Gas Separations Using Ceramic Membranes

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Executive Summary

This study covers a comprehensive evaluation of existing ceramic membranes for high temperature gas separations. Methodology has been established for microporous characterization stability and gas separation efficiency. A mathematical model was developed to predict gas separations with existing membranes. Silica and zeolitic modifications of existing membranes were pursued to enhance its separation efficiency. Some of which demonstrates unique separations properties. Use of the dense-silica membranes for hydrogen enrichment was identified as a promising candidate for future development. In addition, the decomposition of trace ammonia contaminant via a catalytic membrane reactor appears feasible. A further economic analysis is required to assess its commercial viability.

1. Introduction

About one-eighth of world's coal production is used to generate electricity in the United States (Schmitt, 1980). Pressure to reduce the cost and environmental impact of producing electricity from coal has stimulated interest in the improvement of advanced power generation systems, such as integrated gasification combined cycle (IGCC) and direct coal-fuel turbine (DCFT) systems.

The advantage of IGCC systems is to allow the most stringent environmental standard to be met economically (Schmitt, 1980). To achieve this clean-up with conventional technology, however, the efficiency loss associated with heat recovery and wet scrubbing is unavoidable (Reed, 1985). Thus it is desirable to perform the clean-up at high temperature and high pressure (HTHP). Hot gas stream clean-up also provides a higher inlet temperature of gas to the combustion turbine, which is critical to the efficiency and electricity cost of IGCC systems (Larson, 1981; Schmitt, 1980). The similar advantages of hot gas clean-up are also applicable to DCFT systems. The ceramic membrane is capable of operating at this condition and could achieve clean-up without a cooling-heating cycle. They have good structure stability and generally can withstand more harsh chemical environments. In addition, the developed HTHP gas separation technology, such as separation of H_2 , can be particularly beneficial in the petrochemical as well as synthetic fuel industries.

Selection of membrane materials was crucial for applications in HTHP conditions. Presently the support of commercial inorganic membranes include carbon, glass and alumina. A commercially available alumina membrane with 40Å pore diameter was identified as one of the potential candidates for HTHP gas separations. It had an excellent stability and acceptable hydrothermal stability at 650°C. The thin membrane layer provided high permeability, which was essential for processing high volume streams involved in IGCC and DCFT systems. Gas separation with such a membrane can perform Knudsen diffusion, i.e. based on molecular weight.

An improved separation efficiency is also highly desirable for applications involving hydrogen separation and catalytic decomposition of contaminants, NH_3 and H_2S . One of the effective avenues is to narrow its pore size through surface modification. Thus, gas separation can be accomplished through molecular sieving. One step further, a dense film membrane can even provide a near infinite selectivity of certain gas, such as H_2 . Both small pore and dense-phase membranes can be readily available through minor modification of existing commercial membranes.

In this project, investigation was focused on: (1) hardware establishment, i.e., membrane modules including housing and end seals for conducting gas separations at HTHP; (2) evaluation of existing alumina membranes with particular emphasis on material characteristics, stability, and gas permeation/separation; (3) study of gas transport phenomenon and development of a mathematical model to verify the results with experimental data using existing membranes, and to simulate gas separation for a range of conditions

encountered in coal-gas cleanup operations; (4) synthesis and characterization of highly selective membranes with small pore and dense film for high temperature gas separations.

2. Characterization of Existing Membranes

The commercial application of microporous ceramic membranes began in the late 1970's and focused primarily on liquid phase microfiltration and ultrafiltration. As a result of the superior mechanical, thermal, and chemical properties of ceramic membranes compared to their polymeric counterparts, considerable interest has been focused on high temperature gas phase applications including filtration, gas separations, and ceramic membrane reactors. Details of membrane synthesis and application have been recently reviewed (Bhave, 1991). Critical to the success of these emerging applications is an understanding of the characteristics of microporous ceramic membranes.

The mechanisms for gas transport through a porous membrane vary primarily with pore size and to some extent with chemical interaction between the diffusing species and the membrane material. At the largest pore size, transport is governed by Poiseuille flow and no separation occurs for multicomponent streams. When the pore size is approximately less than 1/10 that of the mean free path of the diffusing species, collisions between the gas molecules and the pore wall control the transport of species through the membrane. This is known as Knudsen diffusion and separation between species is inversely proportional to the inverse square root of their molecular weights. When pore dimensions approach those of the diffusing species, separations can occur by size exclusion or molecular sieving. In this regime nearly infinite separation factors are theoretically attainable. Under circumstances where adsorption of a species occurs onto the surface of the membrane, transport can be enhanced due to surface diffusion. Finally, for condensable vapor species, capillary condensation can occur in the pores of the membrane and transport through the membrane is governed by pseudo-liquid phase diffusion.

Important parameters for characterizing the performance of a membrane include membrane structure or morphology, gas permeability, multicomponent gas separation factors, and pore size distribution of the separating layer. For applications involving high temperatures and/or severe environments, thermal stability, hydrothermal stability, and chemical stability of the membrane are also critically important.

2.1 Morphology

The membranes investigated in this study are asymmetric, composite ceramic membranes, commercially available as tubular elements under the trade name Membralox®. A cross section of this configuration is shown in the SEM micrograph in Figure 2.1.

The support shown in Figure 2.1 is an extruded α -alumina with a average pore diameter of approximately 10 μm and a porosity of approximately 45%. the support layer is approximately 2 mm thick. A second layer, approximately 50 μm thick, is slip-cast onto this support and fired to yield an α - Al_2O_3 layer with an average pore diameter of 0.8 μm and a porosity of

Figure 2.1 SEM Micrograph of a Cross Section of a Nominal 40Å Asymmetric Alumina Membrane

Layer 1 : Pore Diameter = 40 Å ; Thickness = 3-5 μm ; Porosity = 50%

Layer 2 : Pore Diameter = 0.2 μm ; Thickness = 15 - 30 μm ; Porosity = 35%

Layer 3 : Pore Diameter = 0.8 μm ; Thickness = 30 - 50 μm ; Porosity = 40%

Support : Pore Diameter = 10 - 15 μm ; Thickness = 1.5 - 2.0 mm ; Porosity = 40 - 45%

40%. Similarly, a third $\alpha\text{-Al}_2\text{O}_3$ layer, approximately 30 μm thick, with an average pore diameter of 0.2 μm and a porosity of 35% is deposited. The final top layer is slip-cast and fired to yield a 5 μm thick, transitional $\gamma\text{-Al}_2\text{O}_3$ layer with a nominal pore size of 40 $\text{\AA}$ and a porosity of 50%. An SEM micrograph of the top surface of this inner layer is shown in Figure 2.2. From there it can be seen that the top layer is defect-free (ie. no pinholes or cracks) This top layer provides a separating barrier capable of Knudsen separation for most gas separations encountered. The asymmetric support structure permits high permeability combined with mechanical strength.

2.2 Pore Size Distribution

2.2.1 Methodology

For microporous membranes, pore diameter is one of the most critical factors in determining membrane performance. For the commercially available, asymmetric 40 $\text{\AA}$ $\gamma\text{-Al}_2\text{O}_3$ membrane however, the separating layer constitutes less than 0.2% by weight of the total sample. As a result, traditional techniques such as nitrogen adsorption or mercury intrusion do not have sufficient resolution to determine the pore size in this small layer. A typical pore size distribution from Hg porosimetry is given in Figure 2.3. From there the 10 μm support as well as the 0.8 μm and 0.2 μm sub-layers can be readily seen. However, the distribution for the nominal 40 $\text{\AA}$ separating layer is broad and diffuse with pores from 30 $\text{\AA}$ to 110 $\text{\AA}$ indicated.

A flow weighted pore size distribution analyzer has been developed which is capable of characterizing this thin layer. A schematic of the apparatus is shown in Figure 2.4. The details of the technique were originally developed from work performed at the Oak Ridge Gaseous Diffusion Plant and described by Fain (1989).

The technique is based on the principle of condensation of a vapor in a capillary as described by the Kelvin Equation:

$$\ln(P_0/P) = 2\gamma V / (rRT) \quad (1)$$

where:

- P_0 = vapor pressure of condensable vapor
- P = partial pressure of condensable vapor
- γ = liquid surface tension of condensed vapor
- V = molar volume of condensed vapor
- r = pore radius where vapor is condensed
- R = gas constant
- T = temperature in the pore

A gas mixture which contains a condensable as well as a

Figure 2.2 SEM Micrograph of the Inner Surface of a Nominal 40Å Asymmetric Alumina Membrane

**Figure 2.3 Pore Size Distribution of a Nominal 40Å Asymmetric Alumina Membrane
by Hg Intrusion Porosimetry**

Figure 2.4 Schematic of a Flow-weighted Dynamic Pore Size Distribution Analyzer

noncondensable gas is fed into the membrane tube and permeates through the membrane layer. When the partial pressure of the condensable gas is raised so as to satisfy Eqn. (1), vapor will condense in pores of radius r , thereby blocking them and resulting in a dropoff in flow. At a pressure approaching the saturated vapor pressure of the vapor, all pores in the membrane can be blocked and no permeate flow is observed. As the system pressure is stepwise lowered, pores are evacuated starting from the largest radius to the smallest. This change in flow can be monitored relative to partial pressure to give a flow weighted pore size distribution.

As shown in Figure 2.4, a stream of nitrogen or helium is saturated with cyclohexane by sparging through the temperature controlled saturator which is maintained so as to generate a 5% cyclohexane mixture. The membrane housing is immersed in a constant temperature bath and fed with a side stream from this flow. Total membrane pressure is varied by varying the reject flow while transmembrane pressure is maintained at a constant 15 Torr by controlling the permeate flow. Permeate and reject flows are monitored with mass flowmeters. Vacuum is drawn on the system with a vacuum pump. This system is interfaced with a Macintosh II computer for process control, data logging, and real time data analysis. Labview software from National Instruments is used for these purposes.

In a typical experiment, full vacuum is drawn on the membrane to evacuate any condensed impurities while gas flow (either N_2 or He) is initiated to the saturator and allowed to equilibrate. The N_2 /cyclohexane mixture is then introduced into the membrane. The total pressure is raised to a sufficient level to fully condense the cyclohexane in the pores completely blocking permeate flow. The system pressure is then stepwise lowered. When a pressure equivalent to a pore radius as determined by Eqn. 1 is reached, those pores are evacuated and flow is initiated. Permeate flow is monitored for each increment and a distribution of incremental permeate flow versus system pressure results. This data is then analyzed via Eqn. 1 taking into account the thickness of the adsorbed monolayer of cyclohexane on the pore wall. The result is a distribution of permeate flow versus pore radius and a flow weighted average pore radius can be calculated.

The primary advantage of this system is that it allows accurate pore size distribution measurement of the thin separating top layer of the asymmetric membranes. In addition, the distribution is based on incremental flow through the membrane rather than incremental volume desorbed (as in N_2 porosimetry) or incremental volume intruded (as in Hg porosimetry). This incremental flow relates directly to membrane performance in gas separation applications. Also, no assumptions are required regarding porosity or tortuosity.

The technique is limited by the constraints of the Kelvin equation. As a result, the lower limit of pore diameter accessible with this technique is approximately 15Å. Below this diameter, surface interactions with the adsorbate become significant, and the assumptions under which the Kelvin equation is derived breakdown. Theoretically, there is no upper limit to the application of the Kelvin equation. However, as noted by Gregg and Sing (Gregg, et al., 1982), the relative pressures for given pore sizes at the upper end of the mesoporous regime are grouped so closely together that experimental error renders the results highly questionable. Therefore, this technique is only used for pore sizes up to approximately 500Å or less.

2.2.2 Results and Discussion

The pore size distribution for several nominal 40Å membranes as received from the manufacturer are shown in Figure 2.5. From there it can be seen that the average flow-weighted pore size is essentially 40Å. The distribution for the as-received membranes ranges from approximately 20Å minimum pore diameter to approximately 55Å maximum pore diameter. These results are in excellent agreement with those reported by Fain (1989) for similar membranes. Figure 2.6 shows the results of an experiment where multiple runs were made on a single membrane. From there it can be seen that reproducibility of the technique is quite good. The average pore diameter was $40.6\text{Å} \pm 1.8\text{Å}$ within 95% confidence limits ($\sigma=0.74\text{Å}$). The resulting reproducibility is $\pm 4.5\%$.

2.3 Pure Component Gas Permeability

2.3.1 Methodology

In gas permeation, the flux of gas through the membrane layer is measured as a function of total pressure, transmembrane pressure, and stage cut (ie., the fraction of gas fed to the membrane that permeates through it). Permeability results are reported as gas flow per unit transmembrane pressure per unit membrane surface area (ie., $\text{m}^3/\text{hr}/\text{atm}/\text{m}^2$).

Figure 2.7 shows a schematic of the high temperature, high pressure gas permeation apparatus used in this study. Gas feed rates into the membrane are controlled by mass flow controllers. Total pressure, transmembrane pressure and stage cut are controlled by backpressure regulators on the exit permeate and reject lines. Feed, reject and permeate pressures are read by precision pressure transducers, and permeate and reject flowrates are measured by calibrated mass flowmeters. The temperature of the membrane module can be varied via an electric tube furnace with a maximum operating temperature of 1000°C. The furnace and module are

Figure 2.5 Pore Size Distribution using the Flow-weighted Dynamic Pore Size Distribution Apparatus of Three Nominal 40Å Asymmetric Membranes as Received from the Manufacturer

Figure 2.6 Repeat Pore Size Distribution Runs on the Same Membrane to Establish the Reproducibility of the Dynamic Pore Size Distribution Apparatus

Figure 2.7 Schematic of the High Temperature, High Pressure Gas Permeation Test Apparatus

housed in a steel enclosure which is purged with N₂ in order to maintain an inert atmosphere allowing the investigation of flammable gases (ie. H₂, CH₄). This inert atmosphere is monitored for O₂ and combustibles, and the furnace and flow controllers are interlocked to shutdown in the event of a leak. The reject and permeate flows are fed to a caustic scrubber allowing for the handling of acid gases such as H₂S and SO₂. After the scrubber, the effluents are fed to a dilution stack and discharged.

2.3.2 Results and Discussion

Permeability vs. transmembrane pressure drop results for H₂, He, N₂, CO₂, CO, and CH₄ at 25°C, 538°C, 650°C, and 815°C are given in Figures 2.8, 2.9, 2.10, and 2.11 respectively. Pure component permeabilities are summarized in Table 2.1 and ideal separation factors based on these permeabilities are summarized in Table 2.2.

The permeability of pure gases through a porous solid will be governed by Knudsen diffusion when the Knudsen number:

$$K_n = \lambda / r \quad \text{Eqn. 2}$$

where:

λ =mean free path
 r =pore radius

is very much greater than 1. Under these conditions, the permeability through the membrane can be described by:

$$P = 2/3 \cdot r \cdot (8RT/\pi M)^{1/2} \cdot (\epsilon/\tau) \cdot (1/RTL) \quad \text{Eqn. 3}$$

where:

P =permeability
 r =pore radius
 R =gas constant
 T =absolute temperature
 M =molecular weight
 ϵ =porosity
 τ =tortuosity
 L =membrane layer thickness

From this it can be seen that in the Knudsen regime, permeability is independent of transmembrane pressure drop and inversely proportional to the square root of molecular weight.

From Figures 2.8-2.11 it can be seen that the permeabilities of all of the compounds studied are essentially independent of transmembrane pressure at all temperatures. The slight deviation

Table 2.1: Average Pure Component Permeabilities as a Function of Temperature

Gas	Permeability (m ³ /m ² /hr/atm)			
	25°C	538°C	650°C	815°C
H ₂	245.4	292.0	297.0	313.2
He	173.0	216.4	220.9	234.0
N ₂	70.0	86.1	85.7	96.9
CO ₂	N/A	61.8	62.2	72.2
CO	73.0	47.3	46.3	42.7
CH ₄	86.0	54.5	50.5	26.1

Table 2.2: Ideal Separation Factors Based on Pure Component Permeabilities Referenced to H₂

Gas B	Actual Perm H ₂ / Perm B				Theoretical Ideal Separation Factor (MW _B / MW _{H2})
	25°C	538°C	650°C	815°C	
He	1.42	1.35	1.34	1.34	1.41
N ₂	3.51	3.39	3.46	3.23	3.74
CO ₂	N/A	4.73	4.78	4.34	4.69
CO *	3.36	6.17	6.42	7.34	3.74
CH ₄ *	2.85	5.36	5.88	12.0	2.83

* Coke formation postulated on membrane surface.

Figure 2.8 Membrane Permeability vs. Transmembrane Pressure for H₂, He, N₂, CO and CH₄ at 25°C

Figure 2.9 Membrane Permeability vs. Transmembrane Pressure for H₂, He, N₂, CO₂, CO and CH₄ at 538°C

Figure 2.10 Membrane Permeability vs. Transmembrane Pressure for H₂, He, N₂, CO₂, CO and CH₄ at 650°C

Figure 2.11 Membrane Permeability vs. Transmembrane Pressure for H₂, He, N₂, CO₂, CO and CH₄ at 815°C

with transmembrane pressure has been shown by Leenaars, et al. (Leenaars, et al., 1984) to be a contribution of Poiseuille flow resistance in the support layers of the asymmetric membrane. Table 2.2 shows the separation factors based on the pure component permeabilities and referenced to H₂. From Eqn. 3, if Knudsen diffusion is the controlling mechanism of transport, the ratio of permeabilities of any two compounds under otherwise similar conditions should be given by:

$$P_A/P_B = (M_B/M_A)^{1/2} \quad \text{Eqn. 4}$$

From Table 2.2 it can be seen that this is in fact the case for all compounds studied at 25°C. At elevated temperatures H₂, He, N₂, and CO₂ continue to follow this trend. For CO and CH₄, however, the separation factors appear to be increasing well in excess of the ideal values. From Table 2.1, it seems that this deviation is due to a decline in CO and CH₄ permeability relative to the other compounds.

For both gases, coking was hypothesized as the reason for the permeability decline at high temperatures. This is supported by the results of Figure 2.12. There the room temperature N₂ permeability of the presumably coked membrane and also the room temperature N₂ permeability of the same membrane after treatment in a 10% O₂/balance He at 538°C for 16 hours is shown. The average N₂ permeability increased from 49.7 m³/m²/hr/atm to 122.5 m³/m²/hr/atm after this treatment. The final permeability value is consistent with that reported above for N₂. The source of this carbon deposition appears to be CO disproportionation and CH₄ decomposition on the acidic sites of the transitional γ-Al₂O₃ layer. As a result, the high temperature permeabilities reported for CO and CH₄ are likely not accurate.

2.4 Thermal and Hydrothermal Stability

2.4.1 Thermal Stability

Many of the emerging applications for microporous ceramic membranes hope to capitalize on the thermal stability of ceramics in comparison to polymeric membranes. However, no assessment of the thermal stability of commercially available, asymmetric membranes has been reported.

2.4.1.1 Methodology

In this study, the thermal and hydrothermal stability of the nominal 40Å membranes were assessed in the apparatus shown in Figure 2.13. Under thermal conditions, an inert gas

Figure 2.12 N₂ Permeability at 25°C of a Nominal 40Å Membrane Before and After Treatment with 10% O₂/balance He at 538°C for 16 Hours Following Exposure to CO and CH₄ at High Temperature (538 - 815°C)

○ Before O₂ Treatment □ After O₂ Treatment

Figure 2.13 Schematic of Thermal and Hydrothermal Stability Test Unit with On-line Gas Permeation Characterization

such as He or N₂ is introduced to the membrane module via mass flow controllers. The module is housed in a tube furnace which allows the membrane to be heated up to 650°C. After the furnace, the permeate and reject effluents are cooled in condensers. During thermal treatment, these effluents are vented to a hood. The permeability of the membrane can be measured periodically via the on-line test gauge and flow measuring set up. Here, reject flow is diverted from the vent through a back pressure regulator in order to vary transmembrane pressure. The permeate stream is diverted from the vent through a calibrated rotameter to monitor permeate flow. Feed, reject, and permeate pressures are monitored with a precision test gauge. This unit is also interfaced with an on-line gas chromatograph in order to assess N₂/He mixed gas separation factors.

2.4.1.2 Results and Discussion

The room temperature N₂ permeabilities of several membranes as received from the manufacturer are given in Table 2.3. There reported values range from 51 m³/m²/hr/atm to 70 m³/m²/hr/atm. However, values as low as 40 m³/m²/hr/atm have been observed. In addition to this wide range of as received permeabilities, the fresh permeability also seemed to vary with time of year, with higher values observed in the less humid winter months and lower values observed in the more humid summer months.

The effect of thermal treatment on the fresh as received membranes are summarized in Figures 2.14, 2.15, and 2.16. Figure 2.14 shows the effect of treatment temperature on N₂ permeability measured at room temperature. Here the membrane was treated in 500 cc/min of flowing N₂ for three hours each at 25°C, 200°C, 400°C, 500°C, and 640°C. Thermal treatment had negligible effect on permeability at temperatures up to 400°C. However, treatment at 500°C and 600°C resulted in a near doubling of the permeability of the membrane.

Figure 2.15 shows the effect of thermal treatment on N₂ permeability measured at room temperature as a function of treatment time and Figure 2.16 shows the effect of this treatment on the pore size distribution of the membrane. Treatment was carried out at 640°C with a 500 cc/min flow of N₂ fed to the membrane module. The permeability of the fresh membrane was approximately 40 m³/hr/m²/atm and the flow weighted average pore size was 39.6Å. As can be seen from Figure 2.14, the permeability rose to a value of approximately

Table 2.3: N₂ Permeabilities of As-Received Membranes at 25°C

Membrane	Permeability (m³/m²/hr/atm)
E11831	70
E11835	62
E12269	53
E12458	53
E12462	51

**Figure 2.14 Permeability Growth as a Function of Treatment Temperature
in Flowing N₂ for a Nominal 40A Membrane**

Figure 2.15 Permeability Change as a Function of Treatment Time for a Nominal 40Å Membrane Exposed to Flowing N₂ for 100 Hours at 640°C

Figure 2.16 Pore Size Distribution of a Nominal 40Å Membrane Before and After Thermal Treatment at 640°C for 100 Hours

110 m³/hr/m²/atm after two hours of exposure and remained unchanged after 100 hours of treatment. While the permeability of the membrane more than doubled with thermal treatment, the pore size grew only slightly to 43.2Å as shown in Figure 2.15. This thermally treated membrane was then stored in the laboratory, exposed to room air. After six months, it was resubjected to thermal treatment. The changes in permeability throughout this process are summarized in Figure 2.17. There it can be seen that after six months storage, the permeability of the membrane reverted to its original, as-received value. Subsequent thermal treatment as before caused a near doubling of the permeability, suggesting that the process is reversible.

Transport through membranes in this pore size range is by Knudsen diffusion and permeability is proportional to pore diameter. Table 2.4 summarizes the predicted pore size change based on the observed permeability increase along with the ratios of porosity to tortuosity (ϵ/τ) calculated using Eqn. 3 and the observed permeabilities and pore sizes. For pore size changes to account for the increased permeability, a pore radius of nearly 42Å should have been observed. Obviously the increase in permeability is far in excess of that accountable by the modest increase in pore size suggesting that some other change in the structure of the membrane layer is taking place. A near doubling of the porosity to tortuosity (ϵ/τ) ratio seems to explain the observations. The problem then becomes one of how to explain this change.

Two possible scenarios are presented in Figure 2.18. The pore structure of γ -Al₂O₃ membranes is thought to be slit shaped (Wefers et al., 1987; Leenaars et al., 1984). In Scenario 1, these slit shaped pores are partially filled with adsorbed moisture leaving a capillary of diameter d_p . This moisture is evacuated during thermal treatment at high temperatures, but readsorbs during subsequent exposure to room air. In each step of this process, the pore size distribution analysis, which is based on capillary condensation, measures the width of the slit, d_p (Gregg et al., 1982). The adsorbed water must be strongly adsorbed since short term exposure to 10 torr vacuum during pore size distribution analysis does not change the observed permeability of these membranes. The high temperature required to observe permeability changes during thermal treatment also supports this statement.

The second scenario in Figure 2.18 involves lateral movement of the stacked plates which form the pore structure. Again, with only lateral movement, pore size analysis would detect the

Figure 2.17 Permeability Changes in a gamma-Al₂O₃ Thermally Treated at 640°C for 36 Hours then Stored at Ambient Conditions for 6 Months

Table 2.4: Characteristics of γ -Al₂O₃ Membrane as a Function of Thermal Treatment at 640°C

	$r(\text{\AA})$	N ₂ Permeability (m ³ /m ² /hr/atm)	N ₂ Permeability (mol/m ² /hr/atm)	Predicted $r(\text{\AA})$	ϵ/τ
Fresh	19.8	52.3	2335	-	0.127
100 hrs	21.6	110.0	4910	41.7	0.244

Figure 2.18 Model of Pore Structure Changes in a $\gamma\text{-Al}_2\text{O}_3$ Membrane Subjected to Thermal Treatment at Temperature up to 640°C

Scenario 1:

Scenario 2:

slit width, d_p . This scenario would require that the plates shift back during exposure to room air. For this scenario to be valid, the length of the slit would have to double in order to account for the observed permeability change. It seems probable that dimensional changes of this magnitude would inevitably induce defects such as cracks in the membrane structure. As a result, Scenario 1 most likely occurs.

These results suggest that the $\gamma\text{-Al}_2\text{O}_3$ membranes are thermally stable at temperatures up to 640°C . All permeability measurements were made at room temperature following incremental periods of thermal treatment. This shows that the membranes are also stable to controlled thermal cycling. The observed changes in permeability appear to be due to desorption of water and other contaminants adsorbed onto the membrane during storage. This also explains the variation in permeability of the as received membranes and suggests that an initial thermal treatment is necessary in order to characterize the true gas permeability of these membranes.

2.4.2 Hydrothermal Stability

2.4.2.1 Methodology

The effect of hydrothermal stability was also assessed using the apparatus in Figure 2.13. For one membrane, however, 24 μL of liquid water was fed to a vaporizer which was purged with 2 L/min of flowing N_2 . This resulted in a stream of approximately 5% by volume water vapor in N_2 at the treatment temperature. For a second membrane, a stream of approximately 90% steam was used. These N_2 /steam streams were fed to the heated module. The water was condensed and collected from both the reject and permeate streams. Before permeabilities were measured, the water flow was halted and the membrane was purged overnight in flowing N_2 .

2.4.2.2 Results and Discussion

The effect of hydrothermal treatment with a 5% steam stream on the first membrane is shown in Figures 2.19 and 2.20. From Figure 2.19, the permeability through the membrane rose rapidly to a value of approximately $110 \text{ m}^3/\text{hr}/\text{m}^2/\text{atm}$, as with thermal treatment. Under hydrothermal conditions however, the permeability rose further, plateauing at a value of nearly $145 \text{ m}^3/\text{m}^2/\text{hr}/\text{atm}$. The pore size distribution of the fresh membrane and after 95 and 117.5 hours of exposure are shown in Figure 2.20. There it is evident that the flow weighted average size has grown from approximately $40\text{\AA}$ for the fresh

Figure 2.19 Permeability Growth in a Nominal 40Å gamma-Al₂O₃ as a Function of Treatment Time at 640°C in a Feed Stream of 5% Steam

Figure 2.20 Changes in Pore Size Distribution of a Nominal 40Å gamma-Al₂O₃ as a Function of Treatment Time at 640°C in a Feed Stream of 5% Steam

membrane to 52Å after 95 hours of treatment. No additional pore enlargement is observed after 117.5 hours of cumulative treatment. The results for the second membrane subjected to 90% steam are shown in Figure 2.21. After 198 hours in 90% steam, the permeability of the membrane grew to 188 m³/m²/hr/atm and the average pore size grew to 65.0Å.

The transitional γ -Al₂O₃ is known to undergo transformation through other transitional forms of alumina towards the thermodynamically stable α -Al₂O₃ form at elevated temperatures (T>900°C) (Wefers et al., 1987). Water is known to accelerate this process as well as to lower the temperature at which it takes place. The results here suggest that such a transformation is taking place resulting in pore growth.

Permeability, pore size, predicted pore size based on observed permeability change, and porosity to tortuosity ratio changes throughout treatment are summarized in Table 2.5 for both membranes. For the membrane subjected to 5% steam treatment, the increase in permeability after hydrothermal treatment can be completely accounted for by pore enlargement:

$$109 \text{ m}^3/\text{hr}/\text{m}^2/\text{atm} \times (24.5\text{\AA}/18.5\text{\AA}) = 144 \text{ m}^3/\text{hr}/\text{m}^2/\text{atm}$$

Likewise for the membrane subjected to 90% steam:

$$109 \text{ m}^3/\text{hr}/\text{m}^2/\text{atm} \times (32.3\text{\AA}/18.8\text{\AA}) = 187 \text{ m}^3/\text{hr}/\text{m}^2/\text{atm}$$

In addition, the porosity to tortuosity ratios (ϵ/τ) are slightly higher than those observed after thermal treatment, suggesting that these pore size increases are accompanied by a slight increase in porosity.

These results suggest that the largest changes in membrane structure occur within the first few hours of treatment. The membrane appears to be relatively stable thereafter. This is consistent with a transformation from γ -Al₂O₃ to another intermediate transitional alumina phase. The higher concentration of steam appears to have an increased mineralizing effect. It is not clear, however, if a truly stable plateau has been reached under these conditions or if the kinetics of the transformation have only slowed to the point where much longer exposure times are necessary to observe significant changes in the membrane structure.

Figure 2.21 Changes in Pore Size Distribution of a Nominal 40Å gamma-Al₂O₃ as a Function of Treatment Time at 640°C in a Feed Stream of 90% Steam

Table 2.5: Characteristics of γ -Al₂O₃ Membranes as a Function of Hydrothermal Treatment at 640°C

Hydro 1 5% steam	r (Å)	N ₂ Permeability (m ³ /m ² /hr/atm)	N ₂ Permeability (mol/m ² /hr/atm)	Predicted r (Å)	ϵ/τ
Fresh (after thermal)	18.5	109.0	4866	-	0.282
95 hours	24.6	148.4	6625	25.2	0.289
117.5 hours	24.5	152.5	6808	25.9	0.298
Hydro 2 90% steam					
Fresh (after thermal)	18.8	109.0	4866	-	0.278
198 hours	32.3	188.0	8392	32.4	0.279

2.5 Chemical Stability

Many of the process streams where high temperature membrane processes may be applied contain compounds which may react with the ceramic membrane. Alkali species are an important class of such compounds which would be present in coal gasifier streams as well as in high temperature petrochemical streams where alkali-promoted catalysts are in use.

2.5.1 Methodology

To assess the potential effect of alkali exposure, a ceramic membrane was packed with a crushed, commercially available K^+ -promoted Fe_2O_3 catalyst then exposed to hydrothermal treatment. The feed to the membrane module consisted of 200 cc/min of N_2 into which was evaporated 1.2 ml/min of liquid water. Exposure was for four hours at 640°C.

2.5.2 Results and Discussion

Results are summarized in Figures 2.22, 2.23, 2.24, and 2.25. As a result of this treatment the K^+ content of the catalyst fell from 8.24% to 7.55% on a K_2O basis. The equivalent alkali flowrate was 2.4×10^{-6} mol/min. Following this exposure, the N_2 permeability of this membrane was observed to be approximately 15 $m^3/hr/m^2/atm$. This is in contrast to a value of approximately 150 $m^3/hr/m^2/atm$ found for membranes undergoing the same hydrothermal treatment in the absence of alkali species. The pore size distribution of the membrane can be seen in Figure 2.22. Approximately 20% of the flow through the membrane after exposure to alkali is attributable to pores with diameters in excess of 100Å.

Figures 2.23 and 2.24 show SEM micrographs of the inner membrane surface following this treatment. The inner surface is decorated with crystallites not seen on the fresh inner surface (see Figure 2). In addition, defects are now evident on the alkali exposed surface. From Figure 2.25, EDAX of the membrane surface showed peaks attributable to both Al and to K.

These results are consistent with the formation of alkali aluminates and possibly β -aluminas (Wefers et al., 1987). They also indicate that alkali species may have a severe effect on the integrity of $\gamma-Al_2O_3$ membranes. The loss in permeability with increasing pore size suggests a loss in porosity in the membrane layer. This could be due to blocking of pores by deposited alkali species or to morphological changes associated with compound formation between alkali and alumina.

Figure 2.22 Pore Size Distribution of a Nominal 40Å gamma-Al₂O₃ After Hydrothermal Treatment at 640°C in a Feed Stream of 90% Steam and in the Presence of Alkali Species

Figure 2.23 Wide View SEM Micrograph of the Membrane Surface After Hydrothermal Treatment at 640°C in a Feed Stream of 90% Steam and in the Presence of Alkali Species

Figure 2.24 Magnified View of the Membrane Surface After Hydrothermal Treatment at 640°C in a Feed Stream of 90% Steam and in the Presence of Alkali Species

Treatment at 640°C in a Feed Stream of 99% Steam and 1% Air
 Presence of Alkali Species

MEMBRANE E12459

ST-4423

SURFACE

TIME- 33LSEC

10mV/cm

E J A X

3. Gas Separations with Existing Membranes

Gas separations using commercial ceramic membranes with 40Å pore diameter were performed for three binary mixtures: H_2/CO , H_2/N_2 and He/O_2 . The experimental conditions covered a wide range of temperature (25 to 815°C) and pressure (3 to 38 atm). A mathematical model based upon Knudsen diffusion and intermolecular momentum transfer was developed to predict gas separation efficiency. The experimental results agreed well with the model prediction. The permeability of CO was substantially lower than the value expected from Knudsen diffusion. Nevertheless, the model developed was able to account for this phenomenon and predicted equally well for a binary mixture containing CO. The effect of key operating parameters on separation behaviors was studied with the model developed.

3.1 Introduction

Gas separations via permselective membranes have been developed in the past few years. Several membrane-based processes have been commercialized using polymeric membranes. Microporous inorganic membranes have also been actively explored due to their better material stability than the polymeric counterparts for high temperature and/or high pressure (HTHP) applications. Materials discussed in the literature include vycor glass, aluminum oxide and others with pore size ranging from several microns to 40Å. Several existing and emerging separations at HTHP could be streamlined with the use of these membranes. For example, separation of H_2S from a high pressure natural gas stream, and recovery of hydrogen from coal gasification products.

Gas separations via microporous membranes involve four mechanisms: Knudsen diffusion, surface diffusion, capillary condensation with liquid flow and molecular sieving. In general, when the mean free path of a molecule is ten times larger than the pore diameter, Knudsen diffusion is predominant (Yang, 1987). At an elevated temperature, capillary condensation unlikely exists in commercial microporous membranes with $\geq 40\text{\AA}$ of pore diameter. Molecular sieving does not take place because the smallest pore size commercially available, i.e., 40Å, is much larger than gaseous molecules. Surface diffusion is possible; but could be negligible for most gases at an elevated temperature. Hwang and Kammermeyer indicated that surface diffusion on microporous vycor glass quickly approached zero with increasing temperature (Hwang and Kammermeyer, 1966). At high temperature ($> 327^\circ\text{C}$), the total flow approaches Knudsen diffusion at a low pressure range ($< 2\text{ atm}$). Shindo, et al. also showed that surface diffusion could be negligible at high temperatures (Shindo et al., 1983). In summary, Knudsen diffusion is a dominant mechanism to be considered in gas separation with commercial ceramic membranes under HTHP environment. Viscous flow, resulted from pressure difference across the pore, is not considered as one of the separation mechanisms.

3.2 Literature Review

Many models were developed to describe gas separation using microporous membranes (Shindo et al., 1984, 1989; Pan and Habgood, 1974, 1978; Kao et al. 1989; Li et al., 1990; Huckins and Kammermeyer, 1953; Tranchino, 1989; Haraya et al., 1987; Tock and Kammermeyer, 1969; Uhlhorn et al., 1989). These models were all based on ideal Knudsen separation. The individual permeability in a multi-component gas mixture was assumed the same as that in a single component, and was independent of pressure. This assumption was valid only at a low pressure range. Practically, membrane-based processes required a transmembrane pressure drop to achieve effective gas separations. Under this circumstance, interaction between components in a mixture could become significant.

Interaction between molecules was first incorporated into a gas kinetic model by Present and deBethune (P-D model) more than 40 years ago (Present and Debethune, 1949). A theoretical model including Knudsen diffusion, inter-molecular momentum transfer and viscous flow was developed to describe the gas flow through a single capillary. Figure 3.1 illustrates the concept of the inter-molecular momentum transfer. In a binary mixture each molecule has three possible collision patterns: one type of molecule collides with the other type, the same type, or the wall. The average momentum remains constant in the collision with the same type of molecules. However, a net momentum transfer occurs for collision between different molecules.

Most literature studies since then have based upon the P-D model. Fain and Brown separated neon isotopes under vacuum in capillary and parallel-plate systems with well-defined geometry (Fain and Brown, 1974). The P-D model was modified empirically to improve the prediction. Haraya et. al., presented the separation of H_2 -CO in porous glass membranes with pore diameter ranging from 31 to 200Å at 5-50 atms and 100°C (Haraya et al., 1986 a, b). They applied the P-D model to the observed Knudsen permeabilities with the assistance of a fitting parameter. Eickmann and Werner incorporated 2 parameters to the P-D model to account for membrane morphology and the reflection of gas molecules (Eickmann and Werner, 1985).

In this paper, a mathematical model has been developed following the approach by Eickmann and Werner for a commercial ceramic membrane unit. Predicted gas separation behaviors have been compared with experimental results at HTHP. This model has then been utilized to analyze the effects of key operating parameters, such as stage cut, feed pressure, pressure ratio of permeate to feed sides and molar composition of the feed.

**Figure 3.1 : Molecular Diffusion Through Capillary
for a Mixture of Nitrogen and Hydrogen**

3.3 Experiment

The material used in this study was a multiple layer microporous asymmetric membrane offered from Alcoa Separations under the trade name Membralox®. The individual layer structure is shown in a cross-sectional SEM micrograph in Figure 3.2. The permselective layer is confined in the top layer with 3 - 5 micron thickness. The nominal pore diameter is 40Å with porosity of ~0.5. The detailed characteristics of this membrane was reported elsewhere (Wu and Liu, 1992). The membrane module contains a tubular membrane with 1" length, which was housed in a stainless steel module and sealed by Grafoil ribbon (graphite based packing material) between the tube and the housing.

Figure 3.3 shows the schematic diagram of the facility used for gas separations at high temperatures. Binary gas mixtures were prepared from single gas components including H₂, O₂, He, N₂, and CO. Each mixture was preheated before entering the membrane module. After separation by a membrane, permeate and reject streams were then cooled down and measured by mass flow meters before the compositional analysis by a GC. A thermocouple was inserted into the center of the membrane to measure the temperature. The operating temperature studied ranged from 20°C to 815°C. Pressure was controlled by regulators installed in the reject and permeate lines. Feed pressure varied from 3 to 38 atm, and permeate pressure from 1.3 to 27 atm. Stage cut was operated from 0.01 to 0.36 by adjusting the feed flows ranging from 10 to 100 l/min. The permeability of the single gas components, i.e., H₂, He, N₂, and CO, was also measured with the same unit. The permeability of oxygen was not measured because of potential oxidation of graphite packing at a high temperature. Separation of O₂/He mixtures was carried out at a dilute oxygen environment (11%) for a short period to avoid the oxidation.

3.4 Mathematical Model

3.4.1 Basic Assumptions

The model developed for gas separation using microporous membranes is based on the following assumptions: (1) ideal gas behavior; (2) a well-mixed flow in both the reject and permeate streams; (3) no pressure drops throughout the reject and permeate sides respectively; and (4) negligible surface diffusion. The collisions between molecules, and between molecule and pore wall are assumed completely elastic. Perfect mixing as shown in Figure 3.4 is justified because the tube length is very short, i.e. 2.54 cm. Two equations derived from material balance for the separator can thus be established as follows:

$$Q_F = Q_P + Q_R \quad [1]$$

$$X_0 \cdot Q_F = Y \cdot Q_P + X \cdot Q_R \quad [2]$$

Figure 3.2 : SEM Micrograph of Alumina Membrane Structure

Layer 1 : Pore Diameter = $40 \text{ \AA}$; Thickness = $3\text{-}5 \text{ }\mu\text{m}$; Porosity = 50%

Layer 2 : Pore Diameter = $0.2 \text{ }\mu\text{m}$; Thickness = $15\text{-}30 \text{ }\mu\text{m}$; Porosity = 35%

Layer 3 : Pore Diameter = $0.8 \text{ }\mu\text{m}$; Thickness = $30\text{-}50 \text{ }\mu\text{m}$; Porosity = 40%

Support : Pore Diameter = $10\text{-}15 \text{ }\mu\text{m}$; Thickness = $1.5\text{-}2.0 \text{ mm}$; Porosity = 40 - 45%

Figure 3.3 : Schematic Diagram of Experimental Facility for Gas Separations Through Membrane

Figure 3.4 : A Perfect Mixing Model for Gas Separation

From Equations 1 and 2, the mole fraction of the permeate side stream can be derived in terms of the stage cut θ :

$$Y = \frac{X_0 - X(1-\theta)}{\theta} \quad [3]$$

where:

$$\theta = \frac{Q_P}{Q_F} \quad [4]$$

3.4.2 Mass Transport Through Porous Membrane

Molar fluxes permeated through the membrane can be calculated according to Eickmann and Werner's model (Eickmann and Werner, 1985).

$$n_1 = -\frac{g'}{L} \left[\frac{\alpha_0}{1+B'p} \frac{d(xp)}{dz} + \frac{f_0 B' x p}{1+B'p} \frac{dp}{dz} + x A' p \frac{dp}{dz} \right] \quad [5]$$

$$n_2 = -\frac{g'}{L} \left[\frac{1}{1+B'p} \frac{d(1-x)p}{dz} + \frac{f_0 B' p(1-x)}{1+B'p} \frac{dp}{dz} + (1-x) A' p \frac{dp}{dz} \right] \quad [6]$$

where $g = \frac{8r_k}{3\pi} \left[\frac{\pi}{2kTm_2} \right]^{1/2}$ [7]

$$A = \frac{3r_k}{16\eta v_2} \quad [8]$$

$$f_0 = \frac{m_2^{1/2}}{m_x^{1/2}} \quad [9]$$

$$\alpha_0 = (m_2/m_1)^{1/2} \quad [10]$$

$$B = \frac{8r_k}{3\pi} \left[\frac{\pi kT}{2m^+} \right]^{1/2} \frac{m_x^{1/2}}{(m_1+m_2)^{1/2}} \frac{1}{pD_{12}} \quad [11]$$

$$m_x^{1/2} = x m_1^{1/2} + (1-x) m_2^{1/2} \quad [12]$$

$$m^+ = \frac{m_1 m_2}{m_1 + m_2} \quad [13]$$

$$v_2 = \left[\frac{8 k T}{\pi m_2} \right]^{1/2} \quad [14]$$

$$g' = n_k \pi r_k^2 \beta g \quad [15]$$

$$A' = \frac{A}{\beta} \quad [16]$$

$$B' = B \beta \quad [17]$$

The diffusion coefficient, D_{12} , can be calculated (Bird et al, 1960) as,

$$D_{12} = \frac{1}{3} v \lambda \quad [18]$$

with the mean molecular velocity

$$v = \left(\frac{4 k T}{\pi m^+} \right)^{1/2} \quad [19]$$

and the mean free path of molecule

$$\lambda = \frac{k T}{\sqrt{2} \pi \sigma^{*2} p} \quad [20]$$

The average collision diameter σ^* of the different molecules is defined as,

$$\sigma^* = \frac{\sigma_1 + \sigma_2}{2} \quad [21]$$

The viscosity (η) of the gas mixture for a binary system is estimated with the corresponding state method using the Lucas mixing rule (Reid et al, 1987).

The molar fluxes, n_1 and n_2 , represent the flux of the light and heavy components, respectively. The first two terms in Eqs. 5 & 6 calculate the flows contributed by Knudsen diffusion and momentum transfer between molecules respectively. The third term calculates the contribution of the viscous flow. The Knudsen term accounts for separation, while the second and third terms dilute the separation

efficiency achieved by the first term.

Eqs. 5 and 6 were originally derived from the momentum balance in a single capillary (Present and DeBethune, 1949). In order to apply these equations to a membrane, two parameters, n_k and β , were introduced by Eickmann and Werner. The former accounts for the theoretical number of capillaries per unit membrane area. The latter accounts for the reflection condition of a molecule on the pore wall. These parameters can be determined from single gas permeability via Eq. 22.

$$C_p = \frac{ns}{\Delta p} = \left[\frac{8}{3} n_k \beta r_k^3 \left(\frac{\pi}{2kT_m} \right)^{1/2} + \frac{n_k r_k^4}{2\eta_v} \left(\frac{\pi}{2kT_m} \right)^{1/2} \bar{p} \right] \frac{1}{L} \quad [22]$$

From permeability, C_p , vs. average pressure, $\bar{p}$, across the membrane, n_k and β can be obtained from the slope and intercept, respectively.

Mathematically, n_k and β are analogous to porosity (ϵ) and tortuosity (τ), adopted in the literature study (Keizer et al., 1988) for gas permeation dominant by the Knudsen diffusion behavior. Similarly, ϵ and τ can be determined from the linear relationship of permeability vs. transmembrane pressure drop. According to the definition and the mathematical derivation, n_k accounts for the morphology of the membrane, including ϵ and τ . β is used to correct behaviors that deviate from Knudsen diffusion. n_k and β thus defined offer expanded meaning and have been successfully applied to a mixture involving CO which deviated away from Knudsen diffusion significantly. This system is discussed later in the paper. Once the values of n_k and β are known, the molar fluxes of a binary mixture through a given membrane can be determined. A given membrane separation system can be described completely by feed composition, temperature, stage cut, and feed and permeate pressures. Mole fractions of reject and permeate as well as its separation factor can then be calculated from the above equations. A trial and error approach is required in this calculation. An initial mole fraction of permeate (Y_0) is given to initiate the iteration. The molar fluxes are calculated according to the initial Y_0 value, then confirmed with the material balance. The trial-and-error is iterated until a correct Y is found to satisfy the material balance. This model is solved by a FORTRAN program. The program list and the method to run this program are in the Appendix.

3.5 Results and Discussion

3.5.1 Permeation with Single Components

Figures 3.5 to 3.7 show gas permeability vs. average pressure at 20°C, 538°C and 815°C, respectively, for H₂, He, CO and N₂. The permeability is relatively independent of the pressure, indicating Knudsen diffusion dominates under these operating conditions. The slight increase in permeabilities along with the pressure increase is attributed to the viscous flow, which becomes significant at a higher pressure. This observation is consistent with our assumption that defect of the membranes is negligible.

n_k and β were obtained according to Eq. 22. Data on permeability vs. average pressure fit well with the curve generated from the linear regression. Since n_k is the characteristic of a given membrane reflecting its porous structure (e.g., porosity, tortuosity, etc.), it should be a constant for a given membrane. To determine n_k from

the slope of C_p vs. $\bar{p}$, pore diameter, $2r_k$, is required. The n_k was determined from the N₂ permeability at 20°C, where the nominal pore diameter of 40Å quoted by the manufacturer was used. The average n_k thus determined, $3.52 \pm 1.09 \times 10^{-16}$ (1/m²), was used to estimate the pore size of the membranes exposed at a higher temperature. According to our previous experience, the pore diameter of the membrane grew from 40 to ~80Å during the thermal treatment at 850°C as a result of phase transition of γ -alumina (Gallaher et al. 1990). The enlargement is highly dependent upon its treatment temperature and is irreversible. A similar result on pore enlargement was reported in the literature (Leenaars et al. 1984). The pore diameter thus derived is listed in Table 3.1, ranging from 44 to 78Å, consistent with the experience reported previously. The pore diameter ranges from 45 to 66Å at 538°C and 61 to 78Å at 815°C. This range of pore diameter, instead of a single number, at a given temperature was resulted from the maximum temperature a membrane was exposed to previously. This approach tacitly assumes a constant ε/τ throughout the pore enlargement during thermal treatment. A similar assumption on ε was verified in the literature (Leenaars et al., 1984). The uncertainty of the pore diameter estimation and its impact on separation efficiency prediction is discussed in the next section.

β represents the reflection condition of molecules after colliding with the pore wall. If the collision between the wall and gas molecules is completely elastic, and the tortuosity of the membrane is one (i.e. straight capillary tube in the membrane layer), the theoretical value of β is 1. β , however, is usually less than one because (a) the tortuosity of most membranes is larger than one; (b) possible non-ideal reflection of some gases from the pore wall due to the

Figure 3.5 : Gas Permeabilities vs. Average pressures at 20°C

Figure 3.6 : Gas Permeabilities vs. Average Pressures at 538°C

Figure 3.7 : Gas Permeabilities vs. Average Pressures at 815°C

Table 3.1 : Experimental Values of N_k and β

	Temp (°C)	Nominal Pore Diameter* (Å)	N _k (1/m ²)	β
He	25	40	3.36E16	0.48
	538	53		0.29
	815	70		0.15
N2	25	40	4.30E16	0.40
	538	45		0.50
	815	61		0.24
H2	25	40	2.43E16	0.66
	538	51		0.32
	815	78		0.10
CO	25	40	4.00E16	0.27
	538	66		0.06
	650	68		0.06
	815	72		0.05
Average 3.52±1.09E16				

* Pore diameters at higher temperatures estimated from the average N_k at 20°C

interaction between molecules and membrane material, and (c) other factors. The factor (b) implies that β could be a function of temperature and gas components. β listed in Table 3.1 varies from 0.05 to 0.66. Due to the limited data available here, no correlation was attempted for each gas. β was treated as a constant in Eickmann and Werner's study in contrary to the observation here.

Compared with the permeability of H_2 , He, and N_2 , the permeability of CO is much lower than the theoretical value based upon Knudsen diffusion. It should locate in the neighborhood of N_2 's according to the molecular weight. A similar observation was reported in the literature (Haraya et al. 1986a). The unexpected behavior of CO may be attributed to the interaction of CO with aluminum oxide surface. This effect is described adequately by Eq. 22 via the correction of β . Another factor, surface diffusion, is possible but negligible because the permeability in this case was reduced not enhanced by this effect.

3.5.2 Separations of Binary Mixtures

Tables 3.2 to 3.4 list the separation results of binary mixtures involving H_2/CO , H_2/N_2 , and O_2/He systems. Pressure ratio (P_r) and selectivity (α) are defined in Eqs. 23 and 24, respectively.

$$P_r = \frac{P_1}{P_h} \quad [23]$$

$$\alpha = \left(\frac{Y}{1-Y} \right) / \left(\frac{X}{1-X} \right) \quad [24]$$

The experiments were carried out at a wide range of feed composition, stage cut, temperature, feed pressure and pressure ratio. Experimental results are presented in terms of the mole fraction of the permeate which is compared with the predicted values from the model. The simulation is generally in good agreement with the experimental results generated from a wide range of operating conditions: 20°C to 815°C, 1 to 34 atm, .01 to .36 for stage cut, and .1 to .8 for pressure ratio. Most of the deviations between the predicted and experimental mole fraction are within 10%. The model, however, consistently overestimates the mole fraction of the light component in the permeate for the H_2/CO and H_2/N_2 .

β for oxygen was not available experimentally. It was assumed similar to nitrogen for predicting the mixture of O_2/He . The deviation, $\Delta Y\%$, for He in O_2 is much less than those for H_2/CO and H_2/N_2 . This may be misleading because only one molar fraction was tested here, i.e., 0.89 for He. Deviation in terms of oxygen is also listed in Table 3.4 for comparison. Deviations for the O_2/He mixtures at high temperatures (i.e., observations 2 and 5 in Table 3.4) are

**Table 3.2 :H₂/N₂ Mixture Separation
Predicted vs Observed Values of Permeate Composition and Separation Factor**

Obs #	Temp °C	Ph atm	P1 atm	Pressure Ratio	Xf (H ₂)	Stage Cut	Yobs	Ycalc (H ₂)	ΔY%	αobs
1	20	6.9	1.3	0.19	0.480	0.07	0.61	0.67	8.96	1.69
2	20	7.0	1.3	0.19	0.47	0.35	0.54	0.58	6.90	1.32
3	20	34.4	6.8	0.20	0.47	0.35	0.50	0.55	9.09	1.13
4	20	34.3	27.05	0.80	0.48	0.10	0.51	0.53	3.77	1.13
5	20	20.7	16.27	0.79	0.49	0.06	0.52	0.54	3.70	1.13
6	20	6.7	5.42	0.81	0.49	0.01	0.54	0.57	5.26	1.22
7	20	20.5	4.20	0.20	0.47	0.36	0.48	0.57	15.79	1.04
8	538	34.0	6.72	0.20	0.48	0.33	0.53	0.60	11.67	1.22
9	538	20.4	4.1	0.20	0.48	0.20	0.57	0.64	10.94	1.44
10	538	20.3	4.1	0.20	0.49	0.33	0.55	0.62	11.29	1.27
11	538	6.9	1.3	0.19	0.47	0.33	0.58	0.63	7.94	1.56
12	538	6.9	1.3	0.19	0.48	0.07	0.66	0.70	5.71	2.10
13	538	5.4	2.39	0.44	0.49	0.03	0.62	0.66	6.06	1.70
14	538	22.4	2.43	0.11	0.48	0.25	0.56	0.64	12.50	1.38
15	538	33.0	2.50	0.08	0.48	0.35	0.54	0.60	10.00	1.27
16	538	37.7	2.43	0.06	0.17	0.28	0.25	0.25	0.00	1.63
17	538	15.9	2.36	0.15	0.21	0.10	0.30	0.36	16.67	1.61
18	538	6.4	2.43	0.38	0.21	0.03	0.30	0.33	9.09	1.61

**Table 3.3: H₂/CO Mixture Separation
Predicted vs Observed Values of Permeate Composition and Separation Factor**

Obs #	Temp °C	Ph atm	Pi atm	Pressure Ratio	Xf (H ₂)	Stage cut	Yobs	Ycalc (H ₂)	ΔY%	αobs
1	20	5.97	1.34	0.22	0.51	0.03	0.69	0.71	2.82	2.16
2	20	6.85	1.41	0.21	0.22	0.02	0.36	0.39	7.69	2.06
3	20	6.88	5.51	0.80	0.50	0.01	0.55	0.57	3.51	1.23
4	20	7.10	1.24	0.17	0.46	0.38	0.55	0.60	8.33	1.44
5	20	21.54	4.09	0.19	0.49	0.10	0.60	0.63	4.76	1.51
6	20	21.61	17.22	0.80	0.49	0.02	0.54	0.54	0.00	1.23
7	300	5.49	1.41	0.26	0.21	0.04	0.35	0.37	5.41	2.02
8	300	5.83	1.41	0.24	0.50	0.06	0.67	0.70	4.29	2.07
9	300	6.51	1.34	0.21	0.79	0.10	0.88	0.90	2.22	1.95
10	300	5.97	3.48	0.58	0.52	0.04	0.63	0.64	1.56	1.58
11	300	13.9	2.73	0.19	0.51	0.12	0.62	0.69	10.14	1.59
12	300	21.6	4.16	0.19	0.51	0.20	0.59	0.67	11.94	1.39

**Table 3.4: He/O₂ Mixture Separation
Predicted vs Observed Values of Permeate Composition and Separation Factor**

Obs #	Temp °C	Ph atm	Pl atm	Pressure Ratio	X _f (O ₂)	Stage cut	Y _{obs} (He)	Y _{calc} (He)	ΔY% (He)	Y _{obs} (O ₂)	Y _{calc} (O ₂)	ΔY% (O ₂)	α _{obs} (He)	α _{ob} (O ₂)
1	537	3.38	2.36	0.70	0.11	0.02	0.921	0.927	0.65	0.079	0.073	-8.22	1.44	0.70
2	537	5.63	2.36	0.42	0.11	0.07	0.927	0.938	1.17	0.073	0.062	-17.74	1.56	0.63
3	650	5.29	3.45	0.65	0.11	0.05	0.924	0.928	0.43	0.076	0.072	-5.56	1.50	0.65
4	815	3.38	2.36	0.70	0.11	0.03	0.920	0.922	0.22	0.080	0.078	-2.56	1.42	0.71
5	815	5.49	2.36	0.43	0.11	0.08	0.924	0.937	1.39	0.076	0.063	-20.63	1.50	0.65

much higher than the rest. The graphite-based end seals could be oxidized under these conditions, causing bypass of the retentate to the permeate through the damaged seal. Experimental values of β for H_2 and CO at 300°C were not available. They were estimated by linear interpolation with β at 20 and 538°C.

3.5.3 Error Analysis

Determination of n_k from the slope of the single component permeation data inevitably involves some uncertainty. The slope should be very gradual intrinsically for the microporous membrane unless the contribution of the viscous flow becomes significant. Sensitivity analysis of n_k was performed for H_2/N_2 mixtures at 538°C (obs # 8-18 listed in Table 3.1). If n_k varies $\pm 30\%$ of the average value used in this study, i.e., $3.52E16$, the associated pore diameter change is $45 \pm 4\text{\AA}$. This degree of variation in n_k and pore diameter resulted in a maximum change of 0.88% of the permeate composition. This range of uncertainty is acceptable, and is much less than the deviation between observed and predicted values.

Based upon the experimental and simulation study, the parameters involved in separation were identified as feed pressure, temperature, stage cut, pressure ratio, pore size and concentration. Effects of these parameters on selectivity are discussed in the following with the model developed.

3.5.4 Effect of Pressure Ratio and Feed Pressure

A binary mixture, H_2/N_2 , was used as a case studying the effect of pressure ratio and feed pressure. Figure 3.8 presents the simulation results in terms of separation factor (α) vs. pressure ratio (Pr) with feed pressure as a parameter. The operating condition is detailed in the figure. Under the selected condition, the lower the pressure ratio, the higher the separation factor is. This is attributed to higher separative driving force at a lower Pr. When the feed pressure is low and Pr approaches zero, the separation approaches the prediction by the ideal Knudsen separation. When the pressure ratio approaches one, no separation is expected.

For a given pressure ratio, the higher the feed pressure, the lower the separation efficiency is as shown in Figure 3.8. The mean free path of a molecule is shorter at a higher pressure (Eq. 20). The frequency of molecular collision thus increases and the inter-molecular momentum transfer becomes more significant. The light component (i.e. H_2) loses its momentum during diffusing through the membrane; meanwhile, the heavy component (e.g. N_2) gains the momentum. The average velocity of the light component thus decreases and that of heavy component increases. The enrichment of

Figure 3.8 : Feed Pressure Effect on Separation of H₂/N₂ Mixture

the light component is discounted away from the ideal Knudsen diffusion, so does the separation factor.

The pressure effect is illustrated in Figure 3.9. It displays the distribution of the individual H_2 molar flux through the membrane for the H_2/N_2 separation. Again, Knudsen represents the separative part of the flow; momentum and viscous represent the non-separative part. The inter-molecular momentum transfer has a significant impact on separation when the feed pressure increases. Furthermore, it shows that the viscous flow is not a major dilution factor even at a very high feed pressure because the pore size is small (56Å) and still within the Knudsen regime. The analysis clearly indicates the importance of intermolecular momentum transfer for gas separations within the Knudsen regime.

3.5.5 Effect of Temperature

It has been commonly accepted that temperature does not affect gas separations based upon Knudsen diffusion because the ideal separation factor is independent of temperature as shown in Eq. 10. The intermolecular momentum transfer, however, is partially dependent upon the mean free path, which is a function of temperature. Figure 3.10 shows the temperature effect on separation factor from room temperature to 815°C. The higher the temperature, the better the separation is. The mean free path is longer at a higher temperature for a given pressure ratio. Thus, less momentum loss is expected for H_2 , which enhances the separation factor. The degree of improvement, nevertheless, is less than the effect of pressure.

3.5.6 Effect of Concentration

Effect of feed concentration on the separation factor is illustrated in Figure 3.11. As the H_2 concentration decreases, the separation factor also decreases under the selected operating condition. When the feed contains less H_2 and more N_2 , the collision frequency of H_2 to N_2 is greater than that of H_2 to H_2 . Therefore, more H_2 momentum is lost at a low H_2 concentration. The separation efficiency of H_2 decreases through this effect. However, the concentration effect is weak compared with those of feed pressure and temperature because the molecule collision on pore wall is much more frequent than collision between molecules.

3.5.7 Effect of Pore Size

Effect of pore size can be described with the intermolecular momentum transfer. As a rule of thumb, Knudsen diffusion would dominate if the mean free path is at least 10 times larger than the pore diameter. It has widely prevailed that the separation factor is

Figure 3.9 : Influence of Feed Pressures on Separation Efficiency of H₂/N₂ Mixture

Figure 3.10 :Temperature Effect on Separation of H₂/N₂ Mixture

Figure 3.11 : Feed Concentration Effect on Separation of H₂/N₂ Mixture

constant once the diffusion through a pore diameter is within the Knudsen regime. A pore diameter $< 100\text{\AA}$ would comfortably provide gas separations according to Knudsen diffusion. A smaller pore diameter, however, means more collision to wall than to another molecule. As a result, the contribution of the inter-molecular momentum transfer is reduced. Figure 3.12 shows the separation factor slightly increases with the pore size decrease from 100 to $20\text{\AA}$. The effect of pore size is less than that of pressure, temperature and concentration and becomes negligible at a high pressure ratio. The effect of pore size discussed here should be treated as theoretical prediction because the experimental study covered in this paper was generated from the membranes with pore size $\geq 40\text{\AA}$.

3.5.8 Effect of Stage Cut

The influence of stage cut on separation factor is simply governed by the material balance. As shown in Figure 3.13, the higher the stage cut, the worse the separation. At a high stage cut, the driving force for gas separation in terms of partial pressure difference is reduced to maintain the material balance. Evidently, a small stage cut is required in order to achieve the enrichment of the light component in the permeate side to the level determined by the ideal Knudsen separation.

3.6 Conclusions

A mathematical model was established for gas separations in a microporous membrane at high temperature, and was verified by experimental data. This model requires the permeability of the single component to determine two parameters, n_k and β , which relate to the morphology of microporous membranes and the reflection behavior of gas molecules, respectively. Gas separations for a binary mixture can then be predicted with the model developed. Gas permeation of CO deviated substantially from the values expected from Knudsen diffusion. This behavior was corrected with the model, which then predicted the gas separation involving CO adequately.

The effect of the key operating parameters is described through the simulation study. Feed side pressure and pressure ratio have much more significant effect on the separation factor than others under the condition studied. A lower feed-side pressure and pressure ratio is required to achieve maximum separation efficiency.

Figure 3.12 : Pore Size Effect on Separation of H₂/N₂ Mixture

Figure 3.13: Stage Cut Effect on Separation of H₂/N₂ Mixture

4. Modifications of Commercial Ceramic Membranes

4.1 Introduction

Currently, the applications of inorganic membranes are limited to UF and MF, because the minimum pore diameter of inorganic membranes available is in the range of 30-40Å. These membranes can separate gas mixtures based on Knudsen diffusion, which is inversely proportional to the square root of molecular mass (Present, 1949). Membranes with a smaller pore size or with a specific surface property can achieve a higher separation selectivity via other separation mechanisms (e.g. surface diffusion, molecular sieving, etc.). The modification selected in this study is to deposit thin films of metal oxides within the wall of porous supports. Deposition of silica oxide via chemical vapor deposition (CVD) has been studied extensively in this project. Deposition of zirconium oxide via CVD and lanthanum oxide via impregnation was also explored to some extent. The deposition methodology, characterization results, gas separation performance and thermal/hydrothermal stabilities of the modified membranes are discussed in detail in this section.

4.2 Literature Review

Modifications of inorganic membranes by chemical vapor deposition have been documented in the literature, specifically on the use of silica and zirconia. Silica modification has several advantages. Niwa et. al. reported that the silica modification of zeolite did reduce the size of the pore opening (Niewa, 1984, 1987, 1989). Silica modification of porous Vycor glass tubes was performed to improve the selectivity for gas separation (Gavalas, 1989; Nam, 1989; Gavalas, 1990; Okubo, 1989). Murrel and Dispenziere (Murrel, 1988) reported that the addition of 5% silica to alumina led to distinct stabilization of alumina under the calcination at 950°C and steam at 870°C.

Zirconia is another candidate as a modifier. Somiya and Yoshimura reported that the addition of ZrO_2 to γ -alumina retarded the phase change of alumina under thermal and hydrothermal treatments and improved its stability (Somiya, 1985). Krishnamoorthy reported that Mg partially stabilized ZrO_2 (PSZ) and Mg-Ti-PSZ showed better corrosion resistance toward coal ash attack than existing γ -alumina (Kirshnamorthy, 1990). Deposition of ZrO_2 on existing alumina membranes evidently is another promising step in improving the thermal/hydrothermal stabilities and chemical resistance of existing alumina membranes.

4.3 Deposition Chemistry and Methodology

Two types of silica modified membranes were obtained by chemical vapor deposition: porous and dense membranes. The resultant porous silica membrane demonstrates a pore size ranging from 65Å to 4Å. The dense silica modified membrane exhibited an exceptional hydrogen separation

selectivity at an elevated temperature. Typically, membranes were modified with silica by introducing tetraethyl orthosilicate (TEOS) into the pores of porous alumina membranes and decomposing on the wall of the pores (CVD). The experimental apparatus for the CVD process is shown in Figure 4.1. Existing tubular membranes with $\sim 40\text{\AA}$ pore diameter and 1" and 10" lengths (US Filter) were used as precursors in these experiments. TEOS was introduced on the inner surface of the membrane. Helium containing 10 to 20% of oxygen was chosen as a carrier gas. The temperature of the furnace varied from 200 to 600°C and the vaporizer was set at 21-150°C. The feed and reject rates were controlled by mass flow meters. The permeate rate was monitored and determined with a soap-film meter. The feed pressure varied from 0 to 60 psi. The deposition process lasted for 15 to 300 minutes.

Thickness and pore size of the modified membrane was controlled through the following parameters: vaporizer temperature, feed, reject and permeate flow rates and deposition temperature, time and pressure. Deposition mechanism of silica on alumina membranes is complex and has not been well understood. The reaction involving TEOS as the source for the deposition of SiO_2 on the membranes is suggested as follows:

$\text{C}_2\text{H}_5\text{OH}$ could further react with O_2 to form CO_2 and H_2O . The final gaseous products depend on the ratio of oxygen to other components and the decomposition temperature.

4.4 Morphological Characterization with SEM/EDAX

Scanning electron microscope (SEM) (WB-6, International Scientific Instruments, Inc.) with energy dispersive spectroscopy (EDAX) (PV9900, EDAX International, Inc.) was used to examine the location and morphology of the modified layer. However, the resolution of the SEM (25 KX) was not sufficient to identify the pore size of the modified layer. If the material of the modifier is different from the support's, the combination of SEM and EDAX can provide the information on the thickness and the location of the modified layer. Typically, the modification of the existing membranes may take place within and/or on the top of the membranes. The former generates less mechanical stress than the latter and is desirable from the material stability standpoint. However, its porosity is further reduced from the precursor's, resulting in the reduction of the permeate.

The SEM image of the inner surface of the modified membrane demonstrates a uniform layer with no pinholes or cracks as shown in Figure 4.2. Figures 2.1, and 4.3-4.6 present the SEM image of the cross-section of the existing and modified membranes, Si001, Si004, Si005 and Si009, respectively. No visible difference was observed between the existing and the modified membrane in each layer along the cross section,

Figure 42
SEM of Inner Surface of Silica Modified Membrane Si005

Figure 4.3
SEM of Cross-Section of Silica Modified Membrane Si001

Figure 4.4
SEM of Cross-Section of Silica Modified Membrane Si004

Figure 4.5
SEM of Cross-section of Silica Modified Membrane Si005

Figure 4.6
SEM of Cross-Section of Silica Modified Membrane Si009

nor any significant increase in the membrane layer thickness. Further EDAX showed a significant silica content on the top surface of the membrane (Figures 4.7 & 4.8). Evidently silica was primarily deposited within the existing porous structure; no additional membrane layer was produced as a result of deposition.

EDAX examination throughout the membrane layer offers information on the thickness of the modified layer. A significant silica content (~1250 counts) was detected on the top surface of Si009 (Figure 4.9). However, the silica content decreased along the depth of the membrane. The silica content at 1.5 μm below the top surface was 250 counts (Figure 4.10). No significant silica content was detected at the position below 1.5 μm depth. This concludes that the thickness of the modified layer is about 1.5 μm . Most of the membranes generated from this method were found to have a similar layer thickness. The EDAX can also provide the information on metal oxide loading of the modified membranes. For example, Si001 showed a higher amount of silica content at its inner surface than Si004 (Figures 4.7 vs. 4.8).

4.5 Characterization of Microporous Structure with Pore Size Distribution Analyzer

A pore size distribution analyzer can be used to identify the average pore size of a membrane and its pore size distribution. However, this instrument is not suitable for a pore size smaller than ~15Å because of the complication of the pore size estimation based upon the Kelvin equation. For membranes with <15Å, however, a pore size analyzer is useful for confirming the non-existence of the pore size larger than 15Å.

A series of modified membranes were produced with a pore size ranging from 31 - <15Å, listed in Table 4.1. For example, the modified membrane, Si211, exhibited a sharp pore size distribution with an average pore size around 23Å (Figure 4.11). The analysis of the modified membranes Si207 and Si209, on the other hand, showed that no significant flow was contributed from a pore size larger than 15Å.

This characterization technique is very informative in directing the synthesis process. For example, a wide pore size distribution (24-65Å) of the modified membrane, Si409, indicated a nonuniform deposition (Figure 4.12). A more narrow pore size distribution (18-50Å) was achieved with some adjustments in the deposition process (Figures 4.13-4.15).

Porous modified membranes with pore size ranging from 40-5Å can also be characterized by gas separations. Relative pore size among modified membranes can be determined by the separation selectivity for N_2 /neopentane, He/SF_6 and He/N_2 mixtures. Gas separations with these modified membranes are discussed in the following sections.

Figure 4.7
EDAX of the Inside Surface of Silica Modified Membrane Si001

Figure 4.8
EDAX of Inner Surface of Silica Modified Membrane Si004

Figure 4.9
EDAX of Top Surface of Silica Modified Membrane Si009

Figure 4.10
EDAX of Cross-Section of Silica Modified Membrane Si009 at 1.5µm Position from Top

Table 4.1 Pore Size vs He/N₂ Separation of Silica Modified Porous Membranes at Room Temperature

<u>Samples</u>	<u>Deposition Time</u> (min)	<u>Pore Size</u> Å	<u>N₂</u> (M ₃ /M ₂ /hr/atm)	<u>He</u> (M ₃ /M ₂ /hr/atm)	<u>He/N₂</u> Selectivity	<u>He/SF₆</u>
R1		70.00	244.53	649.22	2.65	
R2		45.00	147.38	362.83	2.62	
Si208	20 _a	31.40	69.55	169.85	2.44	
Si210	25 _a	27.60	48.08	115.66	2.41	
Si212	70 _b	24.80	17.62	36.87	2.09	
Si211	71 _b	22.80	18.07	37.79	2.09	
Si224	133 _b	22.76	10.24	21.65	2.12	
Si220	37 _c	20.00	8.16	18.90	2.30	
Si221	91 _c	-	2.78	9.62	3.46	
Si209	30 _a	< 15	1.010	3.91	3.86	2.06
Si207	35 _a	< 5.5	0.048	1.76	36.59	9.63

He/N₂ separation selectivity is based on single gas ratio.

He/SF₆ separation selectivity is based on binary mixture separation.

_a, _b and _c indicated three different deposition conditions.

Figure 4.11 Pore Size Distribution of Silica Modified Membrane Si211

Figure 4.12 Pore Size Distribution of Silica Modified Membrane Si409

Figure 4.13 Pore Size Distribution of Silica Modified Membrane Si415

Figure 4.14 Pore Size Distribution of Silica Modified Membrane Si416

Figure 4.15 Pore Size Distribution of Silica Modified Membrane Si416

4.6 Characterization with Gaseous Molecules as Probes

The modified membranes were first characterized by the pore size analyzer. If the modified membranes had no pore sizes larger than 15Å, the membranes then were characterized by the probe gases based on size exclusion. Neopentane, SF₆, nitrogen, helium and hydrogen having kinetic diameters of about 6.2Å, 5.5Å, 3.64Å, 2.8Å and 2.96Å, respectively were used. Binary gas mixtures of H₂/N₂ (50:50), N₂/neopentane (92.5: 7.5) and He/SF₆ (90.0:10.0) were selected. Mass flow meters and an on-line gas chromatography were equipped with FID and TCD to measure the composition and flow rate of the feed, reject and permeate streams.

4.6.1 Porous Membranes

The silica modified membrane Si018 demonstrated a selectivity in N₂/neopentane and H₂/N₂ based on Knudsen diffusion. Since hydrogen, nitrogen and neopentane can permeate through the silica modified membranes, Si018, the pore size of this membrane must be larger than the kinetic diameters of neopentane, nitrogen and hydrogen. Accordingly, the pore size of the modified membrane was assigned to 15-6Å.

It is difficult to assign the actual pore size of the membrane with pore size in the range of 15-6Å. However, relative pore size can be obtained based on their gas separation selectivities and/or liquid separation selectivity. A series of modified membranes with pore size less than 15Å were prepared. The N₂/neopentane selectivity of these membranes ranges from 2.5 to 28.7 (Table 4.2). No molecular sieving separation was observed for these membranes, therefore the pore sizes of these membranes are assigned in the range of 15-6Å. Since the modified membrane Si064 has the highest N₂/neopentane separation selectivity, one concludes that this membrane may have the smallest pore size. These gas separation results also are consistent with the liquid separation results.

The modified membranes with pore size less than 6Å were prepared. A N₂/neopentane separation selectivity around 405 was delivered by the modified membrane Si019 (Table 4.2). This high separation selectivity indicates that the separation is likely based on the molecular sieving effect. Since nitrogen, but not neopentane, permeated through this membrane, the pore diameter of this membrane should be smaller than the kinetic diameter of neopentane (6.2Å) and larger than that of nitrogen (3.6Å).

4.6.2 Dense Phase Membranes

Although a series of silica modified membranes with a variety of pore size distribution were synthesized, it is difficult to synthesize a porous membrane to separate hydrogen from nitrogen because of the

**Table 4.2 Separations of Silica Modified Porous Membranes
with Pore Size of 15 - 6Å**

<u>Samples</u>	<u>Nominal Pore Size (Å)</u>	<u>N₂ Permeability (M³/M²/hr/atm)</u>	<u>Pyrene/hexane Rejection</u>	<u>N₂/Neopentane Selectivity</u>
Alumina	40	79.100	0%	1.6(ca)
Si033	15-6	0.972	30%	2.5
Si038	15-6	0.196	33%	15.3
Si025	15-6	0.113	76%	24.4
Si064	15-6	0.252	78%	28.7
Si019	6-4	0.130	-	405.0

1. % rejection is based on concentration of permeated flux/concentration of feed flux.
2. N₂/Neopentane separation was conducted by feeding 10% of neopentane in nitrogen to the membranes at room temperature and transmembrane pressure of 35psi.

small difference in their kinetic diameters ($0.75\text{\AA}$). A different separation mechanism is needed for efficient H_2/N_2 separation. Dense silica modified membranes can achieve a high selectivity in H_2/N_2 separation at high temperature based on activated diffusion.

A series of hydrogen selective membranes were synthesized, including Si009, Si024, Si187, Si195 and Si215 on 1" supports and Si403, Si404, Si412 on 10" supports. Their N_2 and He permeabilities at room temperature were .06 - 2.2 and 0.13 - 0.35 $\text{M}^3/\text{M}^2/\text{hr}/\text{atm}$ (Table 4.3) respectively. The He permeabilities increased with temperature while N_2 permeabilities decreased, resulting in the enhanced selectivity for helium at a high temperature. The He/ N_2 selectivities at 600°C were enhanced significantly, i.e., 10^{-59} .

With adjustments in our deposition procedure, several silica dense phase membranes, Si418, Si421, Si428, Si432 and Si438 with an improved selectivity were synthesized on 10" supports. The N_2 and He permeabilities of these membranes at room temperature are 0.001 - 0.006 and 0.004 - 0.018 $\text{M}^3/\text{M}^2/\text{hr}/\text{atm}$ (Table 4.4) respectively. The He/ N_2 separation selectivity of these modified membranes at 600°C ranges from 125 to 473 which is higher than the modified membranes listed in Table 4.3. The separation selectivity was probably reduced due to the leakage of the graphite packing. This small leakage attributes to 30-100% of the total N_2 flow and only 1% of total He flow. The detailed evidence to prove this assumption is discussed in section 4.9. If we take this leakage into consideration, the He/ N_2 separation selectivity of the modified membrane could reach infinity.

These He selective membranes also demonstrated a high separation selectivity in hydrogen as observed in Table 4.3. For a given modified membrane, the H_2/N_2 separation selectivity is about one half of its He/ N_2 separation selectivity at 600°C . Therefore, we can estimate the H_2/N_2 separation selectivity based on their He/ N_2 separation. In summary, hydrogen selective membranes have been achieved. The challenge in the future is to obtain hydrogen selective membranes with high permeate flux and eliminate the small leakage from packing.

4.7 Reproducibility and Scale-up of Chemical Vapor Deposition

Two factors affect the reproducibility of the CVD process: variation of the precursor microporous structure and the control of the operating condition. A series of commercial ceramic membranes with an average pore size of $40\text{\AA}$ were characterized by nitrogen permeabilities and pore size distribution before the chemical vapor deposition. The nitrogen permeabilities of these membranes range from 86 to 144 $\text{M}^3/\text{m}^2/\text{hr}/\text{atm}$ (Table 4.5). Due to the slight difference in the pore size distribution, the

Table 4.3 He, N2 and H2 Permeabilities of Modified Dense Membranes at Various Temperatures

<u>Samples</u>	<u>Length</u>	<u>Temp.</u>	<u>N2</u>	<u>He</u> (M3/M2/hr/atm)	<u>H2</u>	<u>He/N2</u>	<u>H2/N2</u>
Si009	1"	25	0.00970	-	0.12300	-	1.25
Si009		500	0.01000	-	0.01250	-	12.68
Si024	1"	500	0.00920	-	0.23000	-	25.00
Si187	1"	25	0.06198	0.12957	0.20871	2.09	3.29
Si187		300	0.03922	0.11736	0.14915	2.74	3.29
Si187		450	0.06032	0.19767	0.14314	3.45	2.34
Si187		600	0.04061	0.32501	0.16842	9.46	4.65
Si195	1"	25	0.22356	0.32249	0.55862	1.44	2.50
Si195		300	0.09686	0.99357	0.52954	10.26	5.47
Si195		450	0.05993	0.03389	0.98864	33.94	16.50
Si195		600	0.049863	2.92653	1.39675	58.70	28.01
Si215	1"	25	0.16000	0.35000	-	2.11	-
Si215		300	0.09300	0.75000	-	8.04	-
Si215		450	0.08100	1.59000	-	19.64	-
Si215		600	0.07500	2.46000	-	32.73	-
Si403	10"	25	0.07678	0.12910	0.15362	1.68	2.00
Si403		300	0.03858	0.32972	0.13011	8.55	3.37
Si403		450	0.03283	0.66927	0.21643	20.39	6.59
Si403		600	0.03021	0.97988	0.25511	31.79	8.28
Si404	10"	25	0.05381	0.09761	0.14271	1.81	2.65
Si404		300	0.03084	0.17520	0.09358	5.68	3.03
Si404		450	0.02399	0.39942	0.12716	16.65	5.30
Si404		600	0.02189	0.60824	0.15884	27.58	7.20
Si412	10"	25	0.10100	0.21300	-	2.10	-
Si412		385	0.05400	0.51900	-	8.04	-
Si412		450	0.04900	0.86600	-	17.70	-
Si412		600	0.04400	1.26600	-	28.71	-

Table 4.4 He, N2 Permeabilities of Dense Silica Membranes with Improved⁺ Deposition

<u>Samples</u>	<u>Length</u>	<u>N2-600°C</u>	<u>He-600°C</u>	<u>N2-22°C</u>	<u>He-22°C</u>	<u>He/N2</u>
			(M3/M2/hr/atm)			600°C
S.S.*1 [*]		0.00011	0.00038	0.00022	0.00040	3.40
S.S.*2 [*]		0.00000	0.00000	0.00000	0.00000	-
Si418	10'	0.00101	0.38356	0.00189	0.01160	380.75
Si421	10"	0.00084	0.39650	0.00114	0.00838	473.79
Si428	10"	0.00340	0.42540	0.00200	0.00400	125.39
Si432	10"	0.00207	0.33393	0.00585	0.01769	160.94
Si438	10"	0.00066	0.25089	0.00115	0.00791	381.39

* S.S.*1 and S.S.*2 are stainless tube reference #1 and reference #2

+ Deposition method used for Table 4.3 was improved to generate this series of membranes.

Table 4.5 N₂ Permeability of Various Starting Materials for CVD

<u>Sample ID</u>	<u>N₂ Permeability (M3/M2/hr/atm) at 25°C</u>
ES105.1.D #01	144
ES105.1.D #15	138
ES105.1.D #20	130
ES105.1.D #22	137
ES105.1.D #25	121
ES105.1.D #28	120
ES105.1.D #33	151
ES105.1.D #33	151
ES105.1.D #33	151
ES105.1.D #34	117
ES105.1.D #34	117
ES105.1.D #35	139
ES105.1.D #36	137
ES105.1.D #37	156
ES105.1.D #38	140
ES105.1.D #39	145
ES105.1.D #40	130
ES105.1.D #40	130
ES105.1.D #41	146

non-uniformity of the layer thickness according to SEM examination was believed to be the source of the variation. We were able to modify these membranes with such a difference in starting materials to obtain membranes with a similar pore size.

Two modified membranes, Si211 and Si212, were obtained at the same condition. The final products had a similar N₂ and He permeability (Table 4.1). The pore size analysis indicated that the average pore of Si211 and Si212 were around 22.8 and 24.8Å, respectively. This 2Å difference in average pore size is within the precision of the instrumentation. The consistent permeability and pore size generated from these two samples lead us to believe that the deposition process is reproducible for a 1" precursor.

We also investigated the reproducibility of the chemical deposition process for a 10" precursor. The modified membranes Si405 and Si406 were deposited under a similar condition resulting in similar He and N₂ permeabilities as well as a similar He/N₂ separation selectivity (Table 4.6). Nevertheless, the deviation increased in the 1" as compared to the 10". Similar results were observed in the modified membranes Si407 and Si409, which were deposited at a different condition from Si405 and Si406. This is a good indication that the large scale deposition process is also reproducible as in the small scale.

However, we discovered the presence of a nonuniform deposition. The analysis of the modified membranes Si405 showed that the pore size distribution of these membranes was wide, 61-24 Å although a great portion of the pores in this membrane was around 50Å.

We further investigated this nonuniform deposition by cutting a modified membrane Si401 into three pieces to inspect the uniformity of the membrane (Table 4.7). The first and final pieces showed similar He and N₂ permeabilities. However, the central piece showed much higher He and N₂ permeabilities. Non-uniformity like this in permeability was also present in the precursor primarily due to the different thickness along the length of existing membranes. This may cause the nonuniform deposition observed in the modified membranes.

Two corrective actions were attempted to overcome this non-uniformity deposition: increasing the deposition rate and/or controlling the permeate flux during the deposition. A modified membrane, Si409, was then synthesized at a higher deposition rate. Its average pore size decreased to about 40.9Å from 50Å (Figure 4.12). However, the pore size distribution remained wide, e.g. 60-24Å.

Control of the permeate flow was attempted to narrow the pore size distribution. The permeate flow rates of the modified membranes, Si415, Si416 and Si417, were fixed at various levels during the deposition process.

Table 4.6 He,N₂ Permeabilities of 10" Modified Porous Silica Membranes

<u>Samples</u>	<u>Permeability (m³/m²/hr/atm)</u>		<u>He/N₂</u>
	<u>N₂-22°C</u>	<u>He-22°C</u>	
Si405	13.32	32.55	2.44
Si406	11.03	26.85	2.43
Si407	6.42	11.43	1.78
Si408	0.64	1.22	1.91
Si409	4.66	10.25	2.49
Si415	7.73	18.31	2.37
Si416	17.40	40.90	2.35
Si417	26.06	62.28	2.39

Table 4.7 He,N₂ Permeabilities of 10" Modified Silica Membrane at Three Different Positions

<u>Samples</u>	<u>Permeability (m³/m²/hr/atm)</u>		<u>He/N₂</u>
	<u>N₂-22°C</u>	<u>He-22°C</u>	
Si401 - End #1	0.094	0.170	1.87
Si401 - Center	1.76	2.910	1.65
Si401 - End #2	0.079	0.140	1.75

The average pore size of Si415, Si416 and Si417 were around 33Å, 33.8Å and 31Å, respectively. Modified membranes Si415, Si416 and Si417 showed a narrower pore size distribution, 48-21Å, than unmodified membranes (Figures 4.13-4.15). The modified membrane Si417 seems more desirable for industrial applications because of a sharper pore size distribution and higher He and N₂ permeabilities.

In summary, the deposition process was successfully scaled up from a 1" to 10" precursor with minor adjustment. Modified membranes with 10" length were synthesized to have a porous or dense phase structure. The reproducibility of this large scale deposition was confirmed.

4.8 Thermal Stability of Silica Modified Membranes

According to our previous experiment, the γ -40Å alumina membranes were thermally stable up to 650°C. These 40Å alumina membranes undergo pore growth to 60Å after being heated in 90% water in nitrogen at 650°C for 24 hours. The nitrogen permeabilities of these membranes increased immediately from 60 to 150 M³/M²/hr/atm at the first three hours in hydrothermal treatment. It is known that at elevated temperature (800-1000°C), γ alumina will transfer to α alumina and results in pore size enlargement. The He permeability of existing alumina membranes rose from 295 to 1113 after being treated at 1000°C for 5 hrs. The average pore size of these membranes increased from 45Å to 89.6Å (Table 4.8). Under a hydrothermal condition, water will promote this transformation at an accelerated rate. Several studies indicated that foreign cations can accelerate or inhibit this transformation.

The thermal stability tests were conducted on both porous and dense modified membranes. An on-line He and N₂ permeability measurement was used to monitor the thermal stabilities of these membranes. Silica modified 1" porous membranes Si071 was subjected to a thermal treatment at 760-800°C for 160 hrs. The N₂ permeability of these membranes decreased from 0.19 to 0.09 M³/M²/hr/atm initially and remained constant at 760-800°C (Table 4.8, Figure 4.16). The decreasing of N₂ permeability was due to densification of the modified membrane. It also indicated that modified porous membrane Si071 was thermally stable up to 760-800°C.

Hydrogen selective membranes Si418, Si421, Si428 and Si432 were subjected to a thermal treatment at 600°C under 390 cc/min He flow. The He permeate flows of these membranes decreased initially and became constant after 48 hours (Table 4.9 - 4.12). However, the N₂ permeate fluxes increased drastically after 48 hours with one exception, Si421 (Table 4.10). Modified membrane Si421 gave a He/N₂ separation selectivity of around 473 initially and decreased to about 320 after 75 hours (Figure 4.17), then remained constant for an additional 145 hours of thermal treatment. This result indicated that the modified membrane Si421 went through densification initially and became stable after 75 hours.

**Table 4.8 He, N₂ Permeabilities of Existing and Modified
During Thermal and Hydrothermal Treatment**

Membrane Material	DESCRIPTION OF MODIFIED MEMBRANES		TESTING CONDITION			RESULTS	
	Pore Size (Å)	Permeability	Temp(°C)	Steam(%)	Time(hrs)	Pore Size(Å)	Permeability
Existing-Al ₂ O ₃	45	295 (He)	650	0	5	48	313 (He)
	45	295 (He)	700	0	10	56	373 (He)
	45	295 (He)	800	0	5	58	471 (He)
	45	295 (He)	1000	0	5	88.6	1113 (He)
Si012	<15	1.30* (N ₂)	600	90	250	<15	2.26* (N ₂)
Si071	<15	0.19* (N ₂)	760-800	0	160	<15	0.09* (N ₂)
Si005		8.9* (N ₂)	600	90	25	28	9.69* (N ₂)
Zr012	26	35 (N ₂)	600	90	14	45	105 (N ₂)
La002	48.8	208 (He)	650	0	5	49.9	261.0 (He)
La003	50.0	107 (He)	700	0	5	-	-
			700	0	10	-	-
			800	0	5	-	-
			1000	0	5	101.8	204.0 (He)
			650	0	5	50	103.4 (He)
			700	0	5	54	148.0 (He)
La004	45.6	62 (He)	700	0	10	56	143.0 (He)
			800	0	5	58	204.0 (He)
			1000	0	5	104	579.0 (He)
			650	0	5	-	-
			700	0	5	-	-
			700	0	10	52.8	160.0 (He)
			800	0	5	-	-
			1000	0	5	110.4	204.0 (He)

* Permeability Measured at Testing Temperature

Figure 4.16 N₂ Permeability of Modified Membrane Si071 during Thermal Treatment

**Temp. : 600°C
Feed rate: 1000cc/min
Feed Composition : N₂**

Table 4.9 The He and N₂ Permeabilities of Silica Modified Dense Membranes Si418 During Thermal Treatment

Sample 418

<u>Treatment Time</u> (hrs)	<u>N₂-600°C</u>	<u>He-600°C</u> (M ₃ /M ₂ /hr/atm)	<u>N₂-22°C</u>	<u>He-22°C</u>	<u>He/N₂</u> 600°C
0.0	0.001010	0.38356	0.00189	0.01160	380.75
15.0	0.000980	0.32000			326.11
23.0	0.000909	0.29511			324.65
40.0	0.000850	0.28040			330.51
48.0	0.000880	0.22859			260.57
63.0	0.002120	0.23476			110.72
69.0	0.003090	0.24116	0.00140	0.00449	78.07

Table 4.10 The He and N₂ Permeabilities of Silica Modified Dense Membranes Si421 During Thermal Treatment

Sample Si421

<u>Treatment Time</u> (hrs)	<u>N₂-600°C</u>	<u>He-600°C</u> (M³/M²/hr/atm)	<u>N₂-22°C</u>	<u>He-22°C</u>	<u>He/N₂</u> 600°C
0.0	0.000840	0.39650	0.00114	0.00838	473.79
22.0	0.000950	0.40760			427.51
26.0	0.001120	0.40480			362.33
41.0	0.001090	0.38400			352.30
47.5	0.000940	0.35980			381.46
49.5	0.000940	0.36196			385.31
75.5	0.001080	0.33927			313.14
84.5	0.001080	0.32807			304.90
99.5	0.001010	0.32570			321.25
106.0	0.000930	0.32050			343.97
150.5	0.000970	0.32050			330.66
219.5	0.001010	0.30930	0.00121	0.00565	307.64

Table 4.11 The He and N₂ Permeabilities of Silica Modified Dense Membranes Si428 During Thermal Treatment

Sample Si428

<u>Treatment Time</u> (hrs)	<u>N₂-600°C</u>	<u>He-600°C</u> (M ₃ /M ₂ /hr/atm)	<u>N₂-22°C</u>	<u>He-22°C</u>	<u>He/N₂</u> 600°C
0.0	0.003400	0.42540	0.00200	0.00400	125.39
19.0	0.003290	0.42664			129.67
24.0	0.003480	0.41921			118.65
64.5	0.014190	0.42339	0.00280	0.00524	29.84

**Table 4.12 The He and N2 Permeabilities of Silica Modified Dense
Membranes Si432 During Thermal/hydrothermal Treatment**

Sample Si432

<u>Treatment Time</u> (hrs)	<u>Permeability</u>				<u>Selectivity</u> <u>He/N2</u> 600°C
	<u>N2-600°C</u>	<u>He-600°C</u>	<u>N2-22°C</u>	<u>He-22°C</u>	
		(M3/M2/hr/atm)			
0.0 (T)	0.002070	0.33393	0.00585	0.01769	160.94
15.0 (T)	0.002470	0.33299			134.89
22.0 (T)	0.002470	0.32724			132.56
42.0 (T)	0.008003	0.32114			40.13
46.0 (T)	0.008590	0.31344	0.00544	0.01351	36.49
47.0 (R,H)	0.005500	0.28619	0.00950	0.01825	52.01
70.0 (H)	0.005340	0.23979			44.88
86.5 (H)	0.005600	0.24378			43.56
94.0 (H)	0.005600	0.24045			42.16
112.0 (H)	0.032548	0.28841			8.86
112.0 (R)	0.006500	0.24996	0.01684	0.03706	38.48
112.0 (E)	-	-	0.00081	0.03100	-

T: Thermal Treatment

H: Hydrothermal Treatment

R: Membrane was repacked

E: The end seal of the membrane was fixed up with epoxy and then the membrane was repacked for determining the permeability at a low temperature

Figure 4.17 He and N₂ Permeabilities of Modified Membrane Si421 during Thermal Treatment

Temp. : 600°C
 Feed rate: 390cc/min
 Feed Composition : He

The increase of the N₂ permeability of the modified membranes Si418, Si428 and Si432 after 48 hours was contradictory with the result from the modified membrane Si421. To elucidate the discrepancy, a reference run was performed, using a stainless steel tube instead of a membrane. The treatment conditions of the stainless steel tube was the same as the modified membranes. The He and N₂ permeate fluxes of SS#1 after the first 25 hours were very small and essentially negligible (Table 4.13). However, both He and N₂ permeabilities increased drastically after 25 hours, possibly due to the leakage of the degraded packing graphite. This small leakage does not affect the separation selectivity of the large-pore-size membranes; however, this small leakage contributes to 30-100% of total N₂ permeate flow and only 1% total He permeate flow of the hydrogen-selective membranes. Therefore, the decrease in He/N₂ selectivity after 48 hours of the thermal treatment for Si418, Si428 and Si432 was likely due to the leakage through the graphite module.

In summary, silica modified membranes went through a densification at the first 48 hours of thermal treatment at 600°C which resulted in the decrease of He permeability. Additional thermal treatment at the same condition did not change the permeability of the silica modified membranes. We conclude that silica modified membranes are thermally stable after the initial densification.

4.9 Hydrothermal Stability of Silica Modified Membranes

In the previous section, we demonstrate that both silica modified porous and dense membranes are thermally stable. The increase of the nitrogen permeability in certain instances during the thermal treatment is due to the degradation of the graphite or membrane packaging. This section focuses on the hydrothermal stability of the silica modified membranes. The N₂ permeabilities of the silica modified porous membranes (Si005*), increased slightly after being heated in 90% of steam at 600°C for 24 hours (Table 4.8). Comparing this result with that of existing alumina membranes, it indicated that the silica modified membranes have a higher hydrothermal stability than γ -alumina membranes. The pore size analysis of Si005** indicated that this silica modified membrane had a pore size around 28Å after the hydrothermal treatment. The SEM cross section images of silica modified membranes Si005 also indicated that no pinhole and pore growth occurred (Figure 4.5). Silica modified membranes Si012 with pore size less than 15Å was also subjected to a hydrothermal treatment at 600°C with 90% steam for 250 hours. Table 4.8 indicated that the N₂ permeabilities of this modified membrane increased from 1.39 to 2.26 M³/M²/hr/atm during the cumulative treatment. This might be due to the leakage of module, graphite or glass end seal of the membrane. We further investigated this leakage with silica modified dense membranes.

We continued studying the hydrothermal stability of silica modified dense

**Table 4.13 The He and N2 Permeabilities of Stainless Steel
Tube as Control for Thermal/hydrothermal Treatment**

S.S.#1 (T)

<u>Treatment Time</u> (hrs)	<u>N2-600°C</u>	<u>He-600°C</u> (M3/M2/hr/atm)	<u>N2-22°C</u>	<u>He-22°C</u>	<u>He/N2</u> 600°C
0.0			0.00022	0.00040	3.40
17.5	0.000110	0.00038			3.84
25.0	0.000110	0.00040			1.54
41.5	0.000650	0.00100			1.40
49.0	0.002820	0.00395	0.00079	0.00136	

S.S.#2(H)

<u>Treatment Time</u> (hrs)	<u>N2-600°C</u>	<u>He-600°C</u> (M3/M2/hr/atm)	<u>N2-22°C</u>	<u>He-22°C</u>	<u>He/N2</u> 600°C
0.0	0.00000	0.00000	0.00000	0.00000	"
17.0	0.00000	0.00000	0.00000	0.00000	"
23.0	0.00000	0.00000	0.00000	0.00000	"
40.0	0.00000	0.00000	0.00000	0.00000	"
48.5	0.00000	0.00000	0.00000	0.00000	"
65.0	0.00000	0.00000	0.00000	0.00000	"
70.5	0.00000	0.00000	0.00000	0.00000	"
88.5	0.00000	0.00000	0.00000	0.00000	"

membranes. The modified membranes Si432 and Si438 were subjected to a thermal treatment at 600°C first, then a hydrothermal treatment at 600°C with 31% H₂O in He. The He permeability of the modified membrane Si432 decreased the first 46 hours of the thermal treatment, however the nitrogen permeability increased (Table 4.12). As we discussed in the previous section, modified membranes went through a densification the first 24-48 hours of thermal treatment, therefore we observed the decrease of He permeability. The increase of nitrogen permeability could be due to the degradation of graphite or glass end seal of the membranes. The decrease of nitrogen permeability and the increase of He/N₂ separation selectivity after repacking at the 47th hour indicated that the degradation of graphite attributed to the observed phenomenon. The nitrogen and helium permeabilities remained constant after the repacking and an additional 48 hours of hydrothermal treatment. Both N₂ and He permeability increased and separation selectivity decreased to 8.86 after 112 hours of total treatment (67 hours hydrothermal treatment). The membrane resumed its permeability and separation selectivity after being repacked (Table 4.12). This indicated that loss of separation selectivity is due to the degradation of graphite. It also indicated that membranes were hydrothermally stable up to 67 hours. The end seal of the modified membrane, Si432, was fixed with epoxyl and the membrane was then repacked. The room temperature nitrogen permeability decreased to 0.00081 M³/M²/hr/atm which is lower than the original N₂ permeability. This showed that there were possibly some microcracking of the end seal of the membrane before the thermal and hydrothermal treatment. This explains why this membrane did not have high separation selectivity as other hydrogen selective modified membranes.

So far, we observed that the nitrogen permeability of the hydrogen selective membranes at 600°C was around 0.0005-0.00008 M³/M²/hr/atm if there was no microcracking of the end seal. The observed nitrogen mostly was due to leakage caused by graphite degradation, as evidenced in the thermal treatment of the stainless tube shown in Table 4.13. If the leakage can be eliminated, the He/N₂ separation selectivity can reach infinity. This is proved by thermal and hydrothermal treatment of the modified membrane Si438.

A second stainless steel tube was used in a hydrothermal test with a new membrane module. No N₂ and He permeate flux was detectable at 50 psi transmembrane pressure and 600°C for 88 hours (Table 4.13). A similar experiment was conducted on the modified membranes Si438. The modified membrane Si438 was subjected to 52 hours of thermal treatment and an additional 264 hours of hydrothermal treatment at 600°C as illustrated in Table 4.14. The membrane went through a densification as did other hydrogen selective membranes during the first 48 hours of thermal treatment. The helium permeability then remained constant after initial densification indicated that the modified membrane was thermally and hydrothermally stable (Figure 4.18). One unexpected result was that there was no detectable permeate nitrogen flux while the helium permeate

**Table 4.14 The He and N₂ Permeabilities of Silica Modified Dense
Membranes Si438 During Thermal/hydrothermal Treatment**

<u>Sample Si438</u>					
<u>Treatment Time</u> (hrs)	<u>N₂-600°C</u>	<u>Permeability</u>		<u>Selectivity</u>	
		<u>He-600°C</u>	<u>N₂-22°C</u>	<u>He-22°C</u>	<u>He/N₂</u> <u>600°C</u>
		(M ₃ /M ₂ /hr/atm)			
0.0 (T)	0.00066	0.25089	0.00115	0.00791	381.39
41.0 (T)	0.00071	0.20363			288.03
47.0 (T)	0.00076	0.19555			267.14
52.0 (T)	0.00076	0.19195			252.95
66.0 (H)	0.00076	0.16029			211.69
72.0 (H)	0.00087	0.16822			192.69
77.0 (H)	0.00080	0.16639			207.75
90.0 (H)	0.00083	0.16205			194.63
97.0 (H)	0.00000*	0.16529			.
114.0 (H)	0.00000*	0.18245			.
120.5 (H)	0.00000*	0.17142			.
138.0 (H)	0.00000*	0.18245			.
144.5 (H)	0.00000*	0.17257			.
166.0 (H)	0.00000*	0.17035			.
187.5 (H)	0.00000*	0.17150			.
211.0 (H)	0.00000*	0.16981			.
217.5 (H)	0.00000*	0.16830			.
234.5 (T)	0.00000*	0.16877			.
240.5 (H)	0.00000*	0.16765			.
258.5 (H)	0.00000*	0.15549			.
264.5 (H)	0.00000*	0.16252			.
282.0 (H)	0.00000*	0.15427			.
289.0 (H)	0.00000*	0.16292			.
306.0 (H)	0.00000*	0.15604			.
313.0 (H)	0.00000*	0.15413	0.00000*	0.00592	.

T: Thermal Treatment

H: Hydrothermal Treatment

*: No nitrogen permeate flow was detectable at 50 psi transmembrane pressure for 1 hrs.

∞: The separation selectivity is infinity

Figure 4.18 He and N₂ Permeabilities of Modified Membrane Si438 during Thermal /Hydrothermal Treatment

flux remained constant after 97 hours of treatment. The He/N₂ separation selectivity remained infinite through an additional 200 hours of hydrothermal treatment. We determined that about .000066 M³/M²/hr/atm of the nitrogen permeability was due to the leakage of graphite. However, we did not understand what sealed the leakage after 97 hours of hydrothermal treatment.

4.10 Thermal/Hydrothermal Stabilities of La₂O₃ Modified Membranes

Another method to improve the thermal and hydrothermal stabilities of existing γ -alumina membranes is to impregnate other metal oxides which can retard the phase change of γ -alumina. According to Schaper, lanthanum oxide decreases the rate of sintering of γ -alumina by the formation of lanthanum aluminate surface layer (Schaper, 1983). The addition of lanthanum oxide also can postpone the phase transformation 100°C by decreasing the rate of nucleation.

The La₂O₃ was introduced by impregnating the existing γ -alumina membranes with an aqueous solution of 5% or 10 % of La(NO₃)₃. The La₂O₃ modified membranes La002, La003 and La004, were calcined in the air at 600°C for 24 hours. In our laboratory, we observed that the pore size of alumina membranes increased 3Å after calcining in air at 650°C for 5 hours, while the pore size of lanthanum oxide modified membrane LA003 remained the same after the same treatment (Table 4.8).

However, the improvement of thermal stability induced by lanthanum oxide only occurred at 650°C. Both γ -alumina membranes and lanthanum oxide modified membranes showed a similar pore growth and permeability increase at 700 and 800°C (Table 4.8). The pore size of existing alumina membranes increased from 45Å to 54Å and 58Å after being calcined at 700°C and 800°C, respectively. The permeability rose from 295 to 376 and 471 M³/M²/hr/atm, respectively.

Lanthanum oxide modified membranes LA003 showed a pore size increase from 50Å to 56Å and 58Å after the same treatment. The permeability of this membrane increased from 107 to 142 and 204 M³/M²/hr/atm, respectively. If the concentration of impregnation solution increased from 5% to 10%, we observed the pore size of La₂O₃ modified membranes La004 increased from 45Å to 56Å after the same treatment up to 800°C.

According to Schaper, the influence of lanthanum oxides is substantial especially at high temperatures such as 1000-1100°C. Further thermal treatments of lanthanum oxide modified membranes at 1000 was conducted to verify the influence of lanthanum oxides on thermal stability of existing alumina membranes at high temperature. Both existing 40Å alumina membranes and lanthanum oxides modified membranes were further treated in the air at high temperatures up to 1000°C for 5 hrs. The pore size

analysis indicated that both have a similar pore growth at this temperature (Table 4.8).

In summary, the lathanium oxide modified membranes show some thermal improvement up to 650°C. However the thermal stability of these modified membranes at 700-1000°C are disappointing. The silica modified membranes demonstrated a better improvement in thermal/hydrothermal stabilities than La₂O₃ modified membranes.

4.11 Zirconia Modified Membranes

The deposition process of ZrO₂ is similar to silica deposition except Zr(OC₃H₇)₄ and Zr(O₂C₅H₇)₄ were used as a chemical source. The CVD apparatus for this process was similar to the one used in SiO₂ deposition (Figure 4.1). Zr(OC₃H₇)₄ or Zr(O₂C₅H₇)₄ vapor was generated by passing N₂ through the vaporizer filled with Zr(OC₃H₇)₄ or Zr(O₂C₅H₇)₄. The feed gas N₂ is controlled by a mass flow meter. Another stream of gas with 10-20% O₂ in He was fed directly to the reactor and was also controlled by mass meter. The vaporize temperature, gas 1 / gas 2 ratio, feed, reject and permeate flow rate and deposition temperature, time and pressure have effects on the thickness and pore size of modified membranes. However, detailed effects of the experimental parameters listed above remain to be studied. Zr(OC₃H₇)₄ and Zr(O₂C₅H₇)₄ react with O₂ as follows and form ZrO₂.

C_xH_{2x} can further react with O₂ to form alcohols, CO₂ and H₂O. Deposition was carried out with Zr(OC₃H₇)₄ as a chemical source initially. Small pore size (~26Å) membranes (Zr008 and Zr012) were obtained through chemical vapor deposition of zirconia on existing membranes (Figures 4.19 - 4.20). However, no zirconia content can be detected by EDAX.

Since it is difficult to maintain a constant concentration of zirconia by using Zr(OC₃H₇)₄ in propanol solution as a chemical source, a new source of zirconia was chosen. Zirconium tetraacetylactonate (Zr(O₂C₅H₇)₄) was in solid form and stable up to 300°C. The concentration of this compound in nitrogen steam can be controlled by varying the temperature of the vaporizer and feed rate of carrier gas (N₂). Balong was able to obtain a uniform zirconia film with this zirconia source at a deposition rate of 7.2 x 10⁻³ mmole/min (Balong, 1977).

We experienced some difficulty in chemical deposition of zirconium tetraactylactonate. However, a zirconia modified membrane with a pore

Figure 4.19 Pore size distribution of zirconia modified membranes Zr008

Figure 4.20 Pore size distribution of zirconia modified membranes Zr012

size around 34Å was obtained after several attempts. The deposition conditions are listed in the Table 4.15. A zirconia modified membrane, Zr020, with a pore size around 24Å was obtained under a similar deposition condition, except that the zirconia feeding rate was increased to 50 cc/min. These membranes also showed some improvement in liquid separation. However, no zirconia content can be detected by EDAX with both zirconia modified membranes Zr019 or Zr020. The reason of this inconsistent result is unknown at the present time.

Zirconia-modified membranes Zr019 and Zr020 have a similar nitrogen permeability (45 and 49 M³/M²/hr/atm, respectively) but have 10Å difference in pore size according to pore size analysis. This indicated that the deposition depth of these membranes might be different. For a given pore size, high permeability is desirable. Therefore, with the combination of pore size analysis and gas permeability one can determine a better deposition procedure and conditions.

Hydrothermal stability are also studied on zirconia modified membranes. The nitrogen permeability of zirconia modified membranes Zr012 increased from 35 to 105 M³/M²/hr/atm after 14 hrs hydrothermal treatment at 600°C with 90% of steam. The pore size of this membrane increased from 26 Å to 45Å (Table 4.8). At present time, it is still a question whether the low hydrothermal stability of this membrane is due to the nature of zirconia modified membranes or the failure of zirconia deposition.

Table 4.15 The Deposition Condition for ZrO_2 on Existing Alumina Membranes

Feed gas 1	N_2 , 25-50 cc/min
Feed gas 2	20% O_2 in He, 400 cc/min
Temperature of Vaporizer	150-200°C
Temperature of Reactor	450-600°C
Reject Flux	420 cc/min

5. Membrane Modification by in-situ Zeolite Crystallization

In the past thirty years, the properties and applications of zeolites have been explored in many scientific disciplines and chemical engineering process technologies. The main commercial applications of zeolites are based on their adsorption, separation, and catalysis characterization (Rojey, 1989; Suzuki, 1989; Goldman, 1989; Kulprathiparija, 1988; Stenzel, 1985). Zeolites, in general, have respectively high thermal and hydrothermal stability (550°C-800°C). Their pore size ranges from 3 to 12Å, which is ideal for using in the separation of small molecules. If zeolites can be formed into membranes, they are expected to have functions both in the molecular sieve separation and catalysis. These zeolitic membranes would be able to serve as separators and reactors at the same time. Therefore, it would have a great economic advantage over direct reaction pathway not only by combining two processes into one, but also by increasing reaction yield through the removal of the desired final or intermediate products.

Zeolitic membranes are superior than other inorganic membranes because of their diverse applications in catalysis and separation. Several polymer-zeolitic membranes demonstrate selective separation in water/ethanol and hydrogen/methane mixtures. Suzuki reported the use of polymer-zeolitic membranes in catalysis (Suzuki, 1985). However, the binder, polymer, used in these membranes have low biological chemical and thermal stabilities. Inorganic-zeolitic membranes also exhibit excellent applications in separation and catalysis but have low economic feasibility because of low permeabilities (Suzuki, 1985; Matsushita, 1985; Ishikoga, 1985; Abe, 1988; Sakurada, 1989; Suzuki, 1987). Despite all the efforts in the synthesis of zeolitic membranes, there is no solid evidence of molecular sieving efficiency of those membranes. The lack of characterization technique for the membranes with small pores is the major task in the research of zeolitic membranes. The preparation and characterization of a new type of silica-ZSM-5 membrane was initiated and studied in Alcoa's Laboratory. Detailed summary of this investigation is disclosed in following sections.

5.1 Pretreatment

The existing polymer-zeolitic membranes as mentioned early have the similar disadvantage as polymeric membranes. Other zeolitic membranes supported on ceramics are still under development. The low permeabilities, low thermal stabilities and high brittleness are still the problems for practical applications.

Our development strategy was to overcome the deficiency of zeolitic membranes listed above. Prior to the preparation of silica-ZSM-5 membranes, several modification methods were considered. Modifications of the outside surface of the alumina supports (e.g. polymer coating) can inhibit the formation of zeolite crystals on the outside surface of the support.

Silica modification of inner surface of alumina supports can ensure that the zeolite crystal will form on the entrance or in the pores of the inside

surface of porous support. Another pretreatment procedure is treating the inner surface of supports with zeolites/sol-gel solution.

Various concentration (2-7%) of ZSM-5 crystals were prepared in the sol-gel solution (Table 5.1). Several supports with different pore size were dipped with the solution described. The membranes then were dried at room temperature for 24 hrs and calcined to 450°C. The membranes then were characterized by their nitrogen and helium permeabilities (Table 5.2 - 5.4). Compared with their support (0.2 μm), zeolitic membranes ZS129, ZS132 and ZS135 have improved in He/N₂ separation selectivity. This improvement indicated that the pinholes of these membranes after pretreatment were smaller than the pore size (0.2 μm) of the supports. However, the He/N₂ separation selectivity of pretreated zeolitic membranes ZS133, ZS134, ZS138, ZS139 and ZS148 remained similar to their support (100Å and 500Å). This indicated that the pinhole from the pretreatment is larger than 500 or 100Å. Therefore, the separation selectivity is based on support material. The SEM of ZS133 (Gel#3 on 100Å) and ZS136 (Gel#3 on 0.2 mm) confirmed this speculation (Figure 5.1 - 5.4). Although a few pinholes were observed on the inside surface of the membranes, a uniform layer was observed (Figure 5.5). It is unlikely to obtain a pinhole free membrane through this method. However, it is possible to narrow down the pinhole to 40Å by altering the zeolite/sol-gel composition. The advantage of this method is that the porosity of these membranes should be higher than those from the direct synthesis.

Once a zeolitic membrane with a small pinhole around 40Å can be achieved through this pretreatment, these pretreated membranes can be used as a starting material for direct synthesis of zeolitic membranes. The pretreatment layer can serve as a seed where the zeolite will grow in place (inside surface of starting material). The other possibility is using the chemical vapor deposition to patch up these ~40Å pinholes.

5.2 Synthesis Procedures

A typical direct synthesis procedure of a silica-ZSM-5 membrane on a Membralox® porous alumina support was as follows: prepare a solution by mixing tetraoxothorylsilica, sodium hydroxide and tetrapropyl ammonium bromide in deionized water; transfer the solution to autoclaves and place a Membralox® porous alumina tube with a top layer pore size of 40Å, 100Å, 500Å and 2000Å in this solution; place the autoclaves in the oven at 80-200°C under autogenous pressure for 1-6 days; remove the Membralox® porous alumina tube and wash with deionized water; calcine the silica-ZSM-5-Membralox® alumina tube to 300-600°C.

Several silica-ZSM-5 membranes were synthesized on the alumina support (ZS001-ZS149). The observation of by-products in the reaction suspension from microscopic study indicated the formation of typical crystals of silica-ZSM-5.

Table 5.1 The Concentration of the Pretreatment Sol-gel of Zeolitic Membranes

<u>Gel</u>	<u>ZSM-5 Concentration</u>	<u>Alumina Concentration</u>
1	4.5%	2.2%
2	6.5%	2.1%
3	7.3%	2.1%
4	2.0%	2.1%

Table 5.2 The Nitrogen and Helium Permeabilities of Various Pretreated Zeolitic Membranes on 0.2mm Support

<u>Samples</u>	<u>Support</u>	<u>N₂ Permeability M³/M²/hr/atm</u>	<u>He Permeability M³/M²/hr/atm</u>	<u>He/N₂ Selectivity</u>
Reference	0.2μm	614.50	2196.51	1.79
ZS129(Gel#1)	0.2μm	298.22	598.86	2.10
ZS132(Gel#2)	0.2μm	462.75	870.19	1.88
ZS135(Gel#3)	0.2μm	379.11	741.02	1.95

Gel composition is listed on Table 5.1

Table 5.3 The Nitrogen and Helium Permeabilities of Pretreated Zeolitic Membranes on 500Å Support

<u>Samples</u>	<u>Support</u>	<u>N₂ Permeability M³/M²/hr/atm</u>	<u>He Permeability M³/M²/hr/atm</u>	<u>He/N₂ Selectivity</u>
Reference	500Å	251.95	535.85	2.13
ZS134(Gel#3)	500Å	254.5	556.95	2.19

Gel composition is listed on Table 5.1

Table 5.4 The Nitrogen and Helium Permeabilities of Pretreated Zeolitic Membranes on 100Å Support

Samples	Support	N ₂ Permeability <u>M₁/M₂/hr/atm</u>	He Permeability <u>M₁/M₂/hr/atm</u>	He/N ₂ <u>Selectivity</u>
Reference	100Å	242	-	2.64(ca) ^a
ZS133(Gel#3)	100Å	190.98	489.8	2.56
ZS138(Gel#3)	100Å	195.39	501.76	2.57
ZS139(Gel#3)	100Å	280.55	671.64	2.40
ZS148(Gel#4)	100Å	164.58	433.58	2.64

Gel composition is listed on Table 5.1.

- ^a The separation selectivity is calculated based on Knudsen diffusion.

Figure 5.1
SEM of Inner Surface of Zeolitic Modified Membrane ZS133

Figure 52
SEM of Inner Surface of Zeolitic Modified Membrane ZS133

Figure 5.3
SEM of Inner Surface of Zeolitic Modified Membrane ZS136

Figure 5.4
SEM of Inner Surface of Zeolitic Modified Membrane ZS136

Figure 5.5
SEM of Cross-Section of Zeolitic Modified Membrane ZS136

The scanning electron micrographs of the inner surface and cross-section of zeolitic membranes on porous alumina support indicated that their inner surface was covered with silica-ZSM-5 crystal (Figures 5.6 - 5.10). This was consistent with the EDAX analysis of the inside surface of the zeolitic membrane (Figure 5.11). The scanning electron micrographs of the outside surface of the sample tube showed that the outside surface still retained its porous structure after hydrothermal reaction (Figure 5.12).

However, not all the alumina supports are stable under the hydrothermal reaction. Efforts have been made in search of a suitable reaction condition for a particular alumina support. For example, ZS011 (40Å), ZS014 (100Å), ZS005 (500Å) and ZS020 (0.2 µm) were synthesized under the same conditions. However, SEM indicated that the alumina supports with a top layer of 40Å might have been damaged after a hydrothermal reaction. All of these zeolitic membranes, except ZS011, exhibited lower permeabilities than their alumina supports (Table 5.5). The increase of the nitrogen permeabilities of ZS011 from 70 to 217 M³/M²/hr/atm indicated that the 40Å γ alumina layer was damaged during the hydrothermal reaction. Since the 40Å alumina membranes are very unstable under the hydrothermal reaction at a high pH solution, a low pH synthesis condition (pH 8-9) may be able to solve this problem. However, a low pH synthesis procedure of silica-ZSM-5 requires a long reaction time (6-24 days) and seeds which will cause a problem to control the growing position of zeolite crystals. Therefore, γ alumina membranes with a top layer of 40Å might not be a good candidate as support in this synthesis.

Other alumina supports with a top layer of 100Å, 500Å, and 2000Å can retain their structure under different reaction conditions. The alumina supports with a top layer of 100Å can be stable under hydrothermal reaction only when the sodium hydroxide concentration is lower than 0.125M. When a 0.25M sodium hydroxide was used, the defects did not occur between the zeolitic membrane and the top layer (100Å) of support, instead it occurred between 100Å and 0.8 µm layer. These results were indicated by the scanning electron micrographs of zeolitic membrane ZS023 (Figure 5.8).

Besides selecting a proper pretreatment procedure and synthesis conditions for a desired support, the cleaning procedure of zeolitic membranes after hydrothermal reaction was investigated. The detailed synthesis conditions of zeolitic membranes ZS104- ZS111 are listed in Table 5.6. Experimental results indicated that these zeolitic membranes have small permeabilities when calcined to 450°C. However, further calcination up to 650°C usually will result in a permeability increase. EDAX analysis of these membranes indicates that there was sodium residue in the alumina support (Figures 5.13 - 5.15). This sodium residue in the alumina support might have attacked support materials at a high temperature and caused the pore growth of support. The cleaning procedure before calcination to avoid such a problem was investigated.

Figure 5.6
SEM of Inner Surface of Zeolitic Modified Membrane ZS117

Figure 5.7
SEM of Cross-Section of Zeolitic Modified Membrane ZS014

Figure 5.8
SEM of Cross-Section of Zeolitic Modified Membrane ZS023

Figure 5.9
SEM of Cross-Section of Zeolitic Modified Membrane ZS076

Figure 5.10
SEM of Cross-Section of Zeolitic Modified Membrane ZS133

Figure 5.11
EDAX of the Inside Surface of ZS005
Developmental Zeolitic Membrane

ZS005
INSIDE SURFACE
MEMBRANE
TIME= 24LSEC

10eV/ch

Figure 5.12
SEM of Outside Surface of Zeolitic Modified Membrane ZS005

**Table 5.5 The Nitrogen Permeabilities of Zeolitic Membranes on Supports
Before and After in-situ Synthesis**

	Support Pore Diameter	N ₂ Permeability (M ³ /M ² /hr/atm)	
		<u>Before</u>	<u>After</u>
ZS011	40.0	109.0	108.3
ZS014	100.0	200.0	72.86
ZS005	500.0	499.0	108.3
ZS020	0.2 μm	614.5	15.1

Table 5.6 Synthesis Conditions for ZS104-ZS110

Samples	Supports	NaOH	:	TPABr:	SiO₂
ZS104	100Å	1	:	2	4
ZS105	40Å	1	:	2	4
ZS106	40Å	1	:	2	4
ZS107	100Å	1	:	2	4
ZS108	500Å	1	:	2	4
ZS109	100Å	1	:	2	4
ZS110	100Å	1	:	2	4

Reaction temperature: 150°C

Reaction Time: 24 hrs

Figure 5.13
EDAX of Inner Surface of Zeolitic Membrane ZS106

RJLEE GROUP JSM 840 SEM
Cursor: 0.000keV = 0

TUE 12-MAY-92 12:19

0.000
60

VFS = 4096 10.240

ALCOA SEP ZS-106 ID CRY5 (9499) D2227/F101

Figure 5.14
EDAX of Inner Surface of Zeolitic Membrane ZS107

RJLEE GROUP JSM 640 SEM
Cursor: 0.000keV = 0

TUE 12-MAY-92 13:57

Figure 5.15
EDAX of Inner Surface of Zeolitic Membrane ZS110

RJLEE GROUP JSM 840 SEM
Cursor: 0.000keV ± 0

TUE 12-MAY-92 13:16

A washing procedure was developed to remove sodium residue before calcination. We discovered that zeolitic membranes are unstable under the sodium cleaning process. For example, the nitrogen permeability of zeolitic membrane ZS106 was $0.013 \text{ m}^3/\text{m}^2/\text{hr}/\text{atm}$ after the first time washed with water and calcined to 600°C . However, further washing and calcining of this membrane up to 450°C caused the nitrogen permeability to increase to $7.45 \text{ m}^3/\text{m}^2/\text{hr}/\text{atm}$. This suggested that the zeolitic crystals synthesized within the porous structure may not form a strong bond with the existing alumina membrane structure.

Therefore, the synthesis conditions have been altered so zeolitic membranes can withstand this cleaning procedure. Zeolitic membranes ZS122-ZS124 were synthesized on $100\text{\AA}$ alumina support. The detailed synthesis conditions are listed on Table 5.7. The nitrogen permeabilities of these membranes remained small and constant after the cleaning process (Table 5.8). The He/N_2 separation selectivity of these membranes were around 2.64.

The pore size analysis indicated that the probe gas, cyclohexane, can condense only on a certain portion of pores of these membranes. The percentage of flow contributed by noncondensable pores of zeolitic membranes ZS122, ZS123 and ZS124 was 57%, 69% and 71%, respectively. The condensable portion of the pore of ZS122 has an average pore size of $36\text{\AA}$, while ZS123 and ZS124 have a wide pore size distribution around $100\text{-}30\text{\AA}$. (Figure 5.16 - 5.18). Further treatment with silica chemical vapor deposition can eliminate those pinholes (Table 5.9). The stability of zeolitic membranes at high temperature was improved once there was no sodium residue.

Along the concept discussed in the previous section, a $100\text{\AA}$ alumina support was pretreated with gel #3, dried at room temperature for 24 hours and calcined to 450°C (ZS139*). The pretreated membrane then was placed in zeolite synthesis solution and sealed in a autoclave at 150°C for 20 hours. The mole ratio of $\text{NaOH}/\text{TPABr}/\text{TEOS}$ used was $1/2/4$. The membrane was washed with deionized water until no sodium residue existed and dried at room temperature. The membrane ZS139(*2) then was dried by further calcination up to 300°C . The permeability of ZS139(2*) is much small after in-situ synthesis (Table 5.10). The pore size analysis indicated a $100\text{\AA}$ - $40\text{\AA}$ pinhole was present in this membrane (Figure 5.19).

A similar pretreatment and in-situ synthesis were conducted on ZS143 and ZS148. The pore size distribution of these zeolitic membranes indicated that the pinholes of these membranes had a similar pore size as that of their supported materials (Figure 5.20 - 5.21). The He and N_2 permeability of these membranes was lower than that of their supports, indicating that a great portion of inner surface was covered with zeolite crystals (Table 5.11).

In summary, the pinholes in zeolitic membranes can be minimized by combining pretreatment and in-situ synthesis.

Table 5.7 The Synthesis Conditions for Zeolitic Membranes ZS122-ZS124

NaOH Concentration:	0.25M-0.5M
TPABr Concentration:	0.065-0.125M
SiO ₂ Concentration:	0.5-2M
Furnace Temperature:	150-200°C
Support:	100Å
Reaction Time:	18-21 hrs

Table 5.8 He and N₂ Permeabilities of Zeolitic Membranes ZS122-ZS124

<u>Samples</u>	<u>Support</u>	<u>Pinholes</u>	<u>N₂</u> <u>(M³/M²/hr/atm)</u>	<u>He</u>	<u>He/N₂</u> <u>Selectivity</u>
ZS122	100Å	~36Å	19.05	40.06	2.10
ZS123	100Å	30-100Å	32.93	77.45	2.34
ZS124	100Å	30-100Å	28.72	78.14	2.72

Figure 5.16 Pore Size Distribution of Zeolitic Membrane ZS122

Figure 5.17 Pore Size Distribution of Zeolitic Membrane ZS123

Figure 5.18 Pore Size Distribution of Zeolitic Membrane ZS124

Table 5.9 He and N₂ Permeabilities of Zeolitic Membranes Before and After Silica CVD Modification

<u>Samples</u>	<u>Before</u>			<u>After</u>		
	<u>N₂</u> <u>M³/M²/hr/atm</u>	<u>He</u> <u>M³/M²/hr/atm</u>	<u>He/N₂</u> <u>Selectivity</u>	<u>N₂</u> <u>M³/M²/hr/atm</u>	<u>He</u> <u>M³/M²/hr/atm</u>	<u>He/N₂</u> <u>Selectivity</u>
ZS111	28.72	78.14	2.72	0.0017	0.036	2.10
ZS123	32.93	77.45	2.34	0.0278	0.0140	1.98
ZS124	28.72	78.14	2.72	0.0689	0.0256	2.69
ZS138	195.39	501.76	2.57	4.52	14.49	3.28
ZS148	8.370	16.100	1.92	1.9183	4.958	2.58

Table 5.10 The Nitrogen and Helium Permeabilities of Zeolitic Membranes ZS139 After Pretreatment and In-situ Synthesis

<u>Samples</u>	<u>Support</u>	<u>N₂ Permeability M³/M²/hr/atm</u>	<u>He Permeability M³/M²/hr/atm</u>	<u>Separation Selectivity</u>
ZS139(1*)	100Å	280.55	671.64	2.40
ZS139(2*)	100Å	15.92	36.63	2.30

The permeabilities of ZS139 after pretreatment with gel #3.

The permeabilities of ZS139 after pretreatment, direct synthesis and calcined to 300°C.

Figure 5.19 Pore Size Distribution of Zeolitic Membrane ZS139

Figure 5.20 Pore Size Distribution of Zeolitic Membrane ZS143

Figure 5.21 Pore Size Distribution of Zeolitic Membrane ZS148

Table 5.11 He and N₂ Permeability of Various Zeolitic Membranes After Pretreatment, In-situ Synthesis and/or CVD

<u>Samples</u>	<u>Support</u>	<u>Treatment</u>	<u>N₂ M³/M²/hr/atm</u>	<u>He M³/M²/hr/atm</u>	<u>He/N₂ Selectivity</u>
ZS139	100Å	Sol-Gel	280.05	671.64	2.40
		in-situ	15.92	36.63	2.30
ZS143	50Å	Sol-Gel#4	98.60	229.0	2.32
		in-situ	0.26	0.72	2.78
ZS146	100Å	Sol-Gel	130.00	324.0	2.49
		CVD	10.96	26.00	2.37
ZS148	100Å	Sol-Gel#4	164.58	433.86	2.64
		in-suite	8.370	16.100	1.92
		CVD	1.9183	4.958	2.58

5.3 Modification

Chemical vapor deposition can be used in the modification of zeolitic membranes to eliminate the pinholes and defects of these membranes. Zeolitic membranes ZS111, ZS123 and ZS124 were modified by silica CVD method. The N_2 and He permeabilities of these membranes decreased drastically after deposition (Table 5.9). The He/ N_2 separation selectivity of ZS124 remained the same while ZS123 decreased. As discussed in Section 6, the He/ N_2 separation selectivity decreased with the pore size of membranes until an optimum pore size was reached which was around 5.5Å. Therefore, the decrease of the separation selectivity in ZS124 might indicate that the pore size of pinholes was less than 40Å but larger than 5.5Å.

This silica modified zeolitic membrane, ZS111, demonstrates a high separation selectivity in the He/ SF_6 separation which indicated that a great portion of the pinholes have been eliminated. A silica modified membrane, Si172, with an average pore size of about 22Å showed a separation selectivity of 1.57 in He/ SF_6 separation while zeolitic membrane ZS111 demonstrated a separation selectivity of around 4.8. Therefore, we concluded that the pinholes in ZS111 were smaller than 22Å. Since ZMS-5 crystals have a pore opening of around 5.2Å X 5.6Å and the kinetic diameter of SF_6 is around 5.5Å, we are not sure that the total molecular sieving separation can be achieved by ZSM-5 zeolitic membranes.

It is possible to block the open pore of zeolitic membranes while trying to patch up the pinholes with chemical vapor deposition. The other possible route of modification is to patch up the pinhole before removing the template of zeolitic membranes. Since the template inside the pores of ZSM-5 will decompose at 450°C, a low temperature chemical vapor deposition should be employed. Zeolitic membranes ZS146 and ZS148 were synthesized and further modified with such a method. The He/ N_2 separation selectivities of ZS146 and ZS148 after chemical vapor deposition and calcination at 520°C were slightly higher than their supports (2.46). This result is similar to the results reported by other ZSM-5 zeolitic membranes.

ZSM-5 zeolitic membranes showed a separation selectivity slightly higher than Knudsen diffusion for the gas molecules which have a kinetic diameter smaller than the pore opening of ZSM-5 crystals (5.6Å). For the molecules which have a kinetic diameter larger than 5.6Å, ZSM-5 zeolitic membranes shall demonstrate a molecular sieving separation. However, so far, the reported zeolitic membranes demonstrate a combined transport mechanism. Gas molecules transport partially through zeolite channels and partially through the microporous defects. Therefore, a separation selectivity higher than Knudsen but lower than molecular sieving separation was observed.

Although it is encouraging that our zeolitic membranes showed a similar or higher He/N₂ separation selectivity than other reported zeolitic membranes, the analytical results can not prove the separation is due to a true zeolitic membrane. In the past, because of the unsteady supply of neopentane, we used SF₆ as a probe gas molecule. However, since the kinetic diameter of SF₆ is 5.5Å, no molecular sieving separation was observed by our zeolitic membrane. Therefore, using probe gas molecules which have a kinetic diameter larger than a ZSM-5 crystal opening is the only way to identify the true zeolitic membranes.

6. Gas Separations Using Modified Membranes

6.1 Introduction

Gas separation mechanisms through a ceramic membrane can be classified in five categories: (a) Knudsen diffusion or free molecular flow requires the pore size of the membrane is ten times less than the mean free path of gas molecules. The pore size is usually in the range of 40 to 100Å which is still much larger than molecular size. The separation efficiency is based on the gas molecular weight. The ideal selectivity is the inverse of the square-root of molecular weight ratio. (b) Molecular sieving or micropore diffusion is based on the size of molecule vs. the pore diameter of a membrane. The pore size required is usually near the molecular size, which ranges from 3 to 10Å. The separation mechanism is simply dependent on the size exclusion. (c) Solid-solution diffusion is based on the gas molecule solubility and mobility in a dense-film of the membrane. The separation mechanism involves three steps, i.e., dissolution, migration, and evolution. (d) Surface diffusion is controlled by the product of molecular adsorb-ability and migration rate on the surface. The separation is dependent on the chemical and physical interaction between gas molecules and membrane surface. (e) pore condensation is determined by the vapor pressure of the gas component, pore size and temperature. The last four mechanisms usually can provide a very high selectivity in certain gas separations. However, the mechanisms d & e are diminished at high temperature (> 200°C).

6.2 Pore Size vs. Gas Separations

According to Present & deBethune's theory, the separation efficiency of the membrane increases with the decrease of the pore size of the membrane (Present, 1949). However, as the pore size decreases, the surface flow through the membranes become important. As a result, the inverse relationship is not obeyed for a certain range of the pore size. Fain incorporated gas molecule adsorption, surface flow and surface momentum accommodation (Fain, 1991) in addition to Knudsen flow into a transport equation. The equation thus developed can predict the unexpected anomaly.

For a given class of membrane materials, the separation selectivity decreases with the pore size reduction of the membrane until a critical pore size is reached. Then the separation selectivity increases drastically as the pore size of the membranes further decreases (Figure 6.1).

This phenomena was observed in He/N₂ separation with our modified porous membranes. The modified membranes Si208 and Si210 with a pore size around 31-27Å showed a Knudsen separation in He/N₂ with a selectivity of 2.4-2.5. However, as the pore size of the modified membrane decreased to 22-24Å (Si211 and Si212), the He/N₂ separation selectivity decreased to 2.09 (Table 4.1). The He/N₂ separation selectivity started

Figure 6.1 The He/N₂ Separation Selectivity Vs Pore Size

increasing as the pore size of the modified membrane is less than 15Å. For example, according to pore size distribution, both modified membranes ZS209 and ZS207 did not have a pore size larger than 15Å. A high He/N₂ separation selectivity was observed in these two modified membranes (e.g., 3.86 and 36.59). These two modified membranes were further characterized with He/SF₆ mixture separation. The He/SF₆ separation selectivity of the modified membranes Si209 is around 2.06 which is slightly higher than that of existing 40Å alumina membranes (Table 4.1). Since there is no molecular sieving separation, we conclude that both He and SF₆ can permeate through this membrane. The kinetic diameter of He and SF₆ are 2.89 and 5.5Å, respectively. Therefore, we concluded that the modified membrane Si209 has a pore size larger than 5.5Å and smaller than 15Å. The modified membrane Si207, on the other hand, demonstrated a He/SF₆ separation selectivity around 9.06 which is much higher than Knudsen separation. Although there is no molecular sieving separation, the high separation selectivity indicates that the pore size of this membrane is close to kinetic diameter of SF₆ which is 5.5Å. This also indicated that in order to obtain a high He/N₂ separation selectivity at room temperature, the pore size of these silica modified membranes should be ~ 5Å. In this section, we will focus on the separation of hydrogen-containing gas mixtures with membranes of a pore size < 5Å or close to dense phase.

6.3 Literature Review on Si-Modified Membranes

SiO₂-modified membranes provide a very high selectivity of hydrogen. It potentially offers a new energy-efficient process to recover hydrogen. Table 6.1 summarizes the permeabilities of the hydrogen-selective membranes discussed in the literature. The separation mechanism, although was explained by those authors, was still not very clear.

Goldsmith et al. (1992) reported the permeation tests of He, CO₂, Ar and N₂ using SiO₂-modified membranes. The permeability of He obtained was 0.155 m³/m²/atm/hr, with a selectivity of 190 over nitrogen at 450°C. The separation mechanism was explained by molecular sieving. The pore size was estimated in the range of 5 to 10Å.

Megiris and Glezer (1992), and Gavallas et al. (1990 and 1989) suggested that a non-porous SiO₂ film was deposited on the porous support of their hydrogen-selective membranes. The gas separation mechanism was "solid solution diffusion" through the dense film. Hydrogen is dissolved and diffused through the dense SiO₂ membrane. The permeation was a function of temperature. Since the H₂ mobility in the SiO₂ film increases with the temperature increase, the hydrogen permeability is significantly increased at a higher temperature. The permeation ratio of H₂ to N₂ was reported from 200 to 3000 at 450 ~ 750°C depending on the permeation rate. In general, the higher the permeation rate is, the lower the selectivity is. They also investigated the hydrothermal stability of their membranes

Table 6.1 : Permeabilities Comparison of High Selectivity Membranes

Authors	Support	Membrane material	Membrane Thickness (μm)	Deposition & Pre-cursor	gas	Permeability ($\text{m}^3/\text{m}^2/\text{atm}/\text{hr}$)	temp ($^{\circ}\text{C}$)	S/M#	Remark
Gavalas et al.(1989)	vycor glass	SiO ₂	~0.1	CVD (SiH ₄)	H ₂ N ₂	0.11~0.33 3.0E-5~0.05	450 450	S S	
Tsapatsis et al. (1991)	vycor glass	SiO ₂ , TiO ₂ , Al ₂ O ₃ , B ₂ O ₃	<100	CVD (MCl _x)	H ₂ N ₂	0.002~0.21 4.0E-6~0.003	450 450	S S	
Megiris & Glezer (1992)	vycor glass	SiO ₂ /C	~3.0	CVD (C ₃ H ₇) ₃ SiH	H ₂ N ₂	0.095~0.21 5.4E-4~0.03	750 750	S S	
Galvas (1991)	vycor glass	SiO ₂	?	CVD (SiCl ₄)	H ₂ N ₂	0.012~0.21 3.9E-6~3.0E-4	450 450	S S	
		TiO ₂	?	CVD (TiCl ₄)	H ₂ N ₂	0.11 4.4E-4	600 600	S S	
Okubo & Inoue (1989)	porous glass	SiO ₂	?	CVD (TEOS)	H ₂ N ₂ O ₂ He Ne Ar	0.00410 0.00037 0.00049 0.00290 0.00098 0.00033	200 200 200 200 200 200	S S S S S S	
				CVD (TEOS)	He O ₂	0.00244 0.00049	200 200	S S	
Goldsmith et al. (1992)	alumina tube	SiO ₂	0.05-0.1	?	He N ₂	0.1547 0.0012	450 450	S S	
Koresh & Sofer (1987)	Carbon	Carbon	3*	pyrolysis	H ₂	9.4E-8	500	M	(H ₂ /CH ₄)

Single or Mixture data

* Assumed thickness is 3 μ (3X10⁻⁴ cm)

(Gavalas, 1991). The test was carried out in an environment that contained 23% H₂, 27% CO, 32% H₂O and 18% CO₂ at 600°C for up to 3 days. The permeation rate of H₂ decreased from 0.31 to 0.075 (cm³/cm²/min/atm), while that of N₂ dropped from 0.0003 to 0.0001 (cm³/cm²/min/atm). The separation selectivity slightly decreased after the 3 days of the hydrothermal treatment.

Okubo and Inoue (1989 a,b) reduced the pore size by SiO₂ through a CVD process. Gas permeation was suggested through "micropore diffusion", thus, gas with a smaller molecular size gave a higher permeability. The permeation mechanism was estimated to be diffusion through the pores small enough to deviate from Knudsen diffusion. The permeation was also a function of temperature, which follows the Arrhenius equation. The solution-diffusion mechanism was ruled out by comparing the apparent activation energies of He permeation in glass and fused silica. The He apparent activation energy of diffusion in their membrane was 3.9 KJ/mole, while that of vycor glass (non-porous) and fused silica were 21 KJ/mole. N₂ with a kinetic diameter of 3.64Å might be larger than the pore diameter, thus no permeation of nitrogen was observed. However, the small N₂ permeation observed was attributed to the minor defect of the membrane. As a result, the permeability of N₂ followed Knudsen diffusion, i.e., decreased with temperature increase.

Based on the above review, the SiO₂-modified membrane was believed to be microporous layer with pore size within the micropore diffusion range or molecular sieving. Goldsmith et al. and Okubo et al. came to the same conclusion. The dissolution process suggested by Gavalas et al. failed to explain the high permeation rate of He reported by Okubo and Goldsmith. He was an inert gas and should not have interaction with the silica surface. In addition, the diffusion activation energies of He in the membrane was far smaller than that of the dense glass film. The molecule of He is so small that it could penetrate the microporous structure of the SiO₂ film, thus it delivers high permeability. The penetration of He through the network of SiO₂ structure is possible but rather unlikely. The He permeation rate (Boyd and Thompson, 1980) in the dense glass was almost 5 to 6 orders of magnitude less than the H₂ permeation rate reported by Gavalas.

6.4 Separations of Gas Mixtures using Si-Modified Membranes

The method of SiO₂-modified membrane was discussed in Section 4. A one inch tube was first synthesized, later a 10" tube was also synthesized. The silica content of modified membranes was determined with electron microprobe (or EDAX) throughout the permselective layer of the alumina membrane. The layer structure was also examined by scanning electron microscopy (SEM).

Single gas permeation test was used to evaluate the separation performance of the 1" SiO₂-modified membrane. The membrane was housed in a stainless steel module. Permeabilities of N₂, H₂, He and Ne, were measured at 300, 450 and 600°C. Feed flow at ~10 l/min, and feed pressure from 20 to 80 psig were selected by adjusting the back pressure regulator of the reject stream. Permeate was open to atmosphere and flow rate was measured by a bubble meter.

6.4.1 Single Gas Permeation

Figure 6.2 presents the permeability at elevated temperatures. He and H₂ permeabilities increased with the temperature increase while the N₂ permeability decreased. In addition, Ne permeability slightly decreased along with the temperature increase. Some of the phenomena were also reported by Gavalas et al. (1989) and Okubo and Inoue (1989) with modified vycor glass membranes. At 600°C, the ratio of He to N₂ is 59 and H₂ to N₂ is 28, which is much higher than the theoretical Knudsen separation. Under the Knudsen regime, the permeability ratio of He to N₂ is 2.6 and that of H₂ to N₂ is 3.7 for a 50Å membrane.

The kinetic diameter of He is the smallest one (2.6Å), followed with H₂ (2.89Å) and Ne (2.75Å). N₂ has the largest kinetic diameter, 3.64Å. It is believed that membrane pores were reduced by SiO₂ deposition. Gas permeation is through "micropore diffusion", thus, gas with a smaller molecular size gave a higher permeability.

6.4.2 Mixture Separation

A gas mixture of 69% N₂ and 30% H₂, was used to simulate the composition of syn-gas provided by METC. Separation was carried out at 538°C and 7 atm at a total flow rate of about 1.0 l/min. Table 6.2 lists the separation results of H₂ and N₂. The H₂ concentration increased from 31% to 73%. The separation factor is 6.1 which is higher than Knudsen (3.74). However, the separation factor is still smaller than the permeability ratio (ca. ~ 22) of H₂ to N₂ of this modified membrane. This phenomenon was also observed in other modified membranes (Table 6.3). Silica modified membranes Si009, Si018, Si019, Si022 and Si024 were investigated. A 47% N₂ in H₂ mixture was used in this binary mixture separation. In general, the separation selectivity observed in binary mixture separation is smaller than that which was based on single gas ratio. The permeated stream of modified membranes Si009 and Si024 show a great enrichment in H₂ (92%). However, the separation selectivity remained around 10.6 and 11.3, respectively. One should note that the permeability ratio of two gases can only present the ideal separation factor. The practical separation factor is determined not

Figure 6.2 : Temperature Effect on Permeability - AS195

Table 6.2 H₂/N₂ Separation in Modified Membrane - AS195

<u>Temperature:</u>	538°C
<u>Feed</u>	
Flow	0.97 l/min
Pressure	7 atm
Composition	
H ₂	31.4 %
N ₂	68.6 %
<u>Reject</u>	
Flow	0.95 l/min
Pressure	6.97 atm
Composition	
H ₂	30.9 %
N ₂	69.1 %
<u>Permeate</u>	
Flow	0.018 l/min
Pressure	1 atm
Composition	
H ₂	73.5 %
N ₂	26.5 %
<u>Pressure ratio</u>	0.143
<u>Stage cut</u>	0.019
<u>Separation factor*</u> (H ₂ /N ₂)	6.1

$$\text{*separation factor} = \frac{(\text{Permeate H}_2\%) / (\text{Permeate N}_2\%)}{(\text{Feed H}_2\%) / (\text{Feed N}_2\%)}$$

Table 6.3 H₂/N₂ Separation Selectivity of Silica Modified Membranes

<u>Samples</u>	<u>Temp.</u> °C	<u>H₂/N₂</u>
Si009	500	12.68 _a
Si009	500	10.59
Si018	20	1.86 _a
Si018	20	0.91 _b
Si018	500	2.66 _a
Si018	500	1.69 _b
Si019	500	3.12 _a
Si019	500	1.27 _b
Si022	500	2.91 _a
Si022	500	1.23 _b
Si022	600	3.72 _a
Si022	600	1.54 _b
Si024	500	25.00 _a
Si024	500	11.34 _b

_a Separation selectivity based on single gas ratio

_b Separation selectivity based on binary mixture separation

only by the membrane property but also by the pressure difference across the membrane. From the viewpoint of gas mixture separation, there is always a limitation in separation factor. Since pressure is the only driving force, the partial pressures of each component in permeate can never be larger than that of the reject. In practice, permeate pressure always exists, so the real separation factor is never equal to the ideal separation factor. Unless a membrane has infinite selectivity, the separation factor never reaches infinity.

As discussed in Sec. 4, a modified membrane with a nearly infinite selectivity of hydrogen over nitrogen was developed via a chemical vapor deposition. Gaseous mixture separations with a membrane like this failed due to the leak of nitrogen through the graphite packing. It is believed that a nearly pure hydrogen stream could be obtained provided a perfect seal could be developed.

6.5 Removal of Trace Contaminants

H₂S and NH₃ are the two trace contaminants which may be removed via decomposition. Ceramic membranes with a selectivity to hydrogen may facilitate the decomposition of these contaminants via the catalytic membrane reactor approach. The concept has been demonstrated experimentally and analyzed mathematically for several key chemical production processes. A mathematical analysis was performed to assess the feasibility of the trace contaminants removal under the coal gasifications environment.

To simplify the analysis, a feed containing H₂, N₂, H₂S and NH₃ was shown in Figure 6.3. Other contaminants, e.g., CO may be present and are ignored without compromising the feasibility analysis. Our analysis selected the extreme temperatures and pressures encountered in the coal conversion environment. That is, temperatures were at 538 and 1093°C and pressures were at 6 and 32 atm, respectively. The simulation conditions are also summarized in Figure 6.3.

The effluent composition is listed in Table 6.4 and summarized in Figure 6.4 for the most favorable condition, i.e., no limitation and reactor kinetics. At 1100°C, the effluent ammonia in the feed should be decomposed nearly completely even without the removal of hydrogen by the membrane. It indicates that the thermodynamics for the decomposition of ammonia is favorable. However, at a lower temperature and a lower pressure, i.e., 540°C and 6 atm, the membrane reactor could enhance the conversion of NH₃ from 50% at equilibrium to 70%. No H₂S decomposition was found for the system with or without the catalytic membrane reactor. The potential pressure of hydrogen required from H₂S decomposition is too low to be practical, (i.e., low equilibrium conversion coupled with low concentration of H₂S). However, the above analysis does not account for the enhancement through reaction rate due to the removal of hydrogen. No simulation was

Figure 6.3 : Simulation Conditions of Catalytic Membrane Reactor

5 Components System - H₂, N₂, S₂, NH₃, H₂S

Plug flow @ Fast reaction rates

Feed conditions :

N ₂	70.5%
H ₂	29.4%
H ₂ S	0.73%
NH ₃	0.44%

$$\text{Conversion} = \frac{\text{Feed NH}_3 - (\text{reject NH}_3 + \text{Permeate NH}_3)}{\text{Feed NH}_3} \times 100$$

Case 1 : T= 811 K P = 6.0 atm

Case 2 : T= 811 K P = 32.0 atm

Case 3: T= 1366 K P = 6.0 atm

Case 4: T= 1366 K P= 32.0 atm

Note : The critical properties of S₂ are the same as O₂ except molecular weight

**Table 6.4 The Simulated Decompositions of NH₃ and H₂S
in Reducing Conditions**

Based on Ideal Knudsen Separations

Temperature (°C)	Total pressure (atm)	NH ₃ (mole %)			H ₂ S (mole %)		
		In	Out	E.Q.	In	Out	E.Q.
538	6.0	0.44	0.13	0.22	0.73	0.73	0.73
538	32.0	0.44	0.54	0.64	0.73	0.73	0.73
1093	6.0	0.44	0.01	0.01	0.73	0.73	0.73
1093	32.0	0.44	0.04	0.04	0.73	0.73	0.73

Figure 6.4 : Summary of The NH₃ and H₂S Conversion

Based on Ideal Knudsen Separation

performed due to the lack of the reaction kinetic information.

The above analysis was further explored using a hydrogen selective membrane, i.e., selectivity of $H_2/N_2 = \sim 25$. The results are summarized in Table 6.5 and Figure 6.5). At high temperature side ($1093^\circ C$), this membrane showed no significant improvement for NH_3 decomposition because the equilibrium conversion is high under such conditions. At low temperature side (811 K), the NH_3 decomposition is greatly increased to 70.5% at 32 atm and 88.6% at 6 atm. This indicated that the H_2 -selective membrane is superior to the existing membrane for NH_3 decomposition. However, there is still no H_2S decomposition using such a membrane due to very small equilibrium constant of H_2S . It is concluded that a hydrogen selective membrane, as those described in Section 4, is promising in removing NH_3 at the lower temperatures of the coal conversion process through the coupling of the hydrogen production enrichment. Further economic analysis is suggested to determine the viability of the proposed process.

Figure 6.5 : Summary of The NH3 and H2S Conversion

Based on H₂/N₂ separation factor = 25
(Ideal Knudsen H₂/N₂ = 3.74)

Conclusion

1. A pore size distribution analysis was established to determine the flow-weighted pore size of an asymmetric membrane. It provides an effective tool for synthesis and characterization of microporous membranes.
2. The smallest pore size of the existing membrane available was confirmed with the pore size distribution analyzer to be 40Å. It shows excellent thermal and moderate hydrothermal stability at 600°C. Deterioration of the microporous structure was observed under an alkali environment.
3. Existing membranes demonstrate gas separation following Knudsen diffusion. A mathematical model has been developed to predict the gas separation efficiency at a high temperature environment.
4. Pore size of the existing membranes was reduced to < 10Å and dense phase via chemical vapor deposition of silica and zirconia. Silica dense-phase membranes show a unique selectivity for hydrogen at a high temperature. Further, the dense membranes demonstrate thermal and hydrothermal stability at 600°C after initial densification.
5. In-situ crystalization was pursued to develop a zeolitic membrane. Our result shows inclusion of zeolitic structure with existing membranes; however, minor cracks exist. Several post-treatment studies show promising results to remedy the cracks.
6. Decomposition of trace ammonia contaminant via catalytic membrane reactor was explored. The hydrogen selective membrane provides a viable avenue for ammonia removal via decomposition. Further economic analysis is required to assess its commercial viability.

List of symbols

A	: coefficient defined in eq. 8
A'	: modified A coefficient defined in eq. 16
B	: coefficient defined in eq. 11
B'	: modified B coefficient defined in eq. 17
C_p	: permeability of single gas [mole-m/(s-m ² -Pa)]
D_{12}	: diffusion coefficient [m ² /s]
f_0	: coefficient defined in eq. 9
g	: coefficient defined in eq. 8
g'	: coefficient defined in eq.15
k	: Boltzmann constant = 1.381×10^{-23} [J/K]
L	: Avogadro number = 6.023×10^{23} [1/mole]
m	: mass of one molecule [Kg]
m^+	: mass defined in eq. 13 [Kg]
m_1	: mass of one molecule of light component [Kg]
m_2	: mass of one molecule of heavy component [Kg]
m_x	: mass defined in eq 12 [Kg]
n	: molar flux [mole/s/m ²]
n_1	: molar flux of light component [mole/s/m ²]
n_2	: molar flux of heavy component [mole/s/m ²]
n_k	: pore number per unit area of membrane [1/m ²]
$\bar{p}$	: average pressure across the membrane [Pa]
p	: pressure [Pa]
P_h	: feed pressure [Pa]
P_l	: permeate pressure [Pa]
P_r	: pressure ratio of permeate to feed [-]
Q_F	: Feed molar flow [mole/s]
Q_P	: Permeate molar flow [mole/s]

Q_R	: Reject molar flow [mole/s]
r_k	: pore radius of membrane [m]
s	: membrane thickness [m]
T	: temperature [K]
v	: mean molecular velocity [m/s]
v_2	: mean molecular velocity of heavy component [m/s]
X	: mole fraction of reject [-]
x	: mole fraction of gas in the feed side of membrane [-]
X_0	: mole fraction of feed [-]
Y	: mole fraction of permeate [-]
z	: axial coordinate in pores [m]

Greek Symbols

α	: separation factor defined in eq. 24 [-]
α_0	: theoretical Knudsen separation factor = $(m_2/m_1)^{1/2}$
β	: reflection coefficient in eq. 22 [-]
η	: gas viscosity [Pa•s]
λ	: mean free path of molecule [m]
θ	: stage cut, the ratio of permeate flow to feed flow [-]
σ	: collision diameter [m]
σ^*	: mean collision diameter [m]

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APPENDIX

FORTRAN Program: Binary Mixture Separation

Notes of the Program for Gas Separations using Ceramic Membrane

This program is used to predict the separation of a binary gas mixture in ceramic membranes at high temperature. Basically it followed the method of Eickmann and Werner's paper (1985). The separation mechanism included Knudsen diffusion, viscous flow, and Poiseuille flow. Two modifications are added in our calculation. When calculating the mole fraction of permeate stream, the stage cut (θ) is introduced to reflect the real membrane separation. The fitting parameters, n_k and β , are averaged by mole fractions of binary mixture in the feed.

The surface diffusion is not considered in the calculation. Pore size growth due to elevated temperatures is considered in the program. However, if the operating temperature is exceeded 811°C, the calculation will be based on the internal data at 811°C. In addition, the n_k and β of H₂ and N₂ are corrected according to the operating temperatures. The rest of components are not corrected by temperatures.

Only binary mixture can be calculated in this program at the present time. There are 13 components listed in the program, and the program can calculate the separation factor of any combination of two components. However, due to the lack of experimental data n_k and β , only 4 components, H₂, CO, N₂, and CH₄ can be calculated. The calculated results from the rest of components are meaningless unless the n_k and β are supplied.

The program runs at interactive mode. At the prompt, users need to input the names of components (either lower or upper cases), the pressures of feed and permeate side, the mole fraction of light components in feed, the operating temperature, and the stage cut (the ratio of permeate to feed).

An example to run this program in VAX computer is following;

```
$ FORTRAN METC.FOR <ret>
$ LINK METC <ret>
  (the above two steps are for the first time only)
$ RUN METC <ret>
ENTER THE FORMULA OF THE FIRST MIXTURE COMPONENT: H2 <ret>
ENTER THE FORMULA OF THE SECOND MIXTURE COMPONENT: N2 <ret>
THIS IS A MIXTURE OF H2    IN N2

ENTER THE FEED SIDE PRESSURE (in atm): 2.85 <ret>
ENTER THE PERMEATE PRESSURE (in atm): 1.34 <ret>
ENTER THE MOLE FRACTION OF H2    IN THE FEED: .48 <ret>
ENTER A VALUE FOR TEMPERATURE (in Kelvin): 293 <ret>
ENTER THE STAGE CUT VALUE (e.g. 0.5): 0.07 <ret>
```

***** Simulation Results *****

H2 Viscosity = 0.7231E-05 N2 Viscosity = 0.1684E-04

The calculated molar fraction of H2 in the permeate stream is 0.6222

of iteration is 10

The pressure at which ALPHA MAX can be obtained is 2.507 atm.

Permeability	H2		N2	
	(m3/m2/atm/hr)	(%)	(m3/m2/atm/hr)	(%)
Knudsen	173.8	49.5	27.7	20.8
Poiseulle	2.0	0.6	1.2	0.9
Viscous	175.4	49.9	104.2	78.3
Total	351.2		133.1	
FORTRAN STOP				

The program is written in FORTRAN code, and is machine-independent. With the proper compilation, it should run in any computer although it has not been tested yet.

In the notation, some variables are defined in the Eickmann and Werner's paper. The equations' number in the notation are matched with those in the paper.

Notation used in FORTRAN program

Name	Symbol		Unit
A	A	Coefficient in eqn. 7	-
ALPHA	α	Separation factor	-
AMU, AMUP		Calculated viscosity	-
APRIME	A'	A/ β in eqn. 26	-
B	B	Coefficient in eqn. 8	-
B1, B2		Dummy variables	-
BETA	β	Fitting parameter in eqn. 25	-
BETAVG	β_{ave}	Molar weighed β	-
BPRIME	B'	B β in eqn. 27	-
BY	b(y)	Coefficient in eqn. 24	-
C3, C4		Coefficients in eqns. 21, 22	-
D12	D ₁₂	Diffusion coefficient	m ² /s
DIP		Dipole moment	debye
DP		Partial pressure difference	Pa
EP	ϵ_p	Porosity of membrane	-
F	f ₀	Coefficient in eqn. 9	-
G	g	Coefficient in eqn. 6	-
GPRIME	g'	Coefficient in eqn. 25	-
I, J, K, ICOUNT, TRY		Counters in program	-
KNUD		Knudsen permeability	m ³ /m ² /atm/hr
L		Avogadro's number	1/mole
LAMBDA	λ	Mean free path	m
MPLUS	m ⁺	Molecule weight in eqn.12	g/mole
MX	m _x	Molecular weight in eqn. 11	g/mole
NK	n _k	Fitting coefficient in eqn. 25	-
NKAVG	n _k	Molar weighed n _k	-
NU	μ	Viscosity	Pa-s
NUBAR	$\bar{\mu}$	Mixture viscosity	Pa-s
PC		Critical pressure	atm
PH		Feed side pressure	atm
PHI	ϕ	Coefficients in eqn. 19	-
PL		Permeate side pressure	atm
POIS		Poiseulle flow	m ³ /m ² /atm/hr
POPT	Ph α_{max}	Feed pressure at α_{max}	atm
Q		number of components	-
QP		Total permeability	m ³ /m ² /atm/hr
R	r	Pore radius	m
RG	R	Gas constant	J/mole/K
RHOC	ρ_c	Critical density	g/cm ³
RK	k	Boltzmann's constant	J/K

SIGMA	σ	Collision diameter	m
T1, T2, T3, T4, T5, T6		Dummy variables	-
T1A, T6A		Dummy variables	-
TC		Critical temperature	K
THETA	θ	Stage cut	-
TL		Thickness of membrane	m
TR		Reduced temperature	-
UK		Shape factor, 1/tortuosity	-
V2BAR	$\overline{v_{12}}$	Mean molecule velocity	m/s
VBAR	$\overline{v}$	Mean molecule velocity	m/s
VC		Critical volume	cm ³ /mole
VISC		Viscous flow	m ³ /m ² /atm/hr
X1		Mole fraction of feed	-
XM		molecular weight	g/mole
XNMAE		molecule name (e.g. H2)	-
Y	y	Mole fraction of permeate	-


```

C     SIMULATION OF MEMBRANE SEPARATION FOR BINARY GAS MIXTURE
C
C     THIS PROGRAM TAKES INTO ACCOUNT THREE TRANSPORT
C     MECHANISMS, KNUDSEN DIFFUSION, VISCOUS FLOW, AND
C     NON-SEPARATIVE DIFFUSION CAUSED BY INTER-MOLECULES
C     MOMENTUM TRANSFER.
C
C     THE PORE SIZES OF MEMBRANE ARE CORRECTED WITH TEMPERATURE.
C
C
C     CHARACTER*5 XNAME(13),NAME
C     INTEGER TRY
C     REAL LAMBDA,NU,NUBAR,NK,MK,MPLUS,PHI,KNUD,L,NKAVG
C     DIMENSION XM(13),TC(13),PC(13),RHOC(13),VC(13),DP(13),
C     &          DIP(13),SIGMA(13),NU(13),NK(13),BETA(13),
C     &          KNUD(2),POIS(2),VISC(2),QP(2),PHI(13,13),
C     &          X_NK(13,4),X_BETA(13,4)
C
C
C     SEQUENCE OF GAS MOLECULES: NH3, CO2, CO, HE, H2, H2S, NO, N2,
C                                NO2, O2, SO2, H2O, CH4.
C
C     DATA1 : CHARACTERISTICS OF GASES
C     XM, MOLECULAR WEIGHT, G/GMOLE
C     DIP, DIPOLE MOMENT, DEBYE
C     SIGMA, COLLISION DIAMETER, METER
C     TC, CRITICAL TEMPERATURE, KELVIN
C     PC, CRITICAL PRESSURE, ATM
C     RHOC, CRITICAL DENSITY, G/CC
C
C     DATA2 : CHARACTERISITCS OF MEMBRANES
C     EP, POROSITY, -
C     UK, SHAPE FACTOR, OR 1/TORTUOSITY, -
C     R, PORE RADIUS, M
C     TL, THICKNESS OF THE MEMBRANE LAYER, M
C
C     DATA 3 : X_NK, 1/M2
C     DATA 4 : X_BETA,-
C
C     PL, PERMEATE PRESSURE, ATM
C     PH, FEED PRESSURE, ATM
C     T, OPERATING TEMPERATURE, KELVIN
C     X1, MOLE FRACTION OF LIGHTER COMPONENT IN FEED, -
C     Y, MOLE FRACTION OF LIGHTER COMPONENT IN PERMEATE, -
C     THETA, STAGE CUT (PERMEATE FLOW/FEED FLOW), -
C
C     NAMELIST /DATA1/ XM,DIP,SIGMA,TC,PC,RHOC
C     &          /DATA2/ EP,UK,R,TL
C
C     OPEN(UNIT=1,FILE='MIX1.DAT',STATUS='OLD')
C     OPEN(UNIT=2,FILE='MIX2.DAT',STATUS='OLD')
C     OPEN(UNIT=3,FILE='MIX3.DAT',STATUS='OLD')
C     OPEN(UNIT=4,FILE='MIX4.DAT',STATUS='OLD')
C     READ(1,DATA1)
C     READ(2,DATA2)
C     DO 1 I=1,13
C 1     READ(3,*) (X_NK(I,J), J=1,4)
C     DO 2 I=1,13
C 2     READ(4,*) (X_BETA(I,J), J=1,4)
C     TRY=0
C 402    WRITE(6,400)
C 400    FORMAT(' ENTER THE FORMULA OF THE FIRST MIXTURE COMPONENT: ',5)
C 10     READ(5,450) NAME
C 450    FORMAT(A5)

```

```

TRY=TRY+1
IF ((NAME .EQ. 'NH3') .OR. (NAME .EQ. 'nh3')) THEN
  I=1
ELSEIF ((NAME .EQ. 'CO2') .OR. (NAME .EQ. 'co2')) THEN
  I=2
ELSEIF ((NAME .EQ. 'CO') .OR. (NAME .EQ. 'co')) THEN
  I=3
ELSEIF ((NAME .EQ. 'HE') .OR. (NAME .EQ. 'he')) THEN
  I=4
ELSEIF ((NAME .EQ. 'H2') .OR. (NAME .EQ. 'h2')) THEN
  I=5
ELSEIF ((NAME .EQ. 'H2S') .OR. (NAME .EQ. 'h2s')) THEN
  I=6
ELSEIF ((NAME .EQ. 'NO') .OR. (NAME .EQ. 'no')) THEN
  I=7
ELSEIF ((NAME .EQ. 'N2') .OR. (NAME .EQ. 'n2')) THEN
  I=8
ELSEIF ((NAME .EQ. 'NO2') .OR. (NAME .EQ. 'no2')) THEN
  I=9
ELSEIF ((NAME .EQ. 'O2') .OR. (NAME .EQ. 'o2')) THEN
  I=10
ELSEIF ((NAME .EQ. 'SO2') .OR. (NAME .EQ. 'so2')) THEN
  I=11
ELSEIF ((NAME .EQ. 'H2O') .OR. (NAME .EQ. 'h2o')) THEN
  I=12
ELSEIF ((NAME .EQ. 'CH4') .OR. (NAME .EQ. 'ch4')) THEN
  I=13
ELSE
  WRITE(6,404) NAME
404  FORMAT(' INCORRECT RESPONSE OF',A5, ' TRY AGAIN')
  IF (TRY .LT. 3) THEN
    GO TO 402
  ELSE
    GO TO 15
  ENDIF
ENDIF
XNAME(I)=NAME
TRY=0
401  WRITE(6,405)
405  FORMAT(' ENTER THE FORMULA OF THE SECOND MIXTURE COMPONENT: ',5)
  READ(5,455) NAME
455  FORMAT(A5)
  IF ((NAME .EQ. 'NH3') .OR. (NAME .EQ. 'nh3')) THEN
    J=1
  ELSEIF ((NAME .EQ. 'CO2') .OR. (NAME .EQ. 'co2')) THEN
    J=2
  ELSEIF ((NAME .EQ. 'CO') .OR. (NAME .EQ. 'co')) THEN
    J=3
  ELSEIF ((NAME .EQ. 'HE') .OR. (NAME .EQ. 'he')) THEN
    J=4
  ELSEIF ((NAME .EQ. 'H2') .OR. (NAME .EQ. 'h2')) THEN
    J=5
  ELSEIF ((NAME .EQ. 'H2S') .OR. (NAME .EQ. 'h2s')) THEN
    J=6
  ELSEIF ((NAME .EQ. 'NO') .OR. (NAME .EQ. 'no')) THEN
    J=7
  ELSEIF ((NAME .EQ. 'N2') .OR. (NAME .EQ. 'n2')) THEN
    J=8
  ELSEIF ((NAME .EQ. 'NO2') .OR. (NAME .EQ. 'no2')) THEN
    J=9
  ELSEIF ((NAME .EQ. 'O2') .OR. (NAME .EQ. 'o2')) THEN
    J=10
  ELSEIF ((NAME .EQ. 'SO2') .OR. (NAME .EQ. 'so2')) THEN
    J=11

```

```

ELSEIF ((NAME .EQ. 'H2O') .OR. (NAME .EQ. 'h2o')) THEN
  J=12
ELSEIF ((NAME .EQ. 'CH4') .OR. (NAME .EQ. 'ch4')) THEN
  J=13
ELSE
  WRITE(6,406) NAME
406  FORMAT('      INCORRECT RESPONSE OF',A5,'      TRY AGAIN')
  IF (TRY .LT. 3) THEN
    TRY=TRY+1
    GO TO 401
  ELSE
    GO TO 15
  ENDIF
ENDIF
XNAME(J)=NAME
IF (XM(I) .GE. XM(J)) THEN
  K=I
ELSE
  K=J
  J=I
ENDIF
WRITE(6,500) XNAME(J),XNAME(K)
500  FORMAT(/,1X,'THIS IS A MIXTURE OF ',A5,'IN ',A5)
WRITE(6,510)
510  FORMAT(/,1X,'THE FEED SIDE PRESSURE (in atm): ',,$)
READ(5,*) PH
WRITE(6,515)
515  FORMAT(1X,'THE PERMEATE PRESSURE,less than 0.8 feed
& P (in atm): ',,$)
READ(5,*) PL
TRY=0
14  WRITE(6,517) XNAME(J)
517  FORMAT(' ENTER THE MOLE FRACTION OF ',A5,'IN THE FEED: ',,$)
READ(5,*) X1
IF (X1 .GT. 1.0) THEN
  WRITE(6,519)
519  FORMAT(' YOU HAVE ENTERED AN INCORRECT VALUE FOR
@THE MOLAR FRACTION.',
@ /,' IT MUST HAVE A VALUE OF LESS THAN ONE.',/)
  TRY=TRY+1
  IF (TRY .LE. 4) THEN
    GO TO 14
  ELSE
    GO TO 15
  ENDIF
ENDIF
WRITE(6,521)
521  FORMAT(' ENTER A VALUE FOR TEMPERATURE (in Kelvin): ',,$)
READ(5,*) T
C
C  MEMBRANE PORE SIZES ARE CORRECTED BY OPERATING TEMPERATURES
C
  IF (T .LT. 673.0) THEN
    R=20E-10
    NK(J)=X_NK(J,1)
    NK(K)=X_NK(K,1)
    BETA(J)=X_BETA(J,1)
    BETA(K)=X_BETA(K,1)

    ELSEIF (T .LE. 867.0) THEN
      R=1.54E-12*T+1.546E-9
      NK(J)=X_NK(J,2)
      NK(K)=X_NK(K,2)
      BETA(J)=X_BETA(J,2)

```

```

      BETA(K)=X_BETA(K,2)

      ELSEIF (T .LE. 1005.0) THEN
        R=2.679E-12*T+6.272E-10
        NK(J)=X_NK(J,3)
        NK(K)=X_NK(K,3)
        BETA(J)=X_BETA(J,3)
        BETA(K)=X_BETA(K,3)

      ELSEIF (T .LE. 1088.0) THEN
        R=4.243E-12*T-8.167E-10
        NK(J)=X_NK(J,4)
        NK(K)=X_NK(K,4)
        BETA(J)=X_BETA(J,4)
        BETA(K)=X_BETA(K,4)

      ELSE
        WRITE(6,502)
502    FORMAT(' THE TEMPERATURE VALUE ENTERED IS OUT OF THE RANGE',
      9    /, ' OF OUR STUDY BUT WILL BE RUN USING 815 C DATA.',/)
        R=38E-10
        NK(J)=X_NK(J,4)
        NK(K)=X_NK(K,4)
        BETA(J)=X_BETA(J,4)
        BETA(K)=X_BETA(K,4)
      ENDIF
      WRITE(6,504)
504    FORMAT(' ENTER THE STAGE CUT VALUE (Must less than 0.5): ',5)
      READ(5,*)THETA

C
C  CONSTANTS - RG : GAS CONSTANT, J/MOLE-K
C              RK : BOLTZMANN'S CONSTANT, J/K
C              L  : AVOGADRO NUMBER, 1/MOLE
C
      RG=8.314
      RK=1.38062E-23
      L=6.022169E+23
      PI=3.1415926
      PH=PH*1.013E+05
      PL=PL*1.013E+05
      P=(PH+PL)/2.0
C  CALCULATE VISCOSITY, NU
      TR=T/TC(J)
      VC(J)=XM(J)/RHOC(J)
      PR=P/(PC(J)*1.013E5)
      PTR=1.058*(TR**0.645)-0.261/((1.9*TR)**(0.9*LOG10(1.9*TR)))
      AMU=33.3*SQRT(XM(J)*TC(J))*PTR/(VC(J)**0.667)*1.0E-07
      NU(J)=AMUP(TR,PR,DIP(J),TC(J),PC(J),AMU)
      TR=T/TC(K)
      VC(K)=XM(K)/RHOC(K)
      PR=P/(PC(K)*1.013E5)
      PTR=1.058*(TR**0.645)-0.261/((1.9*TR)**(0.9*LOG10(1.9*TR)))
      AMU=33.3*SQRT(XM(K)*TC(K))*PTR/(VC(K)**0.667)*1.0E-07
      NU(K)=AMUP(TR,PR,DIP(K),TC(K),PC(K),AMU)
      PHI1=(SQRT(1/8.))
      PHI2=((1+(SQRT(NU(J)/NU(K)))*((XM(K)/XM(J))**0.25))**2)
      PHI3=(SQRT(1+(XM(J)/XM(K))))
      PHI4=((1+(SQRT(NU(K)/NU(J)))*((XM(J)/XM(K))**0.25))**2)
      PHI5=(SQRT(1+(XM(K)/XM(J))))
      PHI(J,K)=PHI1*PHI2/PHI3
      PHI(K,J)=PHI1*PHI4/PHI5
      WRITE(6,950)
950    FORMAT(/,18X,'***** Simulation Results *****')
      WRITE(6,101) XNAME(J),NU(J),XNAME(K),NU(K)

```

```

101 FORMAT(/3X,A5,' Viscosity = ',E11.4,8X,A5,' Viscosity = ',E11.4)
C
C ADJUST MOLECULAR WEIGHT FROM G/MOLE TO KG/MOLE
DO 3 I=1,13
3 XM(I)=XM(I)/1000.0

SS=(SIGMA(J)+SIGMA(K))/2.0
LAMBDA=RK*T/((SQRT(2.))*PI*SS*SS*P)
MPLUS=XM(J)*XM(K)/(XM(J)+XM(K))
VBAR=SQRT(4.0*RG*T/(PI*MPLUS))
D12=VBAR*LAMBDA/3.0
V2BAR=SQRT(8.0*RG*T/(PI*XM(K)))
ALPHA=SQRT(XM(K)/XM(J))

C
C INITIAL VALUES
ICOUNT=1
Y=0.5
X0=X1

C
C MIXTURE VISCOSITY, NUBAR
200 NUBAR=X1*NU(J)/(X1+(1-X1)*PHI(J,K))+
    @ (1-X1)*NU(K)/(X1*PHI(K,J)+(1-X1))
MX=(X1*SQRT(XM(J))+(1-X1)*SQRT(XM(K)))**2
F=SQRT(XM(K))/SQRT(MX)
A=3.0*R/(16.0*NUBAR*V2BAR)
B1=(8.0*R/(3.0*PI))*(SQRT(PI*RG*T/(2.0*MPLUS)))*(SQRT(MX))
B2=((SQRT(XM(J)+XM(K)))*P*D12)
B=B1/B2
NKAvg=NK(J)*X1+NK(K)*(1.0-X1)
BETAavg=BETA(J)*X1+BETA(K)*(1.0-X1)
BPRIME=B*BETAavg
APRIME=A/BETAavg
G=(8./3.)*(R/PI)*SQRT(PI/(2.0*RK*T*XM(K)))*SQRT(L)
GPRIME=NKAvg*PI*R*R*BETAavg*G
DP(1)=X1*PH-Y*PL
DP(2)=(1-X1)*PH-(1-Y)*PL
KNUD(1)=GPRIME/L*ALPHA/(1.0+BPRIME*PH)*DP(1)/TL
POIS(1)=GPRIME/L*F*BPRIME*X1*PH/(1.0+BPRIME*PH)*(PH-PL)/TL
VISC(1)=GPRIME/L*X1*APRIME*PH*(PH-PL)/TL
QP(1)=KNUD(1)+POIS(1)+VISC(1)
KNUD(2)=GPRIME/L/(1.0+BPRIME*PH)*DP(2)/TL
POIS(2)=GPRIME/L*F*BPRIME*PH*(1.0-X1)/(1.0+BPRIME*PH)
    @*(PH-PL)/TL
VISC(2)=GPRIME/L*(1-X1)*APRIME*PH*(PH-PL)/TL
QP(2)=KNUD(2)+POIS(2)+VISC(2)

C SOLVING PERMEATE MOLE FRACTION Y BY ITERATIONS
C
YCALC=QP(1)/(QP(1)+QP(2))
XCALC=(X0-THETA*Y)/(1-THETA)
IF (((ABS(XCALC-X1).GT.5.E-4).OR.(ABS(YCALC-Y).GT.5.E-4))
    @.AND.(ICOUNT.LT.300)) THEN
    X1=(XCALC+X1)/2.0
    Y=(YCALC+Y)/2.0
    ICOUNT=ICOUNT+1
    GO TO 200
ELSE
    IF(Y.GE.1.0) GO TO 1000
    IF (ICOUNT.GE.100) WRITE(6,170)
    WRITE(6,160) XNAME(J),YCALC,XCALC,ICOUNT
160    FORMAT(/,1X,'The calculated molar fraction of ',
    @ A5,'in the permeate stream is ',F6.4,
    @ /,41X,'In the reject stream is ',F6.4,
    @ /,1X,'# of iteration is ',I3)

```

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170  FORMAT(//,10X,'!! WARNING !! The answer may not be correct')
      ENDIF
      SEP_FACTOR=YCALC/(1.0-YCALC)*(1-X0)/X0
      WRITE(6,960) SEP_FACTOR
      WRITE(6,900) XNAME(J),XNAME(K)
      WRITE(6,910) KNUD(1),KNUD(1)/QP(1)*100.,KNUD(2),
      @ KNUD(2)/QP(2)*100.
      WRITE(6,920) POIS(1),POIS(1)/QP(1)*100.,POIS(2),
      @ POIS(2)/QP(2)*100.
      WRITE(6,930) VISC(1),VISC(1)/QP(1)*100.,VISC(2),
      @ VISC(2)/QP(2)*100.
      WRITE(6,940) QP(1),QP(2)
      GO TO 15
1000  WRITE(6,970)
900   FORMAT(//,25X,A5,25X,A5,/, ' Molar flux ',7X,'(mole/m2-s) ',
      @6X,'(%)',10X,'(mole/m2-s)',11X,'(%)')
910   FORMAT(/,1X,'Knudsen diffusion',4X,E9.2,7X,F5.1,9X,E9.2,11X,F5.1)
920   FORMAT(/,1X,'Momentum transfer',4X,E9.2,7X,F5.1,9X,E9.2,11X,F5.1)
930   FORMAT(/,1X,'Viscous flow',9X,E9.2,7X,F5.1,9X,E9.2,11X,F5.1)
940   FORMAT(/,1X,'Total',16X,E9.2,21X,E9.2)
960   FORMAT(//,10X,'SEPARATION FACTOR = ',F6.2)
970   FORMAT(//,1X,'THE CALCULATIONS FAILS.',/,1X,'THE PRESSURE
      @ DIFFERENCE OF FEED AND PERMEATE MAY BE TOO SMALL')
      CLOSE(UNIT=1, STATUS='SAVE')
      CLOSE(UNIT=2, STATUS='SAVE')
      CLOSE(UNIT=3, STATUS='SAVE')
      CLOSE(UNIT=4, STATUS='SAVE')
15    STOP
      END
C *****
C FUNCTION TO CALCULATE PURE GAS VISCOSITY AT DIFFERENT PRESSURES
C
      FUNCTION AMUP(TR,PR,DIP,TC,PC,AMU)
      A=1.9824E-03/TR*EXP(5.2683*TR**(-0.5767))
      B=A*(1.6552*TR-1.2760)
      C=0.1319/TR*EXP(3.7035*TR**(-79.8678))
      D=2.9496/TR*EXP(2.9190*TR**(-16.6169))
      DIPR=52.46*DIP*DIP*PC/(TC*TC)
      O=1.-5.655*DIPR
      AMUP=B*PR+1./(1.+C*PR**D)
      AMUP=O*A*PR**1.5/AMUP
      AMUP=AMU*(1.+AMUP)
      RETURN
      END

```

(MIX1.dat)

\$DATA1

XM=17.03,44.01,28.01,4.00,2.016,34.08,30.01,28.02,46.01,32.0,64.06,
18.016,16.04
DIP=1.5,0.0,0.1,0.0,0.0,0.9,0.2,0.0,0.4,0.0,1.6,1.8,0.0
SIGMA=2.624E-10,3.996E-10,3.59E-10,2.7E-10,2.968E-10,
2.655E-10,3.47E-10,3.681E-10,4.29E-10,3.433E-10,4.29E-10,
2.655E-10,3.882E-10
TC=405.6,304.2,134.2,5.25,33.2,373.6,179.2,126.2,431.0,
154.6,430.4,647.3,90.65
PC=113.5,73,35,2.26,12.8,88.9,65,33.5,100,49.7,77.7,
218.4,45.8
RHOC=0.235,0.46,0.311,0.0693,0.031,2.86,0.52,0.311,
1.785,0.43,0.52,0.323,0.162\$END

(MIX2.dat)

\$DATA2

EP=0.5
UK=0.339
R=20.0E-10
TL=5.0E-6\$END

(MIX3.dat)

6.5E15,6.5E15,6.5E15,6.5E15
2.5E15,2.5E15,2.5E15,2.3E15
6.5E15,6.5E15,6.5E15,6.5E15
2.1E15,2.9E15,2.9E15,4.1E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
6.5E15,6.5E15,6.5E15,6.5E15
3.4E15,8.5E15,8.8E15,8.8E15

(MIX4.dat)

0.5000,0.5000,0.5000,0.5000
0.5000,0.5637,0.5637,0.3857
0.5328,0.0873,0.0840,0.0793
0.9593,0.5383,0.5383,0.2540
1.3191,0.6332,0.6332,0.1529
0.5000,0.5000,0.5000,0.5000
0.5000,0.5000,0.5000,0.5000
0.7522,1.1109,1.1109,0.4643
0.5000,0.5000,0.5000,0.5000
0.5000,0.5000,0.5000,0.5000
0.5000,0.5000,0.5000,0.5000
0.5000,0.5000,0.5000,0.5000
0.5000,0.5000,0.5000,0.5000
0.3481,0.0580,0.0588,0.0944

END

**DATE
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