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Gas Separations Using Inorganic Membranes

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FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Chemical Technology Division

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This report summarizes the results from a research and development program to develop, fabricate, and evaluate inorganic membranes for separating gases at high temperatures and pressures in hostile process environments encountered in fossil energy conversion processes such as coal gasification. The primary emphasis of the research was on the separation and recovery of hydrogen from synthesis gas. Major aspects of the program included assessment of the worldwide research and development activity related to gas separations using inorganic membranes, identification and selection of candidate membrane materials, fabrication and characterization of membranes using porous membrane technology developed at the Oak Ridge K-25 Site, and evaluation of the separations capability of the fabricated membranes in terms of permeabilities and fluxes of gases.

Porous, tubular alumina membranes with a diameter of ~9 mm and a wall thickness of ~0.5 mm, having pore radii ranging from <10 Å to >150 Å, have been fabricated and tested. These membranes are capable of withstanding >600 psi (4 MPa) pressure and operating at temperatures up to 1000°F.

The permeabilities of pure gases, including He, N_2, CO_2, and SF_6, and the separation of gas mixtures containing H_2, CO, CO_2, N_2, and CH_4 were measured over a range of pressures and temperatures. The primary mechanism of gas transport across the membranes appears to be Knudsen diffusion. When the membranes were tested for separating gas mixtures, the permeate gas was enriched in hydrogen, primarily at the expense of carbon dioxide.

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1. INTRODUCTION

This report summarizes the results from a research and development program to develop, fabricate, and evaluate inorganic membranes for separating gases at high temperatures and pressures in hostile process environments encountered in fossil energy conversion processes such as coal gasification. The primary emphasis of the research was on the separation and recovery of hydrogen from synthesis gas. Major aspects of the program included assessment of the worldwide research and development (R&D) activity related to gas separations using inorganic membranes, identification and selection of candidate membrane materials, fabrication and characterization of membranes using porous membrane technology developed at the Oak Ridge K-25 Site, and evaluation of the separations capability of the fabricated membranes in terms of permeabilities and fluxes of gases.

2. BACKGROUND

2.1 COAL GASIFICATION

Hydrogen is an important and valuable raw material that has numerous uses in the chemical and fuel industries. Synthesis gas produced in coal gasification is primarily H_2 and CO, but may also contain N_2, CO_2, H_2S, H_2O, aliphatic hydrocarbons, and other gases, depending on the particular gasification process. Isolating the H_2 from the other gases requires low-temperature operations, such as solvent extraction, pressure-swing adsorption (at 40 to 100°F) or cryogenic separation. If technology could be developed to separate the hydrogen from the raw gas at high temperatures, it would significantly lower the cost of hydrogen production.

Commercially, at present, bulk removal of acid gases from raw process gas, such as synthesis gas containing hydrogen, is carried out by using solvent scrubbing processes like methyldiethanolamine (MDEA), Selexol, and Rectisol. Although solvent scrubbing processes can be designed to operate at temperatures up to 450°F (e.g., the Benfield and Catacarb processes), most commercial acid gas removal processes operate at temperatures below 200°F. Consequently, the gases are cooled to near room temperature during cleanup and separation. Research is being conducted to develop acid gas removal processes, such as the zinc ferrite process, capable of operating at temperatures up to 1200°F. The proposed membrane separation process would operate at conditions closer to the exit gas conditions from typical entrained flow gasifiers than the presently known processes. Satisfactory operations under these adverse operating conditions would significantly improve coal conversion process efficiencies.

Figure 1(A) is a simplified block flow diagram of a typical integrated, entrained-bed coal gasification-combined cycle (IGCC) process. Present technology requires cooling theproduct gases from ~1500°F to ~100°F to permit removal of carbon dioxide, hydrogen sulfide, and other contaminant gases. The cleaned fuel gas (CO-H_2) must then be reheated to 500 to 600°F for downstream combustion in a gas turbine to generate power. The efficiency of the process would be increased substantially if the hydrogen and carbon monoxide could be recovered at the higher downstream operating temperature. A block flow diagram for a conceptual membrane gas separation system for this application is shown in Fig. 1(B). Briefly stated, the gas cooling and the gas cleanup system would be replaced with a membrane separation system operating at high temperature.

An alternative conceptual process might include a shift reactor to convert the carbon monoxide to hydrogen and increase the hydrogen yield. The hydrogen would then be separated using a membrane separation process (Fig. 2). This would simplify the gas separation problem while allowing the recovery of the carbon monoxide energy value.

2.2 MEMBRANE TECHNOLOGY

Significant advances in the field of membrane technology have occurred during the last few years.[1] Recent developments in this area have led to major improvements in both performance and economics in gas processing applications. The development of membranes with high selectivity and flux capabilities has led to the commercial-scale use of membranes to separate gaseous components from gas mixtures. For example, modular membrane separation systems are now commercially available for hydrogen purification and recovery in ammonia plants, manufacture of oxygen-enriched air, sweetening of sour natural gas, and recovery of carbon dioxide from wellhead gas in enhanced oil recovery operations.[2-7]

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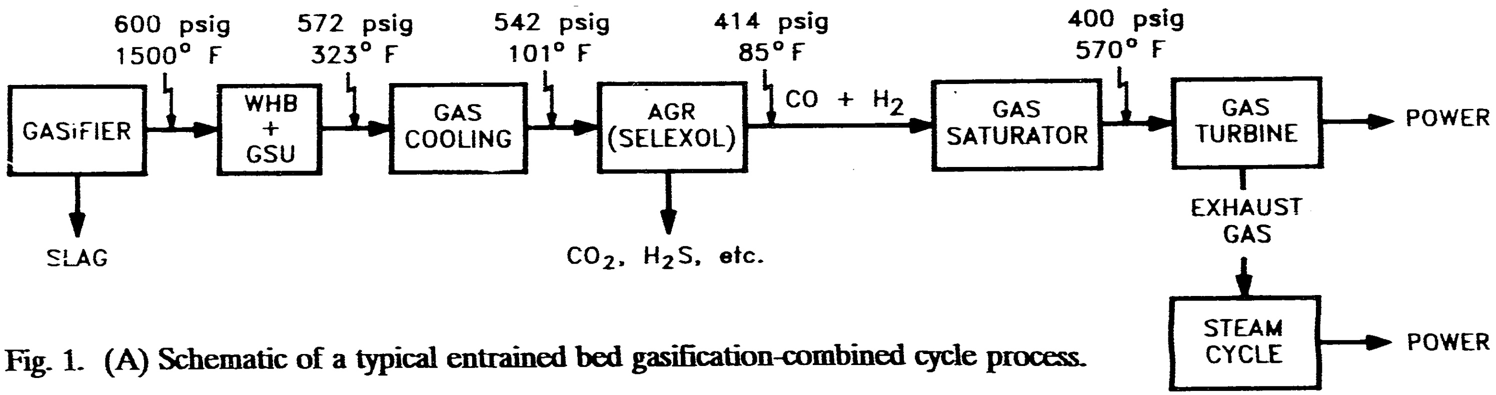
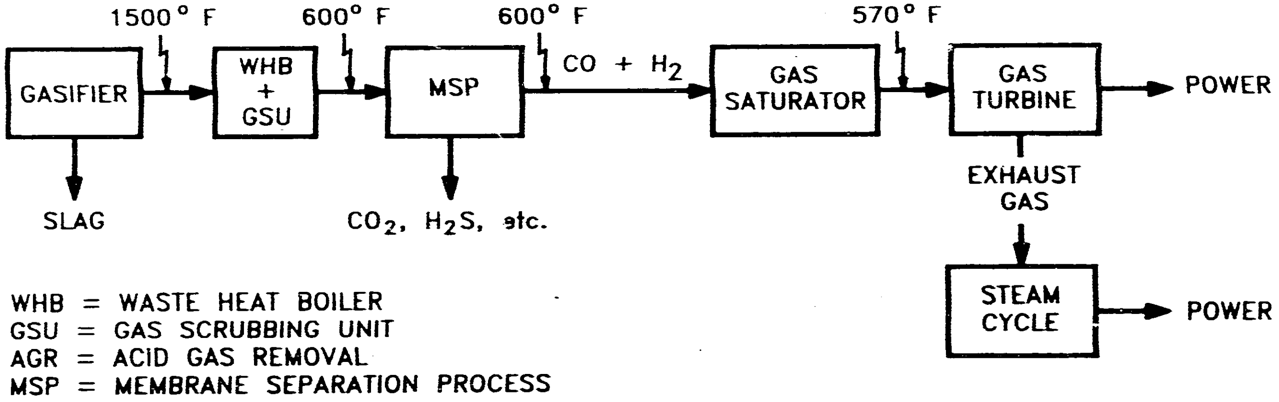


Fig. 1. (A) Schematic of a typical entrained bed gasification-combined cycle process.



WHB = WASTE HEAT BOILER
GSU = GAS SCRUBBING UNIT
AGR = ACID GAS REMOVAL
MSP = MEMBRANE SEPARATION PROCESS

(B) Schematic of a conceptual process using a membrane gas separation system.

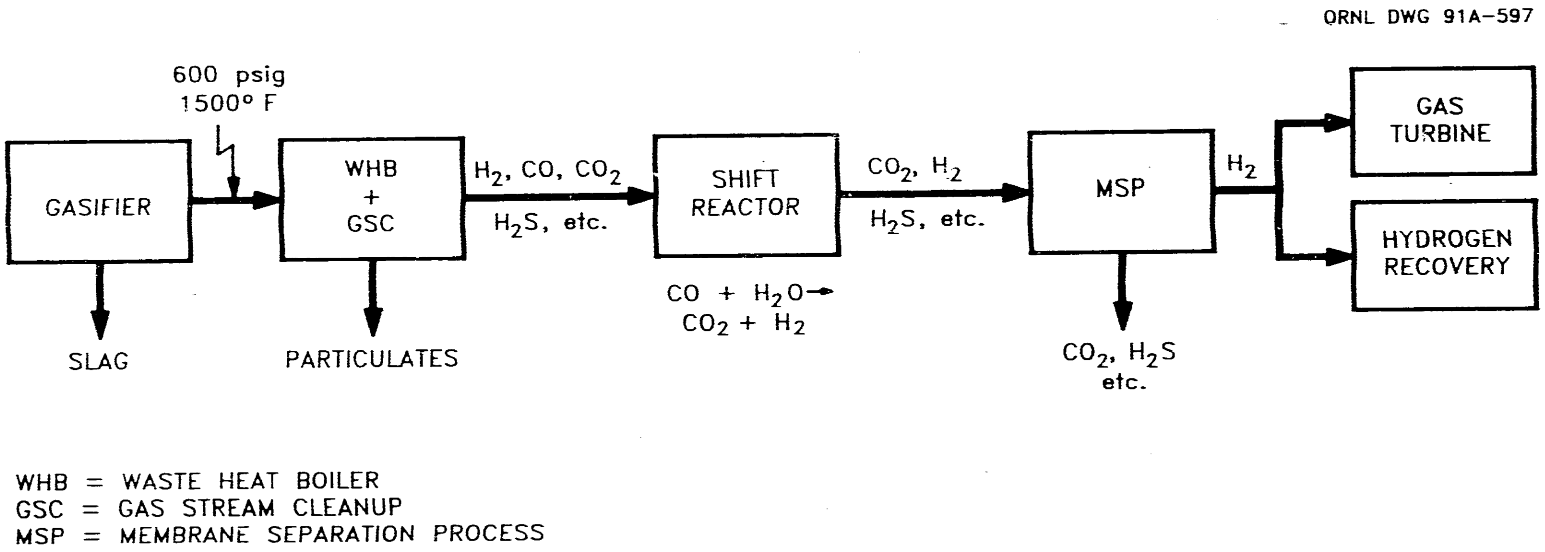


Fig. 2. Conceptual process for hydrogen separation from coal gasification gases.

However, the membranes used in these systems are thin film composites of polymeric organic materials, which have limited thermal stability and are susceptible to abrasion and chemical attack in harsh environments. Therefore, these membranes have not found applications in separation processes where hot, reactive gases are encountered. Inorganic membranes could potentially be used in such hostile environments.

Until recently, inorganic membranes have been used primarily for microfiltration and ultrafiltration. Although the permeability of several gases in various inorganic materials has been studied, there has been no large-scale application of inorganic membrane separations of gases except for uranium enrichment. Gas permeabilities of metals such as W, Mo, Fe, Cu, Ni, Ag, and Pd, and alloys of these metals have been studied.[8] Ceramics and porous metals have also been tested as supports for deposition of metal films of V and Al, and for membrane coatings of ZrO_2, NiO, and TiO_2. Inorganic polymeric membranes, such as polyphosphazenes and organic-inorganic membranes containing heteropoly acids and salts, have also been prepared.[9-11]

2.3 GAS TRANSPORT MECHANISMS

The major types of gas transport through porous membranes are viscous flow, free-molecule or Knudsen flow, surface diffusion, capillary condensation, molecular sieving, and ion exchange. If the pores are much larger than the mean free path of the gas molecules, then viscous flow predominates and no significant gas separation occurs. If the pores are much smaller than the mean free path of the gas molecules, then Knudsen or free-molecule diffusion occurs, and the separation factor for binary gas mixtures can be estimated from the square root of the ratio of molecular weights; the lower molecular weight molecules with a higher velocity move through the pores faster. As the pore size approaches the size of a gas molecule, molecular sieving or screening can occur. If the membrane has pore sizes between the diameters of the smaller and larger molecules, then only the smaller molecule can permeate, and the separation factor approaches infinity. Gas adsorption on the surface of the pore wall may result in surface flow or surface diffusion, and it also effectively decreases the pore size. Capillary condensation occurs when the pore becomes filled or partially filled with a condensed phase; then condensate flow and/or vaporization of the condensate may affect the apparent gas flow or flux through the membrane. Other gas transport mechanisms such as ion exchange, solution diffusion, and solid diffusion involve interaction between gases and the membrane.

2.4 RELATED MEMBRANE RESEARCH

Inorganic membranes are being investigated worldwide for separating gases on a laboratory scale.[12] Membrane materials include porous metals, glass, and ceramics.

Metals, particularly palladium and palladium alloys, have been used to separate hydrogen isotopes from each other and hydrogen from various other gases.[13] The separation of hydrogen from gases such as CO_2, N_2, H_2S, CO, and CH_4 with porous glass membranes has been demonstrated at the laboratory scale.[14-16] Metallic oxides, porous glass, and ceramics have been used to separate a large variety of gases; many involve the separation of hydrogen from other gases. Alumina and silica are the most frequently used materials for metallic oxide membranes.[17, 18] Membrane preparation methods are based on sol-gel,[19] slipcasting,[20] anodic oxidation (metallic oxides),[21] and phase separation/leaching (porous glass)[22] techniques.

Metallic membranes have been used primarily for separating hydrogen isotopes and for separating hydrogen from other gases. Many of the studies are directed toward separating hydrogen, deuterium, and tritium isotopes. Frequently, palladium is alloyed with silver to improve the physical and mechanical properties of the membrane material.

The separation of several gases with porous glass membranes has been shown at the laboratory scale. Some of the gases that have been separated using porous glass membranes include H_2, He, Ar, N_2, O_2, CO_2, CO, and light hydrocarbons. Many of the applications of porous glass for gas separations have come from Japan.

The most frequently used materials for metallic oxide membranes are alumina and silica. Some membranes contain mixtures of these along with other oxides such as zirconia or titania. Alumina is also frequently used as the support for other membrane materials.[23] Most of the metallic oxide membranes are made by sol-gel/slipcasting or anodic oxidation techniques. Other preparation techniques include chemical vapor deposition, sputtering, precipitation/compaction, and phase leaching. Membranes with pore sizes ranging from several angstroms to nearly a micrometer have been prepared. The permeation behavior of several gases has been studied using alumina or alumina-containing membranes. These gases include H_2, N_2, CO_2, He, Ar, O_2, H_2S, SO_2, H_2O, alcohols, and light hydrocarbons.

The Department of Energy has supported programs at Alcoa, SRI International, CeraMem, Air Products, Oak Ridge National Laboratory, Oak Ridge K-25 Site, Idaho National Engineering Laboratory, and several universities to develop and test inorganic membranes for high-temperature gas separations.

Several universities have established membrane research centers or programs to carry out membrane R&D. Many have financial support from industry. Various aspects being addressed by these centers include: preparation and characterization of inorganic polymers, ceramics and metals; membrane applications; modeling and simulation; membrane reactor development; transport mechanisms; and membrane catalysis.

Research on ceramic membranes in Europe is concentrated at the Ecole Nationale Superieure de Chimie de Montpellier, Laboratoire de Physicochimie des Materiaux, in France, and at Twente University of Technology, Enschede, the Netherlands.

3. TECHNICAL APPROACH

Several porous inorganic materials that could be used as membranes are commercially available in disk, tube, and monolith form. Materials include metals, glass, and ceramics with pore sizes ranging from a few nanometers to several micrometers.[12] However, the minimum pore size is in the range of 30 to 40 Å. This limits their applicability primarily to filtration. While some gas separations can be achieved with these materials (primarily by Knudsen diffusion), it is generally accepted that smaller pore sizes or other membrane modifications will be needed for efficient gas separations. Of course, it is necessary to maintain high gas permeability while reducing the pore size. Generally, this means developing a very thin membrane.

Table 1 shows the effect of membrane pore diameter on the calculated separation factors for binary mixtures of hydrogen with N_2, CO_2, CO, and H_2S. At larger pore sizes, the primary transport mechanism is free-molecule or Knudsen flow, and the separation factor can be estimated from the square root of the ratio of the molecular weights of the gases. However, as the pore size decreases, some molecular screening can occur. At some point, if the membrane has no pores greater than the diameter of the larger gas molecule, then the membrane will not be permeable to the molecule and the separation factor will approach infinity. In practice, however, there will be a distribution of pore sizes and other transport mechanisms may be operative. Also, as the pore size decreases, the membrane porosity may

Table 1. Calculated separation factors based on molecular size with various pore diameter membranes

PORE DIAMETER (Å)	GAS PAIRS			
	H_2/N_2	H_2/CO	H_2/H_2S	H_2/CO_2
10000.00	3.73	3.73	4.11	4.67
100.00	3.81	3.80	4.21	4.82
12.00	4.77	4.62	5.36	6.71
10.00	5.14	4.92	5.81	7.51
8.00	5.90	5.54	6.74	9.27
7.00	6.68	6.16	7.73	11.30
6.00	8.33	7.42	9.84	16.18
5.00	13.6	11.2	17.0	38.7
4.00	126	59.4	237	8E+07

decrease, resulting in a lower gas flow through the membrane. So these two factors much be balanced before a practical, efficient membrane can be developed. Nevertheless, this illustrates the potential advantage of smaller pore sizes. Development of improved inorganic membranes with these properties could provide significant advantages for gas separations. Preliminary calculations were made to estimate the size of a conceptual commercial membrane separation unit to recover, for example, 90% of the hydrogen in a typical gas mixture produced in an entrained-bed coal gasifier. Assuming a very high separation factor for hydrogen relative to the other gases present in the raw synthesis gas, and based on a hydrogen permeability of 0.01 $cm^3 / cm^2 \cdot s \cdot (cm\ Hg)$, the calculation showed that to recover 1.8 kg-mol/s (~14,000 lb-mol/h) would require 1580 m^2 (~17,000 ft^2) of membrane surface area. This would translate into a membrane separation unit that is similar in design to a conventional shell-and-tube heat exchanger that is 3 m (10 ft) in diameter by 3.7 m (12 ft) long.

4. RESULTS

4.1 MEMBRANE FABRICATION

Several materials, such as alumina, zirconia, and titania, were identified as potential membrane materials. Both alumina and zirconia membranes were prepared. However, alumina was selected as the primary material for fabricating the membranes. The selection of alumina was based on several factors, including thermal and mechanical stability, chemical stability in the expected gas environment, and fabricability into appropriate tubular configurations. Over 200 of these alumina membrane tubes have been fabricated. The tubes have an outside diameter of ~9 mm and a wall thickness of ~0.5 mm. Fabrication of the membranes involves the use of classified technology and consequently cannot be discussed in this report.

During the course of the program, significant improvements were made in fabricating alumina membranes. The average pore radius of the membranes was reduced from ~150 Å for the initial membranes to <10 Å for the latest membranes. This pore-size reduction was accomplished while maintaining an acceptable membrane permeability. A relatively high leak flow was detected in some of the earlier membranes. It was determined that this leak flow was caused by small cracks at the ends of the tubes, which resulted during the handling and testing procedures. Metal ferrules were attached to the ends of the tubes to facilitate the handling and testing and to alleviate the cracking problem.

For ambient temperature measurements, metal ferrules were attached to the ends of the membrane tubes with epoxy. However, for higher temperature tests, other sealing methods had to be developed for attaching the membranes to the test system. First, we attempted to braze the alumina membrane to ferrules made of 446 stainless steel, which provides good sulfidation resistance as well as relatively low coefficient of thermal expansion. However, during thermal cycle tests, some of the assemblies developed leaks resulting from crack formations in the alumina membranes. To minimize stresses on the alumina membrane, a ring of niobium, which has a thermal expansion coefficient similar to alumina, was joined to the alumina tube, and a stainless steel ferrule was joined to the niobium ring. An active metal brazing technique was used to join the three components in a single brazing cycle. A silver/copper braze material containing titanium as the active metal was used to form a "butt-type" joint. The membranes were then attached to the test system through the ferrules using compression fittings adapted to autoclave fittings. Test assemblies that were fabricated in this manner remained leak-tight following thermal cycling to 1000°F and back to room temperature.

A screening procedure that used air permeability, as well as pore-size distribution measurements, was used to evaluate the membrane samples. Results from these tests were used as a guide to determine the effects of various fabrication parameters on the membrane product and to decide which membranes should be further evaluated.

4.2 MEMBRANE CHARACTERIZATION

4.2.1 Pore-Size Distribution

A dynamic, flow-weighted pore-size distribution test, developed at the Oak Ridge K-25 Site,[24] was used to measure the pore-size distributions of the tubular alumina membranes. Such flow-weighted pore-size distributions can be measured by using a binary mixture of a condensible gas (carbon tetrachloride) and a noncondensible gas (nitrogen). As the absolute pressure of the mixture, and, therefore, the pressure of the condensible gas, is increased incrementally, the condensible gas is capillary condensed in progressively larger pores. The condensed liquid fills and plugs the pores of the material so that the noncondensible gas cannot flow through these pores. The gas flow rate is measured at each change in pressure. The pore size and flow rate are corrected for adsorption of the carbon tetrachloride on the surface of the membrane. Then the corrected flow rate is plotted against the corrected pore radius to give a cumulative flow-weighted pore-size distribution.

The pore-size distributions of experimental alumina membranes were measured using the dynamic pore-size measurement technique. An example of the pore-size distribution of an early alumina membrane is shown in Fig. 3. As shown in the figure, these early

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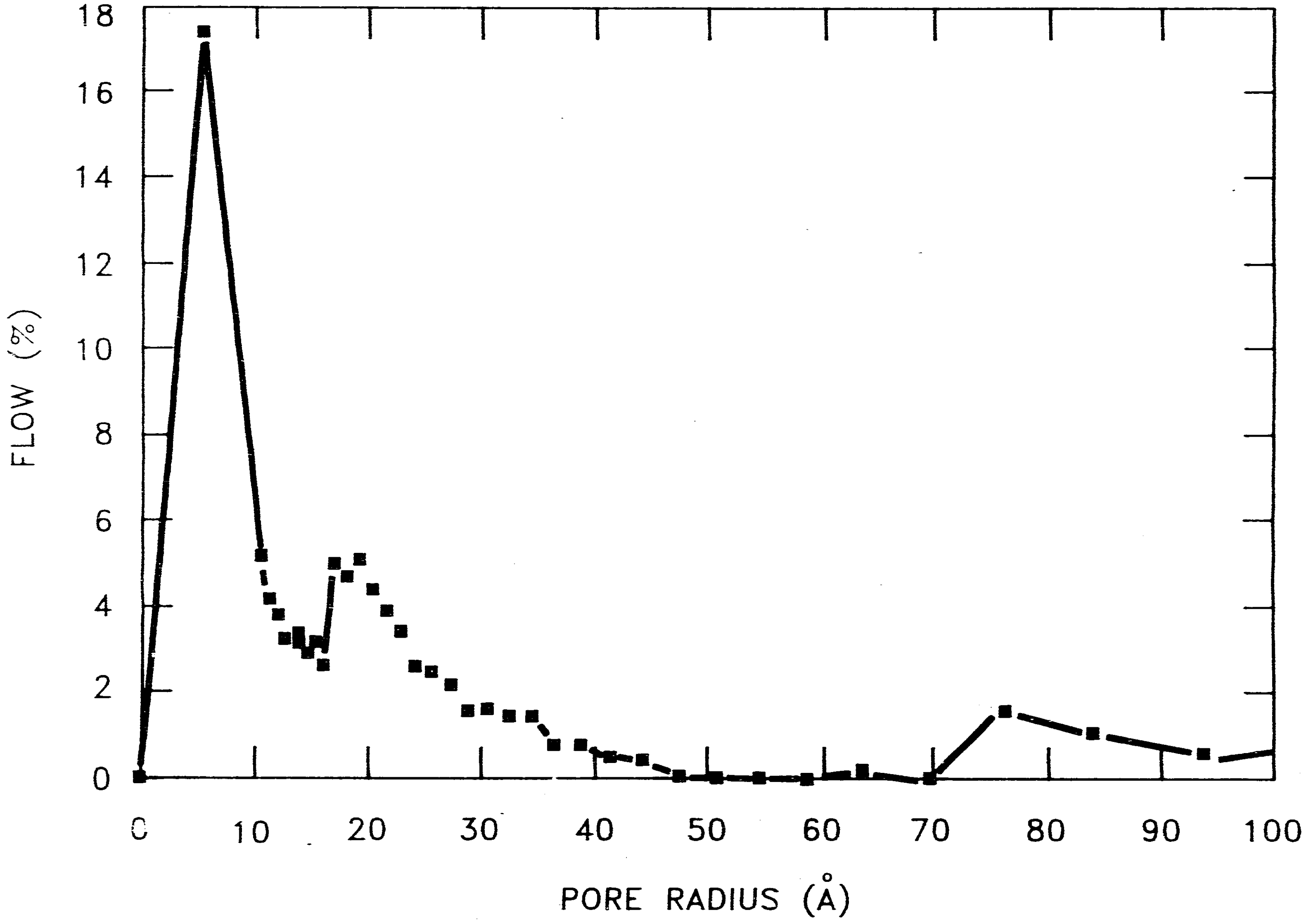

Fig. 3. Pore-size distribution of an early membrane fabricated at the Oak Ridge K-25 Site.

membranes contained some larger pores, and <20% of the gas flow was through pores with a radius of <10 Å. Several process improvements were incorporated to reduce pore size and to improve the pore-size distribution. The improvements can be seen in the example shown in Fig. 4. The mean pore radius of the improved membrane is <10 Å, with essentially no pores with a radius larger than 20 Å. In these improved membranes, over 60% of the gas flow is through pores with a radius <10 Å.

Some commercially available porous materials were also obtained and evaluated. By our measurements, these materials had an average pore radius of ~20 Å.

4.2.2 Burst Strength

Hydrostatic tests were made on six of the tubular membranes to determine their burst strength at room temperature. The burst strength at 1000°F is expected to be ~90% of the value determined at room temperature. As shown in Table 2, the burst strength values ranged from 800 to 1600 psig, with a mean value of about 1300 psig. Based on these results, it was concluded that the membranes with this configuration should operate well in gasifiers up to pressures of 600 psig, which was the initial goal.

4.3 MEMBRANE TEST SYSTEM

A test apparatus for measuring the gas permeabilities of membranes at high temperatures (up to 500°C) and pressures (up to 4 MPa) was designed and constructed. For safety reasons, the total gas flow was restricted to 1.0 L/min.

A flow diagram of the apparatus is shown in Fig 5. Gases are supplied from cylinders through high-pressure regulators and an associated manifold. Pressures are set by

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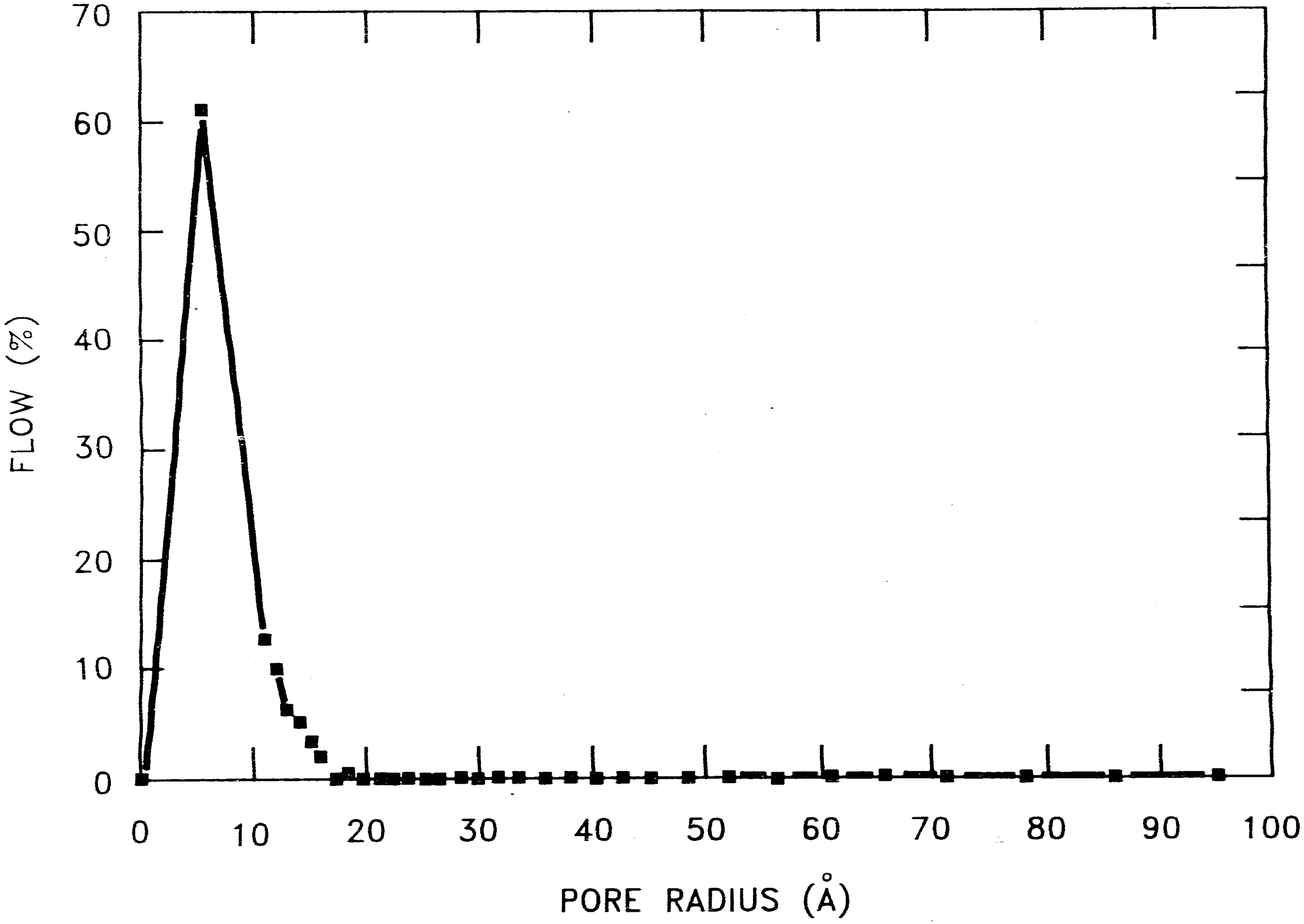

Fig. 4. Pore-size distribution of an improved membrane fabricated at the Oak Ridge K-25 Site.

Table 2. Burst strength of typical tubular alumina membranes

Membrane Sample	Rupture pressure (psig)
1	1450
2	1350
3	820
4	1500
5	1300
6	1600
Mean	1340
Standard Deviation	275

pressure-control valves, and gas flows are measured with differential pressure transmitters. Pressures are measured with pneumatic pressure transmitters connected to chart recorders. Pressures are measured upstream of the membrane, downstream of the membrane, and on the permeate side of the membrane. Research control valves, located in the feed, raffinate, and permeate streams, can be used to control gas pressures and flows. Differential pressure (d/p) cells with integral orifices are used to measure feed, permeate, and raffinate gas flows. The d/p cells are connected to controller/recorders. The d/p cells in the feed and raffinate gas streams have 0.010-in. orifices with an output range of 0 to 20 in. of water; the permeate d/p cell has a 0.007-in. orifice with an output range of 0 to 5 in. of water.

The gases are preheated in a three-zone tube furnace, which also houses the membrane assembly. Temperatures are measured with thermocouples, and exit gases are cooled with heat exchangers, if necessary, and analyzed by gas chromatography.

Shutoff valves are operated by air-controlled actuators, supplied through solenoid-operated valves. The recorder/controllers, thermocouple readouts, and valve switches are

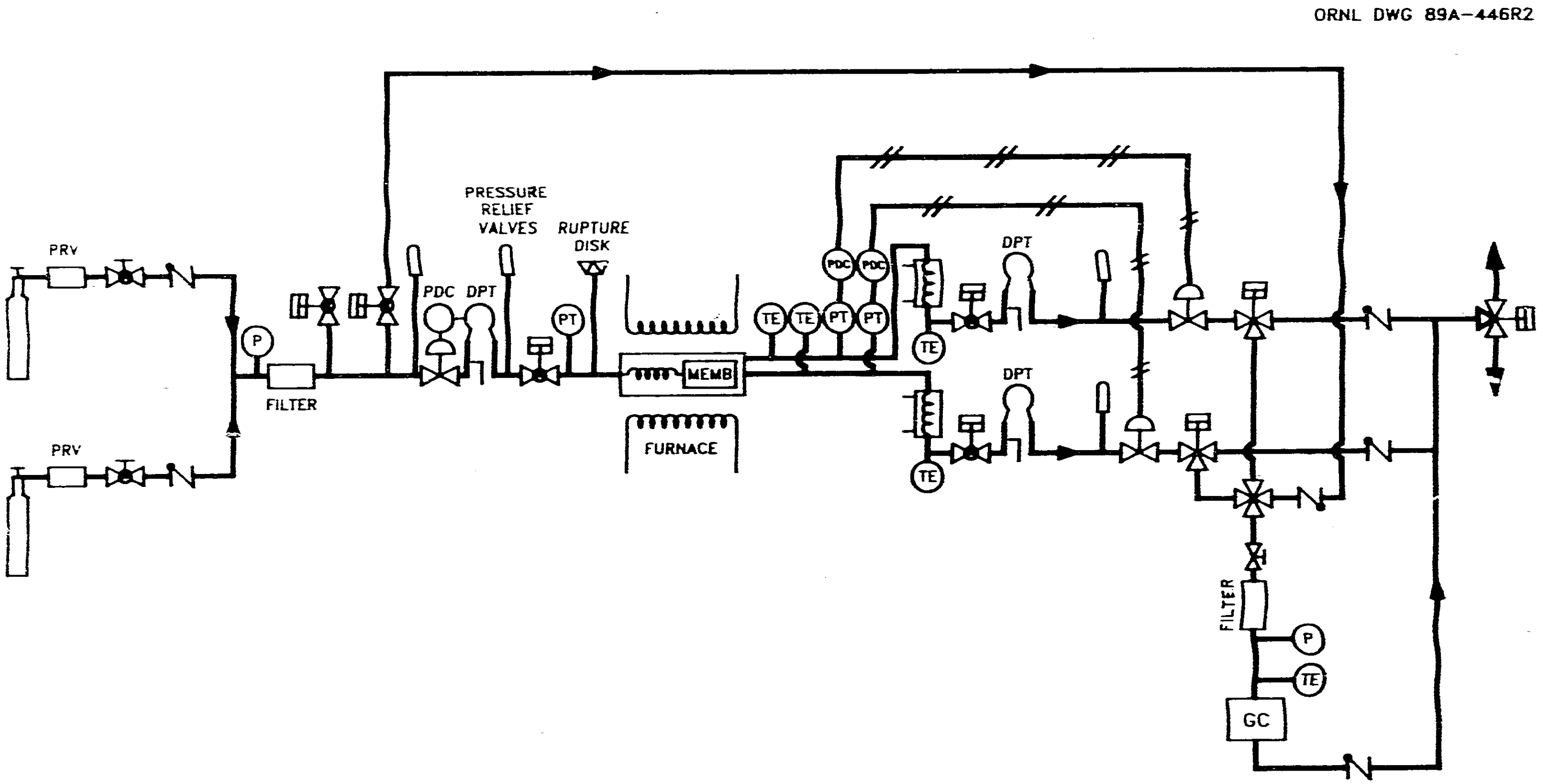

Fig. 5. Test apparatus for gas permeability measurements.

installed in a separate instrument cabinet. The apparatus is contained in a floor-standing hood (Fig. 6).

The feed and raffinate d/p cells were calibrated by measuring the flows of helium and nitrogen at different pressures, using a mass flowmeter and a bubble flow meter equipped with an electronic timer. A modified Darcy equation for calculating noncritical flow through an orifice[25] was used to calculate the gas flows at other measured pressures and differential pressures across the d/p cell.

The errors associated with gas flow calculations, chart recorder readings, etc., were evaluated to better define the limitations of the test system. The readability of the pressure indicators and d/p cell outputs was ~0.5%. In calculating gas flows, the readability limitations result in an error of ± 0.65% at full scale, increasing to ± 5% at 10% of full scale. The resultant error in calculating gas flows was estimated to be ~5.5% at the higher flows and pressures.

4.4 PERMEABILITY MEASUREMENTS

Permeability is defined as the volume of gas flow per unit of time for a given membrane area and pressure difference across the membrane. The membrane thickness is not a variable in this definition. The units for gas permeability are cubic centimeters of gas flow per minute per square centimeter of membrane area per centimeter-of-mercury pressure differential across the membrane.

Several alumina membranes having pore radii ranging from ~7 to 22 Å were fabricated, and their permeabilities were measured in different pressure ranges using pure gases, including He, N_2, CO_2, and SF_6. Measurements were made on selected membranes at

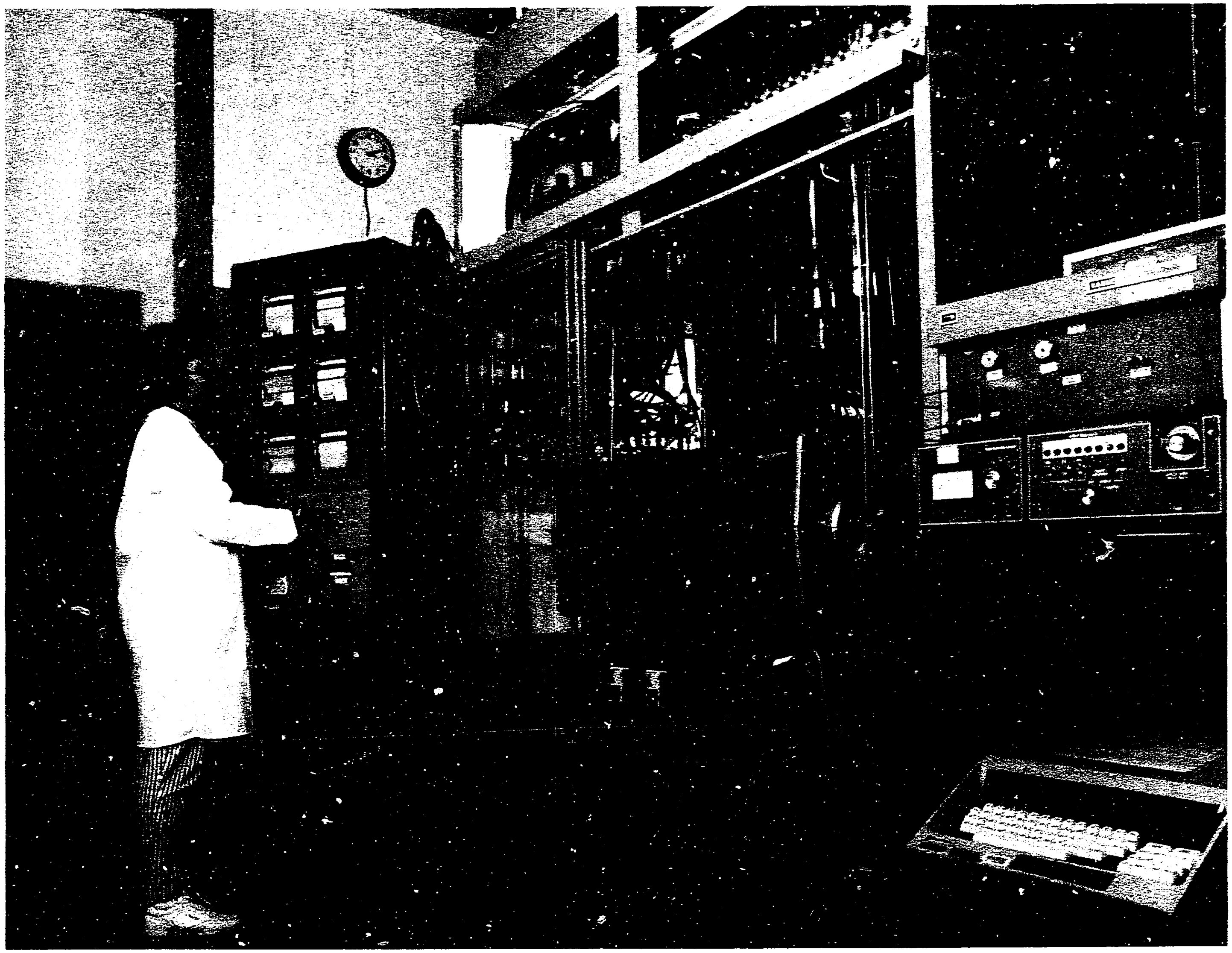

Fig. 6. Photograph of the gas permeability test system.

higher temperatures and pressures using helium and nitrogen. Several membranes were tested for separating gas mixtures simulating a coal gasifier product gas.

4.5 ROOM TEMPERATURE TESTS

A series of six different membranes (Series A), having different pore sizes ranging from ~9 to 22 Å pore radius, was initially characterized. The permeabilities of the membranes were measured at room temperature using pure gases: He, N_2, CO_2, SF_6, and air. Typical results from these measurements are illustrated in Fig. 7, in which the permeability is plotted against the pressure summation, i.e., the sum of the feed and permeate pressures. The permeability of the gases did not vary appreciably with pressure for the gases and pressure ranges that were tested. In general, the order of permeability was $He >> air \geq N_2 \geq CO_2 > SF_6$. The data for the series of membranes are summarized in Fig. 8, in which the calculated separation factors (ratio of permeabilities) for helium/nitrogen and helium/carbon dioxide are plotted versus the average pore size for the different membranes. Also shown in Fig. 8 are the calculated ideal separation factors, assuming a Knudsen gas transport mechanism. It is apparent that other gas transport mechanisms play a role, particularly in the case of carbon dioxide. The enhanced permeability of carbon dioxide, probably due to adsorption and surface diffusion, reduces the helium/carbon dioxide separation factor. The helium/nitrogen separation factor is also reduced somewhat as the membrane pore size decreases.

Figure 9 shows an example of similar types of data obtained for another series (Series B) of alumina membranes. Again, helium and nitrogen exhibit behavior more characteristic of predicted Knudsen transport, while other gas transport mechanisms, probably due to surface adsorption or other membrane interaction, play a larger role in carbon dioxide

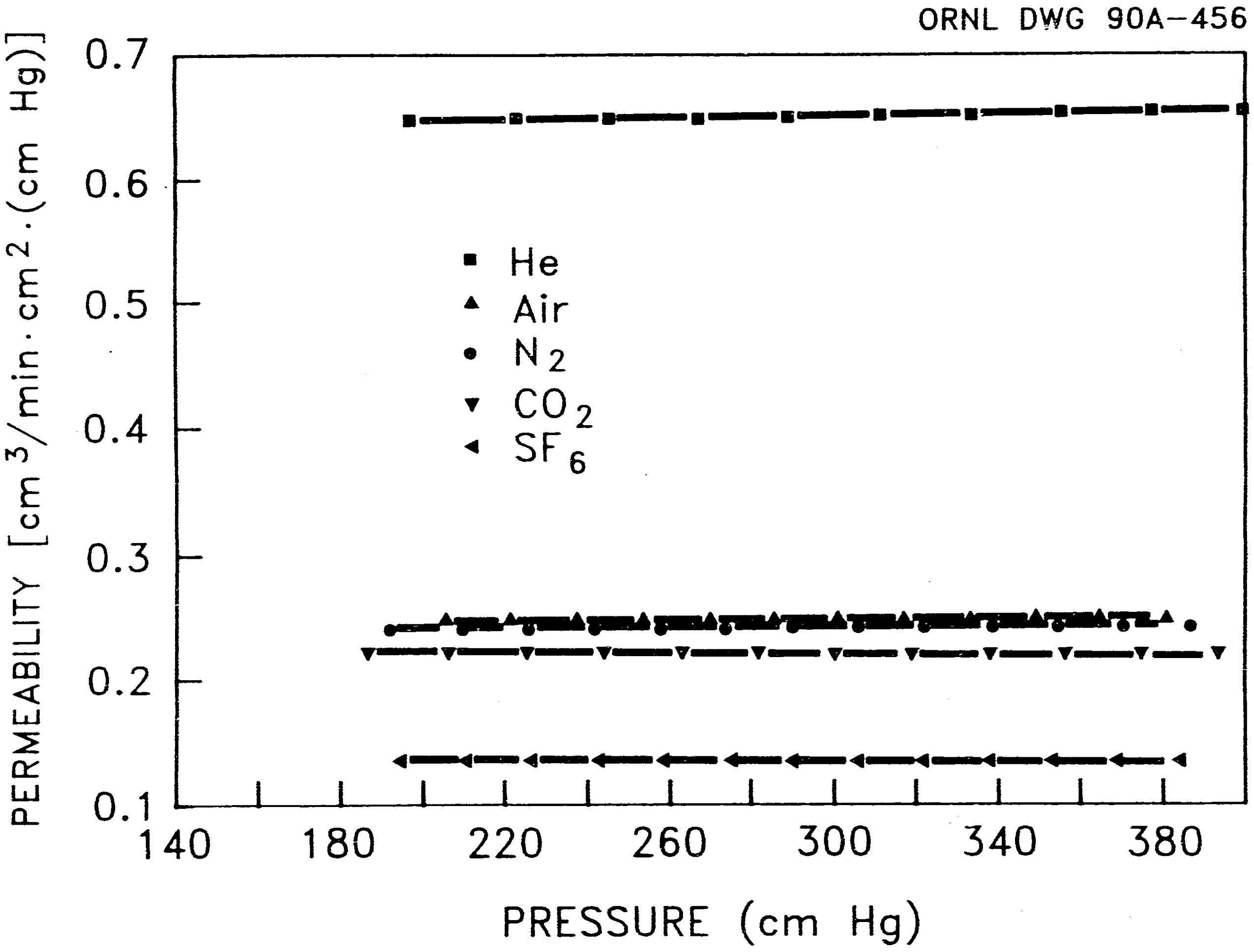

Fig. 7. Typical gas permeabilities of a membrane fabricated at the Oak Ridge K-25 Site.

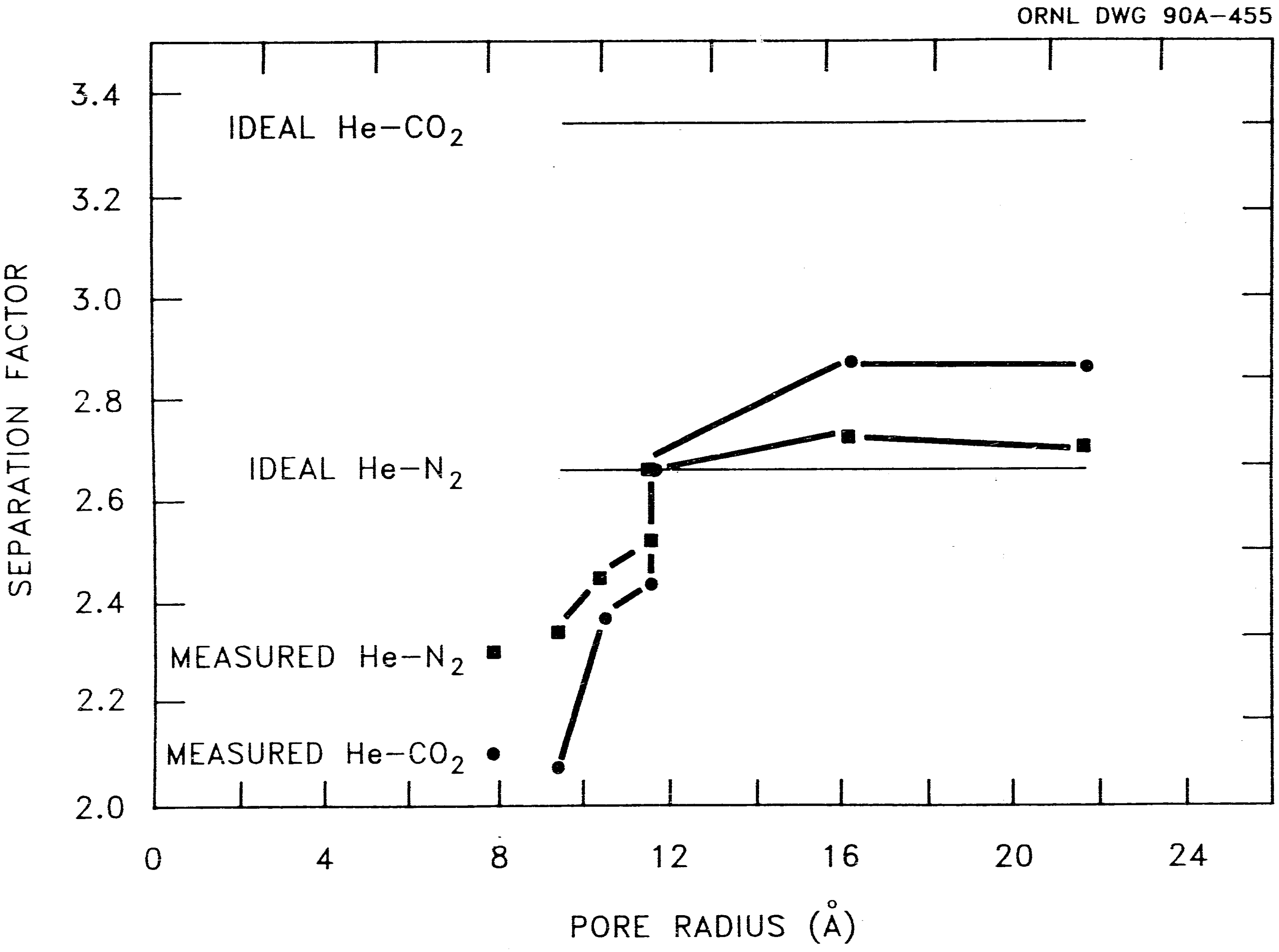

Fig. 8. Separation factors for helium/carbon dioxide and helium/nitrogen for Series A membranes with different pore sizes.

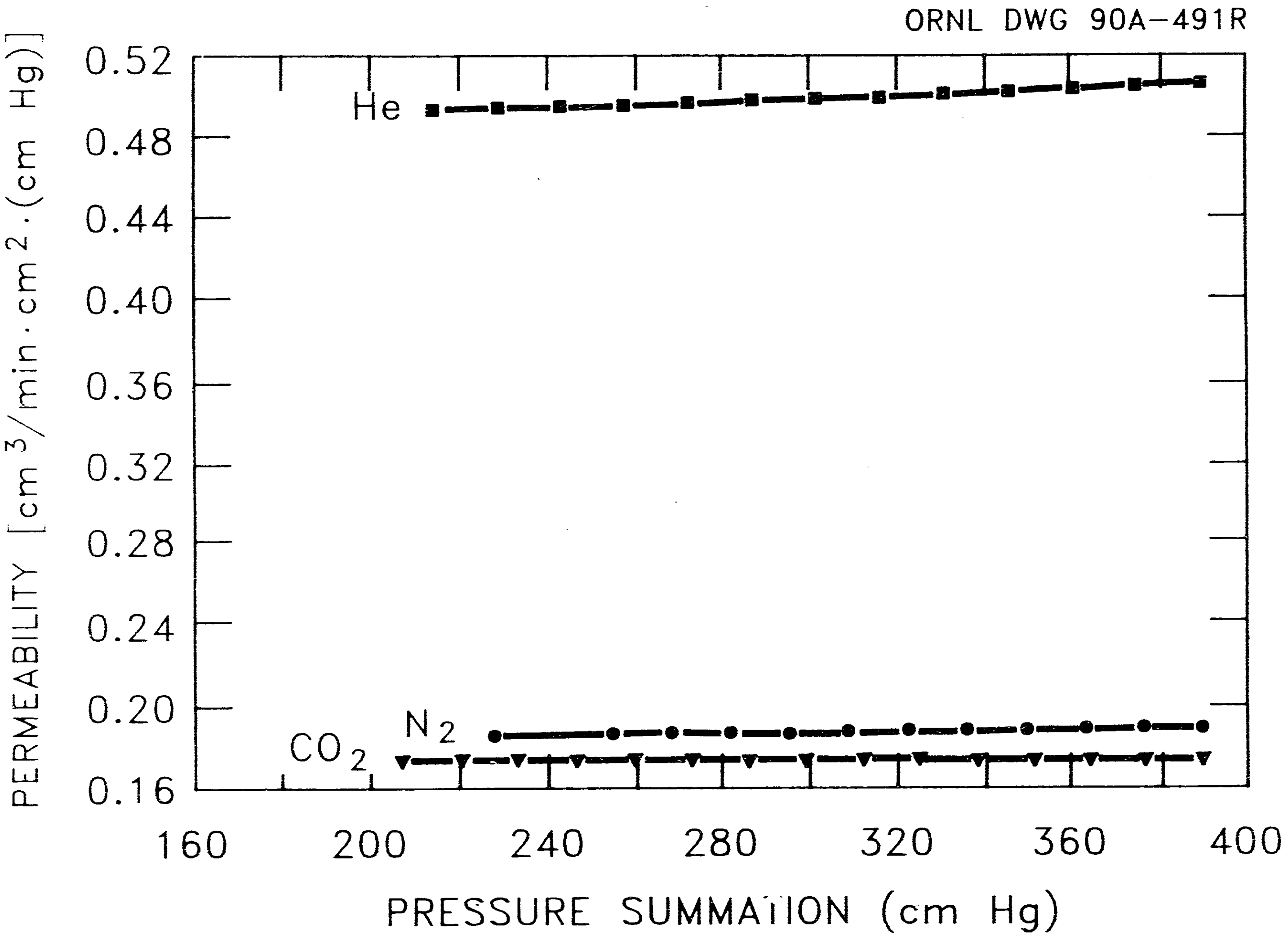

Fig. 9. Gas permeabilities of an alumina membrane fabricated at the Oak Ridge K-25 Site.

transport. Figure 10 summarizes the permeability data for the series of seven membranes having pore radii ranging from ~7 to 18 Å. Figures 8 and 10 are unique plots in that separation factors were determined for a series of similar membranes having different pore sizes in the range below 25 Å pore radius.

4.6 HIGH-PRESSURE TESTS

Gas permeability measurement were also made at higher pressures with helium, nitrogen, and carbon dioxide, using the test apparatus described in Fig. 5. These measurements were made at room temperature (20°C) in the feed-gas pressure range of 50 to 150 psi (0.34 to 1.02 MPa). As seen in Fig. 11, the permeability behavior of these gases in this pressure range is qualitatively similar to the results obtained in the lower pressure range.

Nitrogen and helium permeabilities of another membrane sample were measured up to a feed gas pressure of 589 psi (4.06 MPa) (Fig. 12). The relative gas permeabilities correlate qualitatively with a Knudsen flow mechanism; however, other gas transport mechanisms may also play a role when a pressure gradient is applied across the membrane.[26,27] Laminar flow may occur when the mean free path of the gas molecules is much smaller than the mean pore radius of the porous membrane. Surface diffusion can occur when the gas molecules are adsorbed on the surface of the membrane and move along the surface. The increase in permeability with increasing pressure, particularly in Fig. 12, may be partly a result of these effects.

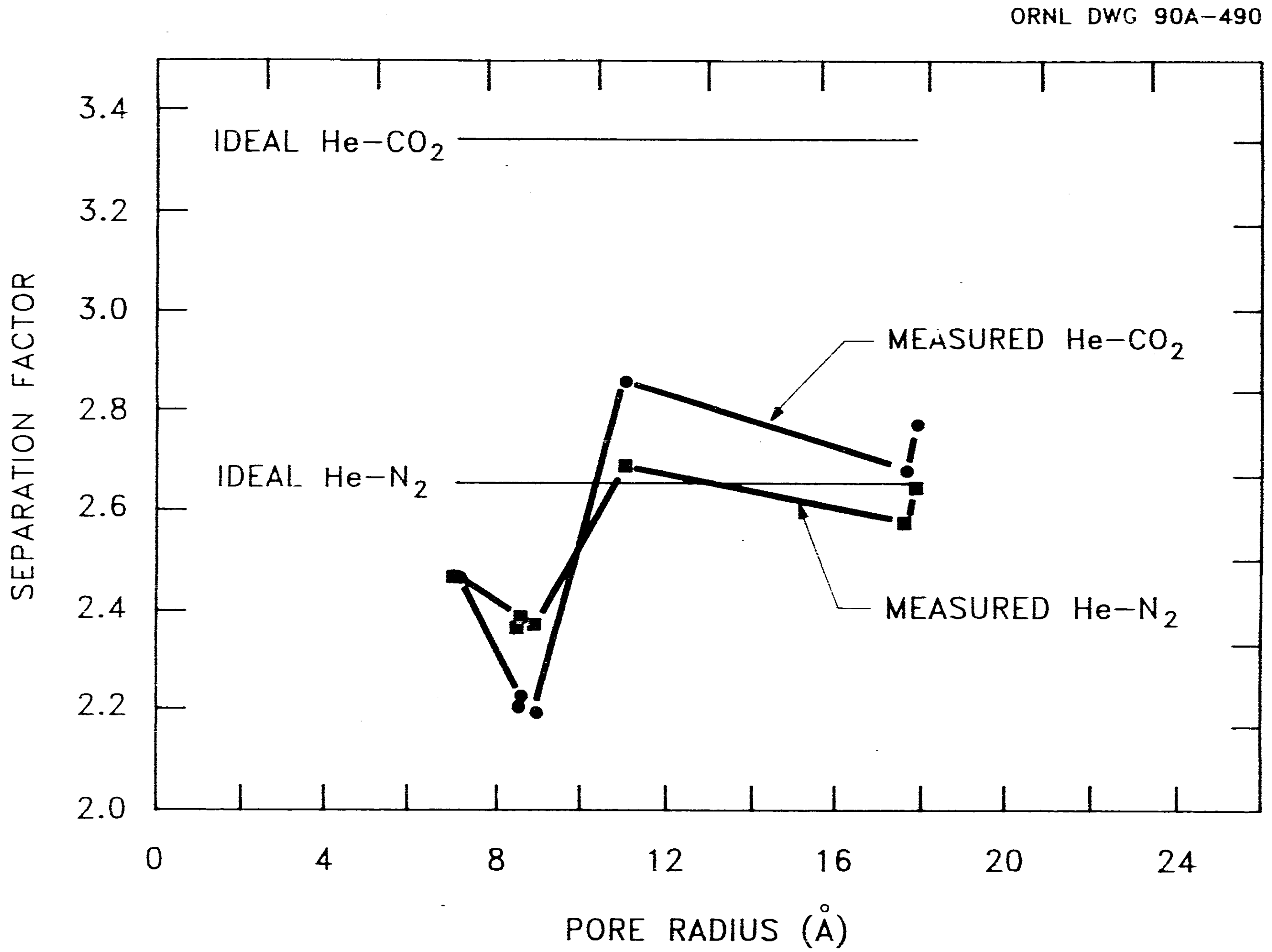

Fig. 10. Separation factors for helium/carbon dioxide and helium/nitrogen for Series B alumina membranes with different pore sizes.

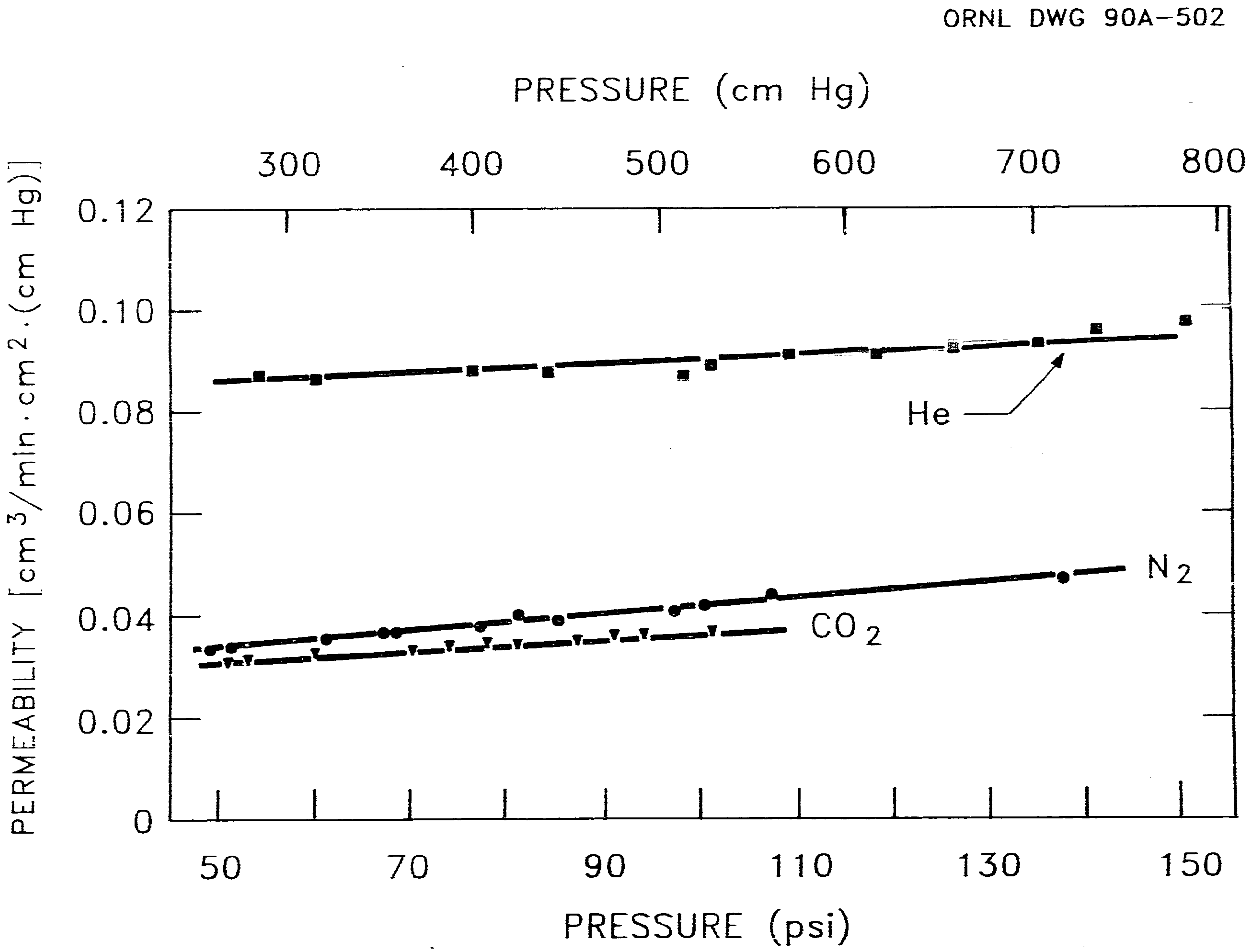

Fig. 11. Gas permeabilities of a fabricated alumina membrane at room temperature.

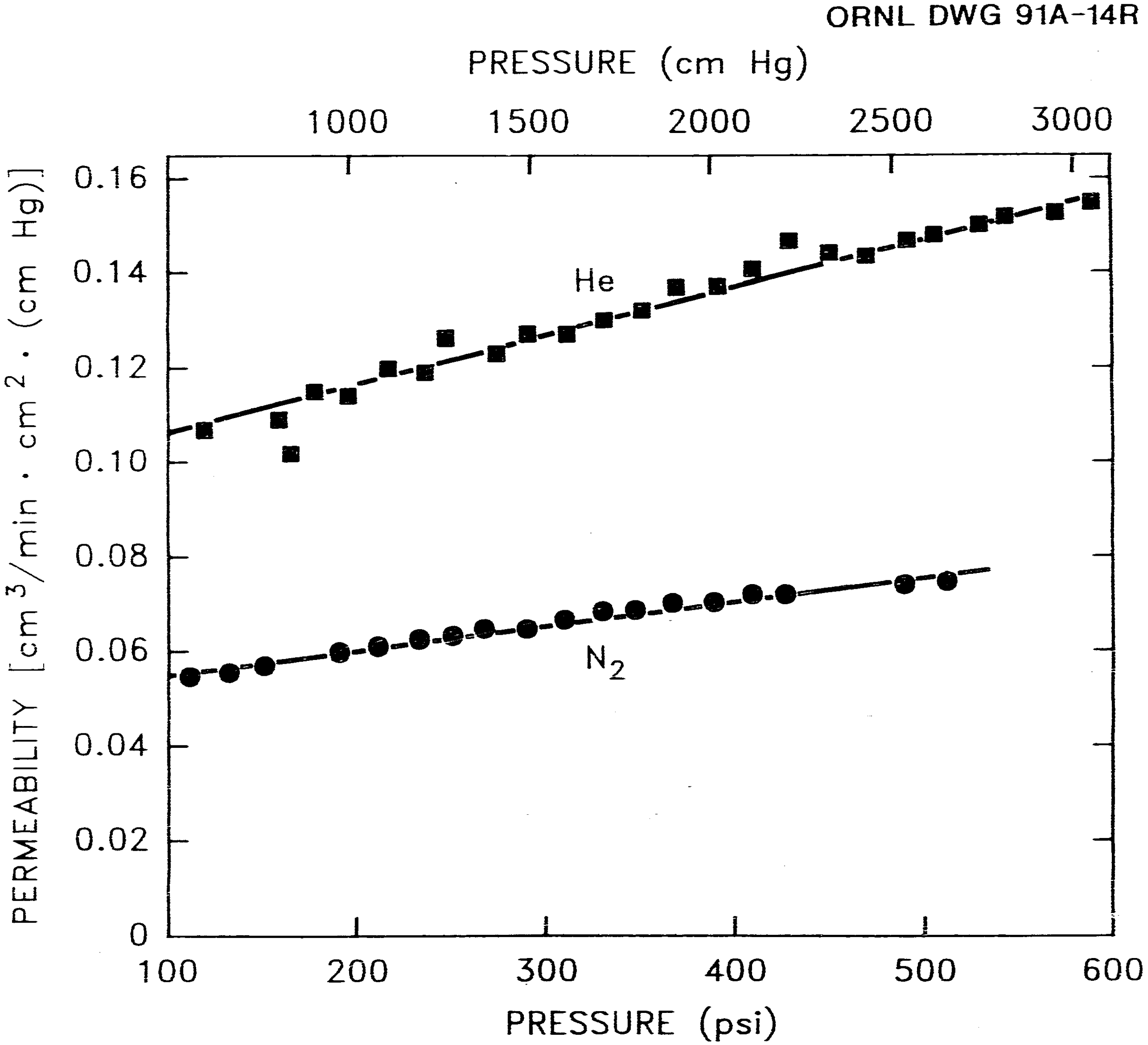

Fig. 12 Helium and nitrogen permeabilities of a fabricated alumina membrane at high pressure (temperature = 20°C).

4.7 PERMEABILITY AT HIGHER PERMEATE GAS PRESSURES

In the permeability measurements described previously, the permeate gas was vented to the atmosphere, so the permeate pressure was constant (atmospheric). The gas permeabilities of several fabricated alumina membranes were measured using a modified membrane assembly in which the permeate gas was contained and the gas pressure on both the permeate side and the feed side of the membrane could be varied. These measurements simulate a more practical situation in which the membrane would be operated at a high feed pressure and the permeate gas would also be maintained at pressures above atmospheric; the differential pressures across the membrane could be varied. The membrane assembly contained an epoxy seal, so tests were made at ambient temperature and at relatively low pressures.

The results of these tests are summarized in Table 3 for three of the membrane samples. The average permeabilities of pure helium and pure nitrogen were determined over a range of feed gas pressures and differential pressures across the membranes. The average permeability of the membranes increased significantly (i.e., from 0.024 to 0.25 $cm^3/min \cdot cm^2 \cdot (cm\ Hg)$ for nitrogen, and from 0.038 to 0.54 $cm^3/min \cdot cm^2 \cdot (cm\ Hg)$ for helium) as the membranes were improved, while the calculated separation factors (ratio of pure gas permeabilities) were maintained and also increased from 1.6 to 2.2.

4.8 PERMEABILITY MEASUREMENTS AT HIGHER TEMPERATURES

The pure gas permeabilities of helium and nitrogen were measured using a fabricated alumina membrane at 200°C and 500°C. For comparison, the gas flows were calculated for 20°C. For the higher temperature tests, the membrane sample was attached to stainless steel ferrules through a niobium spacer using a brazing technique as described previously. The gas

Table 3. Summary of gas permeability measurements at higher permeate gas pressures

	Membrane Sample		
	1	2	3
Membrane Area (cm^2)	11.9	6.3	6.4
Nitrogen			
Feed pressure (psig)	36-158	58-124	39- 74
Permeate pressure (psig)	16- 68	45- 80	33- 56
Pressure differential across membrane (psi)	20- 91	13- 44	6- 18
Average permeability ($cm^3/min\cdot cm^2\cdot$(cm Hg)	0.0237	0.169	0.245
Helium			
Feed pressure (psig)	43-170	50-113	48-103
Permeate pressure (psig)	20- 78	43- 87	41- 86
Pressure differential across membrane (psi)	23- 91	7- 26	7- 16
Average permeability ($cm^3/min\cdot cm^2\cdot$(cm Hg)	0.038	0.329	0.537
Calculated separation factor (He/N_2)	1.6	1.9	2.2

flows through the membrane were measured at different feed gas pressures; the permeate gas was vented to the atmosphere. The results were calculated as the gas flux per unit pressure differential across the membrane and referenced to a temperature of 20°C. The measurements were made sequentially at 20°, 200°, and 500°C. The membrane was then cooled back to 20°C, and the measurements were repeated. Table 4 shows the pressure ranges, the average gas fluxes, and the calculated separation factors based on the ratio of the average gas fluxes of helium and nitrogen, at 20°C (before heating), 200°C, 500°C, and again at 20°C (after heating). The helium flux increased as the temperature was increased. The nitrogen flux decreased by about 18% when the membrane was heated to 200°C, with no significant change when heated further to 500°C. The fluxes of both gases were significantly higher at 20°C after the membrane had been heated to 500°C. The calculated separation factors increased as the temperature was increased, reaching 2.66 at 500°C. The ideal Knudsen separation factor is 2.65.

These results indicate that: (1) heating removes water and other adsorbed materials from the pores of the membrane, resulting in a higher flow of both gases after the membrane

Table 4. Comparison of gas fluxes through an alumina membrane at higher temperatures

	Temperature (°C)			
	20[a]	200	500	20[b]
Helium				
Pressure range (psig)	35-63	33-66	31-61	29-55
Avg. Flux (cm^3/min·psi)	7.82	8.23	9.78	11.7
Nitrogen				
Pressure range (psig)	34-81	35-87	34-89	29-73
Avg. Flux (cm^3/min·psi)	4.42	3.62	3.67	6.21
Calculated separation factor (He/N_2)	1.77	2.27	2.66	1.88

[a] Before heating.
[b] After heating.

was heated; (2) higher surface adsorption of nitrogen at 20°C results in more surface flow and a lower separation factor; (3) surface adsorption is negligible at higher temperatures, and the separation factors approach the ideal value expected from Knudsen diffusion.

4.9 SEPARATION OF GAS MIXTURES

Two different mixtures of gases were used to simulate coal gasifier synthesis gas products. The compositions of the two mixtures obtained from Matheson Gas Company are shown in Table 5. One of the gas mixtures contained H_2, CO, CO_2, and CH_4; the second mixture contained these gases, along with nitrogen. The alumina membranes were tested for their ability to separate hydrogen from the gas mixtures. The membranes were tested at different feed gas pressures, ratios of permeate to residue gas flows, and differential pressures across the membranes. For these tests, the membrane assembly contained epoxy seals, so the tests were made at room temperature. The feed, raffinate, and permeate gas streams were analyzed by gas chromatography. Typically, the pressure on the feed side of the membrane ranged from 65 to 75 psig, and the permeate pressure ranged from ~23 to 29 psig. The permeate gas was enriched in hydrogen, primarily at the expense of carbon dioxide (reduced carbon dioxide content).

Figure 13 compares the chromatograms of the permeate and residue gases from one test using gas mixture 2. In this test, the feed gas pressure was 66 psig, and the permeate pressure was 50 psig for a differential pressure across the membrane of 16 psi. The gas flows were adjusted so that ~15% of the gas was allowed to flow through the membrane as permeate. It can be seen that qualitatively the relative amount of hydrogen compared to carbon dioxide is higher in the permeate gas and lower in the residue gas. In tests similar to

Table 5. Composition of simulated coal gasifier gas mixtures

	Content (%)	
Gas	Mixture 1	Mixture 2
Hydrogen	35.30	19.85
Carbon dioxide	19.86	5.01
Carbon monoxide	35.54	19.97
Methane	9.50	4.99
Nitrogen	----	50.18

this, the hydrogen content in the permeate gas compared to the feed gas increased from 35.3% to 45.5% for mixture 1 and from 19.85% to 24.5% for mixture 2.

5. SUMMARY AND DISCUSSION

Porous tubular alumina membranes with a diameter of ~9 mm and a wall thickness of ~0.5 mm, having pore radii ranging from <10 Å to 150 Å, have been fabricated and tested. These membranes are capable of withstanding >600 psi (4 MPa) pressure and operating up to 1000°F.

The permeability of pure gases, including He, N_2, CO_2, and SF_6, and the separation of gas mixtures containing H_2, CO, CO_2, N_2, and CH_4 were measured over a range of pressures and temperatures. The primary mechanism of gas transport across the membranes appears to be Knudsen diffusion. Consequently, the separation factors for the gases are determined, and limited, by their relative molecular weights. When the membranes were

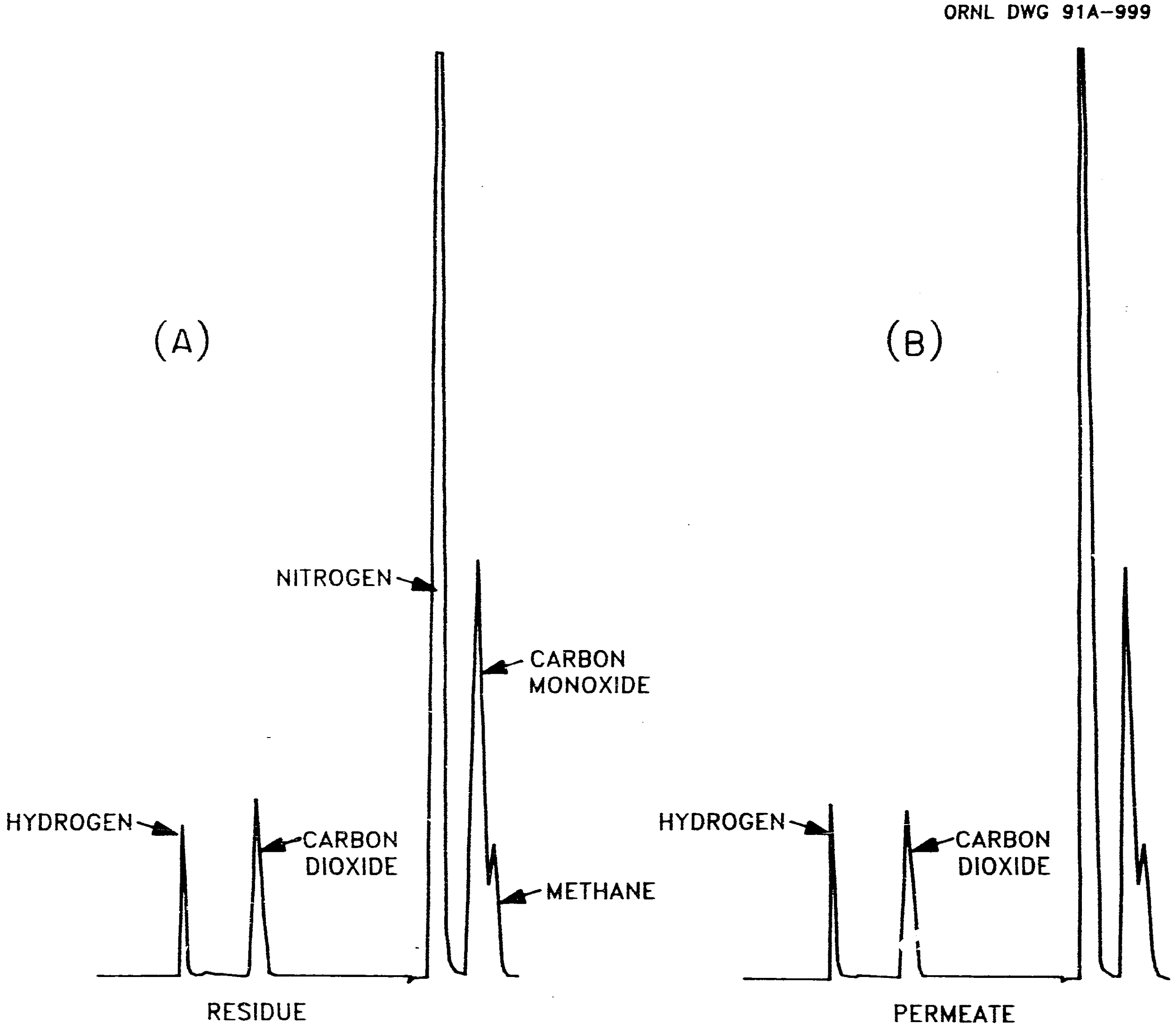

Fig. 13. Gas chromatograms of permeate and residue gases from a test on a gas mixture using a fabricated alumina membrane: (A) residue, (B) permeate.

tested for separating gas mixtures, the permeate gas was enriched in hydrogen, primarily at the expense of carbon dioxide (reduced carbon dioxide in the permeate and increased carbon dioxide in the residue gas).

When a "Knudsen flow" gas transport mechanism is operating, the ideal separation factors are <10 for gases of general interest. For example, the calculated separation factors for hydrogen/nitrogen and hydrogen/carbon dioxide are 3.73 and 4.67, respectively. Separation factors >10 would be preferred for practical and economical process applications. Consequently, it will be necessary to take advantage of other gas transport mechanisms to improve separation factors. One approach is to develop membranes with smaller pores to take advantage of a molecular sieving effect. We are continuing to work in that direction. Mathematical models[28] indicate that membranes with radii <3 Å will be required. The measurement of pore sizes in this range becomes very difficult. These pores approach the size of crystal lattice dimensions, and the gas permeability would be expected to decrease significantly. Other gas transport mechanisms such as adsorption and surface diffusion may become more important.

Another approach that might be used to improve the gas separation factor is to modify the membrane through incorporation of catalysts, either dispersed throughout the membrane or as an ultrathin layer. The catalyst would promote the chemical transformation of some of the gases to yield products that could be separated more easily. This approach has been discussed in a recent review[29] and is being pursued by other investigators.

An active metal brazing technique was used to seal the alumina membrane tubes to a niobium spacer, which was then brazed to stainless steel. When ceramic membranes are used at higher temperatures and pressures, the seals required to assemble the membrane into a configuration for testing or module fabrication become most important. Seals must be compatible with both the membrane materials and the structural component, and they must also be able to withstand both the temperature cycling and chemical environment encountered in process applications. Many seal materials become brittle and permeable to hydrogen under these conditions. Additional research and development is required to develop metal-to-ceramic seals with better mechanical strength and chemical resistance.

Inorganic membrane materials appropriate for gas separation are currently limited to certain metals, alumina, and silica, although membranes have also been produced from zirconia and titania. Other metal oxides and carbides, such as HfO_2, MgO, SiC, TiC, and HfC might be considered as membrane materials for use at higher temperatures.

Inorganic membranes are currently expensive, although they generally have a longer lifetime than polymeric membranes. This cost is expected to decrease as fabrication techniques improve. Ceramic membranes also have higher structural stability toward compaction and swelling, but they are more brittle. The surface area-to-volume ratio of inorganic membranes needs to be improved to decrease the size of the separation unit. This will improve as the membranes become thinner and the tube diameters decrease.

It is preferable in many coal conversion processes to retain the lower-molecular-weight gases, such as hydrogen, on the high-pressure side of the membrane while allowing the contaminant gases to permeate the membrane.[30] Such separations will require a more reactive membrane (or membranes) which does not rely on Knudsen diffusion alone for gas transport, as discussed earlier. It would not be economical to recompress the gases and use additional separation stages. Consequently, present inorganic membranes are not readily adaptable to the Integrated Gasification Combined Cycle, Molten Carbonate Fuel Cell, and Direct Coal-Fueled Turbine cleanup processes but are more appropriate for hydrogen enrichment or recovery.

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