

# Development of Microporous Inorganic Membranes for Separation and Purification of Hydrogen\*

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## Abstract

Activities are discussed concerning the development of microporous inorganic membranes at Oak Ridge National Laboratory (ORNL). These membranes have effective pore diameters of less than 2 nm. The International Union of Pure and Applied Chemistry designation for membranes of this pore size is microporous, although descriptively, they are nanoporous. Results of recent developments (i.e., from about January 2002 to the present) are discussed. Current development is directed toward the fabrication of tubular metal-supported ceramic membranes. The thin membranes are applied to the inner surface of the tubular supports, in part to prevent damage to the membranes during handling and installation into a separation system. Metal-supported membranes also have advantages over ceramic-supported membranes with respect to integration into gas-separation units because they can be welded to metal support structures such as tube sheets. Characterization, flow, and separation performance data are discussed. Separation factors for hydrogen, which are indicative of the selectivity of the membranes for hydrogen in a binary gas mixture, are very high and are coupled with very high permeances, (the volumetric flow per unit of surface area per unit of transmembrane pressure difference). Reported performance data include permeance, ideal separation factors, and separation factors for actual gas mixtures. Physical properties of these membranes are also reported. This paper will also address the status of classification and nonproliferation reviews, which are required prior to release and use because of legacy classified technology issues.

## Introduction

ORNL has engaged in the development of microporous membranes for hydrogen separation for several years. Prior to 1999, this effort was directed to very high temperature (i.e.,  $\geq 600^{\circ}\text{C}$ ) all-ceramic membranes. As a result of changing system requirements in, for example, coal gasification, the temperature at which hydrogen separation may be conducted is decreased to about 250 to 350°C. The lower temperature operation negates the need for all-ceramic structures and suggests that metal-supported membranes would be an option. Certain advantages accrue from the use of metal-supported membranes. The metal supports provide much greater flexibility in fabrication and in system integration. End fittings and subsequent system connections may be accomplished by brazing or welding. The metal-supported membranes are much more robust and resistant to damage, especially catastrophic breakage, than all-ceramic

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membranes. The ORNL membranes are composite structures consisting of a macroporous support tube (pore diameter  $> 50.0$  nm, usually about  $2.0$ – $5.0$   $\mu\text{m}$ ) coated with one or more membrane layers. The layers are thin, about  $2.0$   $\mu\text{m}$  thick, and, for hydrogen separation, the separative layer pore size is typically  $< 1.0$  nm.

A microporous membrane is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a membrane with a pore diameter  $\leq 2.0$  nm. Such membranes may be more accurately described as “nanoporous” because the pore diameters are in the nanometer range. However, for consistency with the IUPAC nomenclature, the term “microporous” is used in this paper. Molecular diffusion, the mode of transport in these membranes, is distinct from the ionic transport in ion-transport membranes and from solution-diffusion transport in palladium membranes. Ion-transport and palladium membranes are fully dense structures, whereas microporous membranes have significant void fractions with open porosity.

For microporous hydrogen-separation membranes, separation probably occurs by a combination of mechanisms. For gas mixtures containing molecules with significantly different molecular diameters, separation may occur via molecular sieving as is depicted in Fig. 1. Other diffusion mechanisms include Knudsen diffusion, surface diffusion or surface flow, and viscous flow (which has no separation function). Membranes are designed to offer the best combination of flux or volumetric flow rate and selectivity for hydrogen. These designs may differ for different gas mixtures. The focus of the ORNL activity has been toward designing membranes with a pore diameter of less than  $1$  nm (i.e., approaching a molecular sieve concept).

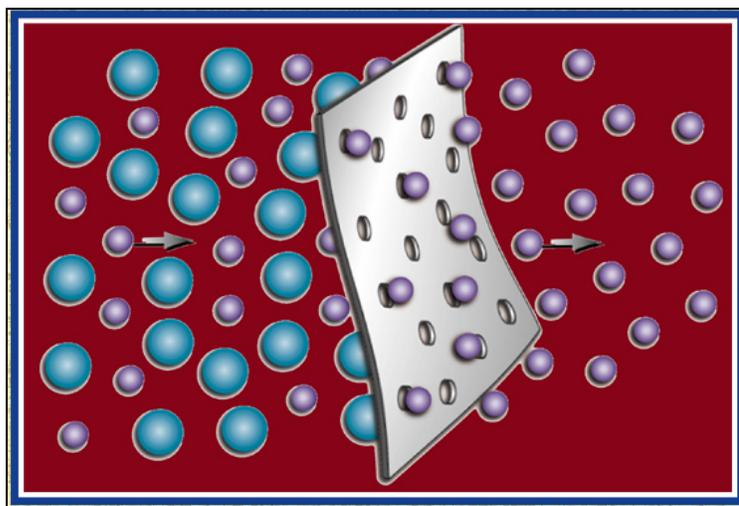


Figure 1. Simplified graphical depiction of a microporous membrane functioning as a molecular sieve.

Inorganic membranes with pore sizes less than  $1$  nm offer many advantages over thin-film palladium membranes and ion-transport membranes for the separation of hydrogen from mixed-gas streams such as reformed natural gas, coal-derived synthesis gas, and refinery purge gases. In microporous membranes, flux is directly proportional to

transmembrane pressure, whereas in palladium membranes, for example, flux is proportional to the square root of transmembrane pressure. Thus, microporous membranes become the preferred option for systems that operate at high pressure (see Fig. 2). The permeance of microporous membranes also increases dramatically as the temperature is increased (see Fig. 3). Also, as will be noted from Fig. 3, the permeances of the lighter molecules, hydrogen and helium, increase more rapidly with temperature than do the permeances of the heavier molecules, propane and carbon dioxide. This difference has positive implications with respect to the selectivity of these membranes for hydrogen because selectivity is directly proportional to the ratio of flows of the respective gases in a gas mixture.

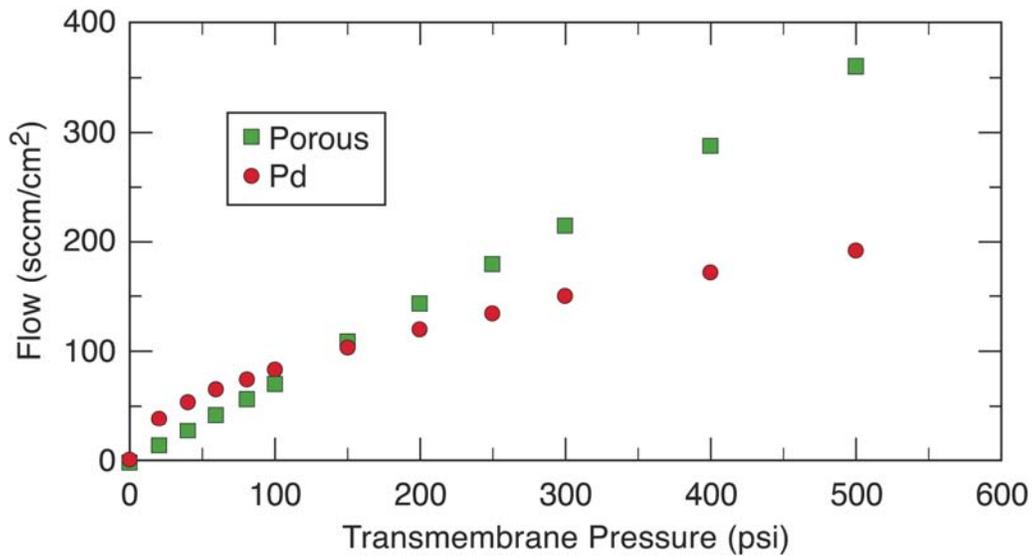


Figure 2. Hydrogen flows as a function of transmembrane pressure ( $\Delta P$ ) for an ORNL microporous membrane and a palladium membrane.

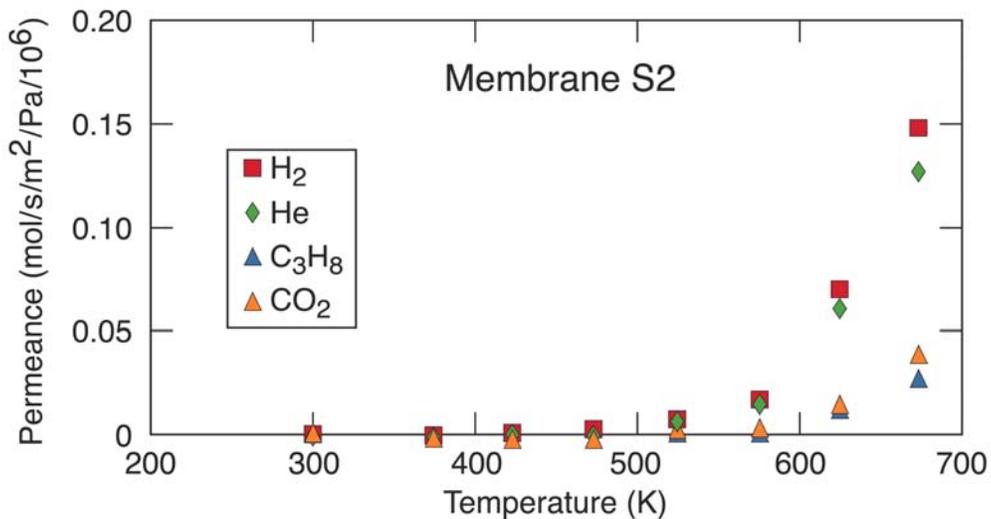


Figure 3. Permeances of several gases as a function of temperature for an ORNL microporous membrane.

The positive dependence of these performance characteristics on pressure and temperature suggests that the membranes have the potential for very high fluxes at elevated temperatures and pressures.

Because the separation process and transport mechanism are purely physical and thus do not involve ion transport, the ORNL membranes can be fabricated of almost any combination of materials, such as a ceramic membrane on a metallic support or a ceramic membrane on a ceramic support. Proper material selection is usually based on environmental compatibility, which can ensure that the membrane will have a long lifetime while maintaining high flux and selectivity. The ORNL microporous membranes are low-cost in large measure because their fabrication does not require the use of strategic materials or precious metals, such as palladium. Because microporous inorganic membranes are porous, they do not provide pure gas streams as do thin-film-palladium or ion-transport membranes. In those instances where pure hydrogen is the desired product, that apparent disadvantage can be overcome by coupling microporous membranes with pressure swing adsorption (PSA) to produce pure hydrogen. In such a scenario, PSA would only be required to separate the final 1% of the impurities, which implies a very compact and efficient separation system. Another approach to obtaining very high purity, but not 100% pure, hydrogen is to use two microporous membrane systems in stages or cascades. The impact of staging membranes in this way may be illustrated by considering that a membrane with a relatively low separation factor of 10 will in a single stage enrich a 50:50 mixture of hydrogen with a second gas to ~91% hydrogen. A two-stage system results in an effective separation factor of 100 (i.e.,  $10^2$ ) and will enrich the initial 50:50 mixture to ~99% hydrogen. Many power generation systems, even hybrid systems using fuel cells, can accommodate less than that purity of hydrogen.

### **Membrane Fabrication**

The permeance of a homogeneous membrane is inversely proportional to the membrane thickness. To be effective for gas separations, the mean pore diameter should be 2 nm or less. With such small pores, the membrane must be very thin, preferably less than 2  $\mu\text{m}$ , in order to have the highest flux at the lowest transmembrane pressure. Such a thin membrane is too weak to support itself and must be applied as a layer onto a strong, porous support material, either metal or ceramic. It is preferable that the separative layer be applied to the inside of the tube. This provides for protection of the membrane from damage incidental to handling. Metal is preferred for the support tube for several reasons. For example, integration into a gas-separation unit is facilitated greatly by the use of metal-supported tubular membranes. The support tubes may be equipped with metal end fittings and welded or brazed into the system support structure, usually a tubesheet type arrangement. Ceramic support tubes are, of course, usually much more brittle than metal support tubes and thus are more prone to catastrophic failure. Should a tube fail catastrophically, broken shards and pieces could result in a cascading effect, causing other elements to break.

The primary or separative membrane layer can be applied directly to the support tube or to an intermediate layer. A layer having an intermediate pore size applied to the support tube first can provide a better surface for the primary separative layer, resulting in a

thinner and more uniform membrane. The primary layer should have a mean effective pore diameter of 10 nm or less and preferably as small as 2 nm. Once the primary layer is in place, various chemical treatments can be used to reduce the effective pore diameter to the desired value (as low as 0.5 nm). A photomicrograph of a microfilter with an approximately 3- $\mu\text{m}$ -thick layer of zirconia is shown in Fig. 4.

It is extremely difficult to fabricate a membrane with absolutely no defects. Fabricated membranes are evaluated by combining measurements made on them with a model<sup>1</sup> to estimate the percentage of flow through the defects and to estimate the amount that the separation factor would be lowered by their presence. Because a defect can allow the unimpeded flow of both the desired product gas and the undesired gases, the number of defects must be minimized in order to achieve a high separation factor. Several methods have been developed to reduce the effective pore diameter of a defect or to eliminate the defect altogether. These defect repair methods do not significantly reduce the number of small pores and thus do not appreciably lower the flux of hydrogen through the membrane.

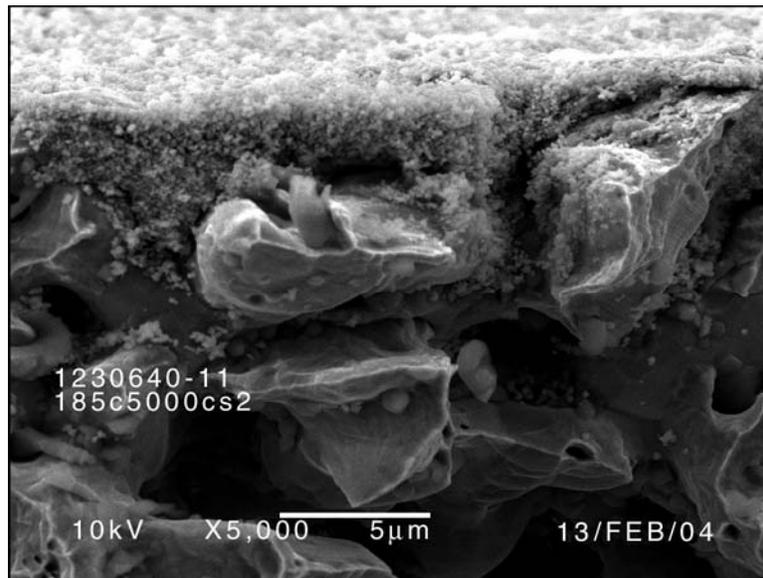


Figure 4. Photomicrograph of a porous zirconia membrane on a porous stainless steel support tube.

### Membrane Characterization and Testing

The two most important performance characteristics of inorganic membranes are permeance and separation factor. Permeance is a measure of the volumetric gas flow rate per unit of membrane surface area per unit of transmembrane pressure. A more fundamental unit is permeability, which is the permeance multiplied by the thickness of the membrane. In most cases, the thickness of the membrane cannot be accurately determined; thus, permeance is a more practical unit. The separation factor is meaningful only with respect to a mixture of two gases. The ideal separation factor is the ratio of the permeance of the two gases measured at zero pressure, where there is no interaction or momentum exchange between them. Each gas flows through the membrane as if the other

gas were not there. The ideal separation factor for a given temperature can be estimated by measuring the permeance of each gas separately as a function of average pressure and extrapolating the permeance to zero average pressure. The ideal separation factor is then the ratio of the zero-pressure permeances.

The transport of gases through membranes behaves differently as the pore diameter is reduced. Gas transport can also be affected by temperature, and a change in temperature can affect diffusion differently at different pore diameters. Measuring pore diameters that are smaller than 2 nm is extremely difficult. Therefore, it is critically important to be able to follow the changes in the transport mechanisms of different gases during pore diameter reduction to help determine the extent to which pore sizes have been reduced. A detailed protocol is followed to monitor changes in transport mechanisms.

Several theoretically based models have been developed to help understand the transport mechanisms. One of the most important is the Hard Sphere Model,<sup>2,3</sup> which combines the effect of the size of the gas molecule with Knudsen diffusion.<sup>4</sup> Separation by Knudsen diffusion generally treats gas molecules as points having no molecular dimensions. In reality, the diameter of a pore relative to the molecule is the pore diameter minus the molecular diameter (or the diameter of an equivalent hard sphere). If molecular diameter is not considered, the separation factor for free molecule diffusion (Knudsen flow) is the square root of the molecular weight ratio. With the molecular diameter consideration, the separation factor for free molecule diffusion (Knudsen flow) is the square root of the molecular weight ratio (Knudsen separation factor) multiplied by the cube of the ratio of the difference between the pore diameter and the molecular diameter for each molecule. The effects that the molecular diameter and molecular size have on the theoretical separation factor are demonstrated in Fig. 5 with several gas pairs. Several gas transport mechanisms may be operative in microporous membranes,<sup>5,6</sup> and this model provides a mathematical formula for what is essentially a bridge between the separation factors for Knudsen diffusion and molecular sieving. If the membrane pore diameter is equal to or less than the diameter of the larger of the two molecules, the larger molecule cannot pass through the membrane and the separation factor becomes infinite (as in a molecular sieve). As is indicated in Fig. 5, the larger the difference in the molecular diameters, the larger the pore diameter can be for the separation factor to become infinite, as is the case with hydrogen/CF<sub>4</sub> and helium/CF<sub>4</sub>.

The effective hard sphere diameters, in nanometers, of the molecules used in the calculations for Fig. 5 are as follows: helium 0.258, hydrogen 0.297, nitrogen 0.368, carbon dioxide 0.399, carbon tetrafluoride 0.47, and sulfur dioxide 0.411. The information in Fig. 5 clearly demonstrates the potential for achieving very large separation factors, even at pore diameters larger than the molecular sieve pore diameter, when there are large differences in the molecular diameters of the gases being separated.

The next most important transport mechanism is surface flow, which occurs with significant adsorption of a gas on the walls of the membrane pores. While the molecules are adsorbed on the membrane surface, they are in motion and can diffuse along it.

Generally, the heavier the molecule or the larger the interaction potential between the membrane surface and the molecule, the greater the adsorption and surface flow will be.

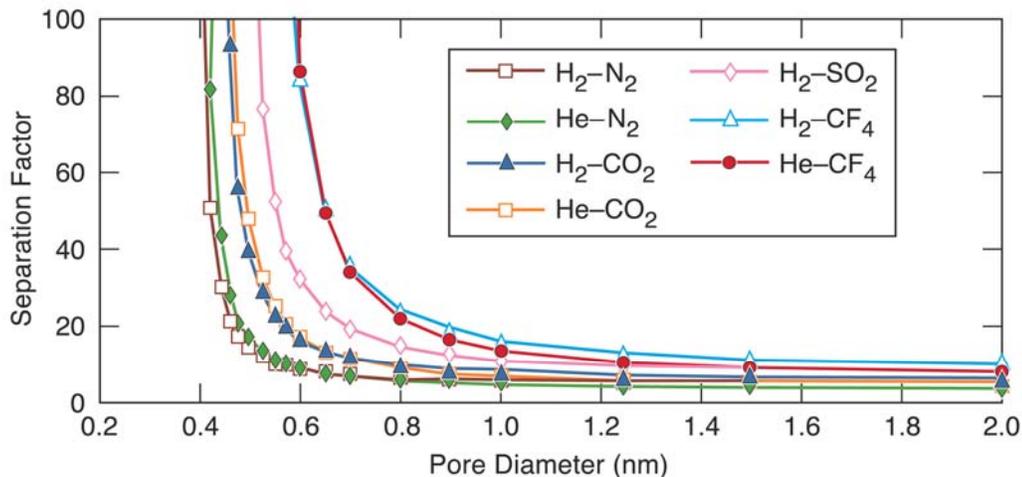


Figure 5. Separation factors for gas pairs with different relative sizes as a function of pore diameter obtained by using the Hard Sphere Transport Model.

Since this transport mechanism favors the heavier molecule, it tends to decrease the separation factor. Surface flow has been included in the full mathematical transport model.<sup>3</sup> However, adsorption and surface flow measurements are required to evaluate constants in the mathematical formulation. To date, these measurements have only been completed for carbon dioxide and an alumina membrane at 25°C. Model calculations were made for the helium and carbon dioxide binary pair. Zero surface flow for helium was assumed. The results of these calculations are shown in Fig. 6. As the pore diameter decreases, the gas-phase diffusion decreases and the surface flow increases, primarily because the amount of surface area increases relative to the pore volume. This decrease in flow causes the separation factor to decrease until the pore diameter approaches the diameter of carbon dioxide, at which point the transport of the carbon dioxide decreases sharply while the separation factor increases sharply. The calculation was based on the flow of the individual pure gases. It does not take into account the fact that adsorbed carbon dioxide molecules may decrease the effective size of the pore diameter and may thus impede the flow of the helium molecules. Therefore, in a mixed-gas separation, the separation factor may be even smaller than is shown in Fig. 6. If the separation factor drops below unity, which is possible under certain conditions, the carbon dioxide permeance becomes larger than the helium permeance.

### Permeance Measurements

Rapid and highly accurate permeance measurements are critical elements of the ORNL membrane development management protocol. Single-point permeance measurements are of little value. Permeance is measured as a function of average pressure. A linear regression of permeance with average pressure provides valuable information. The actual measurement made is the sum of the feed and permeate pressures, which is twice the average pressure and is called  $\Sigma P$  or pressure summation. Initial testing is performed

with air at room temperature. A series of 5 to 25 permeance measurements is made over an average pressure range from about 50 to 200 cm Hg.

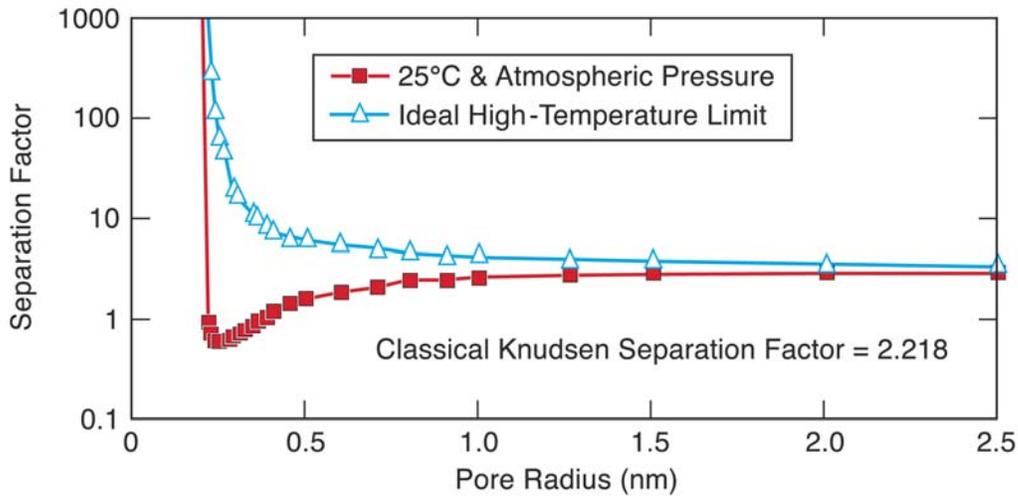


Figure 6. He-CO<sub>2</sub> separation factors at 25°C calculated from the Full Transport Model compared with the Hard Sphere Free Molecule Diffusion Model.

A linear regression is calculated, and then calculations are made of zero-pressure permeance, a permeance deviation factor, and the permeance at an average pressure of 75 cm Hg. The permeance deviation factor is the ratio of the slope of the linear regression to the zero-pressure permeance. A positive value may indicate viscous flow through defects in the membrane. These measurements are made on the membrane at every stage of development. Membranes that have a small permeance deviation factor are advanced to the next level of permeance testing, in which permeance measurements are made over the same average pressure range but at a multiplicity of temperatures, typically 25, 150, and 250°C. This series of measurements is made with three or four pure gases selected from helium, hydrogen, oxygen, argon, carbon dioxide, carbon tetrafluoride, propane, and sulfur hexafluoride. A linear regression with pressure summation (the sum of feed and permeate pressures) is made at each temperature and for each gas. The ideal separation factor for each gas with respect to helium is calculated from the zero-pressure permeances. The ideal separation factor is extrapolated to infinite temperature ( $1/T = 0$ ). At  $1/T = 0$ , no adsorption would be expected. Therefore, the flow is primarily free molecule diffusion. The equation used to calculate the results in Fig. 5 can be used with the ideal separation factor at  $1/T = 0$  and the molecular diameters to calculate a mean pore diameter for the membrane. While the accuracy of this pore diameter calculation is indeterminant, it does provide a parameter to track the progress in reducing the membrane pore diameter.

### Separation Factor Measurements

Separation factors are meaningful only in the context of binary gas mixtures and are measures of the relative flow rates of the two gases through a membrane. As was explained in the previous section, ideal separation factors are determined by establishing the permeances of the pure gases that are components of the binary gas mixture under

identical conditions. Ideal separation factors eliminate any interactions between molecules of different types. Actual separation factors are determined by separating gas mixture components in a mixed-gas-separation system. Both of these measurement techniques are useful for understanding fully the gas-separation mechanisms and are valuable for establishing models for the separations.

Prior to 2002, most of the membrane development at ORNL focused on the development of very high temperature, all-ceramic membranes. Significant progress in this development was made, and membranes with hydrogen-separation factors of up to ~165 were fabricated. Figure 7 is a photograph of an alumina membrane on an alumina support and is typical of the all-ceramic membranes that were fabricated.



Figure 7. Photograph of an alumina hydrogen-separation membrane on an alumina support.

All-ceramic hydrogen-separation membranes were developed for application at very high temperatures (up to about 1000°C) in the very aggressive environments typical of coal gasification systems. During the last few years, system changes and system reconfigurations have been made that have resulted in a lessening of the temperature capabilities of gas cleaning and purification devices in general, and gas-separation membranes in particular. As a result of these system differences, ORNL's hydrogen-separation membrane development was redirected to ceramic membranes on porous metal supports. As indicated in the "Membrane Fabrication" section of this paper, the use of metal-supported membranes greatly facilitates integration of the membranes into a gas-separation system. Although the metal-supported membranes cannot achieve the high-temperature capability of all-ceramic membranes, judicious materials selection can result in membranes that can function at temperatures up to about 800°C.

#### **Status of Development of ORNL Microporous Hydrogen-Separation Membranes**

ORNL has developed metal-supported hydrogen-separation membranes with ideal separation factors as high as ~140. Figure 8 presents data for several of these membranes and demonstrates to some degree the advancements that have been made in ORNL's membrane fabrication technology during the last two years.

## Results

Helium has been found to behave similarly to hydrogen in microporous membranes and is much safer to use in the laboratory. Therefore, most of the preliminary testing has employed helium as a surrogate for hydrogen. Because much of the testing takes place at temperatures less than 250°C and because sulfur hexafluoride is more inert than most hydrocarbons or carbon dioxide, sulfur hexafluoride is often employed to simulate larger hydrocarbons that may be present in a gas stream.

Only membranes with small permeance deviation factors (as determined by testing them with air at room temperature) were advanced to the next stage of testing with multiple gases at higher temperatures. Results of tests on membranes selected from recent membrane development work are presented in Table 1. The most recent work is presented at the top of table; the data at the bottom of the table were obtained early in 2002.

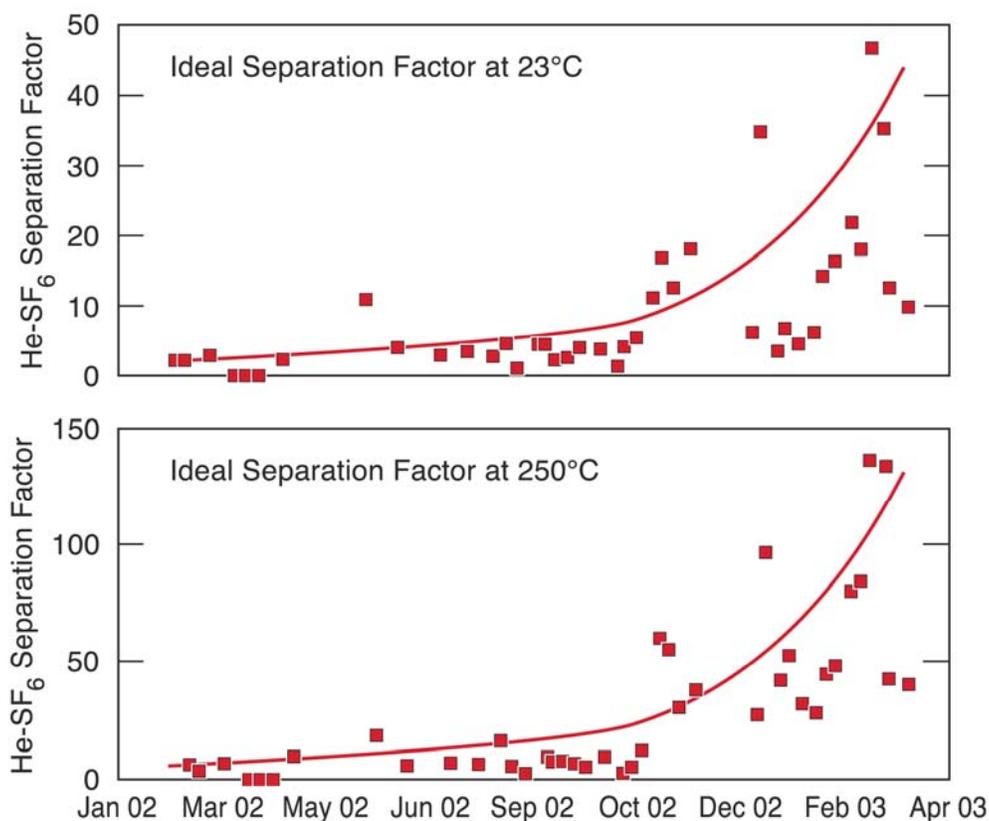


Figure 8. Ideal separation factors for He-SF<sub>6</sub> for an ORNL metal-supported microporous hydrogen-separation membrane.

Recent membranes were found to have ideal separation factors for helium from sulfur hexafluoride of over 30 at room temperature and over 100 at 250°C. Work earlier in the year resulted in He/SF<sub>6</sub> separation factors mostly in the single digits and often less than would be expected from Knudsen diffusion. The large improvement in the separation

factor is believed to be attributable to a recent improvement in the process to eliminate defects.

For ideal free molecule diffusion, the ratios of the permeances predict Knudsen separation factors of 3.316 for He/CO<sub>2</sub>, 2.827 for He/O<sub>2</sub>, and 6.041 for He/SF<sub>6</sub>. A larger ideal separation factor would indicate a higher-than-expected separation factor than would be predicted if Knudsen diffusion alone were the mechanism governing gas flow through these fine pores. Table 1 also shows how the permeance consistently increased as the temperature increased for all gases (except carbon dioxide, which is not included in Table 1). Depending on the membrane, the permeance of carbon dioxide sometimes increased and sometimes decreased with increasing temperature. This is believed to be a function of the amount of surface flow occurring along the walls of the pores at room temperature. An increase in permeance with temperature is contrary to what would be predicted if transport were governed by Knudsen diffusion. This phenomenon is believed to be caused by a thermally activated diffusion process that is not well understood at this time.<sup>8</sup> One interesting feature of this mechanism is that it does not seem to affect all gases in the same way. With the most recent membranes (e.g., 2528b and 5021b), the permeance of helium increased by a factor of between five and six when the temperature was increased to 250°C while the permeance of sulfur hexafluoride only increased by a factor of less than two. It may be possible to take advantage of this phenomenon, which only appears to occur in very fine pores (or at least is much more pronounced in fine pores). Adjustment of the temperature may result in both an increase in hydrogen flux and an increase in the separation factor.

The separation factors extrapolated to  $1/T = 0$  and the Hard Sphere Model were used to calculate pore diameter (see Table 1). It is clear from the results that the Hard Sphere Model does not always accurately describe the transport of molecules through these small pores. The model does not incorporate surface diffusion, nor does it account for increase in permeance that was found when the temperature was increased. More work is in progress to better understand these mechanisms so that they can be incorporated into an expanded, more comprehensive predictive model.

### **Status of Approval of Membranes for Commercialization and Use**

Legacy classified technology issues impose the requirements for classification and nonproliferation reviews of membranes fabricated by ORNL's Inorganic Membrane Technology Laboratory. A hydrogen membrane classification and nonproliferation review package was submitted for review on January 16, 2004. ORNL obtained approval from DOE on July 9, 2004. The implications of this approval are that the membranes may be distributed to outside laboratories for characterization and testing, and scale-up, pilot testing, and demonstration of the membranes may be accomplished. Hydrogen membranes approved as unclassified are those with any type 300 or 400 stainless steel, Hastelloy X, or iron aluminide support tube; a membrane layer of alumina; and a final separative layer of any oxide of aluminum, zirconium, titanium, or silicon.

This hydrogen-separation membrane product concept was developed as a part of the DOE Office of Fossil Energy's (FE's) Coal and Power Systems Advanced Research Program.

Its further scale-up, proof testing, and implementation will be conducted as part of the President's Hydrogen Fuel Initiative. Advanced hydrogen-separation membranes are among the technologies that will be evaluated in FutureGen, DOE-FE's Integrated hydrogen, electric power production and carbon sequestration research initiative. Upon approval of this product concept and as hydrogen membrane prototypes are developed, testing will occur under plant conditions at an appropriate development facility in FY 2006/2007.

**Table 1. Permeance, separation factor, and pore diameter for a series of membranes based on measurements at room temperature and at 250°C.**

Membrane	He permeance (scc/cm <sup>2</sup> ·s·cm Hg)		SF <sub>6</sub> permeance (scc/cm <sup>2</sup> ·s·cm Hg)		Ideal He/SF <sub>6</sub> separation factor		Calculated membrane pore diameter, Å
	23°C	250°C	23°C	250°C	23°C	250°C	
25227a	6.71e-04	3.20e-03	6.58e-05	7.77e-05	10.20	41.16	6.69
2528b	8.77e-04	5.03e-03	1.86e-05	3.65e-05	47.18	137.85	6.34
5021b	5.93e-04	3.22e-03	1.66e-05	2.39e-05	35.68	134.86	6.24
5022a	1.67e-03	5.71e-03	1.26e-04	1.32e-04	13.18	43.36	6.82
2527b	5.30e-04	3.36e-03	2.86e-05	3.93e-05	18.54	85.46	6.30
2527a	1.22e-03	4.36e-03	7.29e-05	8.85e-05	16.72	49.32	6.83
5021a	1.59e-03	4.44e-03	2.42e-04	1.57e-04	6.56	28.30	6.87
25221a	5.11e-04	2.96e-03	7.27e-05	5.61e-05	7.03	52.70	6.25
25210a	1.56e-03	4.62e-03	8.35e-05	1.17e-04	18.63	39.39	7.36
2525a	1.93e-03	5.79e-03	1.67e-04	9.47e-05	11.58	61.14	6.36
108b	2.46e-04	6.51e-04	4.35e-05	5.01e-05	5.65	12.99	8.95
60b	4.06e-04	4.10e-04	9.47e-05	7.15e-05	4.28	5.74	30.71
106a	1.24e-03	2.49e-03	7.96e-04	8.76e-04	1.55	2.84	273.62
108a	1.15e-03	3.19e-03	2.94e-04	3.05e-04	3.92	10.47	9.00
5426a	4.52e-05	6.37e-05	1.06e-05	9.30e-06	4.25	6.87	15.76
54212A	1.05e-03	2.32e-03	7.74e-04	7.05e-04	1.36	3.28	20.45
12305422B	8.70e-05	1.30e-04	1.76e-05	2.14e-05	4.94	6.06	36.74
12305429A	1.40e-03	4.39e-03	4.62e-04	2.57e-04	3.03	17.06	6.98
1230530-94A	2.20e-02	2.65e-02	5.00e-03	3.68e-03	4.40	7.21	14.85
1230530-109A	3.13e-03	4.54e-03	2.76e-04	2.31e-04	11.37	19.66	8.84
1230530-89B	1.39e-02	1.78e-02	4.44e-03	2.45e-03	3.13	7.28	10.99
1230530-89A	2.07e-02	2.59e-02	8.07e-03	5.66e-03	2.56	4.58	22.48
1230530-86a	9.74e-03	1.54e-02	3.63e-03	2.36e-03	2.69	6.54	11.25

### Implications for the FutureGen Initiative

DOE-FE has embarked on an ambitious Integrated Sequestration and Hydrogen Research initiative that has the sobriquet, "FutureGen." The first FutureGen plant is envisioned to be a 275-MW (nominal net equivalent output) facility that produces both electricity and hydrogen and that sequesters one million metric tons of carbon dioxide per year. The plant will employ coal conversion technology to gasify coal to produce a hydrogen-rich synthesis gas. The synthesis gas will be subjected to conventional shift reactions to produce a concentrated gas stream of hydrogen, steam, and CO<sub>2</sub>. The gas mixture will be

separated to yield high-purity streams of the individual components. The hydrogen may be used to power gas turbines and/or fuel cells to generate electricity. Some or all of the hydrogen may also be used as a feedstock for chemical plants or petroleum refineries.

According to DOE's program plan for FutureGen, currently available technology for production and purification of hydrogen, such as solvent-based absorption followed by PSA, are very energy intensive and would adversely affect the thermal efficiency of the plant.<sup>9</sup> Thus, alternative advanced approaches to hydrogen production and purification are being pursued in DOE's Coal R&D Program. These advanced approaches are being directed to reduce cost and improve the efficiency of hydrogen production. The FutureGen Program Plan anticipates that the first membrane modules could be tested at the Power Systems Development Facility (PSDF) in FY 2006/2007. Further, these novel hydrogen production technologies are significantly more thermally efficient than existing conventional technologies and have the potential to reduce the cost of hydrogen by nearly 25%. ORNL's microporous inorganic membranes are included in these novel hydrogen production technologies.

Air Products and Chemicals, Inc., is the largest supplier of commercial natural-gas-reforming/PSA-based hydrogen production and purification systems to the petroleum refinery industry. An example of a very large plant that delivers one million cubic meters of hydrogen per day is shown in Fig. 8. As is obvious, hydrogen production and purification using PSA is a well-established technology. That fact notwithstanding, microporous inorganic hydrogen-separation membrane systems potentially offer certain efficiency and cost advantages.



Figure 8. A 35 million scf/day hydrogen production plant. (Photograph courtesy of Joe Abrado of Air Products and Chemicals, Inc.)

Parsons Infrastructure & Technology Group Inc. has described a conceptual hydrogen-separation device based on ORNL's porous inorganic membranes.<sup>10</sup> Based on the Parsons data, a microporous inorganic membrane system to process one million cubic meters of hydrogen per day would be very compact compared with natural-gas-reforming/PSA systems such as that shown in Fig. 8. In an approach similar to that used by Parsons (i.e., three vessels in series), a membrane-based hydrogen-separation device to process one million cubic meters per day would require three 1-m-diam, 1.5-m-long vessels.

## Conclusions

Much of the work during the past year has been directed toward increasing membrane permeance, achieving repeatability with defect-free membranes, and using materials and techniques that can be approved by the DOE review process and manufactured on a large scale. Significant progress has been made in all these areas. We are significantly expanding our understanding of gas transport in inorganic membranes. Recent results have shown ideal separation factors for helium over sulfur hexafluoride of more than 45 at 23°C and more than 140 at 250°C. Also, it has been observed that the permeance of helium increases significantly with increasing temperature. As a result, even higher permeance and separation factors should be attainable at higher operating temperatures.

Future work will include testing some of the new membranes that have shown high ideal separation factors for helium over sulfur hexafluoride with hydrogen to confirm that our results also apply to hydrogen. Also, efforts will be made to test the best membranes at temperatures approaching 600°C to empirically determine how much the permeance and separation factors increase with increasing temperature. Finally, the membranes need to be evaluated under simulated coal-derived synthesis gas conditions to determine their actual separation performance and long-term stability.

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