The Potential for Separation and Capture of Carbon Dioxide at High Temperatures Using Inorganic Membranes

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ABSTRACT

Gas separation has been identified as a critical enabling technology for Vision 21 and various technologies that might be included in some Vision 21 plant configurations. Principal among these is the separation of hydrogen from reformed natural gas and coal-derived synthesis gas. Also of interest is the pre- and postcombustion separation and capture of carbon dioxide. Oak Ridge National Laboratory (ORNL) is engaged in the development of both high-temperature and low-temperature gas separation devices. ORNL has developed high-temperature (>600°C) inorganic membranes for gas separations of interest in fossil energy systems. For many processes of interest, particularly natural gas reforming and coal gasification, hydrogen and CO_2 are in the same process streams. Thus, separation of these components is of considerable interest. The H_2–CO_2 separation is addressed in this paper. At least two approaches may be used for the separation of CO_2 by using these membranes. For separation of H_2 and CO_2, the usual approach has been to fabricate inorganic membranes with sufficiently small pore size, i.e., ~0.5 nm diameter, so that they function as molecular sieves for H_2.[1] Another approach has been to fabricate surface flow membranes in which CO_2 adsorbs on the pore surfaces and is transported through the membranes. Only molecular sieving, i.e., the high-temperature approach, is discussed in this paper. Results of these efforts are presented as well as a discussion of the potential for the use of these membranes.

INTRODUCTION

Separation of hydrogen from high-pressure gas streams can be used to advantage in a carbon mitigation strategy in which carboniferous materials are subjected to conversion processes to form hydrogen and CO_2. Oak Ridge National Laboratory (ORNL) has developed membranes that are capable of separating hydrogen from larger molecules via molecular sieving. The approach involves, in simplistic terms, the preparation of membranes with pores larger than the smallest molecule in a gas mixture but smaller than the larger molecules. Thus, separation is accomplished by size discrimination of molecules. Molecular sieving of hydrogen from gas mixtures requires membranes having

[1] In the separation literature, membranes with pore sizes of 2 nm and less are described as "microporous", in accordance with an IUPAC definition of some years ago [Sing, 1985]. However, in view of the actual diameter of the pores of order nm, and in harmony with the current major thrusts of U.S. R&D funding agencies in nanoscience, nanoengineering and nanotechnology (NSET) we refer to membranes with pore sizes of order nm as nanoporous.

pore diameters of ~0.5 nm. Such membranes have been successfully fabricated using the ORNL technology. Figure 1 depicts molecular sieving of gas molecules.

The goals of this work included the development of hydrogen separation membranes that could separate ninety percent of the hydrogen in a gas stream at ninety percent or greater purity at 600ºC. Furthermore, the performance criteria for these membranes required that they be quite strong, with a burst pressure >4.2 MPa.

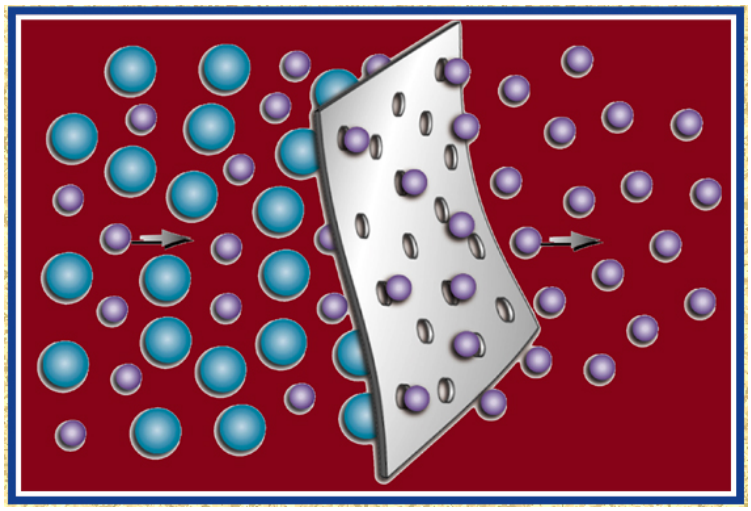

Fig. 1. Representation of membrane separation of gas molecules via molecular sieving.

Figure 2 is a photograph of an ORNL porous support tube, which would have a thin ~2-µm-thick membrane applied to the inner wall to create a composite layer structure. The support tube pictured is an all-ceramic (alumina) structure. Glass seals are on each end of the tube so that it can be incorporated into a separation system support structure. Figure 3 is a simplified depiction of the type module that would be used for the separation of hydrogen from gases having higher molecular weight and larger molecular size. In operation, a gas mixture containing hydrogen and CO_2 would be fed under pressure to the inside of a set of tubular membranes. By appropriate adjustments of the pressures of the permeate (hydrogen) and raffinate streams, hydrogen may be separated from CO_2 and the CO_2, at high pressure, may be directed to a storage device for further treatment prior to sequestration.

Figures 1 through 3 illustrate the principles of separation, an actual membrane, and operation of a membrane separation system. Alumina membranes have been tested for short periods at >600ºC with no apparent damage. However, the preferred approach is to use metallic support tubes with ceramic, metallic, or other membrane layers (e.g., carbon). Metallic support tubes are much more amenable than ceramics to incorporation into a separation system via welding or other joining process. The ORNL approach is to weld tubular metal ferrules to the ends of the membrane tubes. The ferrules may then be attached to a tube-sheet structure by welding or rolling the ferrules into the receiver holes in the tube sheet. One of the principal issues related to the use of metallic support tubes, and ceramic structures as well, is the environmental compatibility of these materials, i.e.,

corrosion resistance, but these issues are addressed through judicious materials selection, as would be the case for any system component.

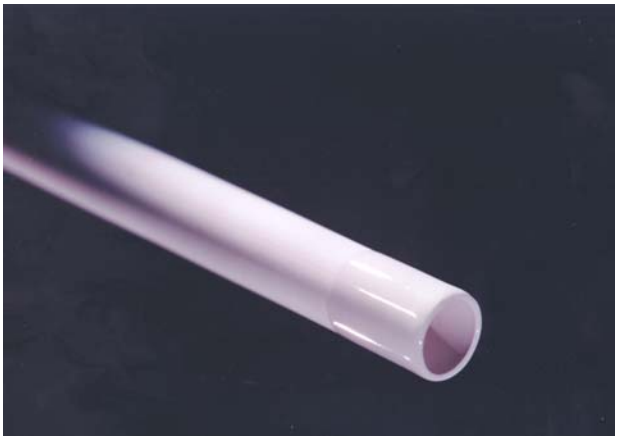

Fig. 2. Photograph of a porous alumina support for high-temperature hydrogen separation membranes.

BACKGROUND

Membranes used for separating mixtures of gases or liquids have a long history of importance to both the security and economic prosperity of the United States. *Inorganic membranes* have been employed for well over half a century for separating uranium isotopes as gaseous UF_6 molecules. In the early 1980s, inorganic membranes began to be applied to the separation of particles from fluids and to the separation of mixtures of fluids, both liquids and gases [de Lange, et al., 1995; Fain, 2000; Ismail and David, 2001; Meixner and Dyer, 1998]. For example, inorganic membranes are now used industrially in catalysis, beverage production, water purification, and gas separation. A number of commercially produced inorganic membranes have been fabricated for various applications. Ismail and David [2001] list 11 commercial trade-name inorganic membranes, which are subdivided into 33 different major formulations. Among the materials employed in these membranes are alumina, zirconia, titania, silicates, zeolites, carbon composites, silicon carbide, and various metals and metal-ceramic composites.

This impressive progress notwithstanding, *organic* membranes have achieved much more commercial success than inorganic membranes [Burggraaf and Cot, 1996]. The use of polymer membranes for separations is now a vast field of application. Some of the many uses of polymers include the separation of liquids, the separation of the component gases in air, the production of hydrogen, and the dehydration of gas mixtures [Meixner and Dyer, 1998; Robeson, et al., 1994]. Polymer membranes are generally less expensive to produce and use than inorganic membranes and can achieve very high separation factors. However, the fluxes or permeances achievable with organic membranes are typically much less, sometimes orders of magnitude less, than can be achieved with inorganic membranes. Also, the materials of which organic membranes are fabricated suffer limitations that exclude their use in potentially crucial areas. For example, polymer membranes cannot be used at elevated temperatures or in some aggressive chemical

environments. Inorganic membranes generally have superior high-temperature behavior and mechanical properties (e.g., wear resistance), are chemically inert, and can maintain a well-defined and stable pore structure. Furthermore, incremental improvements in polymer membranes, even in regimes in which suitable polymer properties are matched to the application environments, have become more difficult to achieve. In terms of a specific figure of merit for separation processes, a combination of selectivity and permeance, polymer membranes are approaching an upper bound for a variety of gas separations [Robeson, et al., 1994; Robeson, 1991]. Inorganic membranes offer a path toward exceptional results without having the same limitations as polymer membranes.

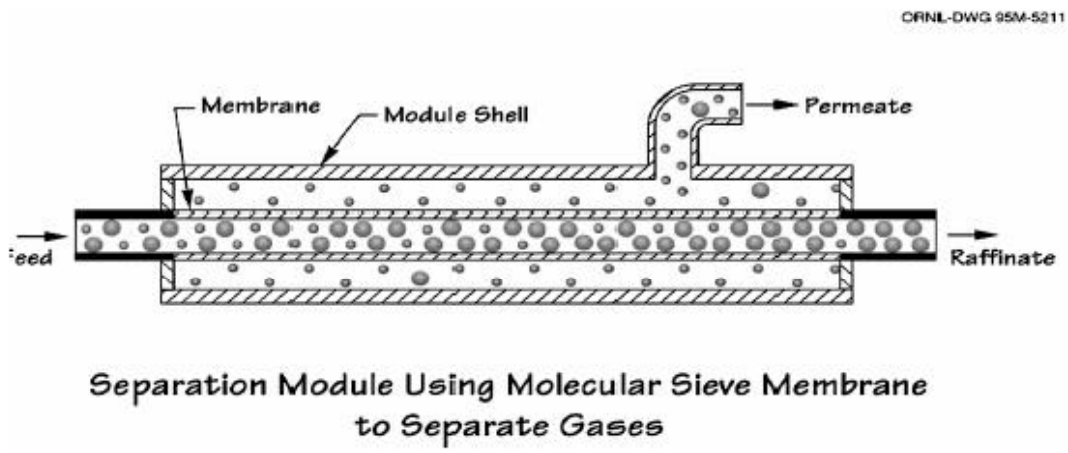

Fig. 3. Schematic drawing of a gas separation membrane module.

Many of the inorganic membranes that have been produced to date have pore diameters of tenths to several micrometers. The smallest pore diameters available in commercial membranes are 4 nm. Primary permeation and separation mechanisms operating in this regime are Knudsen diffusion and surface transport. Knudsen diffusion [Knudsen, 1909; Burggraaf, 1999; Lee and Oyama, 2002] refers to gaseous diffusion within the confining channels (pores) of the membrane, where the mean free path for molecule-molecule interactions is much larger than the pore diameter. The molecules migrate through the membrane by random straight-line jumps in empty space that are traversed at a velocity dictated by the temperature. One jump is terminated and the next one begun by a collision with a pore wall. It is assumed that the molecule is adsorbed on the wall and the molecule vibrates on the wall until it has no recollection of its incident momentum. When it picks up enough energy from the motion of the wall to escape from the wall, its escape is in a random direction. While adsorbed and oscillating on the wall, it undergoes surface diffusion in which it hops randomly from surface site to surface site. In the case of a two-component gas mixture present on the feed side of a membrane, the operation of these two mechanisms results in the gas molecules having different mean velocities and they emerge on the other side of the membrane at a different relative concentration. Because these two separation mechanisms dominate, membranes with pore sizes of several nanometers and above generally have relatively low selectivity for separating gas mixtures [Fain, 2000; Meixner and Dyer, 1998; Uhlhorn, et al., 1992]. For example, the maximum separation factor that can be achieved by Knudsen diffusion is limited to the square root of the ratio of molecular masses of the gases to be separated. For a mixture of

hydrogen in typical hydrocarbon gases or in CO_2, the separation factor under ideal conditions is limited to less than about 5 to10.

From the mid-1980s onward, a concerted effort has been made to decrease the pore sizes of separation membranes to diameters of 2 nm or less [deLange, et al., 1995]. Membranes with such small pore sizes can have very high separation factors for mixtures of gases. One important application of gas separation that is of great interest to ORNL is to recover H_2 from mixtures of gases. Hydrogen is presently a significant contributor to the U.S. economy, and it is destined to become of dominating importance in the future [*National Hydrogen Energy Roadmap*, 2002].

As an example of what can be achieved for hydrogen, a separation factor of 200 has been measured for a mixture of H_2 and C_3H_6 gases by a supported silica membrane with a pore diameter of approximately 1 nm [Uhlhorn et al., 1992]. Furthermore, they found that a key figure of merit for separation processes, the product of the measured selectivity and permeance, is among the highest ever reported. However, much of the hydrogen visualized for the future hydrogen economy will have to be obtained in high-temperature processes between 400 and 800˚C or higher, and where the feed gases contain water. The use of silica is prohibited above about 500˚C or in high-temperature feed gas streams containing water. High temperatures are required for some hydrogen-releasing chemical reactions, and it would be energy inefficient to provide cooling simply to separate hydrogen.

Although they are the most highly developed and well-understood separation processes, Knudsen diffusion and surface diffusion fail to describe permeation and separation processes of inorganic membranes at pore sizes below 2 nm, and especially below 1 nm, where high separation factors can be achieved [Burggraaf and Cot, 1996]. Gas transport through inorganic membranes in this regime is not well understood quantitatively. Qualitatively it is clear, however, that diffusion through smaller and smaller pores can be visualized to more closely approach the regime of solid-state diffusion, which is a well-developed field of study. Additional physical mechanisms to those described above become operational. The physics of gas transport in pores on the order of 1 nm is complex. Gas transport under these conditions occupies a realm at the convergence of gaseous diffusion, surface diffusion, and solid-state diffusion.

ORNL has developed several variants of porous inorganic gas separation membranes. Membranes that are capable of separating hydrogen from various gas mixtures, particularly gas mixtures containing CO_2, have been of particular interest because of the implications to the separation and capture of CO_2. The fabrication process is quite versatile, and membranes may be made of almost any material.

The ORNL inorganic membranes are porous materials in which molecular transport of gaseous species via several possible mechanisms occurs. Manipulation of membrane characteristics, primarily pore size, enables effective separation of gases by Knudsen diffusion, molecular sieving, or surface flow processes. These inorganic membranes are composite structures consisting of a microporous tubular support structure with a

membrane layer or layers on the inside of the tube. The support tube and the membrane layers may be of the same or different materials. The current focus of the ORNL effort is directed toward fabrication of ceramic membranes on metallic supports.

MEMBRANE FABRICATION

For highly efficient gas separations, the effective mean pore diameter must be 2 nm or less. One of the desirable attributes of any membrane is to have high rates of transport of separated gases through the membrane. Permeance is a useful parameter to describe gas transport. Permeance is defined as flow rate per unit of membrane surface area per unit pressure drop across the membrane. For a homogeneous membrane, permeance is inversely proportional to membrane thickness. At the very small pore sizes required for hydrogen separation, the membrane must be very thin (preferably < 2 μm). Such a thin membrane would be too weak and fragile to be sufficiently durable for applications of commercial interest. Thus, the ORNL approach (and that of many others) is to fabricate composite structure membranes in which a thin membrane is layered on a strong porous support material. Metal support tubes are preferred because module construction is facilitated greatly and because the modules will be less expensive than ceramic structures. The primary membrane layer may be applied directly on the support material or on an intermediate-pore-size layer. The multiple layer approach aids the fabrication of a thinner and more uniform primary membrane layer. The primary layer should have a mean effective pore diameter of 10 nm or less and preferably as small as 2 nm. Various chemical treatments are used by ORNL to reduce the effective pore diameter to the desired value, which may be as small as 0.5 nm.

Elimination of defects is a critical issue because non-separative flow may occur through defects that are larger than the desired pore size, and the overall separation efficiency may be reduced. Thus, one of the most important elements of the fabrication process is the elimination or repair of defects. Defects may result from, among other factors, cracks, voids, or inclusions. Although fabrication of defect-free membranes is, of course, extremely difficult, ORNL has developed several methods to eliminate defects or to reduce their effective pore diameters. In addition, the ORNL measurement technique can be used with a model developed in-house to estimate the percentage of flow through the defects and thus provide an indication of the impact of the defects on the separation efficiency [Fain and Roettger, 1996].

DETERMINATION OF PERMEANCE

Rapid and highly accurate permeance measurements of pure gases are critical to the ORNL membrane development protocol. Ideal separation factors are calculated ratios of the zero pressure permeance values for a pair of gases. Ideal separation factors represent the highest separation that can be achieved with a given gas pair because there is no interaction or momentum exchange between the gas-pair molecules. Thus, ideal separation factors are useful for evaluating performance of membranes in a mixed-gas system.

Because single-point permeance measurements can be misleading, permeance is determined as a function of a sum of the feed and permeate pressures, called the pressure summation, which is twice the mean pressure. A linear regression analysis of permeance vs pressure summation, ΣP, provides valuable information. The standard test membranes are tubes about 1.1 cm in diameter and 20 to 25 cm long. Initial testing is performed with air at room temperature. About 5 to 25 permeance measurements are made over an average pressure range of about 0.067 to 0.27 MPa. A linear regression is calculated, and the zero pressure permeance, a permeance deviation factor, and the permeance at an average pressure of 0.1 MPa are reported. The permeance deviation factor is the ratio of the slope of the linear regression to the zero pressure permeance. A positive value most likely indicates viscous flow caused by defects in the membrane.

The measurements necessary to obtain the data for determination of these parameters typically take less than 10 min to obtain and are made on the membrane at every stage of development. The permeance data are obtained for the support tube and after each membrane layer is applied. For single-membrane development, several (10 to 100) similar membrane formulations may be investigated. Typically, 1000 or more permeance measurements are made on a single set of membranes during a year.

Membranes that show particular promise or membranes that are being used to monitor the progress of fabrication steps go to the next level of permeance testing. At that level, permeance measurements are made over the same ΣP range at 25, 150, and 250°C. These measurements are made with three or four pure gases selected from helium, hydrogen, oxygen, argon, carbon dioxide, carbon tetrafluoride, and sulfur hexafluoride. In the Oak Ridge studies, helium has been determined to be an excellent surrogate for hydrogen. A linear regression with ΣP is made at each temperature and for each gas. The ideal separation factor for each gas at each temperature with respect to helium is calculated from zero pressure permeances. For each gas, a linear regression of the natural logarithm of the ideal separation factor is calculated with respect to the inverse of the absolute temperature. This calculation usually results in a linear relationship, which can then be used to estimate the ideal separation factor at any temperature. The intercept at $1/T = 0$ provides a significant parameter (i.e., free molecule diffusion) because, at infinite temperature ($1/T = 0$), adsorption of gas molecules is eliminated. The correlations between ideal separation factors at $1/T = 0$ and the gas molecule diameters may be used to calculate a mean pore diameter for the membrane. Although the accuracy of this pore diameter calculation is unknown, it is precise and provides a useful parameter to evaluate progress in reducing membrane pore diameter.

Variations in permeance with ΣP at 25ºC are shown in Fig. 4 for a membrane with minor but significant defects. For free molecule diffusion, permeance is invariant with pressure. The positive slopes of the linear regressions for these two gases indicate some viscous flow. For viscous flow, the slopes of these lines would be proportional to the product of the viscosity and the molecular velocity. Line slopes that are not proportional to the product of the viscosity and the molecular velocity are indicative of other transport mechanisms. For Knudsen flow, the permeance is proportional to the inverse square root

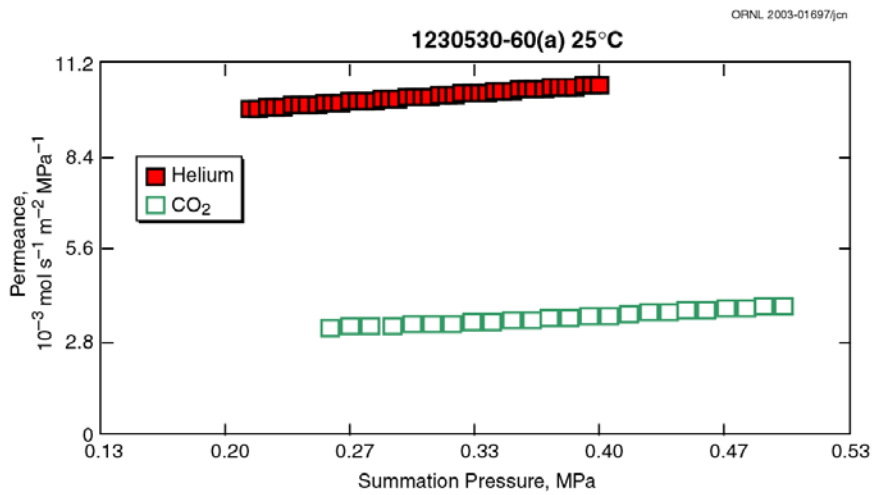

Fig. 4. Variation of permeance of He and CO_2 with summation pressure, ΣP, at 25ºC for a membrane with minor defects.

of the product of molecular mass and absolute temperature. Thus, multiplication of the permeance of any gas by the square root of the product of molecular mass and absolute temperature yields an intercept at zero pressure that is the same for all gases and all temperatures for Knudsen flow. Deviations from a common intercept at zero pressure indicate that different transport mechanisms are involved. Molecular size effects can increase the separation factor, and surface flow can decrease the separation factor. Deviations from ideal Knudsen separation factors are indicative of transport mechanisms other than classical Knudsen flow. An example of this principle is demonstrated in Fig. 5. With this membrane the permeance of carbon dioxide at 25°C is about 2.5 times larger than the permeance of helium, whereas at 250ºC, the carbon dioxide permeance is less than one-half the permeance of helium (for Knudsen flow it would be about one-third). This indicates a high degree of CO_2 surface flow with this membrane at 25°C and some residual surface flow at 250°C. In addition, the linear regression shows a negative slope at 25°C, likely indicating that the adsorption of carbon dioxide is large enough that it reduces the pore size of the membrane as the pressure increases. This implies that, in a gas pair mixture with helium, the adsorption of carbon dioxide would also reduce the pore size for helium and would reduce the helium permeance to a value less than what it was for the pure gas. This effect would make the separation factor for carbon dioxide even higher than is indicated by the individual pure gas permeances.

The surface flow component for CO_2 shows up most prominently in the zero pressure permeance. Apparently, the surface flow component depends more on the relative amount of time the adsorbed molecules spend on the surface rather than the surface population. Only a small amount of surface flow is evident at 250°C, and the permeance of carbon dioxide at 25°C is more than four times its permeance at 250°C. That is also true for sulfur hexafluoride. When normalized as described above, these deviations from a common intercept indicate that different transport mechanisms are involved. For free molecule diffusion (Knudsen flow), the ideal separation factor is the square root of the molecular weight ratio. Deviations from square root of the molecular weight ratio ideal separation factors indicate that other transport mechanisms are involved. As shown in

Fig. 5, the permeance of helium increases with temperature, whereas the permeances of other gases decrease with increasing temperature. The variation of the permeance with pressure is essentially constant at 250°C, where the ratio of the permeances (ideal separation factors) for helium and carbon dioxide is only about 2.3, indicating some remaining surface flow of carbon dioxide.

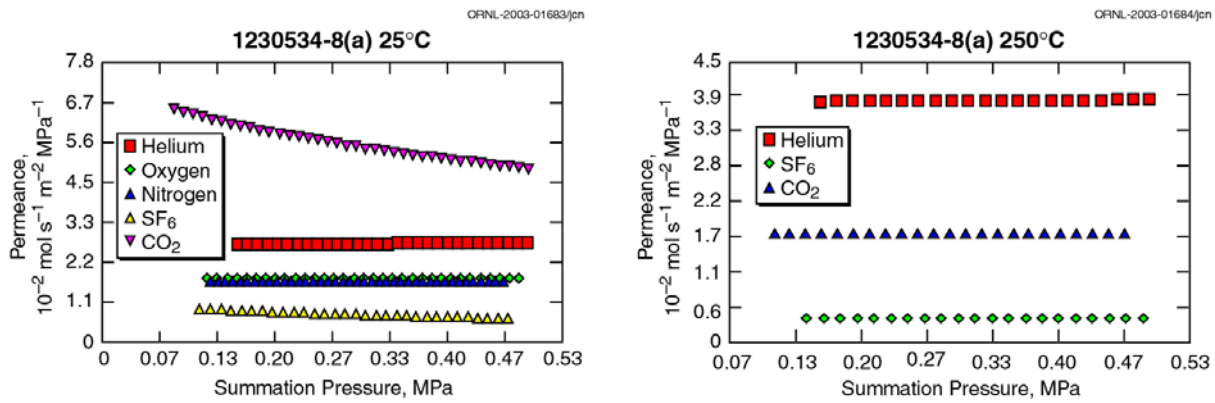

Fig. 5. Variation in Permeances with pressure at 25 and 250 °C for a defect-free membrane showing the effects of temperature on the large surface flow component for CO_2.

Recently, experiments have been performed by several groups on alumina, silica, and zeolite membranes having nanometer-diameter pores with H_2, He, Ar, Ne, and a number of other gases [Burggraaf, 1999; de Lange, et al., 1995; Fain, 2000; Lee and Oyama, 2002; Uhlhorn, et al., 1992]. Results from experiments at ORNL for He permeation through a nanoporous ceramic membrane are shown in Fig. 6. Results from experiments in the Netherlands for H_2 permeation through a nanoporous silica-modified γ-alumina membrane [Uhlhorn, et al., 1992] are shown in Fig. 7. These plots represent the trend of a large number of permeation tests on nanoporous membranes. The temperature dependence has an opposite sign to Knudsen and classical surface diffusion processes discussed above. The permeance and its rate of increase both increase with increasing temperature. Fain [2000; 2002] makes the point that this behavior is not understood. However, the appearance of Fig. 6 and many similar results in the literature mentioned above exhibit the signature of thermally activated processes.

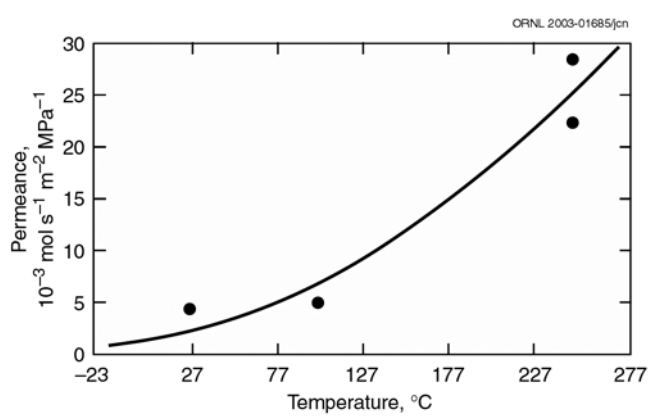

Fig. 6. Variation of He permeance with temperature for an ORNL alumina membrane.

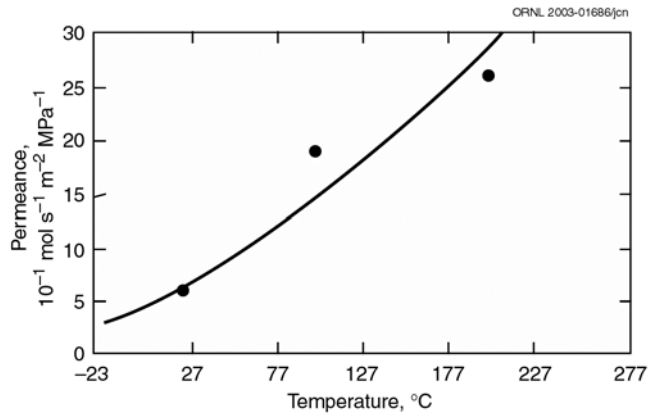

Fig. 7. Variation of H_2 permeance with temperature for a nanoporous silica-modified γ-alumina membrane.

A considerable amount of information can be acquired from individual pure gas permeance data when a sufficient amount of precise data is acquired over a range of pressures and temperatures.

MIXED-GAS SEPARATION MEASUREMENTS

Permeance measurements on pure gases are invaluable in the evaluation of membrane performance. However, in gas mixtures, the interactions of gas molecules with each other and with the membrane pores can have significant effects on gas separations. For example, in the separation of hydrogen from a hydrogen-CO_2 mixture, adsorption of CO_2 on the pore surfaces effectively decreases the size of the pores, and in turn the achievable separation factor may be changed. As a gas pair travels through a membrane, the different species can collide with each other and transfer momentum. Present and deBethune [1948] have derived a method for calculating this momentum exchange. To the first order, the momentum exchange depends on the pressure difference across the membrane.

In an operating separation system such as that depicted in Fig. 3, a gas mixture is fed into a membrane module, and a portion of the gas, the permeate, passes through the walls of the membrane and a portion, the retentate or raffinate, exits the membrane at the opposite end of the membrane. The fraction of the feed gas passing through the walls of the membrane is enriched in the gas with the higher permeance. The retentate is depleted in the gas with the higher permeance, and, of course, for a molecular sieve, only the smaller gas molecules permeate the membrane. The ratio of the permeate flow rate to the feed flow rate is usually called the *cut*. The major variables in an operating gas separation system are the *pressure ratio*, the *pressure difference* across the membrane, the *cut*, and the *temperature*. These variables affect the separation factor in different ways, and, in an operating gas separation system, the actual separation factor is strongly dependent on these operating conditions. As an example, concentration polarization effects can develop near the membrane surface as a result of withdrawal of the gas with greater permeance and can thus decrease in its concentration in the feed gas. Concentration polarization effects may be addressed through changes in the geometry of the feed flow path to the

membrane. Generally, the separation factor measured in an operating mixed-gas separation system will be significantly less than the ideal separation factor.

ORNL's mixed-gas separation system is, in effect, a small single-stage gas separation module. The standard test membranes are 25-cm-long, 1.1-cm-diam tubes such as that depicted in Fig. 3. In operation, the feed gas enters one end of the tube, a fraction of the gas passes through the walls of the tube, and the balance of the gas exits the tube at the opposite end. The system can be operated at feed pressures up to 0.67 MPa, permeate pressures as low as 0.05 MPa, and cuts between about 0.1 and 0.5 (although higher cuts may be achieved), and temperatures from ambient to 600°C. The principal issue for high-temperature separations testing of ceramic membranes relates to difficulties in sealing the membranes above 300°C. This is not a significant issue for metal-supported membranes, which can be sealed by welding. Feed, permeate, and retentate/raffinate mole fractions are determined by gas chromatography. Pressures are measured with high-precision capacitance transducers, and temperatures are measured with high-precision thermistors. Flow rates are determined with a flow meter; however, flow rates are not critical to the determination of separation factors. Although cut is a critical measurement, it may be calculated from the gas chromatography data for the three streams, especially if only binary mixtures are involved.

The ORNL mixed-gas separation system permits the acquisition of data to calculate actual separation factors over the operating range of the system. With properly acquired data, measured separation factors may be extrapolated to the ideal separation factor for any gas pair. Fain [2002] has reported such information for two different membranes. The extrapolated ideal separation factor from the binary mixed-gas separation was, within experimental error, the same value as the ideal separation factor calculated from the pure gas permeance measurements. This is a result of considerable importance in that it establishes the validity of using pure gas permeances to estimate the efficacy of membranes in separating gases contained in gas mixtures.

CONCLUSIONS: IMPLICATIONS OF RESULTS TO CO_2 SEPARATIONS

Thousands of membranes have been tested during the development work in Oak Ridge on inorganic membranes for hydrogen separation. Most of the data were obtained to understand transport mechanisms of different gases at different temperatures, pressures, and pore sizes. These data were essential to the development of the models and evaluation methods. Over that period, more than a dozen membranes have been made that have ideal separation factors significantly greater than the Knudsen ideal separation factors. Table 1 presents Knudsen ideal gas separation factors. Table 2 presents separation factors for several membranes that have been determined to establish the efficacy of the membranes for hydrogen separation. As will be noted from the data contained in Table 2, considerable progress has been made toward achieving very high separation factors. Also, the data are consistent with the models developed.

The data presented in Table 2 reveal quite clearly that surface flow of the heavier molecules in a binary mixture (e.g., He and CO_2) has a significant role in reducing the

value of the ideal separation factor at lower temperatures and that surface flow becomes more significant for smaller mean pore diameter membranes. For the gases investigated and reported here, surface flow is essentially negligible at 250°C and higher. This may or may not be the case for other gases. For a given membrane and at temperatures of 250°C and higher, the ideal separation factor increases with the increasing difference in molecule size between the two gases used in a binary mixture. Helium has been shown to be a good surrogate gas for hydrogen, and the permeances of helium and hydrogen are observed to increase with increasing temperature. This behavior with temperature is of opposite sign to the temperature dependence of Knudsen diffusion. More importantly, the rate of increase in helium permeance with temperature increases with a decrease in membrane pore diameter. This effect is not expected classically, but it is fortunate because it contributes significantly to higher ideal separation factors. Current work involves developing a theoretical model for thermally activated diffusion in porous membranes that explains this behavior on a physical basis. The model shares some features with diffusion in the solid state in the presence of traps [Mansur, 1981].

These membranes, which Parsons suggests may cost on the order of $\$1100/m^2$, have operated up to 600 ºC. Membranes for the separation of H_2 from synthesis gas have apparent pore diameters of 0.5 nm. As noted previously herein, the small pore size of these membranes notwithstanding, very high fluxes or permeances may be achieved. The membranes have a positive flux dependence on temperature. At about 350°C, the H_2 permeance of these inorganic membranes will be about 0.558 $mol \cdot s^{-1} \cdot m^{-2} \cdot MPa^{-1}$.

The data in Table 3 and Parsons' conclusions on costs suggest that an H_2-separation device based on these inorganic membranes would be highly efficient and compact. A membrane system capable of very high efficiency separation of CO_2 and providing high-purity H_2 at minimal costs is possible with these membranes. Thus, the Parsons paper focused on the engineering aspects of a system based on these membranes, whereas this paper focuses on the principles of use of these membranes in a high-temperature carbon dioxide mitigation strategy. These complementary studies suggest that the membranes have great potential for the separation and capture of carbon dioxide at high temperatures.

Table 1. Knudsen ideal gas separation factors

	Gases				
	He	CO_2	CF_4	SF_6	Ar
Molecular weight	4.0026	44.0098	88.0046	146.01	39.948
Diameter, nm	0.256	0.399	0.470	0.551	0.342
Knudsen separation factor	Basis	3.316	4.689	6.040	3.159

Table 2. Membranes with high Knudsen ideal gas separation factors

Sample ID	Permeance at 25°C[b]	Separation factors for gas pairs[a]							
		He/CO_2		He/CF_4		He/SF_6		He/Ar	
		250°C	600°C	250°C	600°C	250°C	600°C	250°C	600°C
1371-37B	0.0084	25.7	64.6	42.4	70.0				
182686	0.0021	24.1		75.0					
1373-37	0.028	20.3	44.7	46.7	59.6				
1373-38a	0.015	10.0				165.9			
1373-19	0.28	4.1		3.0	9.3	109.0		6.0	9.8
1373-19c		7.6				26.1			
1373-11	0.028	2.7		16.4		29.0		5.4	
1373-62b	0.0073	5.0		10.3					
1373-97		2.7		10.3				4.4	
1373-62d						18.4			
1373-43	0.14	4.5				9.5			
1373-94b	0.056	4.3		8.4		10.9			

[a]Separation factors calculated from ratios of zero pressure permeance. Values at 600°C were extrapolated from values taken at 250°C.
[b]Permeance units: $mol \cdot s^{-1} \cdot m^{-2} \cdot MPa^{-1}$.

Table 3. H_2 separation device designs[a]

Device design	Baseline	Revised	Revised
Operating temperature (°C)	761	600	300
H_2 production			
Rate (kg/h)	15,969	16,285	16,585
Temperature (°C)	761	600	300
Synthesis gas inlet conditions			
Flow rate (kg/h)	310,257	310,257	310,257
Pressure (MPa)	6.895	6.895	6.895
Temperature (°C)	513	318	207
Flow rate (m^3/s)	5.78	4.90	3.20
Membrane area			
Minimum (m^2)	3,271	3,335	3,397
Increased ~25% (m^2)[b]	4,181	4,181	4,181
Vessel ID (m)	2.4384	2.4384	2.4384
Tube dimensions			
OD (mm)	15.875	15.875	15.875
ID (mm)	12.7	12.7	12.7
Preliminary length (m)	8.84	8.84	8.84
Tubes per vessel	11,800	11,800	11,800
Gas velocity through tubes (m/s)	3.87	3.29	2.13
Gas retention time (s)	2.3	2.7	4.1
Reynolds number	~19,000	~22,500	~28,000
Number of vessels	3	3	3
Configuration of tube bundle (m)	2.4 × 3	2.4 × 3	2.4 × 3
Flow arrangement	Series	Series	Series

[a]Adapted with permission from Michael Rutkowski, the Parsons Infrastructure & Technology Group Inc [Badin, et al., 2000].
[b]Membrane area increased to meet design specifications of Parsons study.

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