960's, the Air Force was involved in an aggressive research program to develop an oxide-based air separation system for use in hypersonic flight. The researchers involved in the project identified a number of candidate oxide systems (Reti and White 1964, 4-11), but eventually proposed a design based on the oxidation of CoO to Co₃O₄ (Reti and Turner 1966, 1). The following is a list of some of the key findings that were made in the process of evaluating the candidate metallic oxides:

- 1) In order for chemical air separation to have utility in hypersonic flight, the bed cycle time must be approximately 0.1 seconds (Hoagland and Turner 1963, 2);

- 2) The rate of Co_3O_4 decomposition is faster than the oxidation rate of cobalt oxide (Reti 1966, 10);
- 3) The oxide particles must be porous with a large surface area available for reaction (Reti and White 1964, 12);
- 4) Significant increases in conversion can be achieved with small drops in the regeneration chamber pressure (Reti 1966, 20); and
- 5) The maximum purity of oxygen that can be obtained from a chemical air separation system designed for use in hypersonic flight is approximately 85% (Reti and Turner 1966, 4-5).

Using the above findings and other pertinent data, the researchers designed metallic oxide air separation systems for at least two different hypersonic applications. The designs utilized rotating drums packed with a thin bed of cobalt oxide cycling between regions of high and low pressure. It was estimated that the separation system designed for an inlet air flowrate of 6,000 lbs/sec with an oxygen recovery of 50% would have a specific weight (defined as the mass of the separator divided by the mass flowrate of the inlet air) between 11.1 and 12.8 lbs/(lbs/s). A second design proposed for a smaller vehicle operating at slower speeds had an estimated specific weight of 36.5 lbs/(lbs/s) (Reti and Turner 1966, 2-15).

Although the 6,000 lbs/s design comes close to meeting the current project's specific weight limit of 10 lbs/(lbs/s) (assuming that the unit could be effectively scaled down to 100 lbs/s), the metallic oxide air separator was given less consideration than other air separation methods due to concerns stemming from the extremely high reaction temperature required for the reversible oxidation of the cobalt oxide (Leingang, Maurice, and Carreiro 1996, 343).

Improvements to the Metallic Oxide Air Separation System. One way to reduce the problem of the extremely high operating temperatures of the metallic oxide air separation system is to replace the cobalt oxide with a material that would operate at a lower temperature. A review of the patent literature indicated that air separation systems based on both strontium oxide (Mullhaupt and Stern 1971, 1) and praseodymium and cerium (Mullhaupt 1976, 2) have been considered in the past for low temperature air separation systems. The advantage of a system using strontium in place of cobalt can be seen by inspecting the data contained in Figure 22 on page 84. This plot shows that the temperature at which the equilibrium oxygen pressure is 1 atmosphere is much lower for a strontium system than for a system designed to utilize cobalt oxide. A further advantage of the strontium system is the potential for higher amounts of oxygen produced per pound of oxide (Mullhaupt and Stern 1978, 169). For example, the maximum amount of oxygen produced per pound of SrO_2 is 13% by weight compared to 7% for Co_3O_4 .

The downfall of an air separation system that uses strontium is slow oxidation and reduction rates (Mullhaupt and Stern 1978, 172). Although the reaction rates can be improved dramatically by the addition of metals such as silver, sodium, and copper, the best rates only average 1.2 - 1.6 wt. percent per minute per atmosphere of oxygen pressure (Mullhaupt and Stern 1971, 12). Bench scale tests on a strontium oxide system doped with copper, nickel, and sodium yielded maximum absorbent productivities of 5.1×10^{-5} pounds of oxygen per second per pound of SrO_2 . It was estimated that a 10 TPD (0.23 lbs/s) air separation system using strontium oxides would require approximately

9,000 pounds of reactant and an inlet air flow of 3.54 lbs/s (Mullhaupt and Stern 1978, 179-180). This combination of reactant mass and air flow equates to a specific mass of approximately 2,500 lbs/(lbs/s) which is several orders of magnitude higher than the project limit of 10 lbs/(lbs/s). Consequently, it appears that a metallic oxide air separation system using strontium does not have utility in hypersonic air separation.

One of the reasons of the poor performance of the strontium oxide system is that the time needed to complete one oxidation and reduction cycle is nearly 20 minutes (Mullhaupt and Stern 1978, 179). In comparison, the cycle time for the high temperature cobalt oxide system was designed to be approximately 0.1 seconds. In order for the strontium oxide system to be competitive with the high temperature cobalt system, it would appear that the cycle time must be drastically reduced. Although increasing the reaction temperature would likely cause the reaction rate to increase and the cycle time to be reduced, thermodynamics would require that the system's operating pressure would also have to increase. Since the equilibrium pressure of oxygen is a very strong function of temperature, even small increases in the reaction temperature would require a large increase in the system pressure.

Conclusions. Air separation systems using metallic oxides have been shown to be capable of producing oxygen with a purity near 90%. However, unless very short reaction times are used, the slow reaction kinetics and the high density of the oxide would make the volume and weight of the system significantly exceed the current project's limits. Although a previous hypersonic air separator designed with fast cycle times had a

specific weight close to the current project's limit of 10 lbs/(lbs/s), the system was rejected based on its high operating temperature. Before low operating temperature metallic oxides could have utility in the area of hypersonic air separation, significant improvements would have to be made in the rates of the oxidation and reduction reactions. Faster reaction rates would lead to reductions in the required amount of oxide which, in turn, would reduce both the weight and the volume of the system. An assessment of low temperature oxides using short cycle times would require bench scale testing to generate the necessary initial reaction rate data.

Transition Metal Complexes

For animals, an essential means of separating oxygen from air is through the binding of oxygen with hemoglobin. Hemoglobin is a complex organic molecule made up of a combination of proteins and aromatic rings. The heme molecule contains four linked, substituted pyrrole units which surround a central iron atom. Although the iron atom is attached to four nitrogen atoms, it can still accommodate additional groups above and below the plane of the ring. It is this property that allows oxygen to reversibly bind to the molecule (Vollhardt and Schore 1994, 1050-1052). The placement of the heme molecule in the protein chain is critical since it is the protective nature of the protein that keeps the iron atoms from being irreversibly oxidized to iron(III) (Ege 1989, 1153).

Use of Transition Metal Complexes for Hypersonic Air Separation

When synthetic oxygen carriers are developed for the purpose of air separation, the molecules must be designed to protect the transition metal so irreversible oxidation is prevented (Busch 1988, 62). The transition metals that have been used in the past to bind oxygen include iron, magnesium, and cobalt (Li and Govind 1994, 774). In air separation with transition metal complexes, the material is contacted with air for a period of time until the desired degree of complex saturation is obtained. To recover the oxygen that has been absorbed, the pressure of the oxidized complex is reduced and/or the temperature is increased (Li and Govind 1994, 772).

In order for a transition metal complex to be effective in air separation, it must possess four important characteristics (Park et al. 1991, 1362):

- 1) The complex must be able to be oxidized and reduced reversibly, have a selective affinity for oxygen, and have an absorption equilibrium constant that is a function of temperature;
- 2) The absorption and desorption of oxygen must occur at rapid rates;
- 3) The complex must be chemically stable and must be able to withstand numerous absorption and desorption cycles without losing a significant amount of its initial absorptive capacity; and
- 4) For liquid solutions, the complex must be very soluble in a suitable solvent.

For a system designed for air separation in hypersonic flight, the first, second, and third items are the most critical. It is extremely important that the reaction rate is fast since slow reactions require large quantities of the complex which will cause the weight and volume of the system to be excessive. It is also important that the amount of oxygen

absorbed per cycle be as large as possible since this will reduce the number of cycles required to recover a specified quantity of oxygen.

Researchers began searching for a transition metal complex for use in air separation as early as the 1940's (Wilmarth, Aranoff, and Calvin 1946, 2263). Although many complexes have been developed which reversibly bind oxygen (Li and Govind 1994, 774), they have not found use in commercial air separation systems (Kulkarni and Govind 1992, 414). A summary of the air separation performance of several transition metal complexes near ambient conditions is presented in Table 4.

Table 4. Summary of the air separation performance of several transition metal complexes.

Reference	Complex (A)	State	Yield (lbs O ₂ /lb A)	Cycle (sec)	Initial Productivity (lbs O ₂ /s)/(lbs A)
Park et al. 1991, 1367	CoSalen	Liquid	1.8×10^{-4}	420	4.3×10^{-7}
Park et al. 1991, 1367	CoSalophen	Liquid	1.3×10^{-4}	450	2.9×10^{-7}
Kulkarni and Govind 1992, 410	Mn(depe) ₂ (NCS) ₂	Solid	2.8×10^{-3}	1800	1.5×10^{-6}
Adduci 1976, 576-577	Fluomine	Solid	4.2×10^{-2}	300	1.4×10^{-4}
Ramprasad et al. 1995, 10696	Li ₃ Co(CN) ₅ ·2DMF	Solid	5.8×10^{-2}	2100	2.8×10^{-5}
Wilmarth, Aranoff, and Calvin 1946, 2263-2264	CoSaEn	Solid	4.1×10^{-2}	1200	3.4×10^{-5}
Wilmarth, Aranoff, and Calvin 1946, 2263-2264	3F-CoSaEn	Solid	4.2×10^{-2}	570	7.3×10^{-5}

There are several points of interest contained in the data presented in Table 4. First, the complexes used in liquid solutions are much less productive than complexes utilized in the solid state. The lower productivity can be attributed to the limited solubility of the complex in the solvent used in the separation tests. Consequently, it appears that the

complex should be in the solid state to maximize the amount of oxygen recovered per pound of complex. Second, fluomine, which is equivalent to 3F-CoSaEn and cobalt bis(3-fluoro-salicylaldehyde) ethylene diimine, has the highest initial productivity of any complex that could be found in the open and patent literature. Fluomine was initially researched in the 1940's and more recently was thoroughly studied by the Air Force to provide oxygen-enriched breathing air for aircraft crew members (Adduci 1976, 575). Assuming that fluomine's oxygen productivity remains constant at 1.4×10^{-4} pounds of oxygen per second per pound of absorbent, nearly 80,000 pounds of the complex would be required to recover 20,000 pounds of oxygen in a 30 minute collection period. In order to reduce the required amount of complex, it would appear that the combined absorption and desorption cycle time of 5 minutes must be substantially reduced. In fact, as was stated in the previous section, earlier research has indicated that the optimum cycle time for a high temperature oxide separation system was approximately 0.1 seconds. In order to accurately assess the use of fluomine for oxygen production for hypersonic flight, the absorption/desorption rate data during the very early stages of the reaction must be obtained. Unfortunately, data published in the literature has a very long cycle time scale compared to the period of interest for hypersonic flight. Consequently, before an assessment of the performance of fluomine operating with short cycle times is possible, initial reaction rate data would need to be determined in bench scale tests.

One complex currently under development by researches at Air Products and Chemicals that has a higher oxygen yield than fluomine is $\text{Li}_3\text{Co}(\text{CN})_5 \cdot 2\text{DMF}$. This compound has been shown to reversibly absorb approximately 5.8% of its initial weight

in oxygen compared to 4.2% for fluomine. According to published data, the combined absorption and desorption cycle times for this complex are 35 minutes in duration (Ramprasad et al. 1995, 10696). This cycle time is clearly too long to have utility in hypersonic air separation. Inspection of a plot of the oxygen gain and loss as a function of time for $\text{Li}_3\text{Co}(\text{CN})_5 \cdot 2\text{DMF}$ shows that although a large portion of the total oxygen uptake occurs in a period of less than five minutes, the rate of oxygen desorption occurs over a substantially longer time period (Ramprasad et al. 1995, 10696). As was discussed previously, in order for this complex to have utility in hypersonic air separation, it appears that the absorption and desorption cycle times must be drastically reduced since a cycle time of 35 minutes is clearly impractical.

Further investigation of the patent literature showed that a cobalt complex currently under development by Praxair appears to have a faster cycle time than Air Products' complex, but its maximum oxygen absorption is only about 1.3% by weight (Mullhaupt et al. 1996, 25). Similar to the two preceding complexes, in order for this cobalt complex to have utility in hypersonic air separation, it would appear that its absorption and desorption cycle times must be substantially reduced.

Conclusions. Transition metal complexes have an advantage over metallic oxide air separation systems since the required reaction temperatures are much lower, generally near ambient conditions. Unfortunately, none of the complexes considered in this review would come close to meeting the current project's weight and volume limits when equilibrium cycle times are utilized. Operating the complexes with a much faster cycle

time could reduce the required amount of the complex if the initial reaction rates were sufficiently high. If bench scale testing showed that the initial reaction rates of the complex systems were promising, a hypersonic air separation system based on transition metal complexes should be considered for further investigation.

CHAPTER 7

SOLID STATE ADSORPTION

Summary of the Technology

Solid adsorbents used in gas separations can be broken into two major groups, equilibrium selective adsorbents and rate selective adsorbents. Equilibrium selective adsorbents, such as zeolite, separate gases by a difference in the relative amounts of a gas species adsorbed at equilibrium. Zeolites are crystalline molecular sieves made of silicate and aluminate units and are generally porous and contain cavities consisting of 8-, 10-, or 12-member oxygen rings. The alumina units provide a negative charge that must be balanced by cations which are present in the crystalline structure. It is the cations, as well as the shape of the zeolite and its degree of hydroxylation, that interact with nitrogen's quadrupole moment and cause it to be more readily adsorbed than oxygen (Tao 1994, 508-509). LiX is considered to be the most effective zeolite commonly used in air separation. Its high polarity gives it greater nitrogen capacities and selectivities than other commonly used zeolites (Cheng and Yang 1995, 2021).

As their name implies, rate selective adsorbents separate gases through differences in their relative adsorption rates. One type of rate selective adsorbent that is commonly used in air separation is carbon molecular sieves (CMS). CMS have a network of

micropores in which oxygen diffuses much more rapidly than the larger nitrogen molecule (Yang 1987, 269-271). CMS have typically been used in systems designed for nitrogen production (Thorogood 1991, 90).

After cryogenic distillation, the most commonly used land-based air separation method is physical adsorption. Since argon does not readily adsorb on the zeolite surface, the maximum purity of the oxygen-enriched air (OEA) obtained from an adsorption process using zeolites is 95% oxygen. For the production of OEA with this purity level and production rates less than 100 TPD, separation by adsorption is more economical than cryogenic distillation (Thorogood 1991, 88-89).

Oxygen production using zeolites generally utilizes multiple adsorption beds that are continually cycled between a high pressure adsorption mode and a low pressure desorption mode. It is this pressure cycling that gives the process its common name of pressure swing adsorption (PSA). The complete PSA cycle time typically lasts for several minutes. Large scale commercial PSA systems generate oxygen-enriched air with a purity of up to 95% with an oxygen recovery ranging from 30 - 60% (Yang 1987, 263-267).

A variation to the common PSA process is known as vacuum swing adsorption (VSA). The VSA process is very similar to PSA with the major difference being that the oxygen adsorption occurs at atmospheric pressure and desorption occurs at vacuum conditions. VSA processes are generally less energy intensive than PSA processes since only the oxygen product requires compression. Furthermore, VSA systems typically have a higher oxygen recovery than PSA processes since the amount of oxygen adsorbed

by the zeolite and consequently lost in the bed regeneration process decreases as the adsorption pressure decreases. VSA processes are more applicable to larger scale operations (greater than 15 TPD) while PSA processes are more often used in small applications (Kumar 1996, 877-878). The capacity of a single train VSA plant is limited to around 100 TPD of oxygen by the size of the vacuum pump necessary to regenerate the saturated adsorption bed (Reiss 1994, 98).

A second variation on the traditional PSA system involves a process known as rapid pressure swing adsorption (RPSA). The differences between RPSA and PSA include much faster bed cycle times (seconds instead of minutes) and the use of a single adsorption bed which leads to simpler process control (Yang 1987, 265-266). RPSA processes are typically used in small scale operations since the process tends to be energy intensive (Kumar, Naheiri, and Watson 1994, 1).

Use of Solid State Adsorption in Hypersonic Air Separation

With the operational principles described in the preceding section, the open and patent literature was searched to obtain data to determine if a separation system using nitrogen selective adsorbents would be practical in hypersonic air separation. The key operating parameters obtained from several references found in the literature search have been summarized in Table 5 on the following page. For all cases listed, the purity of the oxygen-enriched air ranged from 90 - 95%.

Table 5. Summary of the air separation performance of several nitrogen selective adsorption systems.

Reference	Adsorbent (A)	System Type	P_h/P_1 (atm)	Cycle Time (sec)	Oxygen Recovery	Productivity (lbs O ₂ /s)/(lbs A)
Sircar and Kratz 1989, 437-439	Mordenite	PSA	3/1	600	42%	1.8×10^{-6}
Kumar 1996, 884	NaX	VSA	n/a	n/a	n/a	1.5×10^{-5}
Kumar 1996, 884	CaA	VSA	n/a	n/a	47%	1.4×10^{-5}
Kumar 1996, 886	CaA	VSA	n/a	n/a	n/a	3.0×10^{-5}
Sircar and Hanley 1993, 2561-2564	CaX	VSA	1.1/0.1	120	24%	1.1×10^{-5}
Farooq, Ruthven, and Boniface 1989, 2812-2813	5A	PSA	4.3/1	160	27%	1.0×10^{-5}
Pritchard and Simpson 1986, 468-469	5A	RPSA	1.8/n.a	3.5	14%	1.1×10^{-5}
Baksh, Kikkinides, and Yang 1992, 284-291	LiX	PSA	5/1	1200	78%	1.9×10^{-5}

Inspection of the data contained in Table 5 shows the limitations of hypersonic air separation by nitrogen selective adsorption. First, the oxygen recoveries are low since any oxygen that is adsorbed in the pores of the zeolite is lost during bed regeneration. Second, since the adsorption takes place on surface sites, only a finite amount of material is able to be adsorbed per bed cycle. Table 5 shows that this quantity results in an adsorbent productivity ranging from 10^{-5} to 10^{-6} pounds of O₂ per second per pound of adsorbent. This productivity would result in a system mass and volume that would considerably exceed the current project's limit. As an example, consider the third entry in Table 5 above. This VSA system has an oxygen productivity of 1.4×10^{-5} pounds of oxygen per second per pound adsorbent. Using the reported oxygen recovery of 47%, the specific mass of the system (defined as the mass of the separator divided by the mass

flowrate of the inlet air) would be approximately 7,800 lbs/(lbs/s). Due to the low adsorbent productivities, an adsorption system designed to meet the current project's oxygen production requirements would exceed the weight and volume limits by several orders of magnitude.

Conclusions

Physical adsorption is a commercially proven method of producing oxygen with purities up to 95%. Since this process does not involve chemical reactions, the material used to adsorb the nitrogen from air is stable and does not have the problem of irreversible oxidation that is known to exist with the transition metal complexes that were discussed in Chapter 6 of this review. The process also has the advantage of being relatively simple and does not require excessive temperatures or pressures for effective operation.

Unfortunately, the data presented in this review indicates that a nitrogen adsorption system designed for the current project's specifications would exceed the weight and volume limits by several orders of magnitude. Although current research has shown some improvement in adsorbent performance (Yang et al. 1996, 3093), significant advancement would be necessary to make adsorption a viable technology for the current project.

Perhaps the best chance for success with a physical adsorption process involves the use of oxygen selective adsorbents. Since the majority of air is nitrogen, it would appear that the size of the adsorption process could be reduced if an oxygen selective adsorbent

was utilized in place of the traditionally used nitrogen selective zeolites. Although oxygen selective adsorbents have typically been used in nitrogen production, it is conceivable that they could be used in oxygen production if the bed cycle times were short enough to limit the adsorption of nitrogen into the pore space of the adsorbent. While the use of a combination of oxygen selective adsorbents and traditional zeolites has been described in the past for the production of ultrahigh purity (99+%) oxygen (Kumar, Mansfield, and Weimer 1995, 1), the feasibility of an oxygen production process using only oxygen selective adsorbents would require further research. If such a system could be developed, a hypersonic air separation system based on physical adsorption should be considered for further investigation.

CHAPTER 8**VAPOR-LIQUID EQUILIBRIUM****Summary of the Technology**

A common method of separating liquid mixtures is through processes utilizing vapor-liquid equilibrium (VLE). VLE separations are based on the principle that within the two phase envelope (i.e. above a mixture's bubble point and below its dew point), the liquid and vapor phases will have different compositions if two or more species are present in the system. The preceding statement only applies to systems that are not at their azeotropic composition. Since the nitrogen/oxygen system does not contain an azeotrope, the statement applies at all points and all operating conditions for VLE air separation systems.

The type of equipment used to carryout VLE separations is based on factors such as the required purity of the product streams, the amount of a given component required to be recovered, and the amount of energy that must be added or removed to reach the product purity and recovery specifications. Because each application has its own unique set of requirements, it is prudent to examine all possible separation techniques and choose the one that is best suited to the project at hand.

Phase Equilibrium in the Nitrogen/Oxygen System

In order to determine which VLE separation method is best suited to separate oxygen from air for hypersonic applications, one must know the distribution of nitrogen and oxygen in the vapor and liquid phases at the system operating conditions. Fortunately, this distribution can be predicted by deriving the equations that describe thermodynamic phase equilibrium. From basic thermodynamic principles (Kyle 1992, 201-238), the chemical potential of a species in a mixture is defined as:

$$\hat{\mu}_i = \mu_i^\circ + RT \ln \hat{f}_i \quad (8.1)$$

Combination of the first and second laws of thermodynamics shows that at equilibrium, the chemical potential of a given species must be equal in all phases present in the system. From this statement and the definition of fugacity presented in equation 8.1, it is easily shown that the fugacity of the given species in each phase must also be equal. Assuming that the Lewis and Randall rule applies to both phases and making the appropriate substitutions for the fugacity in the vapor and liquid phases, the governing equation for phase equilibrium is given by equation 8.2.

$$Py_i\phi_i = P_i^{sat} x_i\gamma_i\zeta_i \quad (8.2)$$

In this equation, P is the system pressure, y_i is the mole fraction of the species of interest in the gas phase, ϕ_i is the species vapor phase fugacity coefficient which corrects for nonideality in the vapor phase, P_i^{sat} is the species vapor pressure, x_i is the species mole fraction in the liquid phase, γ_i is the liquid phase activity coefficient which corrects for

nonideality in the liquid phase, and ζ_i is the species Poynting correction which accounts for liquid phase compressibility. With the exception of the activity coefficient, all of the parameters in equation 8.2 are able to be calculated or measured directly. When the liquid phase behaves ideally, the value of the activity coefficient is by definition unity, and is removed from the expression. Since published VLE data for the nitrogen/oxygen system indicates the mixture is slightly nonideal (Liley, Reid and Buck 1984, 3-173 to 3-175), the activity coefficient must be used when accurate VLE calculations are required.

Values of the activity coefficient as a function of liquid composition can be predicted by any one of a number of models based on the Gibbs-Duhem equation. Of the three common activity coefficient models (Wilson, Margules, and Van Laar), the Wilson equation has been shown to be the most effective in predicting VLE in the widest range of systems (Walas 1985, 203). In order to use the Wilson equation to predict VLE in the oxygen/nitrogen system, binary interaction parameters (BIP's) must be regressed from a set of known VLE data. Using published data, the CHEMCAD III process simulator regressed the Wilson BIP's to be 42.132 and 2.3525 cal/g-mole. When these BIP's are substituted into the Wilson equation, the activity coefficients for both nitrogen and oxygen can be predicted at any system pressure and any liquid composition.

Since all of the parameters in equation 8.2 are now known or are able to be calculated, it is easy to predict the vapor phase composition as a function of liquid phase composition at a given system pressure. This calculation can be quickly made with a process simulator. Figure 23 is an example of the equilibrium curve predicted by CHEMCAD III for the nitrogen/oxygen binary system at several different system pressures.

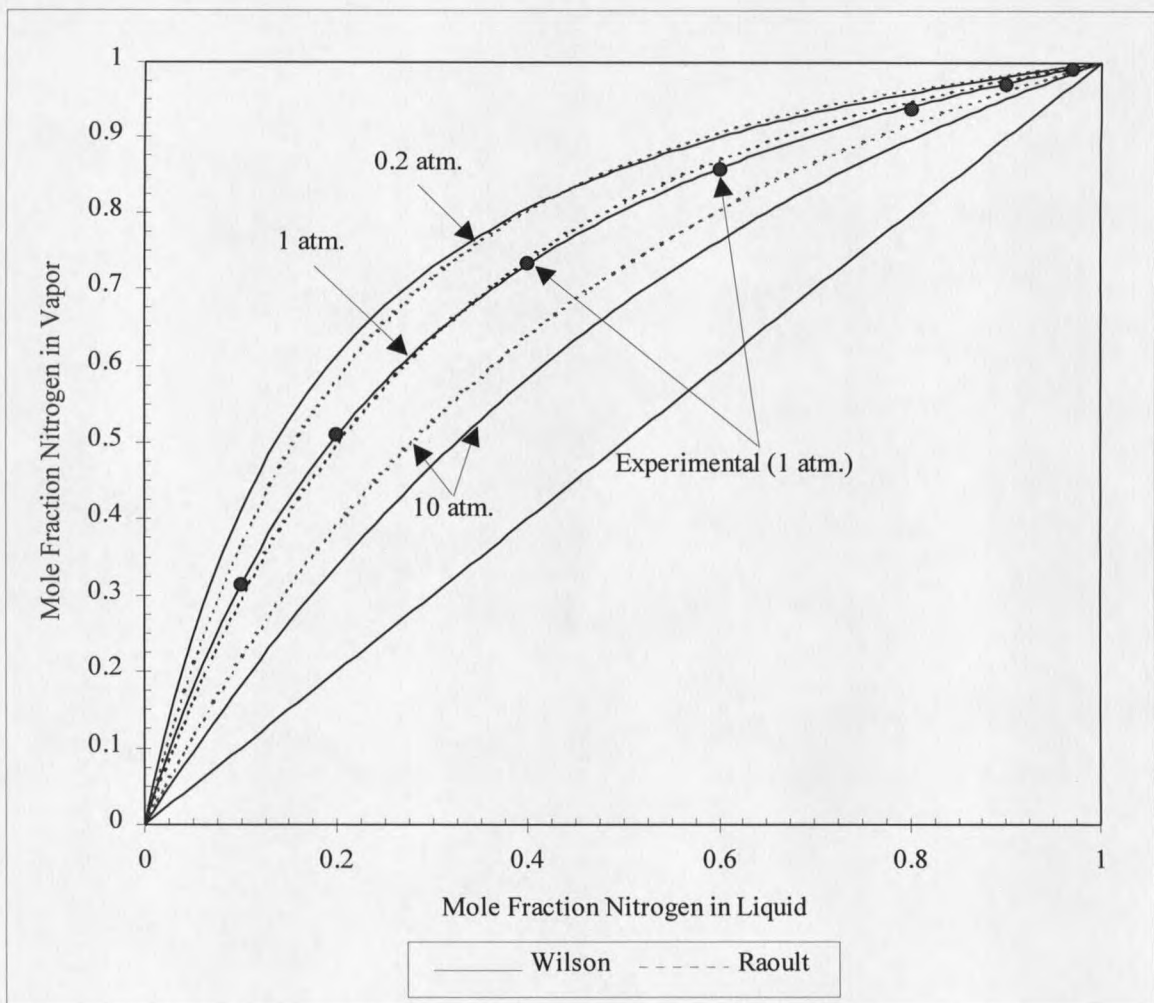


Figure 23. Comparison of predicted VLE with experimental data for the nitrogen/oxygen system.

The data contained in this plot indicates that the simulator very accurately predicts VLE for the nitrogen/oxygen system. The plot also shows the error that would be present if it was assumed that both the liquid and vapor phases behaved ideally (Raoult's Law).

Inspection of Figure 23 also shows that it may be beneficial to operate a VLE separation system at pressures below one atmosphere since the difference between the vapor and liquid composition increases substantially with decreasing pressure. This

statement can be quantified by calculating the system's relative volatility which, for a binary system, is given by equation 8.3.

$$\alpha_{ij}^* = \frac{y_i(1-x_j)}{x_i(1-y_j)} \quad (8.3)$$

As a mixture's relative volatility increases, the concentration of the low boiling component (nitrogen) will increase in the vapor phase and the concentration of the high boiling component (oxygen) will increase in the liquid phase. In general, the higher the system's relative volatility, the easier it will be to separate the components.

It has been shown that the relative volatility in the nitrogen/oxygen system is fairly constant along isobars (Dodge 1928, 622). An average value of the relative volatility can be obtained by simply averaging the individual values of the relative volatility throughout the composition range of interest. For the nitrogen/oxygen system, the average relative volatility ranges from 6.09 at a pressure of 0.2 atmospheres to 2.12 at a pressure of 10 atmospheres. The lower pressure limit is 0.2 atmospheres since, at pressures below this point, the system temperature would approach nitrogen's freezing point of 63 K (Scott 1959, 286).

Use of Vapor-Liquid Equilibrium in Hypersonic Air Separation

In the following sections of this chapter, several VLE separation methods will be examined for potential use in hypersonic air separation.

Flash Distillation

Flash distillation is the simplest VLE separation technique. The process consists of vaporizing a fraction of a liquid feed in a way such that the produced vapor is in equilibrium with the residual liquid. The vapor phase is then removed and can either be condensed or left in the gaseous state (McCabe, Smith, and Harriot 1993, 521-523).

In a binary system operating at a given system pressure, the composition of the vapor phase is fixed when either the temperature or the liquid composition is specified. The amounts of the liquid and vapor phases can be determined by writing total and component material balances for the species of interest in both phases.

$$F = L + V \quad (8.4)$$

$$Fz_i = Lx_i + Vy_i \quad (8.5)$$

In equations 8.4 and 8.5, F represents the inlet stream feed rate, L is the liquid product rate, V is the vapor product rate, and z_i is the concentration of the species of interest in the feed stream.

Using a combination of equations 8.4 and 8.5 and the equilibrium relationship, it is possible to calculate the liquid phase composition as a function of the fraction of feed that is vaporized in the flash distillation process. Calculations of this type were made with the CHEMCAD III process simulator and the results are shown in Figure 24. The pressure of 0.68 atmospheres represents the outlet pressure from the process that will supply carbon dioxide free, dry air to the inlet of the VLE separation system.

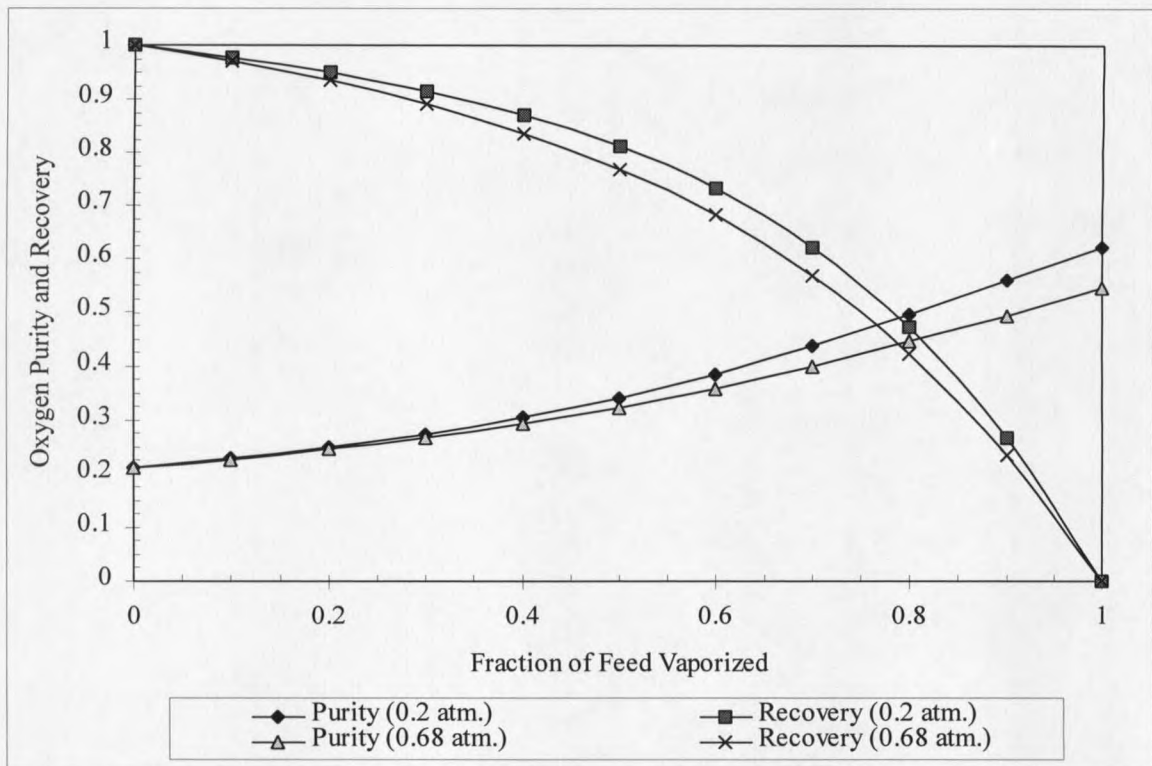


Figure 24. Oxygen purity and recovery as a function of pressure and the fraction of feed vaporized in a single stage flash distillation unit.

Inspection of the data contained in Figure 24 shows that the oxygen content of the residual liquid increases with the fraction of the feed stream that is vaporized. The maximum oxygen concentration of 62% occurs in the limit of complete liquid stream vaporization. Since the required product purity is 90%, a single stage flash distillation unit is not a viable option for hypersonic air separation.

In order to increase the purity of the oxygen product, it would be possible to connect several flash units in series similar to connecting polymeric membrane modules in series. As an example, if one assumes that three flash units are connected in series with each unit operating at 0.2 atmospheres and vaporizing 67% of the liquid they receive, the purity of

the oxygen product would be approximately 91%. The downfall to this system is that the oxygen recovery is only 16% since the oxygen that is contained in the vapor from each unit is not recovered.

In order to increase the oxygen recovery, it would be necessary to use a recycle cascade similar to the countercurrent recycle membrane cascades previously described in Chapter 4 of this review. Based on previous experience in modeling recycle cascades, it is likely that a system could be designed that would produce 90% oxygen with an oxygen recovery of at least 50%. However, before this option is explored, the size of an individual flash vessel should be considered to determine if the use of flash distillation could meet the current project's weight and volume limitations. Although specific flash vessel sizing guidelines for the nitrogen/oxygen system could not be found, application of a general flash vessel sizing procedure (Wankat 1988, 68-73) indicates that the volume of a single vertical flash vessel operating with a stage cut of 0.5, a pressure of 0.68 atmospheres, and a feed rate of 100 lbs/s would exceed 600 ft³. Considering that the project volume limitation is only 50 ft³, it would appear that the use of a flash distillation cascade would not be feasible for air separation in hypersonic flight.

Partial Condensation

The process of partial condensation involves passing a vapor stream through a condenser in which a portion of the feed is liquefied. The operation is carried out such that the liquid that is produced is in equilibrium with the uncondensed vapor (Robinson and Gilliland 1950, 115-116). Using a combination of equations 8.4 and 8.5 and the

