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Membrane Separation Processes at Low Temperatures

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Abstract

The primary focus of Kennedy Space Center's gas separation activities has been for carbon dioxide, nitrogen, and argon used in oxygen production technologies for Martian *in-situ* resource utilization (ISRU) projects. Recently, these studies were expanded to include oxygen for regenerative life support systems. Since commercial membrane systems have been developed for separation of carbon dioxide, nitrogen, and oxygen, initially the studies focused on these membrane systems, but at lower operating temperatures and pressures. Current investigations are examining immobilized liquids and solid sorbents that have the potential for higher selectivity and lower operating temperatures.

The gas separation studies reported here use hollow fiber membranes to separate carbon dioxide, nitrogen, and argon in the temperature range from 230 to 300K. Four commercial membrane materials were used to obtain data at low feed and permeate pressures. These data were used with a commercial solution-diffusion modeling tool to design a system to prepare a buffer gas from the byproduct of a process to capture Martian carbon dioxide. The system was designed to operate at 230K with a production rate 0.1 sLpm; Feed composition 30% CO_2, 44% N_2, and 26% Ar; Feed pressure 104 kPa (780); and Permeate pressure 1 kPa (6 torr); Product concentration 600 ppm CO_2.

This new system was compared with a similar system designed to operate at ambient temperatures (298K). The systems described above, along with data, test apparatus, and models are presented.

Introduction

The use of *in-situ* resources for exploration beyond low-earth-orbit (LEO) is considered to be a major enabling resource. The trade between the added mission complexity and risk versus reduction of power and weight has been and continues to be discussed. These discussions have led to numerous studies that have sought to optimize the use of *in-situ* resources, while lowering the mission risk. This paper addresses a study designed to maximize the use of gases captured from the Martian atmosphere for propellant production and buffer gases to blend with oxygen for manned missions, tank purges, and interlocks.

On Mars production propellant can be accomplished by using carbon dioxide captured from the Martian atmosphere, with hydrogen brought from earth. The primary options proposed for this task are adsorption and freezing. Both methods must deal with the minor Martian atmospheric components, argon and nitrogen, which quickly retard the capture process. Essentially, the initial step of either the adsorption or freezing process is pressure driven by the reduced pressure created over the capture bed, but this condition rapidly changes as argon and nitrogen fill the volume around the capture point. When the volume is full of argon and nitrogen and the pressure in the capture volume equals the ambient pressure, then the rapid capture of carbon dioxide stops. At this point the capture of carbon dioxide becomes diffusion driven. Therefore, to rapidly capture carbon dioxide the argon and nitrogen must be actively removed from the volume around the capture bed. One way to remove the gases (argon, nitrogen, and carbon dioxide) that blocks the capture bed is to use a small compressor. A buffer gas can be prepared by reducing the carbon dioxide concentration in gases removed from the capture bed below 600 ppm. Other fractions with higher concentrations of carbon dioxide could be used for purges gases, while even higher concentrations of carbon dioxide could be returned to the capture bed.

The work reported here describes the experimental procedures used to measure the relative permeabilities of carbon dioxide, nitrogen, and argon at temperatures from 230 to 300 K. These studies included both pure gases and mixtures of all 3 gases. The data generated was used to develop a separation system for a typical mixture that might be removed from a capture bed.

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*Senior Chemist, NASA KSC: Non-member AIAA was used to develop a separation system for a typical mixture that might be removed from a capture bed.

Experimental Procedures

The experimental procedures used in this investigation have involved the control of the pressure drop across the membrane, control and measurement of the gas flow to the membrane, and measurement of the gas composition. A testbed was designed that combined the gas composition control, pressure control, flow control, temperature control, and composition analysis.

Testbed

The testbed, which is illustrated in Figure 1, provided a method to control the composition, pressure of the feed and permeate, and temperature of the membrane. Wet meters with thermometers were use to measure the volume of permeate and raffinate gas flows. Sample points (S) were located after the mass flow controllers (MFC), and after the pumps to measure composition of the gas streams. The pressure (P) of the feed, permeate and raffinate gases were measured with pressure transducers. The pressures of the feed (raffinate) and permeate were controlled with pressure controllers (PC). The temperature (T) of the feed, permeate, and raffinate flows were controlled by a refrigerated cooling bath. All mass flow controllers, pressure transducers, wet test meters, and pressure controllers were calibrated in the KSC NASA calibration laboratory. Samples taken at the sample points were analyzed by gas chromatography (GC).

The testbed was designed so redundant measurements could be made to provide check on the quality of the data. For example, the total gas flow could be determined from the output of the mass flow controllers and that value could be compared with the total gas volume measured by the wet test meters. Similar comparisons could be made with the compositions of the permeate and raffinate streams, where the total amount of each gas added to the system could be compared to the sum of each component as measured by the GC.

Control of the membrane temperature was a major concern, since the membranes and their housing were constructed of polymeric materials that are thermal insulators. To overcome heat transfer problems, a copper coil was added to cool the feed gas stream and bring it to the same temperature as the membrane. Thermocouples positioned in the gas streams at the exits for the permeate and raffinate gases, provided a good measure of the gas temperatures. The temperatures of the feed gases before and after the copper coil were significant, but there was little difference between the feed gas temperature and the temperatures of the exiting gases. Therefore, only two measurements of the gas temperatures were made. The only other gas temperature that was important to this study was the temperature of the wet test meters. The wet test meters were equipped with thermometer wells, so the temperature of the exiting gas could be measured. In addition, pressure-drops due to the wet test meters and membranes were tested and found to be

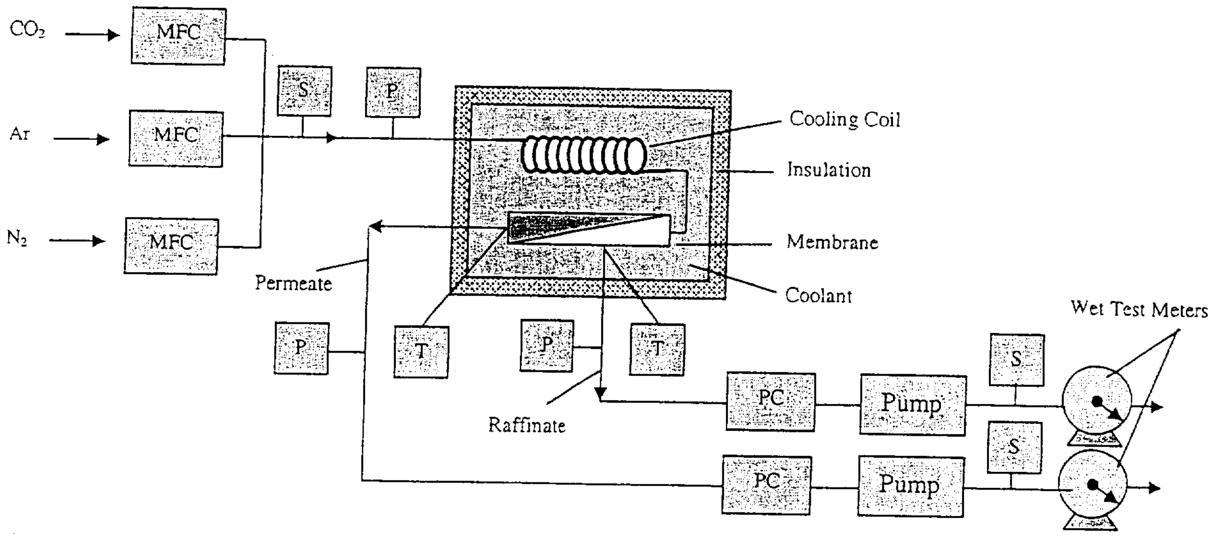


Figure 1. Test bed used to measure the permeate and raffinate flow rates through the membranes at various temperatures, pressures, and compositions

negligible. Since the wet test meters discharge the gases at ambient pressures and the pressure-drops across the meter were negligible, it was possible to use the measured values and calculate the gas flow rates at standard conditions of temperature and pressure (STP). The standard conditions used in this paper for temperature was 273 K and 101.3 kPa (1 atmosphere) pressure.

GC Analysis

Samples were taken at the indicated points (S) in Figure 1 by diverting the flow at that point through a sample loop of known volume on the GC. This sample was then automatically diverted to the GC column for analysis. The GC used for these measurements was manufactured by Quadrex Corporation and used 2 columns for the separation of carbon dioxide, nitrogen, and argon. A thermoconductivity detector was used for the composition analysis. The system was calibrated with several mixtures of known composition. Typical calibration curves used 4 to 5 compositions and the results from 3 injects for each composition were averaged, then plotted. The equation of the resulting line was used for subsequent analysis of samples collected. The procedure followed for analysis of the feed, permeate, and raffinate samples was to make 3 injections, then average the resulting area count. This area count was then used in the calibration equation to calculate the composition. All of the gas measurements were reduced to STP conditions.

Test Procedure

A set procedure was followed to help overcome variations in the test conditions. The procedures followed are listed below:

1. Set the composition of the gases to be measured into the mass flow controllers. Use the proper correction factors.
2. Once steady flow is established from the mass flow controllers, measure the composition of the feed gas stream with the GC. Capture two additional samples and inject them into the GC to confirm the composition.
3. Establish flow through the membrane system, and take several wet test meter readings until the flows are stable. Once the flow is stable, measure the composition of the feed gas 3 times.
4. Check the temperature of the permeate and raffinate gases, then record them once they are stable.
5. Measure the composition of the permeate and raffinate gas stream on the GC. Take 3 samples for the GC measurements.
6. Once the composition measurements are constant, start recording the volume of gas that flows through the wet test meters. Take 3 measurements of the volume flow per minute and note the temperature of the water in the wet test meter.
7. Record all data including the membrane type and model number; barometric pressure; temperature of the permeate, raffinate, wet test meters, and cooling bath; mass flow rates for the test gases; GC analysis of the feed, permeate, and raffinate; and pressures of the feed, permeate, and raffinate gas streams.

The temperatures and pressures were varied, but limited to the structural properties of the membranes and their housings. The results of these tests are summarized in the following section.

Results

The raw volumetric data obtained during this study were converted to STP conditions. Gas compositions obtained from GC analysis were expressed as mole percent of the sample, which is the same as volume percent under ideal conditions. The volume flux (j_i expressed as $cm^3/cm^2 \cdot s$ or cm/s) and the pressure-normalized flux [$j_i/(p_{io}-p_{il})$ expressed as $cm^3/(cm^2 \cdot s \cdot cm\ Hg)$] were used to compare the relative permeabilities of carbon dioxide, argon and nitrogen in the membranes tested. The pressure-normalized flux can be expressed in gas permeation units (GPU), which is 10^{-6} $cm^3/(cm^2 \cdot s \cdot cm\ Hg)$. The membrane selectivity, α_{ij} for 2 gases i and j, is the ratio of their permeabilities, $\mathcal{P}_i$ and $\mathcal{P}_j$. The actual permeability values for these gases and membranes were not calculated, because the membrane thicknesses were not known. However, the membrane thickness information was not needed to obtain relative permeability information, which could be used to calculate α, the membrane selectivity.

Permea Membrane

Air Products manufactures brominated polysulfone membranes under the trade name Permea Prism® Alpha Separators that were designed to separate hydrogen from nitrogen in ammonia plants (1). The new commercial hollow-fine-fiber membranes produced today have higher selectivity than those produced just 10 years ago (1).

Based on commercial experience, the Permea PPA-20, Prism® Alpha Separator was selected as the first

Determination of the pressure-normalized flux at various temperatures is determined by plotting the permeate flow rate versus pressure drop across the membrane. Data like that plotted in Figure 2 was generated for several temperatures over a range of pressures for each of the gases used in this study carbon dioxide, argon, and nitrogen.

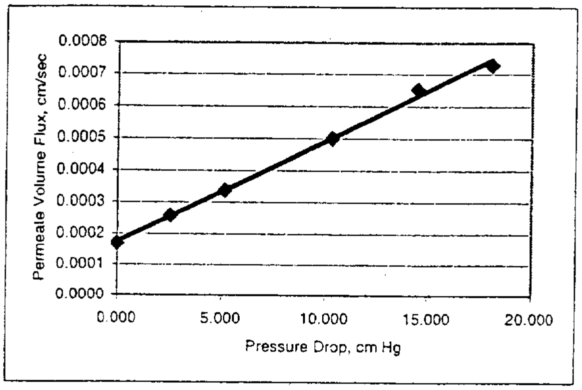


Figure 2. Volume flux versus pressure drop at 10.3° C for argon with the Permea PPA-20 membrane

The slope of the line is $j_i/(p_{io}-p_{il})$, the pressure-normalized flux, which can be expressed as GPUs at different temperatures. The slope of each line was determined from the linear trendline and the results summarized in Table I.

Table I. GPUs for Carbon Dioxide, Argon, and Nitrogen at Various Temperatures

Temp °C	CO_2 GPU	Temp °C	N_2 GPU	Temp °C	Ar GPU
22	163	19.1	32.6	10.3	31.6
10	128	9.6	33.0	0.5	29.6
0	104	-0.2	34.1	-10.5	28.4
-10	103	-9.7	35.1	-14.6	28.3

From the data shown in Table I several interesting trends exist: (1) the GPU decrease with decreasing temperature for carbon dioxide and argon, but increases for nitrogen, (2) the selectivity for carbon dioxide to nitrogen and for carbon dioxide to argon decreases with decreasing temperature, increases for nitrogen to argon. These results from Table I are plotted to illustrate the trends in the data in Figures 3, 4, and 5.

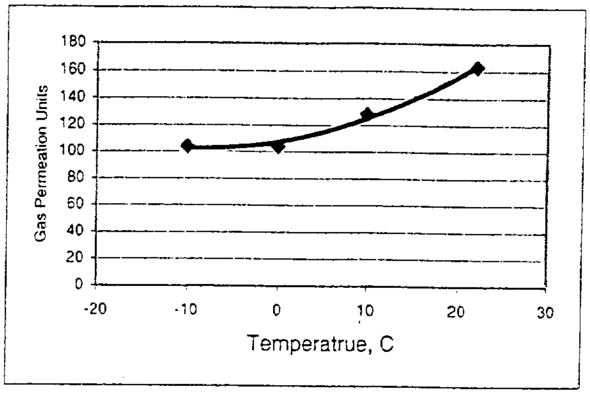


Figure 3. Gas permeation units versus temperature for carbon dioxide with the Permea PPA-20 membrane

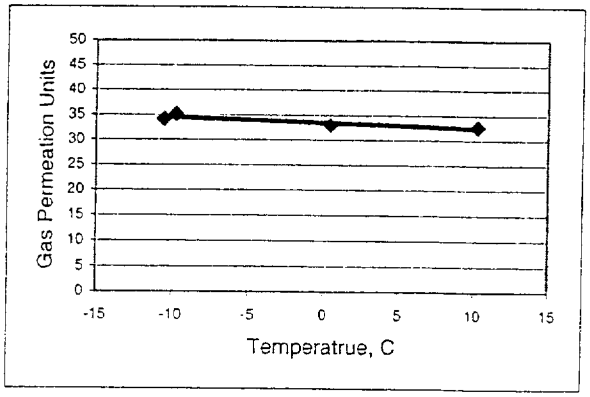


Figure 4. Gas permeation units versus temperature for argon with the Permea PPA-20 membrane

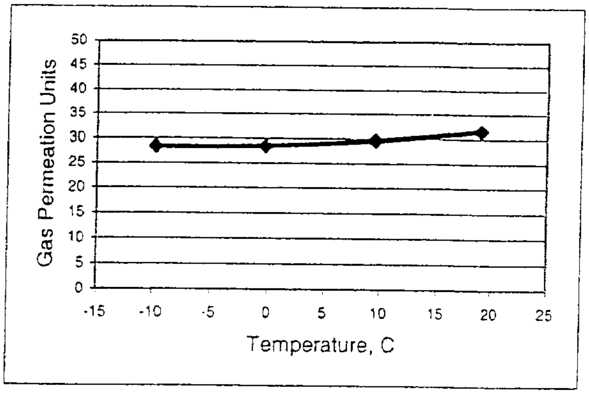


Figure 5. Gas permeation units versus temperature for nitrogen with the Permea PPA-20 membrane

The behavior of gas mixtures on the Permea PPA-20 membrane is illustrated in Figures 6 and 7. In Figure 6 the normalized permeate flow rate in STP cm^3/sec versus the pressure drop across the membrane expressed as cm of Hg at 19.2° C and -12° C is plotted.

These data indicate that all three gases (CO_2, N_2, and Ar) increase the permeate flow with temperature and pressure drop.

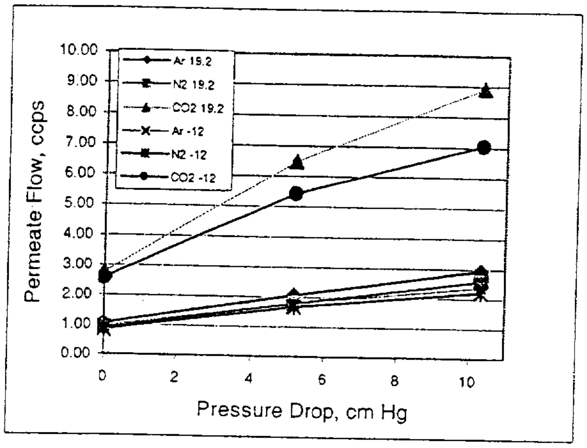


Figure 6. Permeate flow rate versus pressure drop is illustrated for CO_2, N_2, and Ar at 19.2° C and -12° C.

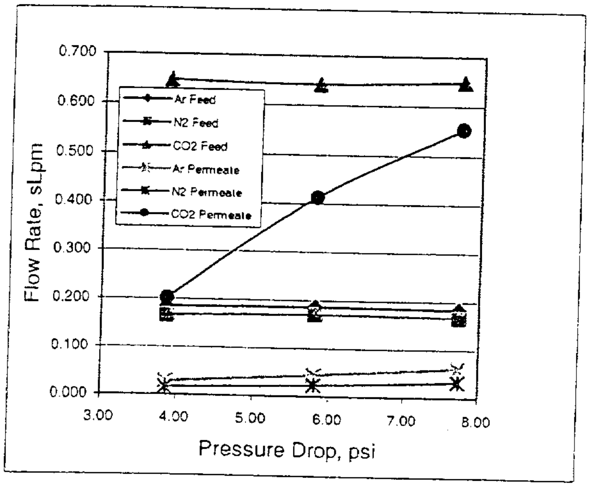


Figure 7. Permeate and feed flow rates versus pressure drop at –0.8° C for CO_2, N_2, and Ar

The data illustrated in Figure 7 confirms that the feed flow rate concentration is constant, while the permeate flow rate increases for all gases, but is greatest for carbon dioxide. The increase in the permeation of N_2 with decreasing temperature does not hold when all three gases are present. Again, the changes in the permeation rate with temperature and composition indicate that a complex mechanism is operating.

Neomecs Membrane

The Neomecs model GT #020101, a high-flow membrane with a 929-cm2 area used in the first stage of the room temperature model is discussed later. The pressure-normalized flux was determined by the same method used for the Permea membrane. Figure 8 shows a representative example of the Neomecs data where the volume flux ($cm^3/cm^2 \cdot sec$ or cm/sec) is plotted against the pressure drop (cm Hg). The slope of this line is the pressure-normalized flux, which can be expressed in GPUs.

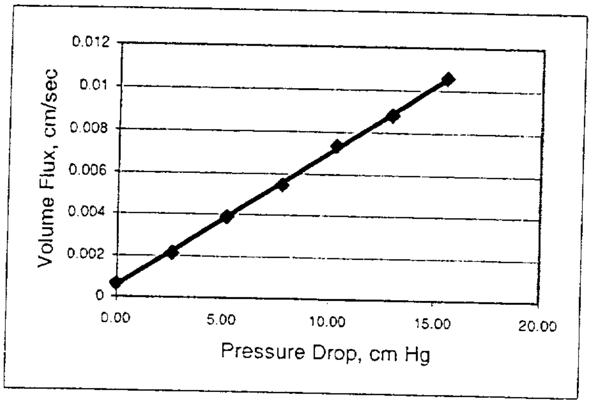


Figure 8. Volume flux versus pressure drop at 19° C for carbon dioxide

Table II summarizes the permeation data for the Neomecs membrane at various temperatures. The results are presented in GPUs for carbon dioxide, nitrogen, and argon.

Table II. GPUs for Carbon Dioxide, Argon, and Nitrogen at Various Temperatures

Temp °C	CO_2 GPU	Temp °C	N_2 GPU	Temp °C	Ar GPU
18.8	644	28	315	28	482
15.2	720	10	259	10	355
10.3	833	-14	190	-3	218
-0.3	1175	-16	200	-9	148
		-17	166	-15	196
		-27	253	-24	170
		-34	231	-30	173
		-38	201	-35	224
		-39	268	-38	195
		-43	233		

There are several interesting trends in the data for the Neomecs membrane. First, all gases permeate faster through this membrane than they did through the Permea membrane. Second, the permeation rate increases with decreasing temperature for carbon dioxide and argon. Third, there is very little change in the GPUs with temperature for nitrogen. To better see these trends the GPU verses temperature is plotted for carbon dioxide, nitrogen, and argon in Figures 9, 10, and 11.

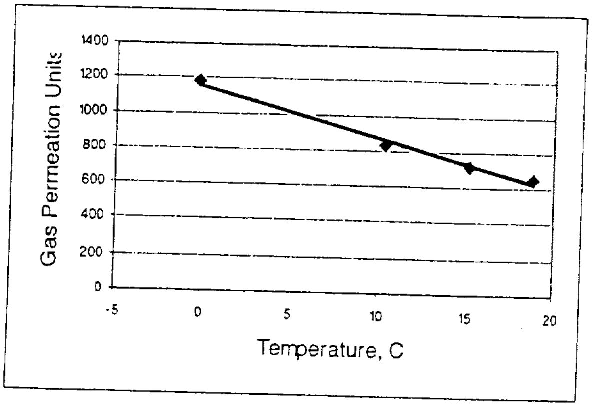


Figure 9. Gas permeation units versus temperature for carbon dioxide with the Neomecs membrane

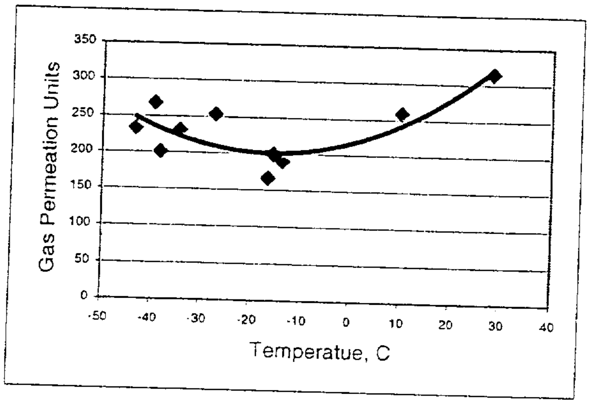


Figure 10. Gas permeation units versus temperature for nitrogen with the Neomecs membrane

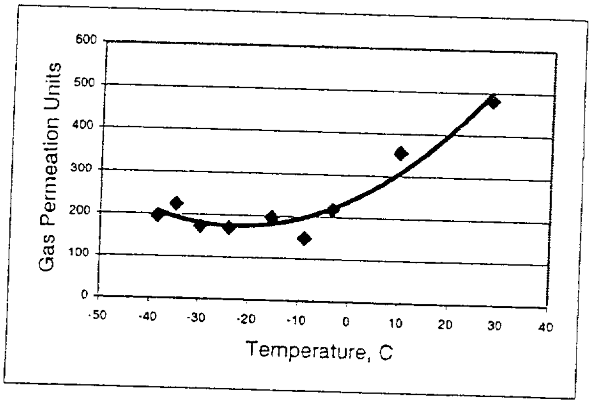


Figure 11. Gas permeation units versus temperature for argon with the Neomecs membrane

The selectivity for the Neomecs membrane is lower than the selectivity for the same gases with the Permea membrane, but the rate is higher. In addition, the permeation rate appears to pass through a minimum with decreasing temperature for nitrogen and nitrogen. These changes indicate that there may be a change in the mechanism of the diffusion process and this change probably applies to carbon dioxide, since the permeation rate is increasing with decreasing temperature.

Enerfex SS Membrane

Enerfex built a small hollow-fiber system that was housed in a stainless steel shell. This system had a membrane surface area of 45 cm^2 and was designed for a 0.25 sLpm feed rate with a 13 psig feed pressure for 100 percent nitrogen.

This membrane system was tested in the same manner as the previous membranes, except at a lower total feed rate. Figure 12 shows a typical plot of the volume flux versus pressure drop, which was the procedure followed to calculate the GPUs for carbon dioxide, nitrogen, and argon.

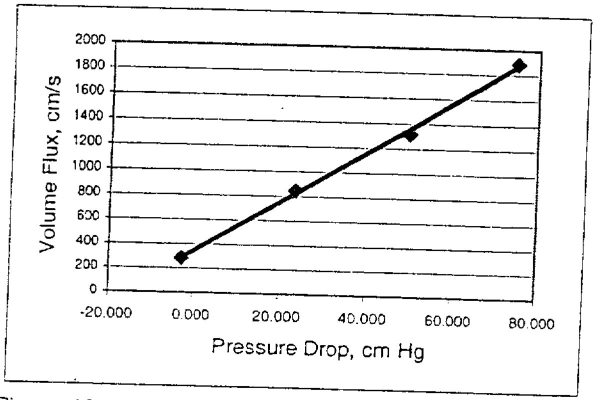


Figure 12. Volume flux versus pressure drop at 22° C for carbon dioxide with the Enerfex SS membrane

The GPUs were determined for carbon dioxide, nitrogen, and argon and tabulated in Table III.

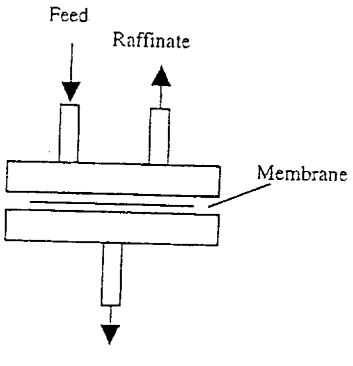
Table III. GPUs for Carbon Dioxide, Nitrogen, and Argon for the Enerfex SS Membrane at Various Temperatures

Temp ° C	CO_2 GPU	Temp ° C	N_2 GPU	Temp ° C	Ar GPU
22	20.4	17	2.41	17	4.52
8	19.7	8	4.20	8	4.15
1.5	23.32	-1.5	3.53	-1.5	12.6

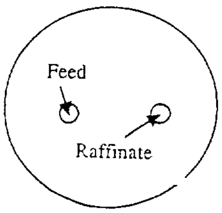
This membrane had good selectivity for all 3 gases at ambient temperatures, but the selectivity decreased significantly for argon versus carbon dioxide. However, it has potential to separate argon and nitrogen at -1.5° C.

SSP-M100C Membrane

This membrane was supplied as a flat sheet and was supported for the test in a 3-inch diameter stainless steel filter housing. The housing was configured so the permeate flowed across the membrane while the raffinate exited on the same side as the feed. This test fixture is illustrated in Figure 13. The housing has a sealing bead, which make a leak-free seal when the two halves are bolted together. The tubing studs were ¼ inch OD, which made it connections to the testbed shown in Figure 1. Once connected, this system was submerged in the cold bath for testing.



Side View



Top View

Figure 13. Test hardware used to support flat sheet membrane material

The SSP-M100C membrane had a 14.8 cm^2 surface area, which is smaller than the other membranes tested in this study. Since the driving force for flow across the membrane is the partial pressure of the permeating component, the flow across a flat sheet would give a constant gradient, while the hollow-fiber membranes have counter flow. This is a major difference between a flat-sheet membrane and a hollow-fiber membrane system. Therefore, it will be difficult to compare the performance of the 2 systems, but the behavior with respect to temperature and selectivity will be helpful.

To determine the performance of the flat-sheet membrane the same test procedures were use. Figure 14 shows a plot of the volume flux versus pressure drop and, as before, this plot is only a representative example of the data. Similar plots were made for all of the test conditions and the slope of the lines were used to calculate the GPUs of this membrane.

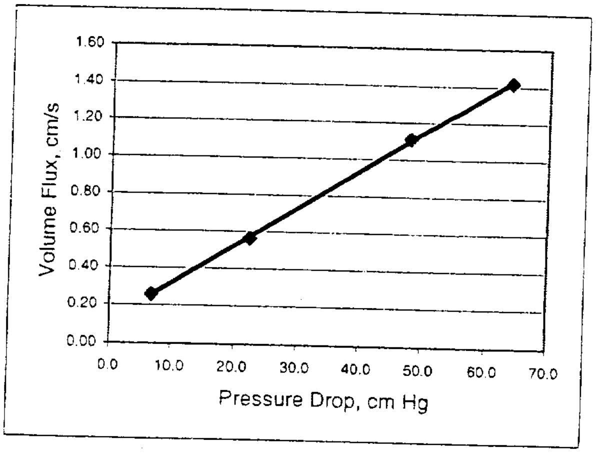


Figure 14. Volume flux versus pressure drop at -19.9° C for carbon dioxide

As with the other membrane systems, plots of the volume flux versus pressure drop showed a good linear fit. The GPUs for the SSP-M100C membrane is tabulated in Table IV.

Table IV. GPUs for Carbon Dioxide, Argon, and Nitrogen for the SSP-M100C Membrane at Various Temperatures

Temp °C	CO_2 GPU	Temp °C	N_2 GPU	Temp °C	Ar GPU
20	19299	18.4	8600	18.5	11623
-0.9	19483	-1.6	8333	-1.6	9634
-19.9	20565	-20.7	8684	-20.7	24199
-25.7	20948				

The data in Table IV show the high permeability of the SSP-M100C membrane for each of the gases studied. However, the selectivity for carbon dioxide is less than the values for the other membrane materials. The only interesting area is the selectivity shown for argon over nitrogen at -20.7° C.

Design of Membrane Separation Systems

Design of a membrane separation system was the primary objective of these studies. The plan focused first on commercial membrane systems that could separate argon and nitrogen from carbon dioxide. We were fully aware of the previous work and the large body of data for gas separations at ambient (298K) and above. However, little data exist at low temperatures.

The primary objective was to develop a simple low-power system that could be used in the Martian atmosphere to capture argon and nitrogen for breathing air, tank purges, and habitat interlocks. One objective was to assess the impact low temperatures on the selectivity commercial membranes with the thought that some system might be more selective at low temperatures.

One membrane (Permea) was selected for the design of a system that could remove carbon dioxide from a mixture of argon and nitrogen. The design conditions are listed below:

1. Initial mixture: 30% CO_2, 26% Ar, 40% N_2
2. Initial temperature: -44° C
3. Initial pressure: 780 mm Hg
4. Final product: Ar/N_2 mixture with 600 ppm CO_2 maximum.
5. Production rate: 100 mL/min Ar/N_2 mixture

These test conditions were based on the production of 1.0 liters per minute of oxygen starting with carbon dioxide and assuming that carbon monoxide would be the other product. It was assumed that the pump that removed the initial gas mixture from the bed, where carbon dioxide was captured, would provide a gas stream at an initial pressure of 780 mm Hg.

The model that generated this design was based on solution and diffusion theory. The model was developed for commercial applications and it is proprietary.[4, 5, 6] Figure 15 shows the initial setup that might be used to capture the carbon dioxide and Figure 16 show the membrane setup.

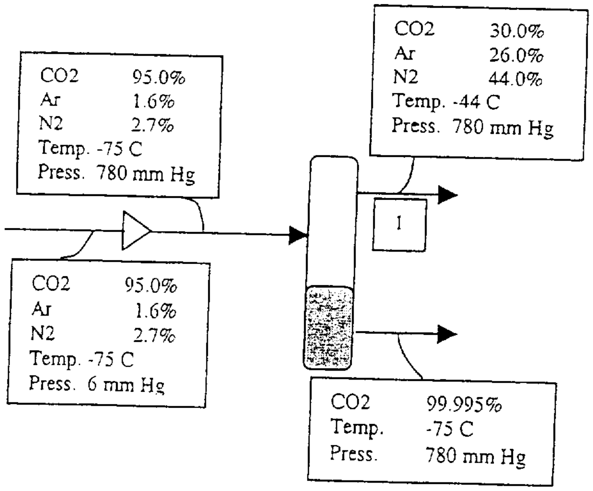


Figure 15. Capture of CO_2 from the Martian atmosphere and feed for the Ar/N_2 purification process

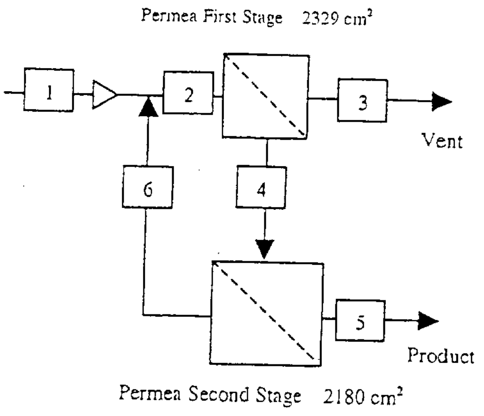


Figure 16. Membrane purification of feed from the capture of CO_2

The membrane design is based on 2 Permea membranes that have a surface area of 2329 and 2180 cm^2. The data that was collected for the mixed gases at –44° C was input to the Enerfex solution/diffusion model and it provided the performance data given in Table V. The stream numbers correspond to the numbers shown on the flow diagram, Figure 17.

Table V. Performance data generated by the Enerfex model

Stream	1	2	3	4	5	6
% CO_2	30.00	27.62	56.53	8.06	0.06	20.04
% Ar	26.00	26.90	15.84	34.37	37.72	29.37
% N_2	44.00	45.48	27.61	57.56	62.22	50.59
Liter/hr	12.77	16.78	6.77	1.01	6.00	4.01
mm Hg	780	6	775	775	6	770

From these results it can be seen that it is possible to separate the CO_2 from argon and nitrogen with 2 membranes to give a final composition that contained only 600 ppm CO_2. The yield of the final product was approximately 47 percent, which means that half of the initial feed stream was purified and suitable for use as a buffer gas.

The initial modeling was done at ambient temperatures based on 15° C and 25° C permeation data. The basic design of these systems is similar, see Figure 17 for the design of the capture system. The design of the separation system requires three membrane units: 2 Permea and 1 Neomecs units, see Figure 18. It was assumed that the feed gas from the capture of CO_2 was at ambient temperatures when the gas went through the membrane system. This initial design was on a mixture of 28% carbon dioxide, 36% argon, and 36% nitrogen. The initial feed pressure was 780 mm Hg and the initial feed rate was 353.3 Liter/hr, see Table VI.

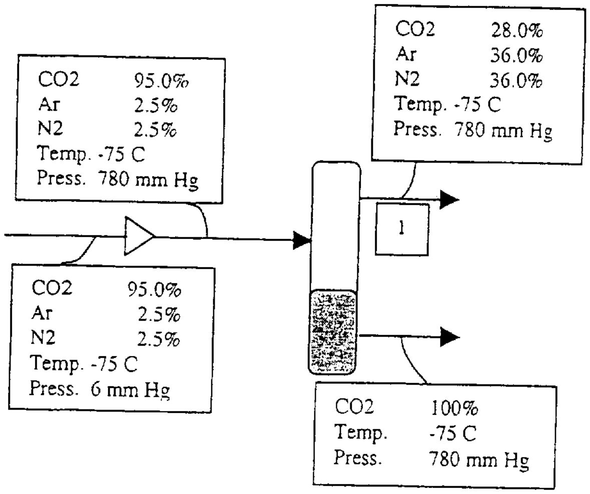


Figure 17. Capture of CO_2 from the Martian atmosphere and feed for the Ar/N_2 purification process

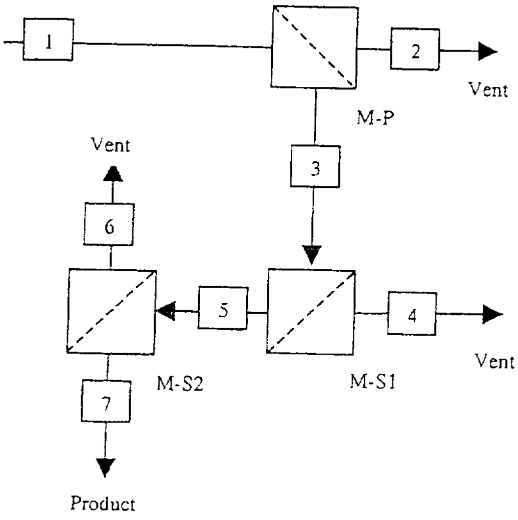


Figure 18. Membrane purification of feed from the capture of CO_2

The 2 Permea membranes are designated M-S1 and M-S2 and the Neomecs membrane is designated M-P.
The results of this design are shown in Table VI where the composition, flow rate, and pressure are listed under the stream numbers.

Table VI. Performance data generated by the Enerfex model

Stream	1	2	3	4	5	6	7
% CO_2	28.0	47.2	7.4	37.6	0.9	6.2	0.1
% Ar	36.0	33.1	39.2	21.4	43.0	33.1	44.4
% N_2	36.0	19.7	53.4	41.0	56.1	60.7	55.5
Liter/hr	353	183	170	30.3	140	17.1	123
mm Hg	780	7	775	7	770	7	765

The results from the ambient design has required 3 membranes to achieve a final product with 1000 ppm carbon dioxide, while the modeling with the low temperature data only required 2 membranes. The percent recovery of useful product was 37 percent for the ambient system, while the recovery was 47 percent at with the low temperature data.

Summary

This study has provided useful information about the low temperature performance of commercial membranes with an improvement in performance based on the permeation characteristics at low temperatures. A design for membrane separation system that could handle the Martian requirement for a buffer gas has been completed. Some unusual trends in the permeation rates at low were observed, which indicated that there was an increase in the permeability for pure gases under some conditions.

Additional reduction of the system weigh and power could be realized by using membranes with higher selectivity and permeability, such as, those based on immobilized liquids $^{(7, 8)}$, microencapsulated liquid membranes $^{(9)}$, or zeolites $^{(10)}$. Membrane systems such as those listed above need to be examined at low temperatures to see if the can provide simple reliable systems with improved performance.

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