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Thermal and Chemical Degradation of Inorganic Membrane Materials

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following most likely degradation mechanisms in hot coal gas and combustion gas environments:

- Hydrothermal sintering
- Reaction with H_2S
- Reaction with ash particles
- Interaction with alkali components
- Deposition of carbon in the pores of the membrane.

Sintering of highly porous inorganic membranes is a degradation mechanism that limits the temperature at which the membranes can be used for gas separation. Also, coal gas streams contain a significant fraction of steam (10 to 30% v/v). At the high temperatures and high pressures encountered in coal gasification, steam can have a deleterious effect on the properties of oxide membrane materials. Metal membranes such as Pd and Pt are not affected by steam, but they are prone to poisoning by H_2S and other vapor impurities in the hot coal gas stream.

SELECTION OF CANDIDATE MEMBRANES AND TEST PROTOCOL

In the experimental testing program, candidate membrane materials were selected in consultation with the DOE program manager according, to three criteria: (1) present development status, (2) future potential, and (3) availability. Suppliers and manufacturers who were possible sources for different membrane materials were contacted to obtain current development status and information regarding demonstrated gas selectivities and permeabilities (at least in the clean laboratory environment). The following membrane materials were selected for testing:

(1) Alumina membranes (Membralox) with a separation layer pore size of 40 Å, supplied by U.S. Filter Corporation

(2) Alumina membranes modified by Media and Process Technologies Inc. to increase membrane selectivity for hydrogen and helium. The membrane was modified by forming a gas separation layer of amorphous silica

(3) Vycor porous glass membranes with a pore size of 40 Å, supplied by Corning, Inc.

(4) Vycor porous glass membranes modified, in Professor George Gavalas's laboratory at the California Institute of Technology, by

depositing amorphous silica to increase membrane selectivity for hydrogen

(5) Platinum foils provided by Bend Research, Inc.

(6) Palladium foils purchased from Aldrich Chemical Company.

Three different test methods were used to evaluate the degradation of these membrane materials:

(1) Characterization of changes in physical and chemical properties of the membranes exposed to simulated IGCC gas streams under well-defined conditions

(2) Measurement of the permeation performance of membranes under simulated coal gas conditions

(3) Determination of changes produced in membrane materials after prolonged exposure to the hot coal gas stream of an operating fixed-bed coal gasifier at the General Electric Corporate Research and Development facility.

The membrane samples were exposed to simulated coal gas at four fixed temperatures in the range 550° to 1000°C at atmospheric pressure. Additional samples were also exposed at 450° and 550°C at a pressure of 270 psig. The exposure duration ranged from 24 to 1000 h. The effect of coal gasifier ash on the membrane samples was determined during both atmospheric and high pressure exposure tests.

Before and after exposure, the membrane samples were characterized by surface area and pore size analysis (BET-N_2), Auger electron spectroscopy, scanning electron microscopy, and dynamic flow-weighted pore size measurements. The membrane permeation performance was determined by pure component permeation rates as well as by mixed gas permeation studies.

TEST RESULTS

Exposure Tests

The pore size of the unmodified Vycor membrane samples increased significantly in simulated coal gas streams at high temperatures and pressures. Exposure at 800°C and 1-atm pressure for 76 h increased the mean pore size from 40 to 120 Å, whereas exposure at 1000°C and 1-atm pressure destroyed all microporosity. The loss of microporosity is likely due to the hydrothermal sintering. It can be also attributed to the presence of alkali vapor released from alumina membrane samples that were present in the same test apparatus. At temperatures lower than 650°C, high pressure conditions enlarged the pores significantly. Whereas the increase in the mean pore size was modest at 550°C and 1 atm pressure, it was severe at 20 atm pressure even at 450°C. The ash from a fixed-bed gasifier did not have a significant effect on the coarsening of Vycor membranes at temperatures below 550°C, indicating the interaction between the ash and the membrane is kinetically limited at low temperatures.

The deleterious effect of coal gas on the relatively large pore Vycor membranes is significant because the pore size needed for good gas separation is less than 10Å. Such a gas separation layer is made by adding or forming an amorphous silica microporous layer. Agglomeration of the amorphous phase is expected to be even more pronounced than observed with the Vycor membrane because of the high surface energy and defect concentration of the microporous layer.

The surface area of all the alumina membrane samples was found to decrease significantly at all exposure conditions, indicating coarsening of the 40 Å layer that contains most of the observed surface area. Dynamic pore size measurements indicated that the membrane pore size increased from 40 to 70 Å when exposed to simulated coal gas at 550°C and 20 atm pressure. Alumina membrane samples also released a significant amount of sodium vapor at temperatures exceeding 650°C, a serious threat to the silica layer in the modified membranes. Evolved sodium vapor actually crystallized the Vycor and quartz materials placed nearby. As with Vycor membranes, the sintering of alumina membranes was not significantly changed at temperatures below 550°C when they were coated with a fixed-bed gasifier ash prior to exposure.

The presence of sulfur on a platinum surface is expected to reduce its permeability to hydrogen. All platinum membrane foil samples exposed to a simulated coal gas containing 1.2% H_2S at 1-atm pressure acquired a surface layer of sulfur about 5 nm deep, whereas platinum samples exposed at 450°C and 20 atm pressure had extensive surface sulfide coatings, more than 20 nm thick. However, as the temperature was increased to 550°C, the extent of sulfidation was limited to the upper 3-nm layer. Precoating of membrane foils by gasifier ash did not significantly affect surface sulfidation. All exposed palladium samples degraded extensively under all exposure conditions because of bulk sulfidation by the H_2S in the simulated coal gas. Thus, palladium is not suitable as a membrane material in direct contact with coal gas.

Membrane Permeation Tests

The permeation performance of modified alumina and Vycor tubular membranes was evaluated at high temperature and high pressure especially in the presence of steam. Initial experiments with both modified membranes produced results different than those reported by the suppliers, possibly as a result of changes that occurred during the 3-month storage of the membranes at ambient conditions in the laboratory prior to testing. In later experiments with two additional modified alumina membranes and one modified Vycor membrane, the observed permeation characteristics under dry gas conditions were consistent with those reported by the suppliers. But, all three modified membrane samples were degraded in a few hours in the presence of a feed gas containing 20% steam in the temperature range 450° to 600°C and at 100 psig total pressure.

In the case of modified alumina membranes, the He/N_2 selectivity (initially 250) decreased to 4 after less than 30 h of exposure to a gas mixture containing 20% steam at 100 psig total pressure in the temperature range 450° to 600°C. During this exposure period, pure-component helium permeance at 450°C decreased from 9.5 to 5.5 cm^3/cm^2-min-atm, whereas that of nitrogen increased from 0.05 to 1.6 cm^3/cm^2-min-atm. Similarly, the He/N_2 permeance ratio of the modified Vycor membrane decreased from 160 to 3.5 upon exposure to a gas mixture containing 25% steam at 100 psig total pressure and 450°C for less than 15 h. During this exposure test, the pure component helium permeance remained constant at 0.45 cm^3/cm^2-min-atm, whereas that of nitrogen increased from 0.005 to 0.14 cm^3/cm^2-min-atm. Thus, degradation of both these membranes resulted in a substantial increase in nitrogen permeation rates indicative of coarsening of the size-selective pores.

Both the alumina and Vycor membranes were modified by depositing a thin silica layer to reduce the membrane pore size. The experimental results indicate that 20% steam at a relatively low total pressure of 100 psig (compared to the typical coal gas pressures of 300 psig) was adequate to increase the pore size of the silica layer, reducing the gas selectivities to those expected from unmodified alumina and Vycor membranes.

Two types of measurements were carried out to determine the permeation characteristics of 25-μm-thick platinum foils. In the first experiment, fresh platinum foil was exposed to a simulated coal gas at 700°C and the permeance of hydrogen present in the coal gas was monitored as a function of time. Periodically, the coal gas flow was interrupted and the permeance of hydrogen was also determined with pure hydrogen as feed gas. Due to burnout/leakage at graphite ferrules and seals, the maximum duration of this experiment was 24 h. The hydrogen permeance decreased from 0.02 to 0.01 cm^3/cm^2-min-atm during the initial 4-h exposure to the simulated coal gas. At longer exposures, the hydrogen permeation rate appeared to remain stable.

In the second type of experiment, the hydrogen permeance through a platinum foil exposed to a simulated coal gas at 550°C and 270 psig for 500 h was determined using pure hydrogen as feed gas at 115 psig pressure and 700°C. The hydrogen permeance increased from an initial value of 0.006 to 0.02 cm^3/cm^2-min-atm, after about 1 h, and then it remained stable. This behavior may be explained by the removal of an adsorbed sulfur layer by reaction with the pure hydrogen feed gas. Both types of experiments confirm that adsorbed sulfur on the surface of a platinum foil reduces its hydrogen permeability.

Exposure to a Coal Gasifier Gas Stream

Alumina, silica, and platinum membrane samples were exposed to hot coal gas stream at about 510°C and 280 psig pressure for 50 h in the General Electric Corporate Research and Development's (GE-CRD) fixed-bed gasifier facility. The samples were exposed at two locations: (1) downstream of the primary cyclone and (2) downstream of a zinc oxide-based H_2S absorber reactor (which had a secondary cyclone). All membrane samples suffered some damage during the exposure test. Many of them were broken, apparently due to high gas velocities and normal pressure fluctuations. The remaining specimens accumulated a substantial amount of a black deposit. The deposit was mainly soot (~98 wt%) with a small amount of ash mixed in it. The mean pore size of the Vycor membrane increased from about 40Å to about 78Å with a corresponding decrease in the surface area from 190 to 85 m^2/g. A modified alumina membrane tube exposed at that location also showed loss of microporosity and a reduced permeation rate indicative of coarsening of the pores along with pore blockage by absorbed tar or fly ash deposits.

CONCLUSIONS AND RECOMMENDATIONS

The experimental tests conducted on the candidate inorganic membrane samples under simulated and actual coal gas conditions indicate that silica- and alumina-based membranes, both modified and unmodified, experience coarsening of their micropores in the high temperature, high pressure, and high steam environment of coal gas streams. The pore coarsening that occurs in the presence of steam at elevated pressures degrades the selectivities of the modified membranes quite rapidly. Such membranes are completely unsatisfactory for use in the coal gas environment for an extended period of time. Platinum membranes experience reduction in the hydrogen permeation rate due to surface sulfidation by H_2S in the coal gas, but they are stable and may be used in coal gas environments if the reduced permeation rate is acceptable. Palladium membranes are degraded extensively by H_2S and are not suitable for coal gas applications. Alternative, chemically and physically stable materials must be identified, or methods must be found to improve the resistance of the current membranes, if porous inorganic membranes are to be used to separate the gaseous components in the coal gas environment.

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I. INTRODUCTION

BACKGROUND

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. The IGCC systems have a high energy conversion efficiency, reduced pollutant emissions, modular construction, and potentially low capital and operating costs. The gasification process allows the contaminants to be removed in their reduced or reactive state. The volume of a coal gas stream is less than that of a combustor flue gas stream in a plant of comparable size; hence, capital and operating costs for contaminant removal are less. Hot gas cleanup minimizes the quantity of waste water requiring treatment and disposal, because the quench/scrubbing operation is eliminated. Fixed-, fluidized-, and entrained-bed reactors have been developed and tested for coal gasification.

Coal is a complex and heterogeneous substance that contains several impurities including sulfur, chlorine, nitrogen, and metal compounds. During gasification or combustion, many of these impurities are converted to gaseous species such as H_2S, HCl, NH_3, SO_2, NO_x, NaCl, and AsH_3. Effective removal of impurities is necessary to protect electric power generating equipment such as gas turbines and fuel cells or to meet environmental standards. Coal gas streams exiting a gasifier are at a high temperature (500° to 1200°C). To preserve the enthalpy represented by this hot gas and thereby improve the thermal efficiency of processes using coal gas, there is a strong incentive to remove impurities at temperatures equal to or above the use temperatures. Indeed, the primary recommendation of U.S. Department of Energy's (DOE) Coal Gasification Research Needs (COGRAN) Panel was to develop efficient and economical hot gas cleanup techniques [COGRAN, 1987]. The use of membranes to separate these noxious gases is an attractive alternative to the use of disposable or regenerable sorbents to remove the gaseous contaminants. Inorganic membranes that have a high separation efficiency and exhibit both thermal and chemical stability would improve the economics of power generation from coal. Furthermore, coal gas contains a significant fraction of hydrogen, a commercially valuable chemical feedstock. Membranes can separate the hydrogen from the rest of coal gas mixture effectively and thus improve the economics of hydrogen production from coal.

PROJECT DESCRIPTION

The overall objective of the program reported here was to evaluate the long term thermal and chemical degradation of inorganic membranes that are being developed to separate gaseous products produced by the gasification of coal in fixed-, fluidized-, and entrained-bed gasifiers. Most inorganic membrane developmental efforts have focused on hydrogen separation membranes which may be used in an IGCC system to maximize hydrogen production from coal gas or to remove H_2S and NH_3 contaminants via thermal or catalytic decomposition of these contaminants.

The specific objectives of this program were to (1) use data from the existing literature to identify and evaluate long term degradation mechanisms for inorganic membranes exposed to hot coal gasification and combustion gas streams, and (2) quantify the extent of the degradation process for the three most serious mechanisms by performing experiments under laboratory-scale conditions. To achieve the above objectives, the program is divided into the following tasks:

Task 1. Development of evaluation methodology

Task 2. Evaluation of potential long term degradation mechanism

Task 3. Submission of a topical report and a plan for experimental testing

Task 4. Experimental testing.

A topical report summarizing the evaluation of potential degradation mechanisms, using existing theories and data available in the literature was submitted in April 1994 [Krishnan et al., 1994] along with a plan for experimental testing in Task 4. The present report summarizes the results of the literature review and describes the results of experimental testing with several membrane materials.

SUMMARY OF LITERATURE EVALUATION

A literature search was conducted using computerized data bases, and several hundred citations were obtained. A critical review of relevant technical articles identified the following as the most likely degradation mechanisms in hot coal gas environments: hydrothermal sintering, reaction with H_2S, reaction with ash particles, interaction with alkali impurities, and deposition of carbon on membranes.

Sintering of highly porous inorganic membranes is a degradation mechanism that limits the temperature at which the membranes can be used for gas separation. Crystallites of the materials used in these membranes are several nanometers in size, but they are in relatively unstable thermodynamic states because of high surface energy. At high temperatures, they tend to revert to a lower energy state by agglomeration or through phase transformations. The pore size distributions in all the oxide membranes significantly enlarged when they were exposed to temperatures above 500°C (Table I-1). Although membranes can be made with a median pore diameter less than 2 nm, the size often increases to about 10 nm when the material is heated to about 500°C. As the temperature is increased further, enlargement of pores and decrease in surface area become more severe. At temperatures above 1000°C, the median pore size is likely to exceed 10 nm. Such changes are due to phase transformation or diffusion of atoms on the surface or in the bulk.

Coal gasification and combustion gas streams contain a significant fraction of steam (10% to 25% v/v). At the high temperatures and high pressures encountered in coal gasification, steam can have a deleterious effect on the properties of the membrane materials. The hydrothermal environment generally enhances sintering of the oxide membrane materials. Similarly, the presence of steam accelerates phase transformations in the oxide ceramics. These effects are attributable to the formation of mobile hydroxide species on the surfaces that interact with ion vacancies normally present in the membrane material. Among common ceramic materials, the hydrothermal effect is most severe in silica, less so in alumina and titania, and minimal in zirconia. Metal membranes such as Pd and Pt are not affected by steam, but they are prone to poisoning by H_2S, arsenic, and other trace metal vapor impurities in the hot coal gas stream (Figure I-1).

A fraction of the mineral matter in coal escapes the gasifier or combustor in the form of fly ash. The composition of fly ash depends on the type of coal, the combustion or gasification conditions, and the particle size of the ash. Although most fly ash is removed by cyclones and barrier filters, a small fraction in the form of fine particulate matter (fume) may still reach the membrane modules. The constituents of these particles are silica, silicates, aluminosilicates, ferrous oxides, alkali and alkaline earth compounds. The alkali compounds especially are likely to react with certain ceramic membrane materials, forming chemical phases that weaken the membrane or modify its permeability (Table I-2).

Table I-1

AVERAGE PORE DIAMETER OF OXIDE MATERIALS AS A FUNCTION OF TEMPERATURE

Material	Treatment Temperature (°C)	Treatment Time (h)	Pore Diameter (nm)
Fumed SiO_2			15.0
SiO_2 aerogel	300	12	11.0
Al_2O_3	500	5	2.0
Al_2O_3	550	5	1.8
Al_2O_3	500	24	7.8
Al_2O_3	900	24	13.0
Al_2O_3	1000	24	14.4
ZrO_2	300	48	1.6
ZrO_2	275	12	3.8
ZrO_2	500	12	5.0
ZrO_2	600	12	5.1
ZrO_2	700	12	7.0
ZrO_2	800	12	10.8
ZrO_2	900	12	13.6
TiO_2	400	3	4.6
TiO_2	450	3	3.8
TiO_2	600	3	20.0
CeO_2	300	3	2.0
CeO_2	400	3	2.0
CeO_2	600	3	>100.0

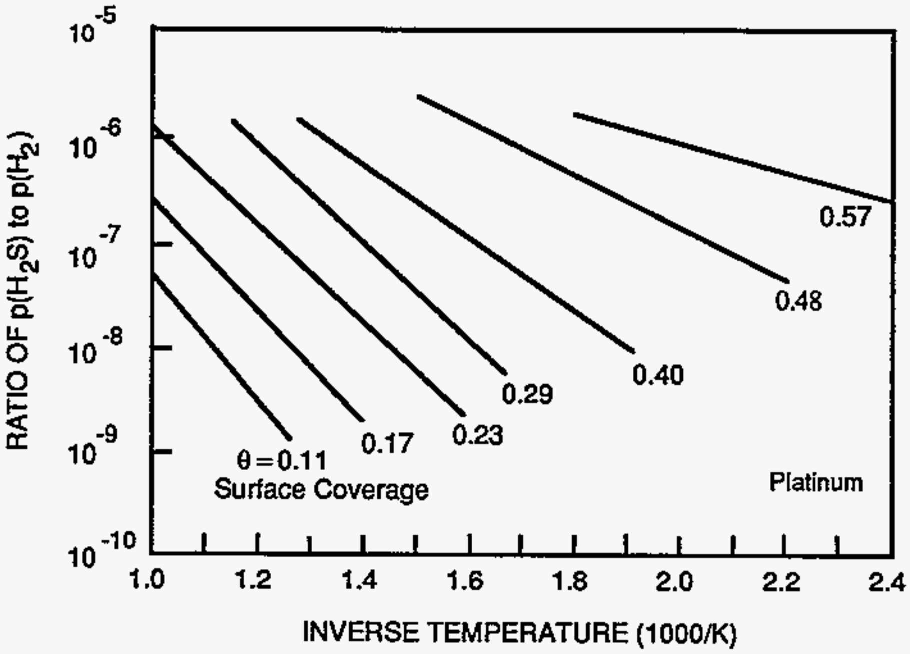

Figure I-1. Variation of surface coverage of sulfur atoms on platinum as a function of temperature.

Table I-2

THERMODYNAMICALLY PROJECTED SOLID PHASES FORMED BETWEEN ASH COMPONENTS AND CERAMIC MEMBRANE MATERIALS IN THE RANGE 500° TO 900°C

	Membrane Material			
Ash Component	**SiO_2**	**Al_2O_3**	**ZrO_2**	**TiO_2**
SiO_2	SiO_2	$Al_2O_3 \cdot SiO_2$ $3Al_2O_3 \cdot 2SiO_2$	$ZrO_2 \cdot SiO_2$	–
Al_2O_3	$Al_2O_3 \cdot SiO_2$ $Al_2O_3 \cdot 2SiO_2$	Al_2O_3	–	$Al_2O_3 \cdot TiO_2$
CaO	$CaO \cdot SiO_2$	$CaO \cdot Al_2O_3$ $CaO \cdot 2Al_2O_3$	$CaO \cdot ZrO_2$	$CaO \cdot TiO_2$ $3CaO \cdot 2TiO_2$ $4CaO \cdot 3TiO_2$
MgO	$MgO \cdot SiO_2$	$MgO \cdot Al_2O_3$	–	$MgO \cdot TiO_2$ $MgO \cdot 2TiO_2$ $MgO \cdot 3TiO_2$
Na_2O	$Na_2O \cdot SiO_2$ $Na_2O \cdot 2SiO_2$ $Na_2O \cdot 3SiO_2$	$Na_2O \cdot Al_2O_3$	–	$Na_2O \cdot TiO_2$ $Na_2O \cdot 2TiO_2$ $Na_2O \cdot 3TiO_2$
K_2O	$K_2O \cdot 4SiO_2$	$K_2O \cdot Al_2O_3$	–	–
Fe_2O_3	$FeO \cdot SiO_2$ $2FeO \cdot SiO_2$	$FeO \cdot Al_2O_3$	–	–

The separation of the various components of the hot coal gas streams during permeation through the membrane changes the gas phase composition and shifts the equilibria between the constituents. In such cases, solids may be deposited by reaction in the gas phase inside the membrane pores. For example, preferential removal of hydrogen from the hot coal gas changes the C/H and C/O ratios, which may lead to deposition of carbon by disproportionation of CO or by decomposition of hydrocarbons.

Thermochemical calculations indicate that the gas stream from an oxygen-blown, entrained-bed gasifier has the potential to deposit carbon (Table I-3). The composition of coal gas from fluidized-bed gasifiers is outside the carbon deposition region only above

800°C. However, preferential removal of hydrogen from the hot coal gas could endow it with enough carburizing potential to deposit carbon. Fixed-bed gasifiers operate at relatively low temperatures and the gas streams contain a significant quantity of tar components. Under hydrogen-deficient conditions, these hydrocarbon components could pyrolyze and deposit carbon in the pores of inorganic membranes.

Table I-3

POTENTIAL FOR CARBON DEPOSITION UNDER EQUILIBRIUM CONDITIONS

	Potential for Carbon Deposition		
Temperature (°C)	Fixed-Bed Gasifier[1]	Fluidized-Bed Gasifier	Entrained-Bed Gasifier
1 atm total pressure			
500	No	Yes	Yes
600	No	Yes	Yes
700	No	No	Yes
800	No	No	No
900	No	No	No
1000	No	No	No
20 atm total pressure			
500	No	Yes	Yes
600	No	Yes	Yes
700	No	Yes	Yes
800	No	Yes	Yes
900	No	No	Yes
1000	No	No	No

[1] Carbon deposition may occur at low temperatures if high molecular weight hydrocarbons (tar) are deposited on the membranes.

In summary, during exposure to coal gasification and combustion gas streams, inorganic membranes could be degraded by thermal sintering, hydrothermal attack, reaction with ash components, attack by vapor- and solid-phase alkali compounds, reaction with hydrogen sulfide, and deposition of carbon from the gas phase. Tables I-4 and I-5 summarize the potential degradation processes with specific membrane materials in coal gasification and combustion gas streams. The gas stream from a fixed-bed gasifier is generally below 600°C and the quantity of fume is likely to be low. Also, because of the low temperature, most of the alkali compounds will be retained in the ash, which can be effectively removed by barrier filters. However, the gas stream contains significant amounts of tar components, which could lead to carbon deposition on a membrane.

Table I-4

LONG-TERM DEGRADATION MECHANISMS FOR INORGANIC MEMBRANES AT 550°C IN HOT COAL GAS STREAMS

	Membrane Material				
Characteristic	**SiO_2**	**Al_2O_3**	**TiO_2**	**ZrO_2**	**Metals[1]**
Phase change	None	None	Yes	Yes	None
Thermal sintering	Small	Small	Significant	Significant	Not applicable.
Hydrothermal sintering	Significant	Small	Significant	Not available	Not applicable.
Vaporization of matrix	Not significant	Not significant	Not significant	Not significant	None
Reaction with H_2S	None	None	None	None	Yes
Reaction with HCl	None	Not significant	Not significant	Not significant	None
Reaction with alkali species	Na_2SiO_2 $K_2O{\cdot}4SiO_2$	$Na_2O{\cdot}Al_2O_3$ $K_2O{\cdot}Al_2O_3$	$Na_2O{\cdot}nTiO_2$	No data	None
Reaction with ash components	$Al_2O_3{\cdot}nSiO_2$ $CaO{\cdot}SiO_2$ $MgO{\cdot}SiO_2$ $FeO{\cdot}nSiO_2$	$Al_2O_3{\cdot}nSiO_2$ $CaO{\cdot}nAl_2O_3$ $MgO{\cdot}Al_2O_3$ $FeO{\cdot}Al_2O_3$	$CaO{\cdot}nTiO_2$ $MgO{\cdot}nTiO_2$	$ZrO_2{\cdot}SiO_2$ $CaO{\cdot}ZrO_2$	None
Carbon deposition:					
Fixed-bed gasifier	No[2]	No	No	No	No
Fluidized-bed gasifier	Yes	Yes	Yes	Yes	Yes
Entrained-bed gasifier	Yes	Yes	Yes	Yes	Yes
Reaction with trace metal species	None	None	None	None	Moderate

[1] Platinum and palladium.

[2] Carbon deposition is possible if tar components are deposited on the membrane.

Table I-5

LONG-TERM DEGRADATION MECHANISMS FOR INORGANIC MEMBRANES AT 700°C UNDER PRESSURIZED-FLUIDIZED-BED COMBUSTOR GAS CONDITIONS

	Membrane Material			
Characteristic	**SiO_2**	**Al_2O_3**	**TiO_2**	**ZrO_2**
Phase change	None	Yes	Yes	Yes
Thermal sintering	Yes	Moderate	Significant	Significant
Hydrothermal sintering	Significant	Moderate	Significant	Not available
Vaporization of matrix	Not significant	Not significant	Not significant	Not significant
Reaction with SO_2	None	$Al_2(SO_4)_3$	Not significant	Not significant
Reaction with HCl	None	Not significant	Not significant	Not significant
Reaction with alkali species	Na_2SiO_2 $K_2O{\cdot}4SiO_2$	$Na_2O{\cdot}Al_2O_3$ $K_2O{\cdot}Al_2O_3$ $Na_2Al_2(SO_4)_4$	$Na_2O{\cdot}nTiO_2$	No data
Reaction with ash components	$Al_2O_3{\cdot}nSiO_2$ $CaO{\cdot}SiO_2$ $MgO{\cdot}SiO_2$ $FeO{\cdot}nSiO_2$	$Al_2O_3{\cdot}nSiO_2$ $CaO{\cdot}nAl_2O_3$ $MgO{\cdot}Al_2O_3$ $FeO{\cdot}Al_2O_3$	$CaO{\cdot}nTiO_2$ $MgO{\cdot}nTiO_2$	$ZrO_2{\cdot}SiO_2$ $CaO{\cdot}ZrO_2$
Reaction with trace metal species	None	None	None	None

Fluidized-bed gasifiers operate at a higher temperature than fixed-bed units and tar generally is not present. The vapor-phase alkali level is high enough to favor attack by sodium and potassium compounds. High steam levels encountered under oxygen-blown operation could lead to hydrothermal sintering of membranes. At temperatures below 800°C, the gas composition is inside the carbon deposition regime and deposition of carbon is likely. Also, removal of hydrogen through the membrane could force the gas to a different equilibrium composition that favors deposition of carbon inside the membrane pores.

The degradation mechanisms that prevail in entrained-bed gasifier streams are similar to those in fluidized-bed gasifier streams, except that alkali levels could be higher in the former. The gas from an oxygen-blown entrained-bed gasifier is sufficiently carburizing that carbon deposition is likely even without removal of H_2. Exposure of membranes to combustor gas streams from direct coal-fueled turbines and pressurized fluidized-bed combustors may lead to degradation by hydrothermal attack, or by reaction with SO_2, alkali sulfates, and ash particles.

In summary, the results of the literature review identified several thermal and chemical mechanisms that could degrade the properties of inorganic membrane materials. In coal gasification streams, the most dominant mechanisms are hydrothermal sintering, attack by fine ash particles (fume) and vapor phase alkali species, poisoning by sulfur and trace metal impurities, and deposition of carbon. In coal combustion gas streams, membrane degradation is most likely to occur by reaction with ash particulates and sulfur oxides.

II. INORGANIC MEMBRANE MATERIALS

INORGANIC MEMBRANES FOR GAS SEPARATION

Inorganic membranes have been an item of commerce for more than 30 years. Many inorganic membrane products available today perform the task of microfiltration and ultrafiltration, and some of the smallest pore size membranes may be used for gas separation applications based upon a Knudsen diffusion mechanism (Table II-1). Glass membranes are made by Corning Glass (Vycor), Asahi Glass, Fuji Filters, and Schott Glass. Commercial alumina membranes are available from U.S. Filter (Membralox) as well as from Golden Technologies Company. These Vycor-like and alumina products can be made in tubular form (6- to 8-mm I.D.). The smallest available pores in these membranes are about 4 to 5 nm in diameter. Pores of this size are much smaller than the mean free path of gaseous molecules under a wide range of pressure and temperature conditions. Consequently, gases are separated according to the well-known Knudsen mechanism, which states that the selectivity for two gases is inversely proportional to the ratio of the square roots of the molecular weights of the gases.

Because the selectivity imparted by Knudsen diffusion is too low to be commercially important for most gas separation applications (a notable exception is the uranium enrichment process at the Oak Ridge Gaseous Diffusion Plant), a variety of research and development efforts have been pursued in recent years to obtain adequate separation factors with industrially acceptable gas fluxes. Many of these efforts have been sponsored by the DOE. Materials of interest include modified alumina and Vycor membranes, platinum and palladium metals, and composite carbon. The metal membranes are designed specifically for H_2 separation (via dissolution/diffusion of H_2), whereas the nonmetals are multilayer membranes with size selective pores as small as the gas molecules themselves, such as in molecular sieves [Wu et al., 1994]. At present, inorganic membranes are not commercially available for gas separation applications in the high temperature-high pressure IGCC gas environments.

Table II-1
POTENTIAL POROUS INORGANIC GAS SEPARATION MEMBRANES

Manufacturer*	Trade Name	Membrane Material	Support Material	Membrane Pore Diameter	Geometry of Membrane Element	Tube or Channel Inside Diameter (mm)
Corning, Inc.	Vycor®	SiO_2	None	4 nm	Tube	4
Alcoa/SCT	Membralox®	ZrO_2 Al_2O_3	Al_2O_3 Al_2O_3	20-100 nm 0.2-5 μm	Monolith, tube	4 and 6
Norton	Ceraflo®	Al_2O_3	Al_2O_3	0.2-1.0 μm 6 μm (symmetric)	Monolith, tube	3
NGK		Al_2O_3	Al_2O_3	0.2-5 μm	Tube	7 and 22
Du Pont	PRD-86	Al_2O_3, Mullite, Cordierite	None	0.06-1 μm	Tube	0.5-2.0
Alcan/Anotec	Anopore®	Al_2O_3	Al_2O_3	20 nm, 0.1 and 0.2 μm	Plate	
Gaston County Filtration Systems	Ucarsep®	ZrO_2	C	4 nm	Tube	6
Rhone-Poulenc/ SFEC	Carbosep®	ZrO_2 ZrO_2	C C	~4 nm 0.08-0.14 μm	Tube	6
Du Pont/ CARRE		$Zr(OH)_4$	SS	0.2-0.5 μm	Tube	~2
TDK	Dynaceram®	ZrO_2	Al_2O_3	~10 nm	Tube	~5
Asahi Glass		Glass	None	8 nm-10 μm	Tube/plate	3 and 10
Schott Glass		Glass	None	10 nm and 0.1 μm	Tube	5-15
Fuji Filters		Glass Glass	None None	4-90 nm 0.25-1.2 μm	Tube	
Ceram-Filtre	FITAMM	SiC	None	0.1-8 μm	Monolith	25
Fairey	Strata-Pore®	Ceramics	Ceramics	1-10 μm	Tube/plate	10
Mott		SS, Ni, Au, Ag, Pt, etc.	None	≥0.5 μm	Tube	3.2-19
Pall		SS, Ni, etc.	None	≥0.5 μm	Tube	60 and 64
Osmonics	Hytrex® Ceratrex®	Ag Ceramics	None Ceramics	0.2-5 μm 0.1 μm	Tube/plate	
Ceramem		Ceramics oxides	Cordierite	0.05-0.5 μm	Honeycomb monolith	1.8

* Some of these manufacturers are not currently producing the identified products.

Developmental efforts are underway to improve the feasibility of inorganic membranes. Media and Process Technology Inc. (MPT) has developed modified silica/alumina and zeolitic membranes [Liu et al., 1992]. Ceramem Corporation is developing asymmetric, porous, silica/alumina membranes and membrane modules made of cordierite for gas separation [Goldsmith et al., 1992]. Hydrogen permselective membranes formed by depositing SiO_2 and other oxides by chemical vapor deposition (CVD) within the pores of a porous silica tube are being investigated at the California Institute of Technology (Cal Tech) [Gavalas, 1992]. Carbon composite molecular sieve membranes are being investigated by Allied Signal Corporation [Yates et al., 1994]. McMahan et al., [1990] studied the use of both Vycor glass and alumina membranes to separate H_2 from a simulated coal gas stream.

Several research programs have focused on separating H_2S and NH_3 from hot coal gas streams using membrane reactors. SRI investigated the use of a catalyst packed inside a tubular alumina membrane to decompose H_2S in He and NH_3 in H_2 and found that removal of hydrogen through the membrane enhanced the decomposition of these compounds to higher than equilibrium levels [Roberts et al., 1993]. Bend Research Corporation used a composite metal membrane to decompose H_2S and found that >99% conversion of H_2S can be attained at 700°C [Edlund and Pledger, 1993]. Molten carbonate salts supported on a porous ceramic substrate were explored by Air Products and Chemicals Corporation and Research Triangle Institute to separate sulfur-bearing gases from simulated coal gas streams [Damle et al., 1994].

Many of the above studies were conducted in relatively clean environments. However, coal gasification and combustion product gas streams at high temperatures can be an aggressive threat to the efficient operation of inorganic membranes. These gas streams contain several components, such as H_2O, CO, H_2S, SO_2, and alkali vapor, that could react with Al_2O_3, ZrO_2, SiO_2, and other membrane materials in the temperature range of interest (500° to 1200°C). High levels of steam can accelerate the sintering of nanopores at high temperatures by forming mobile hydroxide species.

In asymmetric membranes in which a selective, microporous, membrane layer is bonded to a coarse-pore substrate, the composition of gas to which the support layer is exposed is different from the composition of gas to which the selective layer is exposed. In addition, under permeation conditions, the total pressure on the feed side of the membrane greatly exceeds that on the permeate side of the membrane. Consequently, the selective layer and support layer are exposed to very different partial pressures of aggressive gaseous components. For example, the high CO/H_2 ratio that would result from the preferential removal of H_2 by the membrane could lead to deposition of carbon inside the pores of the membrane. Also, residual particulate material, if present after passage through cyclones or filters, contains components such as alkali salts that could react with the membrane materials at high temperatures to form different phases that alter their properties. High temperature coal gas streams are so severe an environment that only refractory materials and noble metals could be considered as membrane candidates.

CANDIDATE MEMBRANE MATERIALS

The developmental, high temperature, inorganic, gas separation membranes may be grouped in five categories:

1) Dense Metallic Membranes

Both palladium and platinum membranes have been investigated for their hydrogen separation ability. Platinum is more resistant to poisoning by H_2S than palladium. Developmental work is underway to increase the permeance by using ultrathin membranes that are supported with base metal (vanadium) and barrier oxide layers.

2) Silica-Based Membranes

Microporous silica/glass membranes are commercially available with pore sizes down to 40 Å (e.g. Vycor glass). Efforts are underway to reduce the pore size of the Vycor-type glass membranes by chemical vapor deposition techniques. Incorporation of silica based zeolitic layers on a porous alumina substrate is also being investigated to separate gases by a molecular sieving mechanism.

3) Alumina-Based Membranes

Similar to silica membranes, microporous gamma alumina/alpha alumina composite membranes are commercially available with pore sizes down to 40 Å (e.g. Membralox membranes). Although, the selectivity afforded by these membranes may be too low for commercial applications, alumina is the most common component of the inorganic membranes available today. Aluminum nitride and lithium aluminate were investigated as support materials for molten-salt-facilitated transport membranes for H_2S removal, although this concept is still far from commercial development.

4) Carbon-Based Membranes

Carbon molecular sieves have been extensively used in the chemical industry for gas separation applications. Efforts are underway to develop carbon/carbon composite CMS membranes, where a top layer of CMS is deposited on a porous carbon support.

5) Zirconia-Based Membranes

Incorporation of zirconia and other oxide gas separation layers, to reduce pore sizes below 40 Å, is also being investigated to separate gases by Knudsen diffusion and molecular sieving mechanisms. As a membrane material, zirconia offers greater resistance to hydrothermal sintering than silica and alumina membranes.

Almost all of the membrane materials described above are intended for hydrogen separation that would maximize hydrogen production from coal gas, for example, in a coal processing plant where hydrogen is needed for coal liquefaction.

Selection of Candidate Materials for Degradation Study

Candidate membrane materials were selected, in consultation with the DOE program manager, according to three criteria: (1) present development status, (2) future potential, and (3) availability. Suppliers of different membrane materials were contacted to learn the development status and to obtain information regarding demonstrated gas selectivities and fluxes, even if only in a clean gas environment. The most promising membrane materials selected for testing were:

- Alumina (Membralox) membranes with a separation layer pore size of 40 Å, supplied by the U.S. Filter Corporation
- Alumina membranes modified by Media and Process Technologies Inc. to increase membrane selectivity for hydrogen and helium
- Vycor porous glass membranes with a pore size of 40 Å, supplied by Corning, Inc.
- Vycor porous glass membranes modified in Professor Gavalas's laboratory at CalTech to increase membrane selectivity for hydrogen
- Platinum foils provided by Bend Research, Inc.
- Palladium foil purchased from the Aldrich Chemical Company, Inc.

Modifications of the Vycor and alumina membrane materials were based on adding a gas separation layer of amorphous silica.

Three protocols were used to evaluate the degradation of these membrane materials during exposure to IGCC gas streams:

- Characterize changes in the physical and chemical properties of the membranes exposed to simulated gas streams under well-defined conditions
- Measure the permeation performance of membranes under representative conditions
- Determine changes produced in membrane materials after prolonged exposure to the hot coal gas stream of an operating coal gasifier.

Before and after exposure, the exposed membrane samples were characterized by BET surface area and pore size analysis, Auger electron spectroscopy, scanning electron microscopy, and dynamic pore size measurements. The membrane permeation performance was determined by measuring both pure component and mixed gas permeation rates. The fixed-bed coal gasifier facility at the General Electric Corporate Research and Development (GE-CRD) at Schenectady, NY was used to expose a set of membrane samples to an actual coal gas environment.

III. LONG TERM MEMBRANE EXPOSURE TESTS

The purpose of the long term exposure tests was to determine the changes in the physical characteristics, chemical composition, and pore size distribution of the membrane materials as a result of exposure to simulated IGCC conditions. In these tests, the membrane materials were placed in an externally heated, pressurized vessel and exposed to a flow of simulated hot coal gas.

The exposure test apparatus consisted of an alloy steel tube, 2.5 cm diameter and 120 cm long with flanged ends, enclosed in a tubular furnace capable of reaching temperatures up to 1000°C (Figure III-1). Alternatively, a fused quartz exposure tube 7.5-cm in diameter was used for 1-atm tests. A movable platform, made of dense alumina or stainless steel, served as a support for the samples. The membrane coupons were mounted on small ceramic supports to prevent contamination. The simulated hot coal gas was generated by adding steam to appropriate dry gas mixtures. The exhaust gas from the exposure tube passed through a steam condenser and then a back pressure regulator that controlled the pressure inside the tube. Thermocouples inserted in the sample zone and the steam generation section provided temperature measurement and control.

EXPOSURE PARAMETERS

Gas Composition

Coal gasification gas streams typically contain N_2, H_2, CO, H_2O, CO_2, H_2S, and NH_3 in proportions that depend on the coal and gasifier type. In general, entrained-bed oxygen blown gasifiers produce a greater fraction of CO and H_2 and a smaller fraction of steam than fixed-bed air blown gasifiers. Table III-1 shows the typical gas compositions produced by different gasifier types. Both the reducing gas conditions and the steam content are likely to contribute to the membrane degradation. Therefore, two gas compositions, covering a wide range in the individual gas species concentrations were used during the exposure studies, as shown in Table III-2. Simulated coal gas streams were prepared by adding an appropriate quantity of steam from a pressurized evaporator to a premixed dry gas from cylinders. The gas mixture flowed through the exposure tube at a rate of about 120 cm^3/min.

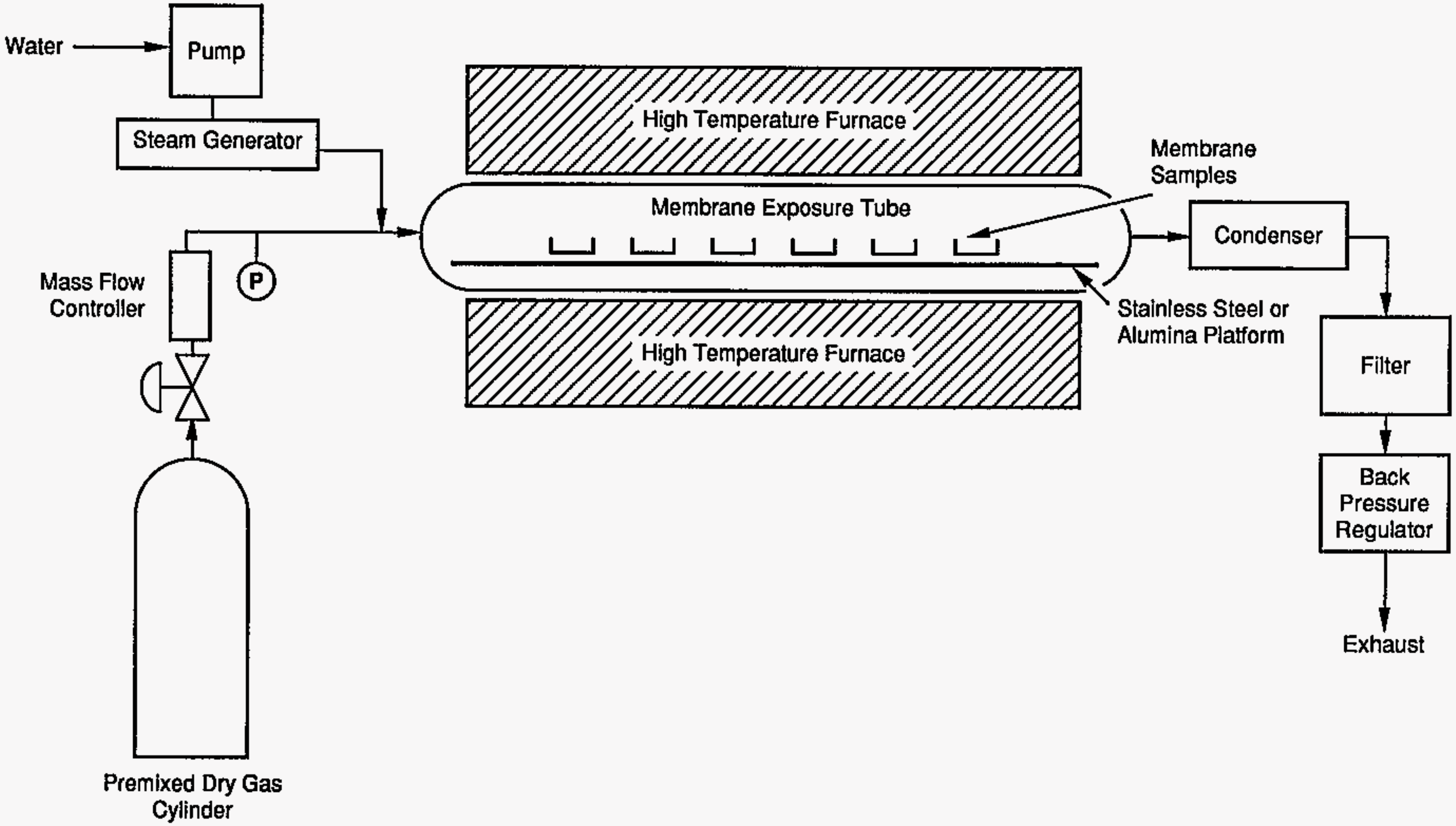

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Figure III -1. Schematic diagram of long term exposure apparatus.

Table III-1
TYPICAL GAS COMPOSITIONS FROM DIFFERENT GASIFIERS

Component	Volume %		
	Entrained Bed Oxygen Blown	Fixed Bed Air Blown	Fluidized Bed Air Blown
CO	44.8	8.0	21.00
CO_2	9.8	11.0	7.00
H_2	30.4	16.0	15.00
H_2O	12.4	30.0	9.00
CH_4	0.2	3.0	1.00
N_2	0.93	29.5	46.89
Ar	1.0	1.0	—
NH_3	0.1	0.5	0.02
H_2S	0.5	3.0	0.08
COS	0.01	—	0.01

Table III-2
COMPOSITION OF DRY COAL GAS MIXTURES USED IN EXPOSURE STUDIES

Component	% of Component (v/v)	
	Mixture 1	Mixture 2
H_2	19.2	31.3
CO	9.6	44.7
CO_2	13.1	10.4
H_2S	1.2	0.5
N_2	33.8	0.0
H_2O	23.0	13.0

The following membrane samples were exposed in these tests: unmodified alumina membranes (Membralox), unmodified Vycor membranes, platinum foils, and palladium foils. Because of the nature and small number of modified membrane samples obtained from MPT and CalTech, these samples were used only in the permeation experiments. The results of the exposure studies on the unmodified parent membrane materials, however, are expected to provide data on the stability of the modified membranes as well.

Temperature

Five exposure temperatures (450°, 550°, 650°, 800°, and 1000°C) were used to cover the wide range of temperatures expected in typical IGCC and hydrogen separation applications. The low temperature regime (<550°C) of this range is representative of the catalytic water gas shift reaction that will likely be used in maximizing hydrogen production from coal gas. The high temperature regime (>650°C) represents the condition of the gas stream from a fluidized- or entrained-bed gasifier that could be used for decomposition of H_2S or NH_3 with hydrogen permeation through platinum membranes.

Pressure

Exposure pressures of 1 and 20 atm (300 psig) were used. The high pressure value is typical of the gasifier product gas conditions, whereas atmospheric pressure is representative of membrane permeate side conditions.

Fly Ash

The effect of fly ash on the membrane materials was investigated by coating the membrane samples with a layer of ash material prior to testing. Ash collected in the secondary cyclone of the GE fixed-bed gasifier facility was used to coat the membrane samples. A small amount of ash was mixed with water to form a paste that was then applied to membrane samples. The samples were dried at 120°C before being loaded in the exposure tube.

Exposure Duration

Test durations of 24 to 1000 h were used. Short durations were used for high temperature runs because accelerated degradation was anticipated. The durations of the tests at 450° and 550°C were in the range 500 to 1000 h.

A total of six exposure tests were conducted in this program. Table III-3 shows the exposure conditions used for each of these tests. Two tests were conducted at 20-atm pressure and at temperatures of 450° and 550°C. Four tests were conducted at 1-atm pressure at temperatures of up to 1000°C. In each test conducted at 450° and 550°C, one set of samples coated with fly ash was included.

Table III-3
EXPERIMENTAL VARIABLES DURING EXPOSURE TESTS

Test No.	Temperature (°C)	Pressure (psig)	Duration (h)	Gas Composition	Ash Coated Samples
1	1000	0	24	1	No
2	800	0	76	1	No
3	650	0	113	2	No
4	550	0	410	2	Yes
5	450	300	1000	1	Yes
6	550	270	500	1	Yes

ANALYSIS OF MEMBRANE SAMPLES

The membrane samples exposed to the simulated coal gas in the exposure tests were analyzed to determine changes in their physical and chemical characteristics. The characteristics that were measured include (Table III-4):

- Surface area and pore size distribution of the membrane samples
- Changes in the physical surface morphology
- Crystalline phases in the membrane
- Elemental distribution in the membrane surface layer.

Surface Area and Pore Size Distribution Analysis

The gas separation ability of the porous Vycor and alumina membranes depends upon the pore size distribution of the gas separation layer. An automated Micromeritics ASAP 2000 surface area and pore size analysis system was used to analyze membrane samples. For homogeneous samples such as Vycor, the BET adsorption isotherm provides both surface area and pore size distribution data. For asymmetric composite samples such as Membralox membranes, the measured surface area arises mainly from the thin microporous layer. However, the amount of gas condensed in the microporous layer was too small to allow precise determination of pore size distribution. Hence, changes in the pore size distribution of the asymmetric membrane samples was inferred from the changes in surface area.

Table III-4
INFORMATION PROVIDED BY ANALYTICAL TECHNIQUES

Technique	Property Measured	Interpretation
BET	Surface area, pore size distribution	Decrease in surface area would indicate grain growth and pore coarsening. Pore size distribution is applicable to pores less than 100 nm.
Mercury porosimetry	Pore size distribution	Data will indicate changes in pores whose size is greater than 20 nm.
X-ray diffraction	Identify crystalline phases	Data will indicate changes in crystalline phases on membrane surface and phase transformations.
Scanning electron microscopy	Surface morphology	Visible indication of grain growth, cracking, and corrosion.
Electron-beam induced X-ray analysis	Elemental distribution in membrane material	Data will indicate extent of bulk reaction of membrane material with reactive gaseous or components or ash components.
Auger electron spectroscopy	Elemental distribution in top 2 to 3 atomic layers on membrane surface	Data will indicate extent of surface reaction between membrane material with gaseous or solid components.

X-Ray Diffraction (XRD) Analysis

X-ray diffraction was used to determine changes in the crystalline phases of a membrane during the exposure tests. Such changes are especially important for silica and alumina membranes that undergo significant phase changes at high temperatures. Initial studies with the alumina membranes failed to distinguish the gamma-alumina phase in the thin micropore layer from the alpha-alumina phase of the support structure. As a result, XRD could not be used to determine the changes in the alumina phase of the gas separation microlayer of the alumina membranes. However, this technique was used to confirm the crystallization of the Vycor membrane samples observed after exposure at high temperatures (650°, 800°, and 1000°C).

Auger Electron Spectroscopy (AES)

The elemental distributions in the metallic membrane surface layers was determined by an Auger electron spectrometer (PHI Model 15-110A) available at SRI. This techniques measures elemental distribution in the surface layers (2 nm thick) of a solid specimen. This technique was useful in determining the sulfur distribution on platinum and palladium membrane surfaces. Using argon ion sputtering, the elemental distribution at various depths (up to ~250 nm) into a solid specimen could be determined.

Scanning Electron Microscopy

A scanning electron microscope (ISI Model SX40) was used to observe changes in the physical morphology of the membrane surfaces. An X-ray detection system (EDAX) attached to the scanning electron microscope was used to determine the elemental distribution on the surface. In contrast to AES, which analyzes only the top 2 nm layer, the EDAX provides an elemental analysis averaged over a 1 μm depth. This technique was used to determine the interaction between the ash layer and the alumina and Vycor membranes.

Dynamic Pore Size Measurement (DPSM) System

Since the BET- N_2 adsorption analysis does not provide adequate resolution to determine the pore size of the alumina membranes, a dynamic pore size measurement system was used. This technique, originally developed at Oak Ridge National Laboratory, provides a flow-weighted pore size distribution by controlled blocking of membrane pores with a condensable liquid [Fain, 1989]. The Kelvin equation correlates the pressure at which a vapor will condense in a pore:

$$\ln(P_o/P) = 2\gamma V/(rRT)$$

where P_o and P are the vapor and partial pressures of the condensable vapor, γ is the surface tension of the condensate, V is the molar volume of the condensate, r is the pore radius where the condensation occurs, R is the gas constant, and T is the temperature of the pore.

In this technique, a gas mixture containing a condensable vapor such as hexane in nitrogen is passed through the membrane (Figure III-2). It permeates the membrane layer

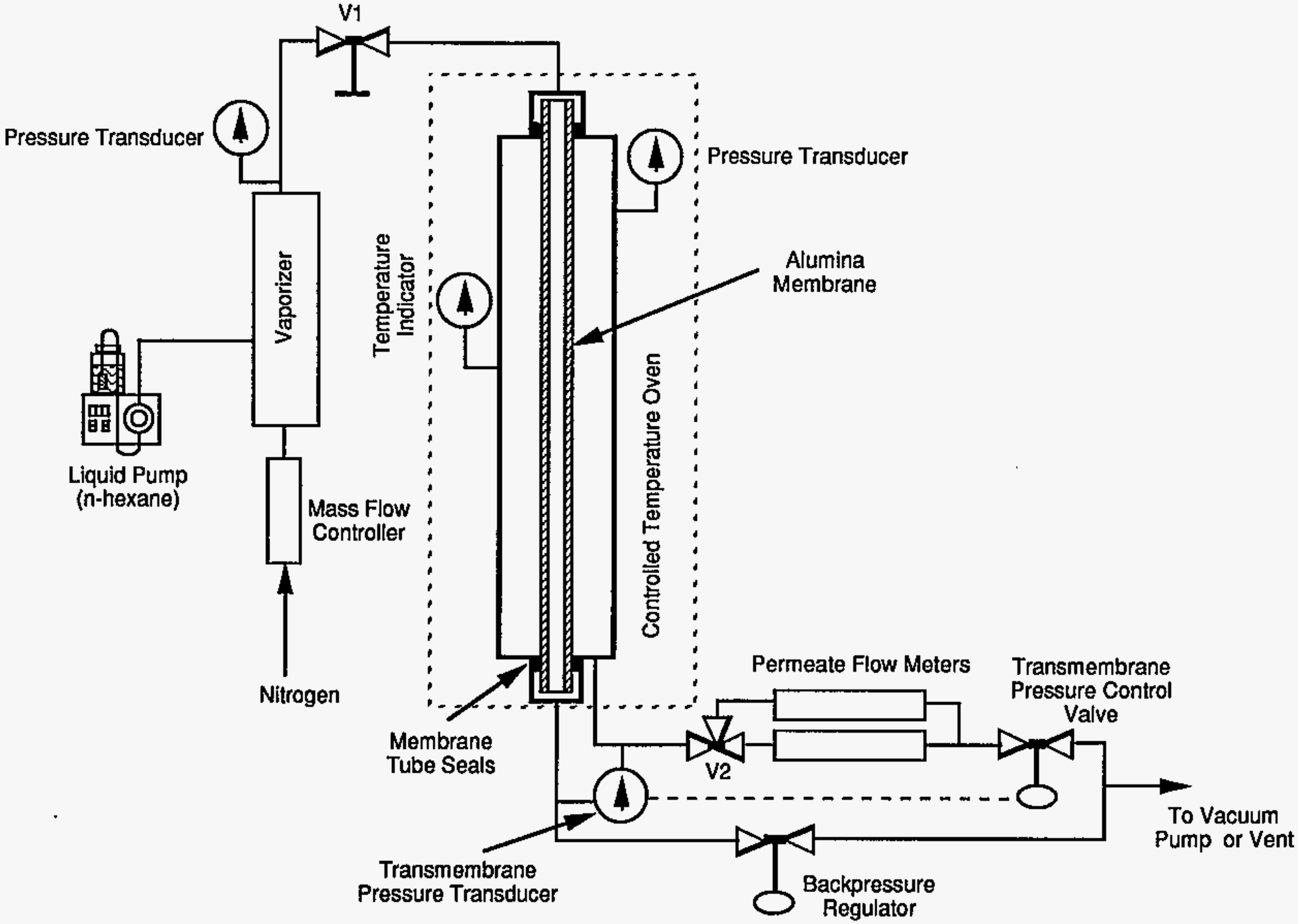


Figure III-2. Schematic diagram of a dynamic pore size measurement system.

under a partial pressure differential of about 0.02 atm. When the partial pressure of condensable vapor is increased to satisfy the Kelvin equation, vapor will condense in pores of radius r, thereby blocking them from permeation and decreasing the permeate flow. As the pressure is raised to a value near the saturation pressure of the vapor, all pores in the membrane are blocked and no permeate flow is observed. If the system pressure is then decreased, the condensate in the pores will evaporate, opening the pores to permeation. Thus, the change in permeate flow as a function of the partial pressure of the condensable species can be correlated to a flow-weighted pore size distribution in the membrane.

The advantage of this technique is that it allows accurate pore size distribution in a thin microporous layer incorporated on supporting thick, macroporous layers. The measurement is based on the incremental gas flow through the membrane rather than the incremental volume of gas adsorbed (as in the BET technique) or the incremental volume of a liquid intruded (as in mercury porosimetry). The smallest pore size that can be measured by the DPSM technique is limited by the constraints of the Kelvin equation and it is generally about 1.5 nm. The upper limit, governed by the precision of pressure measurement, is about 50 nm in the present case.

Effusion Cell Vaporization Measurements

During the atmospheric pressure exposure studies at 800° and 1000°C the alumina membrane samples evolved a significant amount of sodium vapor, enough to damage the exposure tube and quartz supports. Discussion with the staff at U.S. Filter Corporation confirmed the presence of sodium compounds in Membralox membrane at about 0.25 wt%. Because the alkali vapors themselves are expected to be detrimental to the membrane performance, the sodium evolution from the alumina membranes was determined in a high-temperature effusion-cell placed in a mass spectrometer. About 1 g of the alumina membrane chips were loaded in a chemically inert platinum Knudsen cell with a 0.1-cm-diameter orifice. The Knudsen cell was heated by a tantalum spiral resistance heater surrounded by a set of radiation shields; the cell temperature was measured with a Pt, 13% Pt-Rh thermocouple.

Gaseous species vaporized from the sample escaped from the cell as a collision-free molecular beam ($P<10^{-4}$ atm). The molecules in the beam were ionized by electron impact and their abudance of a function of their mass to charge ratio (AMU) was determined using a mass spectrometer. Effusion beam species from the cell could be clearly distinguished from the instrument background by the response to movement of a beam-defining slit interposed between the cell and the ion source of the mass spectrometer. The neutral vapor species were identified by masses and threshold appearance potentials of the ions. Because rapid depletion of the signals precluded the normal recording of ionization efficiency curves, threshold energies for formation of the observed ions were quickly evaluated by lowering the electron energy stepwise until the signal intensities vanished. The determined values agreed with the accepted values within 0.5 eV. Absolute pressures of the neutral gas species were evaluated from the parent ion intensities measured at 3 eV above their threshold appearance potentials by the expression:

$$P_i = (k/\sigma_i) \cdot I_i^+ \cdot T \qquad (2)$$

where I_i^+ is the ion intensity, T is the temperature in Kelvin, σ_i is the relative ionization cross section, and k is an instrument sensitivity constant evaluated using a high-purity sample such as Sn as a vapor pressure standard. The low pressure detection limit of the experiment was about 5×10^{-11} atm.

Table III-5 lists the partial pressures of the observed vapor species evolved from the alumina membrane sample. The sample was heated slowly from room temperature. A brief search over the range 7 to 400 AMU was made at each temperature. Relative species pressures are only qualitative, since at a given temperature all species ion intensities decreased with time, some more rapidly than others, and steady state conditions were never really achieved. CO_2 was observed at all temperatures. H_2O disappeared by 480°C. Na and Zn vapors appeared when the cell temperature reached 480° and 850°C, respectively. The decrease of species pressures with time is indicated by two consecutive measurements at each temperature.

EXPERIMENTAL RESULTS

The untreated Vycor membrane samples had a surface area of 190 m^2/g and a mean pore size of 40 Å (Figure III-3). The surface area of the alumina membranes was about 2 m^2/g, as determined by the BET analysis. Mercury porosimetry analysis of the alumina membranes indicated that nearly 95% of the pore volume was in pores larger than 20 nm, but the surface area of these large pores was only 0.09 m^2/g. This results confirm that nearly all the surface area of the alumina membranes is associated with the microporous layer. The surfaces of Pt and Pd specimens, before exposure tests, were relatively free of impurities, as determined by AES analysis.

Table III-5

PARTIAL PRESSURES OF GASEOUS SPECIES EVOLVED FROM AN ALUMINA MEMBRANE SAMPLE AT VARIOUS TEMPERATURES

		Partial Pressure (atm)			
T(C)	Time (min)	Na (g)	Zn (g)	CO_2 (g)	H_2O (g)
190		N.D.	N.D.	1.36×10^{-7}	1.62×10^{-7}
278		N.D.	N.D.	1.39×10^{-7}	2.55×10^{-7}
368		N.D.	N.D.	1.35×10^{-6}	5.38×10^{-7}
368		N.D.	N.D.	4.04×10^{-7}	8.07×10^{-8}
479		3.05×10^{-10}	N.D.	2.84×10^{-6}	
	60	⇓		⇓	
479		1.27×10^{-10}	N.D.	4.23×10^{-7}	
546		1.15×10^{-9}	N.D.	1.38×10^{-6}	
	110	⇓		⇓	
547		8.02×10^{-10}	N.D.	3.44×10^{-8}	
677		7.18×10^{-9}	N.D.	2.66×10^{-8}	
	43	⇓		⇓	
677		5.32×10^{-9}	N.D.	1.33×10^{-8}	
782		3.25×10^{-7}	N.D.	1.33×10^{-7}	
	31	⇓		⇓	
782		3.33×10^{-7}	N.D.	6.65×10^{-8}	
849		1.44×10^{-6}	4.71×10^{-10}	2.83×10^{-7}	
	28	⇓	⇓	⇓	
849		8.38×10^{-7}	4.71×10^{-10}	9.43×10^{-8}	
922		2.09×10^{-6}	5.52×10^{-9}	1.67×10^{-7}	
	40	⇓	⇓	⇓	
922		5.52×10^{-7}	2.68×10^{-9}	2.51×10^{-8}	
1023		1.20×10^{-6}	7.26×10^{-9}	5.44×10^{-8}	
	26	⇓	⇓	⇓	
1023		3.72×10^{-7}	2.90×10^{-9}	3.63×10^{-8}	

N. D. = Not detected

In general, the exposure tests indicated that degradation occurs in all membrane samples. The observed degradation included loss of surface area, enlargement of pores, phase changes, interaction with ash, and attack by H_2S. The experimental results observed in the exposure tests are described below.

Exposure Test 1

This test at 1000°C and 1-atm pressure lasted for 24 h. The quartz exposure tube, as well as the quartz specimen supports, were devitrified, presumably due both to high temperature and attack by sodium vapor evolved from the alumina membranes. The Vycor membrane sample also turned opaque due to crystallization. BET analysis indicated that the Vycor membrane had lost all of its microporosity resulting in a surface area of only 1.9 m^2/g. The alumina membrane sample also appeared to have degraded and its surface area was reduced to 1.3 m^2/g. The palladium membrane sample melted due to reaction with H_2S present in the coal gas. The phase diagram of the Pd-S system indicates that the addition of sulfur decreases the melting point of Pd drastically. Pure Pd melts at 1555°C but an eutectic alloy of Pd containing 11.5 wt% S melts at 635°C [Massalski, 1986]. Although the Pt samples did not appear to degrade, AES analysis revealed a layer of S atoms on the surface, about 1 nm deep. In contrast to the Pd-S system, the addition of S to Pt does not decrease the melting point severely. The data for Pt-S are not as reliable as for the Pd-S system. Pt_3S has been reported to melt at about 1550°C [Massalski, 1986].

Exposure Test 2

This test at 800°C and 1-atm pressure lasted for 76 h. The quartz supports and Vycor membrane samples turned opaque due to crystallization. BET analysis indicated that the surface area of the Vycor membrane had decreased to 33 m^2/g and the mean pore size had increased to 117 Å (Figure III-4). XRD analysis confirmed the formation of crystalline silica in this exposure test. The surface area of the alumina membrane sample was also reduced significantly to 0.43 m^2/g. The palladium membrane sample was melted due to reaction with H_2S present in the coal gas. The Pt samples did not appear to degrade, but AES analysis revealed a sulfur adlayer on the surface, about 2 nm deep.

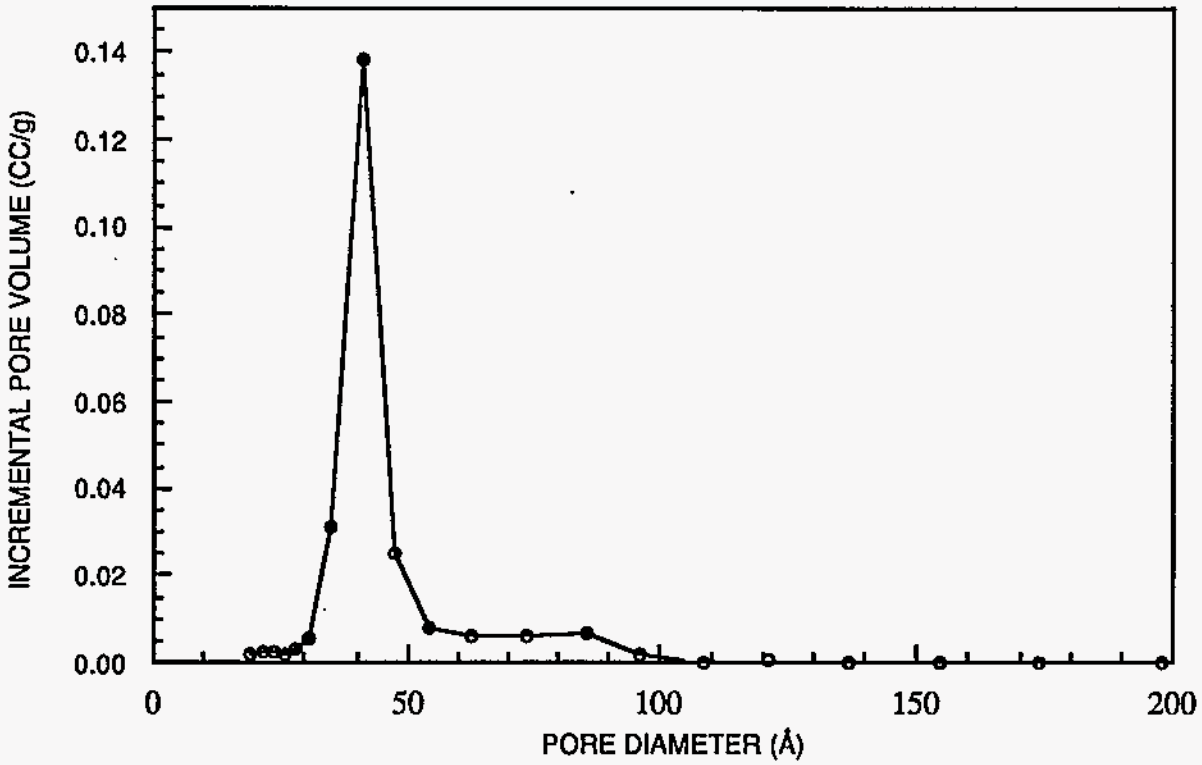


Figure III-3 Pore size distribution of a Vycor membrane in as received condition.

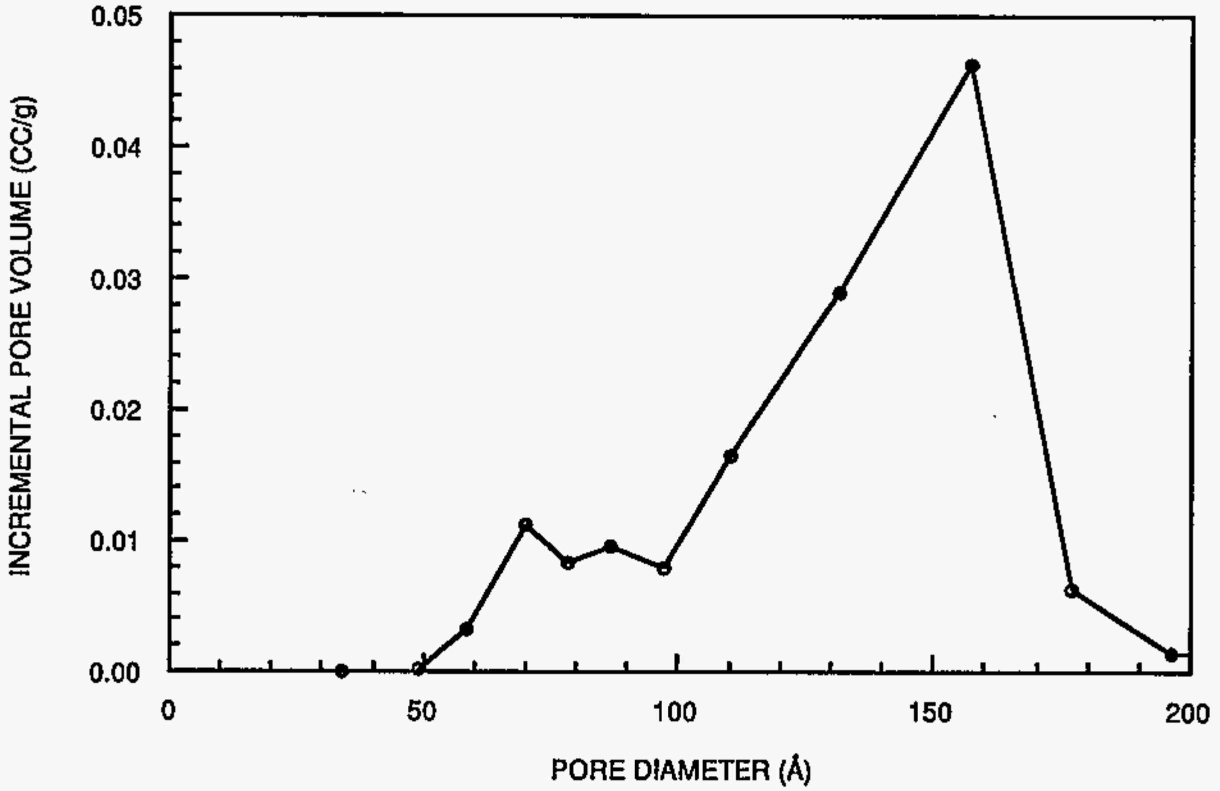


Figure III-4. Pore size distribution of a Vycor membrane after exposure at 800°C and1 atm for 76 h.

Exposure Test 3

This test at 650°C and 1-atm pressure lasted for 113 h. The Vycor membrane samples remained in their glassy state, but a reduction in the surface area (140 m^2/g) and an increase in the mean pore size (45 Å) were observed after the test (Figure III-5). The surface area of the alumina membrane sample was again reduced significantly from 2.1 to 0.9 m^2/g. The palladium membrane sample was deformed extensively. AES analysis of the palladium sample indicated that sulfur was not only a predominant component of the surface, but upon depth profiling by argon ion bombardment, it continued to remain at a high level within the bulk of the metal foil. Pt samples did not appear to degrade, but AES analysis demonstrated that a sulfur adlayer had accumulated on the surface of the samples. The sulfur concentration decreased rapidly with argon sputtering and no sulfur was detected at depths greater than 5 nm. Thus, platinum sulfidation appears to be confined to the surface. Figure III-6 shows the typical depth profiles of the sulfur observed on the surface of the exposed platinum and palladium foils.

Exposure Test 4

This test at 550°C and atmospheric pressure lasted for 410 h. Half of the membrane specimens were coated with gasifier fly ash obtained from GE fixed-bed gasifier facility at Schenectady, NY. Visual inspection of exposed samples showed degradation of palladium samples with and without ash coating. Vycor glass membrane samples appeared unaffected. BET analysis of the samples indicated surface areas in the range 150 to 160 m^2/g and a mean pore size of 44 Å, which shows slight coarsening of initial pore size of 40 Å and about 20% reduction in the surface area (Figure III-7). The presence of the ash coat appeared to have only minimal effect on the degradation of the Vycor membrane samples. EDAX analysis of the Vycor sample coated with ash did not show the presence of any elements other than silicon and oxygen, indicating there was negligible interaction between ash components and silica. XRD analysis did not indicate any crystallization of silica in this exposure test.

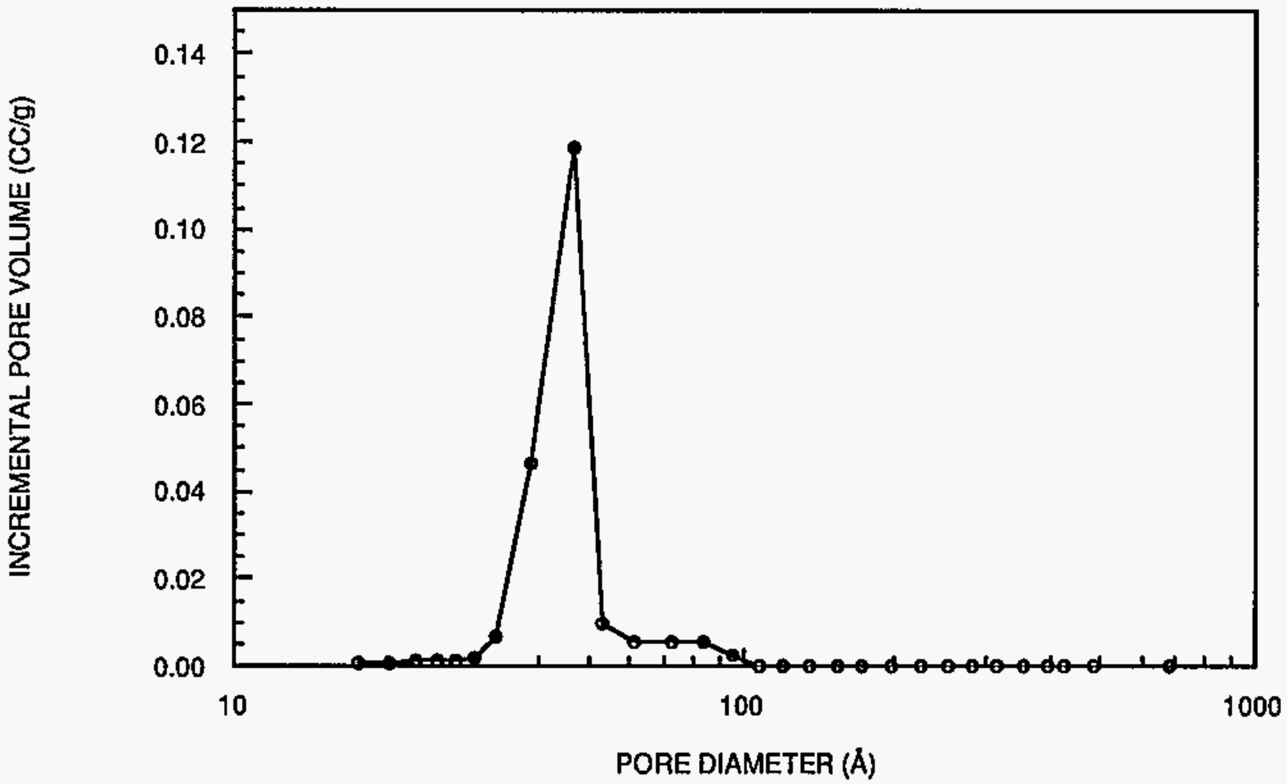


Figure III-5. Pore size distribution of a Vycor membrane after exposure at 650°C and 1 atm for 113 h.

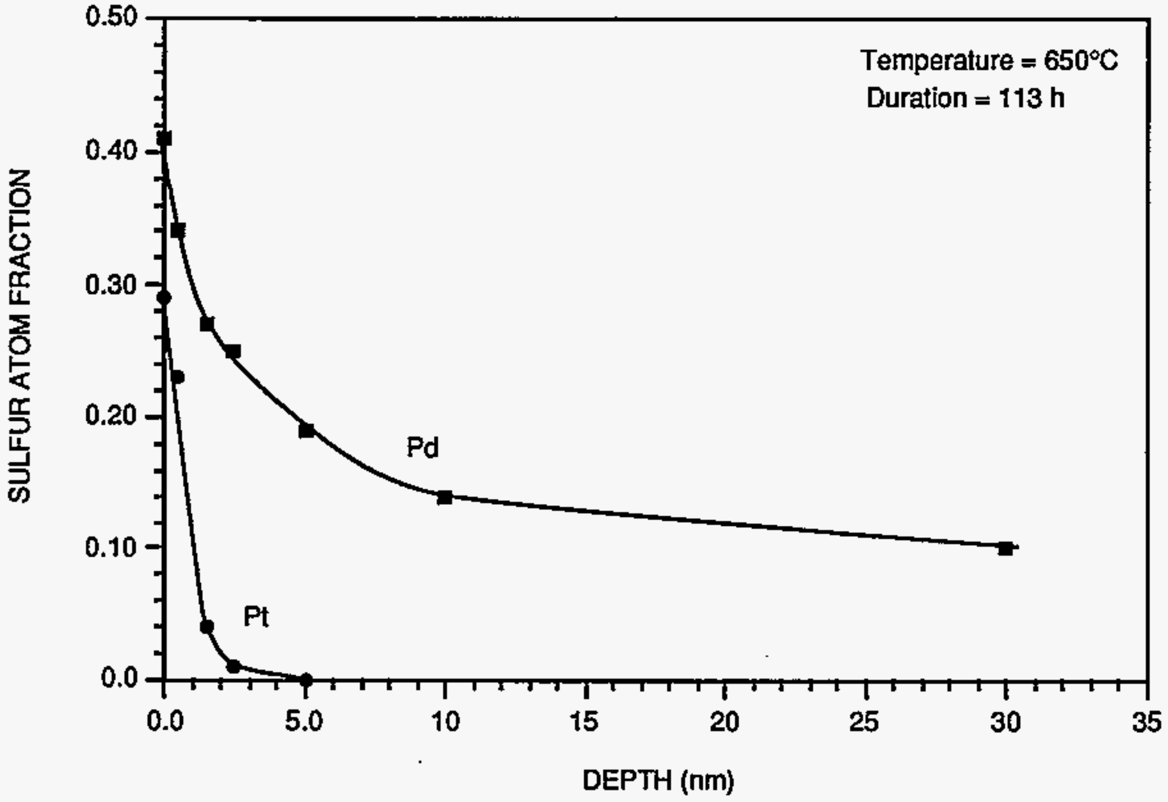


Figure III-6. Distribution of sulfur as a function of depth in the exposed Pt and Pd foils.

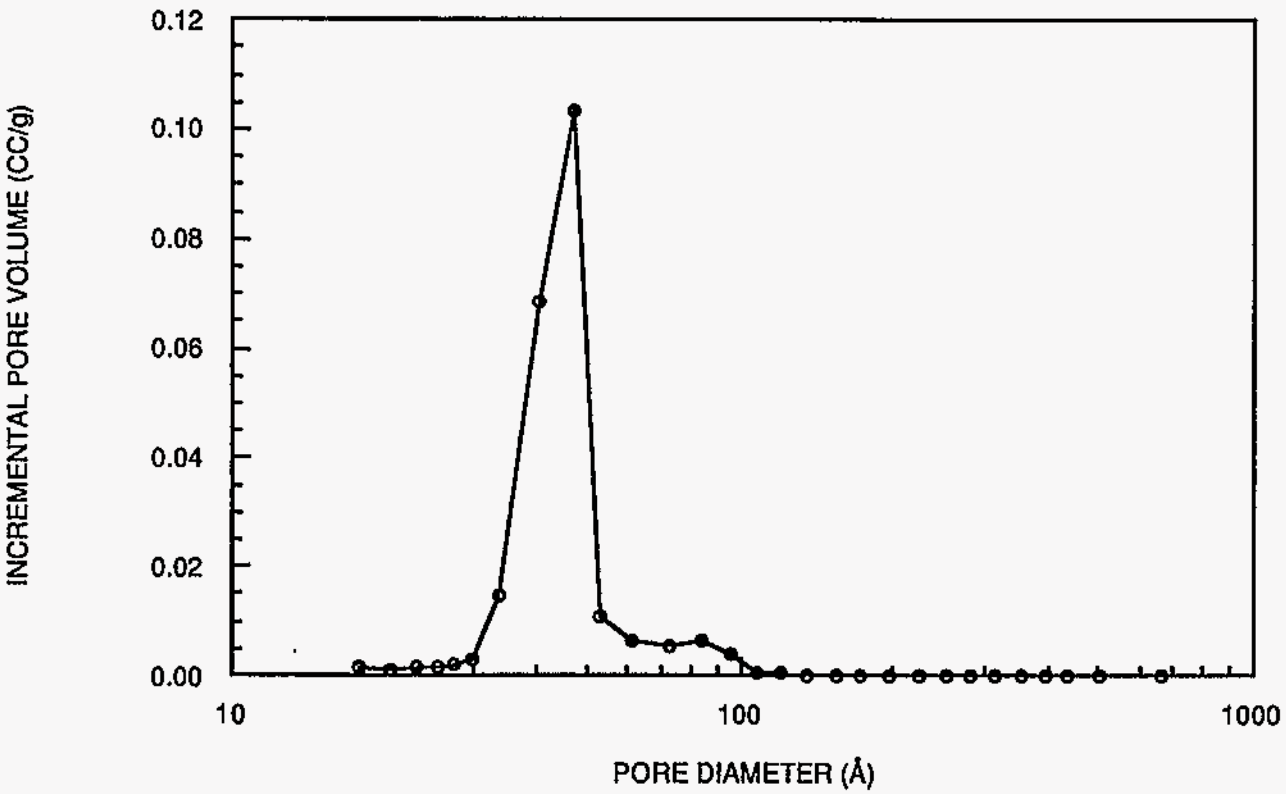


Figure III-7. Pore size distribution of a Vycor membrane coated with fly ash after exposure to 550°C and 1 atm for 410 h.

BET surface area analysis of alumina membrane samples indicated that their surface areas were reduced to about 0.4 and 0.8 m^2/g. As with Vycor samples, the ash coat on alumina membranes did not lead to increased degradation. EDAX analysis of the membrane sample coated with ash showed the presence of Na, Si, and S along with Al even though the sample was ultrasonically cleaned before this analysis. This observation indicates some interaction between alumina membrane and ash components.

Both palladium samples had become gray and very brittle, indicative of bulk sulfidation. AES analysis confirmed this condition, as sulfur was detected even after argon sputtering to a depth of 0.02 μm. Platinum samples with and without ash coat as well as both of the metal membrane foils provided by Bend Research, appeared unaffected by exposure. AES analysis of all four samples indicated adsorbed sulfur on the surface. The sulfur concentration decreased sharply with argon sputtering of the sample surfaces and it was negligibly small at depths greater than 5 nm.

Exposure Test 5

This test, conducted using coal gas at a pressure of 300 psig and a temperature of 450°C, lasted for 1020 h. One set of samples was coated with fly ash obtained from the GE fixed-bed gasifier. The test was interrupted at an elapsed time of 10 h because of an instrumental problem. Visual inspection of these samples with 10 h of exposure indicated that the palladium foils had become brittle and disintegrated. The platinum foil samples without the ash coat had become significantly bluish. AES analysis of these samples indicated deep surface sulfidation of the platinum foils. The surface penetration of the sulfur was estimated to be about 10 nm. A new set of samples without ash coat was then added to the previous two sets before resuming the exposure test.

All the platinum samples at the conclusion of 1020-h test had a strong bluish tinge (including those with the ash coat). Auger analysis and depth profiling of the platinum samples including the two samples coated with fly ash, indicated that sulfur layers were on the order of 30 nm thick (Figure III-8).

The Vycor membrane samples had turned brownish although they still appeared transparent without any indication of crystallization. BET analysis of all three Vycor samples indicated surface areas of 102±3 m^2/g, which represents almost 50% reduction in surface area. Coarsening of the pores to a mean diameter of about 60 Å was also observed (Figure III-9). The occurrence of pore enlargement, even at the relatively low temperature of 450°C, is significant for gas separation applications.

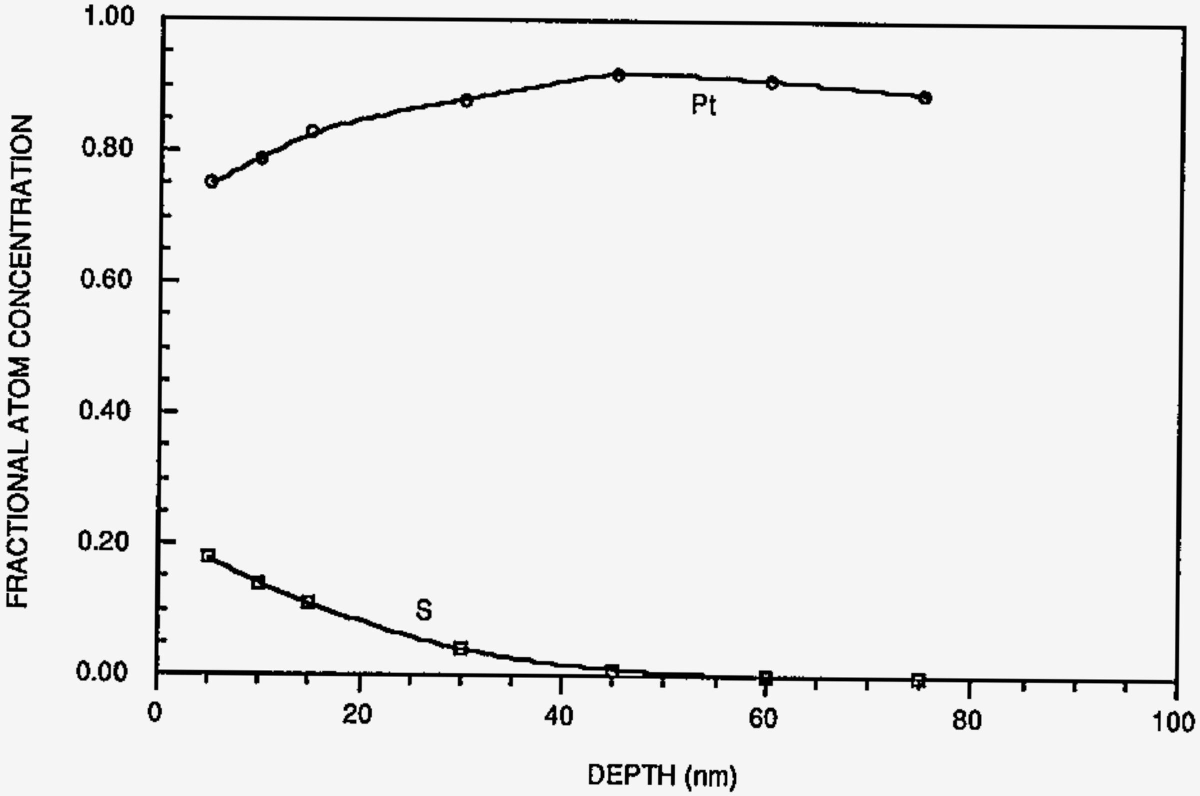


Figure III-8. The depth of sulfidation layer on a platinum sample exposed to a gas stream at 300 psig containing 1.5% H_2S at 450°C for 1020 h.

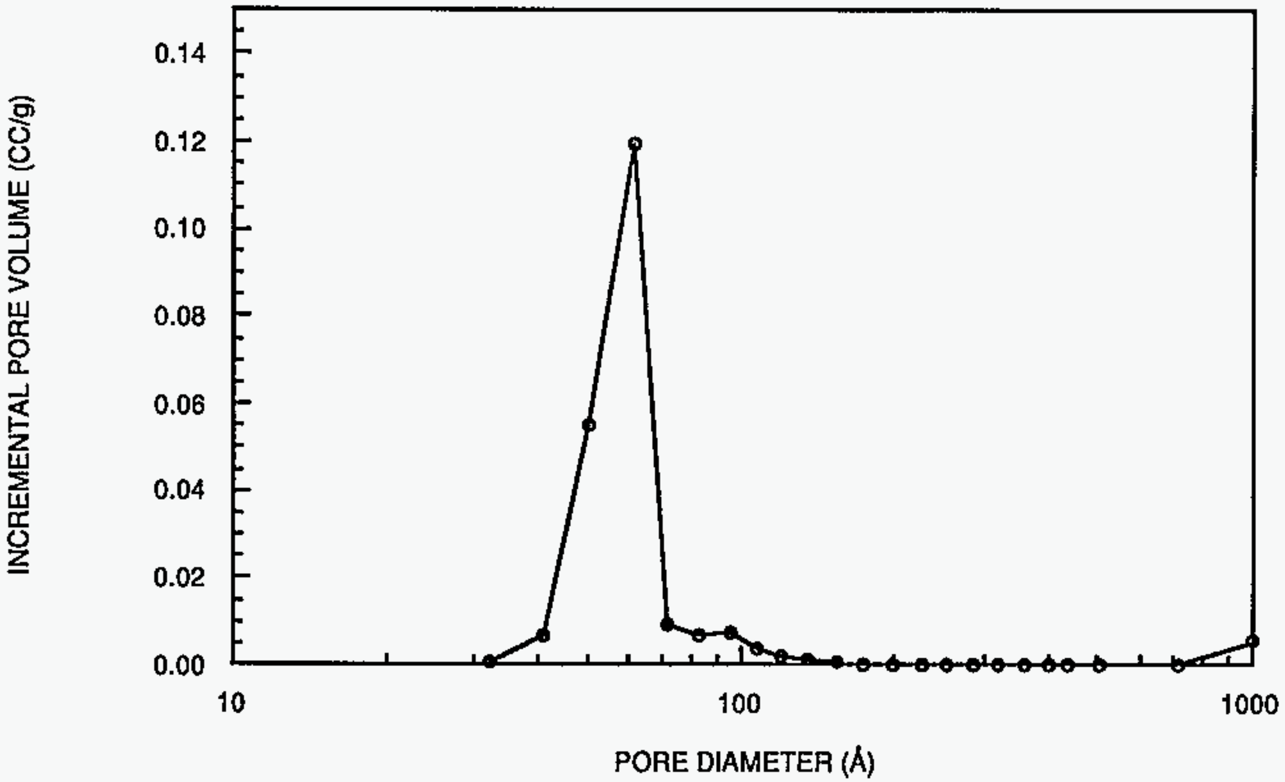


Figure III-9. Pore size distribution of a Vycor membrane after exposure to a simulated coal gas at 450°C and 300 psig for 1020 h.

The effect of pressure on the coarsening of pores in the Vycor membrane is apparent when the result from this test at 450°C and 300 psig is compared with the observation that the pores were enlarged only slightly (a mean pore diameter of 44 Å) when the membrane was exposed at 1 atm pressure at 550°C. Thus, high pressure steam accelerates the pore coarsening process in silica materials.

The alumina membrane samples appeared unaffected. But BET surface area analysis of the alumina samples without the ash coat indicated an almost 50% reduction in the surface area from 2.1 m^2/g to about 1 m^2/g. The surface area of the sample with the ash coat was about 1.4 m^2/g.

Exposure Test 6

This test conducted at a pressure of 270 psig and a temperature of 550°C, lasted for 500 h. One set of samples was again coated with fly ash obtained from the GE fixed-bed gasifier. The Vycor membrane samples turned brownish although they still appeared transparent without any visual indication of crystallization. BET surface area analysis of these Vycor samples indicated surface areas of 103 and 110 m^2/g, which represents an almost 50% reduction in surface area. The pore size analysis of these samples again indicated coarsening from 40 Å to about 60 Å (Figure III-10). The effect of high pressure on the enlargement of pores is apparent when the results from Exposure Test 5 are compared with these data.

The alumina membrane samples appeared unaffected. BET surface area analysis of the alumina samples without the ash coat indicated more than 50% reduction in the surface area from 2.1 m^2/g to about 0.9 m^2/g. As observed in Test 5, the surface area reduction was somewhat less for the sample with the ash coat. The pore size of one, short, 5-cm section of the alumina membrane tube exposed during this test was determined by the DPSM technique. The mean pore size of the exposed sample was found to be about 70 Å compared with a mean pore size of 40 Å for the unexposed membrane sample, as shown in Figures III-11 and III-12. This pore size measurement by the DPSM technique also establishes an approximate correlation between coarsening of the membrane pores and the reduction in surface area.

The AES analysis of both the platinum samples surprisingly indicated very little sulfur on the surface, even less than that observed during the atmospheric exposure test at the same temperature. Reasons for this finding were not clear. Oxidation of adsorbed

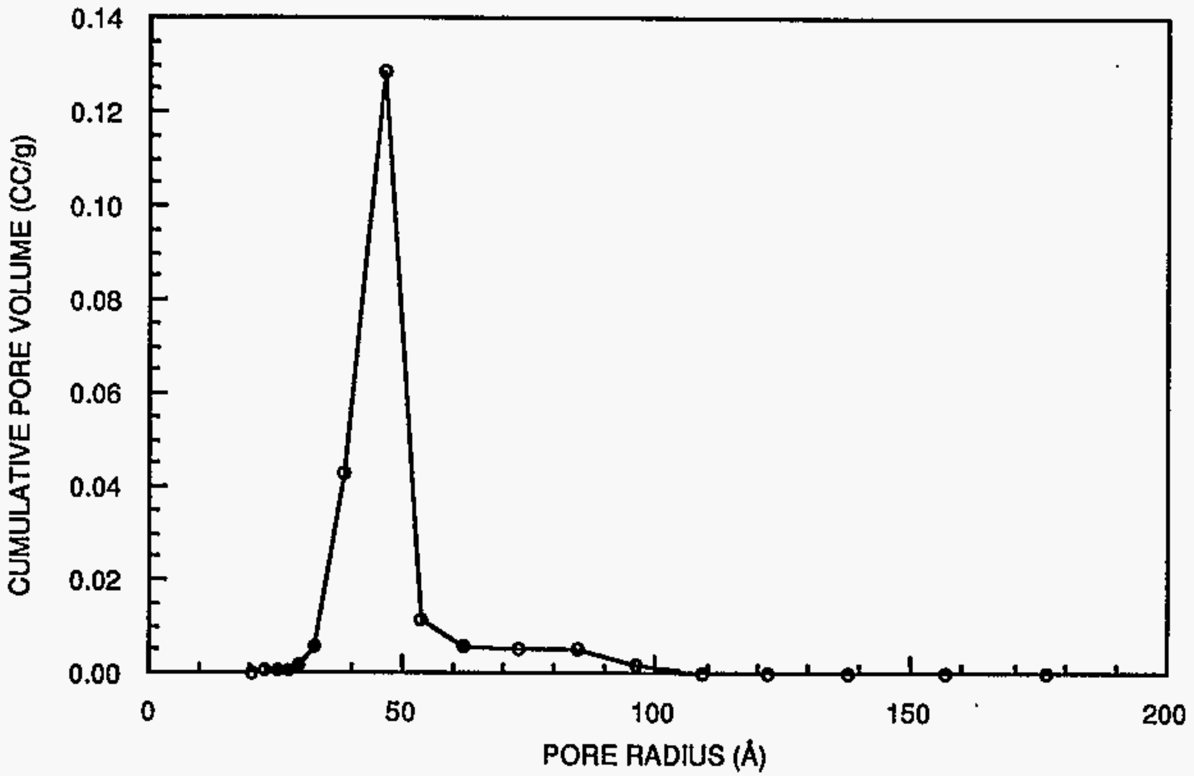


Figure III-10. Pore size distribution of a Vycor membrane after exposure to a simulated coal gas at 550°C and 270 psig for 500 h.

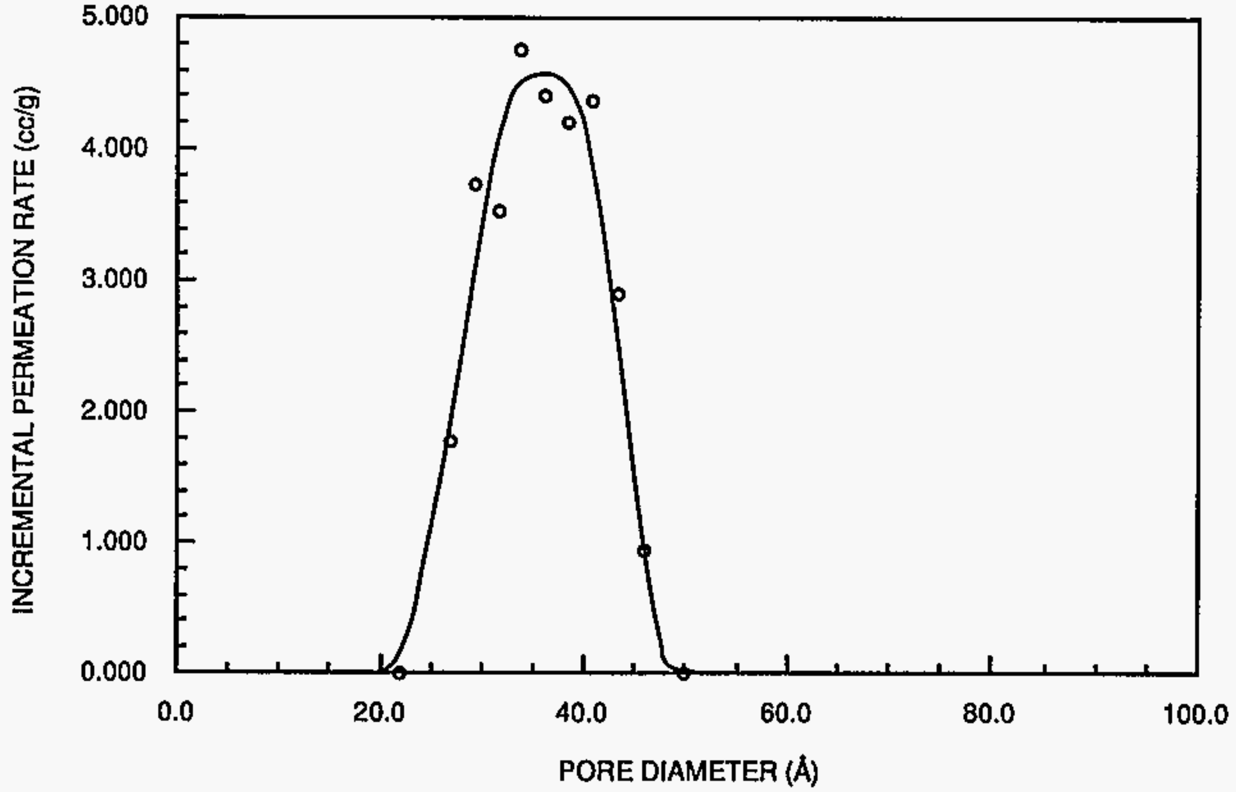


Figure III-11. Pore size distribution of an alumina memberane as determined by dynamic pore size measurement.

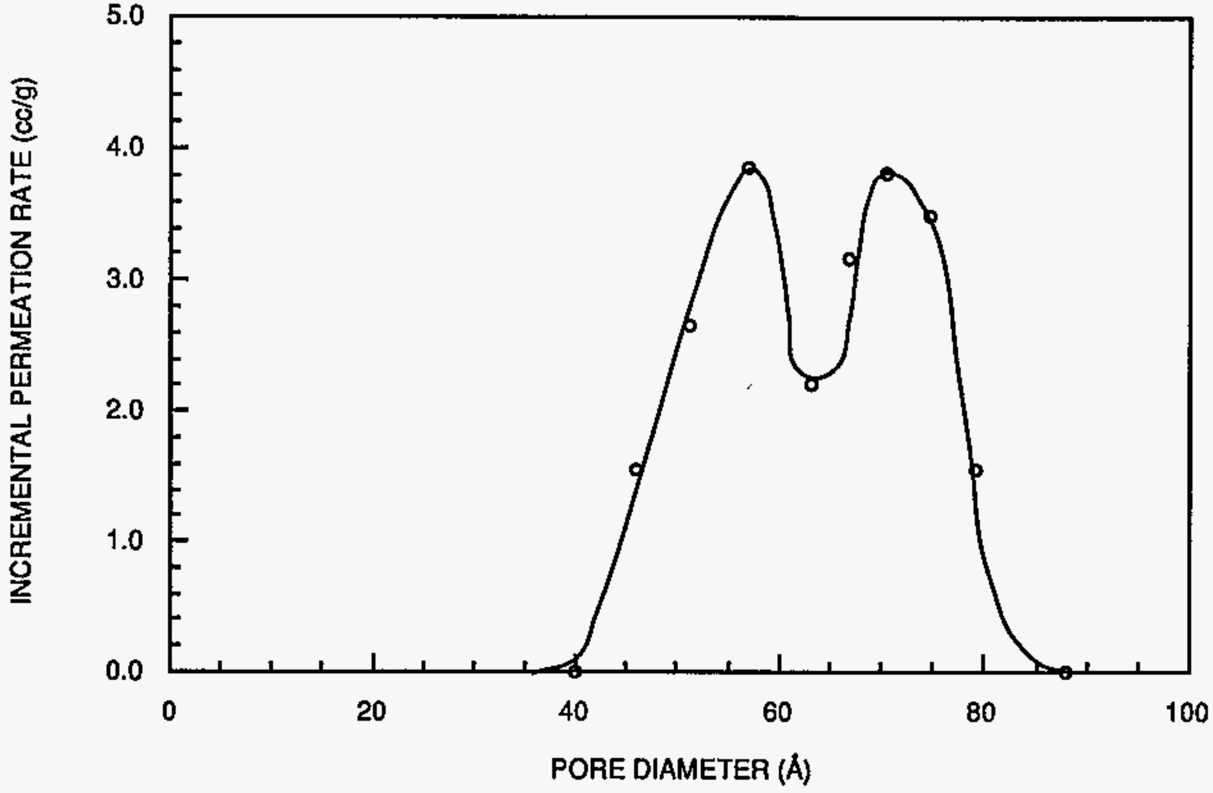


Figure III-12. Pore size distribution of a Membralox membrane after exposure at 550°C and 270 psig for 500 h.

sulfur during the withdrawal of the membrane samples before they were completely cooled is one possible explanation. Platinum is known for its good catalytic oxidation activity.

DISCUSSION

Tables III-6 and III-7 summarize the surface area and mean pore size of Vycor and alumina samples after various treatments. The pore size of the Vycor membrane samples increased significantly during high temperature and high pressure coal gas exposure. Exposure at 1000°C destroyed all the microporosity even at 1-atm pressure. Exposure at 800°C and 1-atm pressure was sufficient to increase the mean pore size from 40 to 120 Å, a result that would be unacceptable for gas separation applications. Even at 650°C, the increase in the mean pore size of Vycor membranes was noticeable after 100 h of exposure to simulated coal gas.

Table III-6
SURFACE AREA AND PORE SIZE OF EXPOSED VYCOR MEMBRANE SAMPLES

Exposure Temperature (°C)	Exposure Pressure (psig)	Exposure Duration (h)	Surface Area (m^2/gm)	Mean Pore Size (A°)
---	---	---	190.0	40.0
1000	0	24	1.9	1000
800	0	76	33.2	116.7
650	0	113	140.5	44.8
550	0	410	150.1	43.8
550 (ash coat)	0	410	160.8	44.0
450	300	1000	100.5	60.6
450 (ash coat)	300	1000	105.3	57.0
550	270	500	102.9	60.1
550 (ash coat)	270	500	109.6	58.2

Table III-7
SURFACE AREA OF EXPOSED ALUMINA MEMBRANE SAMPLES

Exposure Temperature (°C)	Exposure Pressure (psig)	Exposure Duration (h)	Surface Area (m^2/gm)
---	---	---	2.1
1000	0	24	1.26
800	0	76	0.43
650	0	113	0.88
550	0	410	0.37
550 (ash coat)	0	410	0.79
450	300	1000	1.0
450 (ash coat)	300	1000	1.48
550	270	500	0.94
550 (ash coat)	270	500	1.4

At temperatures lower than 650°C, the total pressure had a significant effect on the enlargement of pores. The increase in the mean pore size was modest at 550°C and 1 atm pressure. However, at high pressure the mean pore size increased to 60 Å, even at 450°C. The deleterious effect of coal gas on the relatively dense Vycor membranes containing 96% silica is significant also for the modified silica and alumina membranes, because the modifications are made by adding an amorphous silica layer. Agglomeration of this low density phase is expected to be even more pronounced than the Vycor because of the granular structure. The effect of gasifier ash at 450° and 550°C was negligible, presumably due to slow reaction kinetics between the two solid phases.

The surface area of the tested alumina samples decreased significantly at the tested conditions indicating coarsening of the 40 Å layer, which is the predominant contributor to the observed surface area. The DPSM technique indicated an increase in the mean pore size of the microporous layer from 40 to 70 Å after exposure to high pressure coal gas at 550°C. The results obtained in this investigation are consistent with those reported in the literature. Gallaher and Liu [1994] showed that heating at atmospheric pressure in dry N_2 at 640°C for 100 h did not change the pore size distribution significantly. But, heating in 5% H_2O-95% N_2 at 640°C for 120 h increased the average pore size from 37 to 49 Å. Increasing the steam concentration to 95%

enlarged the pores even further; after 100 h at 640°C, the average pore size increased from 38 to 65Å.

The evolution of sodium vapor from the alumina membranes at temperatures exceeding 650°C is likely to have a deleterious effect on the silica layer in the modified alumina membranes. Evolution of sodium vapor actually caused crystallization of the quartz glass of the exposure tube and the membrane supports. Similar transformations and loss of microporosity may happen to the gas separation layer of modified alumina membranes. At temperatures below 550°C, the interaction between gasifier fly ash and alumina membranes is negligible, presumably due to slow reaction kinetics between the two solid phases.

H_2S present in the coal gas deposits an adlayer of sulfur on the surface of platinum membranes. The extent of sulfidation depends on the partial pressure of H_2S and the temperature. High H_2S partial pressure and low temperature increase the thickness of the sulfur adlayer. At an operating pressure of 300 psig, extensive sulfidation, up to a thickness of 20 nm, could be expected at 450°C. However, at the recommended operating temperature of 700°C the adsorbed sulfur layer would likely be less than 5 nm. The presence of sulfur on the platinum surface reduces hydrogen permeability. Coatings of gasifier ash did not significantly affect the surface sulfidation of the membranes. All exposed palladium samples degraded extensively at all exposure conditions because of bulk sulfidation by H_2S in the coal gas. Thus, palladium is not a suitable membrane material in a direct contact with coal gas.

IV. MEMBRANE PERMEATION TESTS

The objective of membrane permeation tests was to determine changes in the long term permeation characteristics under controlled, realistic, IGCC conditions. Specifically, changes in membrane permeation and selectivity characteristics were determined as a function of time for a variety of experimental conditions. The permeation data were used to identify key operating variables leading to loss of performance. Because of their relatively large pore size (40 Å), Membralox alumina and Vycor membranes could not provide practical gas separations in the high pressure coal gas environments. Hence, only the modified membranes were used in the permeation tests. These included four modified-alumina membranes supplied by Media and Process Technologies Inc., and three modified-Vycor membranes provided by Dr. Gavalas's laboratory at CalTech. Permeation tests were conducted in a high temperature, high pressure (HTHP) tubular membrane test apparatus. The permeation performance of 25-µm-thick platinum foils supplied by Bend Research Inc. was determined in an HTHP disc membrane test apparatus.

EXPERIMENTAL APPARATUS

Tubular Membrane Test System

Figure IV-1 is a schematic diagram of the test apparatus used for long term permeation testing of the tubular membranes. The test system consisted of a gas mixing and delivery manifold, a steam generator, a controlled temperature furnace, a gas chromatograph (GC) system equipped with gas sampling valves, and a computer that commands the GC system to take samples and logs GC data automatically. The gas delivery system provided multicomponent feed and sweep gases. Premixed dry gas in cylinders provided a simulated coal gas of a constant composition. Pure helium, nitrogen, and hydrogen from cylinders were used for both pure component and mixed gas permeation tests. The steam generation system consisted of a high pressure, positive displacement pump that injected water at a selected rate into a controlled- temperature evaporator. A 40-cm long tubular furnace capable of operating at temperatures up to 1200°C controlled the temperature of the membrane samples.

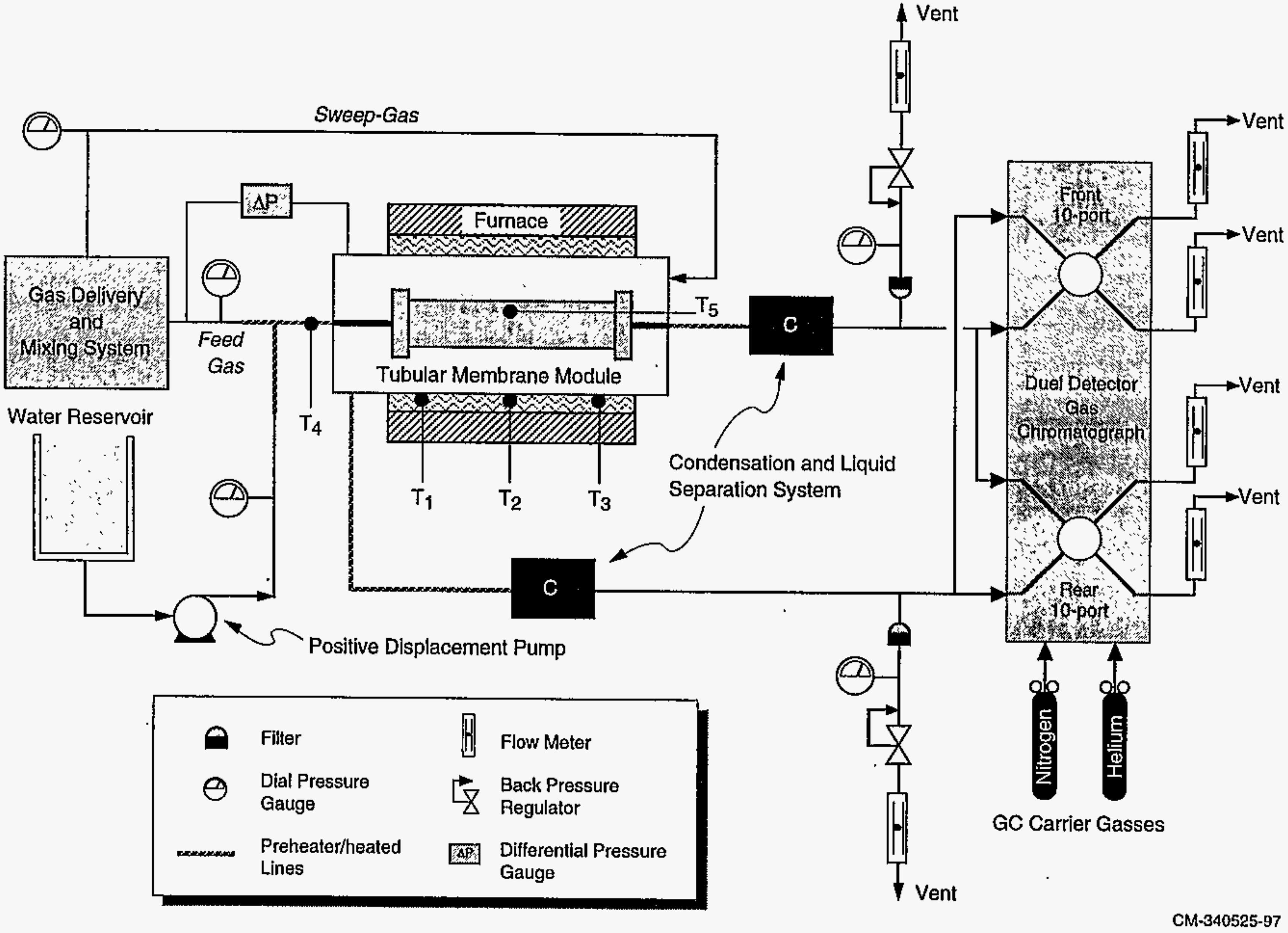


Figure IV-1. Testing apparatus for membrane modules.

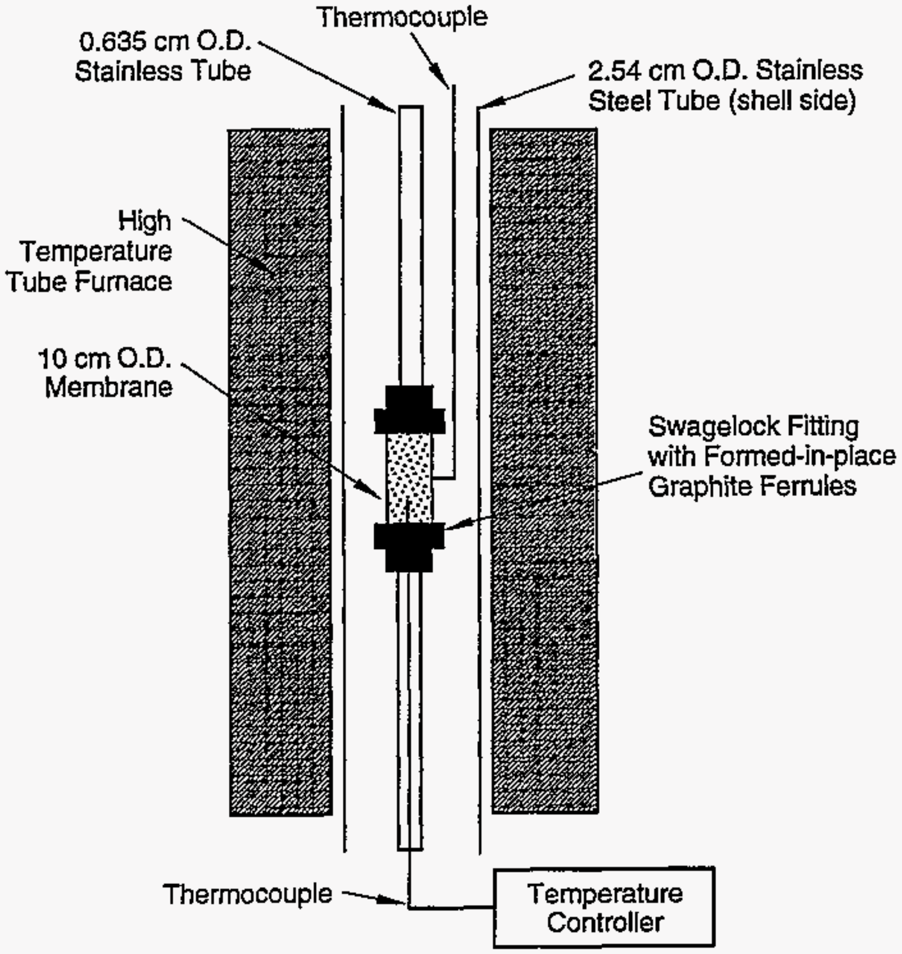
Both the feed exhaust and permeate gases were passed through condensers to remove steam and through filters to remove any particulate matter. Back pressure regulators (BPRs) controlled the feed and permeate side pressures at the desired levels. The GC samples were drawn from both the raffinate and permeate lines. Because the permeation rates were usually small and permeate side pressure was at near 1 atm, all of the permeate flow was often sent to the GC sampling line by shutting off the permeate BPR.

A cylindrical membrane housing module was fabricated for both the modified alumina and Vycor membranes (Figure IV-2). The short (7.5-cm long) modified-Vycor membrane central section was fused to nonporous-quartz tube ends effectively extending the length of the tubular membranes to 53 cm. This arrangement allowed the Viton elastomer seals to be placed outside the furnace at a relatively low temperature while maintaining the membrane section at a high temperature. The 25-cm long modified-alumina membranes were sealed by in-place-formed graphite ferrules, which provided satisfactory seals up to 700°C in the reducing or inert test atmospheres used during all of the permeation tests.

The HTHP membrane test system operated satisfactorily at up to a pressure of 300 psig and a temperature of 800°C. Two ten-port sampling valves were used to sample both the permeate and raffinate streams. Two GC columns were required to analyze all of the typical components of the coal gas mixture: H_2, N_2, CO, CO_2, and H_2S. One column with nitrogen carrier was used for H_2 analysis; the other column with helium carrier was used to analyze all other components. The GC data were collected and processed directly by a dedicated microcomputer.

Disc Membrane Test System

Figure IV-3 is a schematic diagram of the apparatus used for testing platinum foil discs. A muffle furnace (15-cm in diameter by 60-cm deep) was used to provide a constant temperature oven for the membrane module. The gas delivery manifold and the steam generator were similar to those in the tubular membrane test system. The hydrogen permeation rate was measured by a soap bubble flowmeter. The membrane module was provided by Bend Research Inc. It consisted of two alloy steel flanges, one with a 0.75 inch cylindrical cavity at its center with gas inlet and outlet lines, and the other with a metal frit in the center to collect permeate. Graphite gaskets sealed the periphery of the platinum foil disc between stainless steel flanges. The permeate side flange contained a



NOTE: The ends of the 1/4" and 1" tubes go into compression fittings to connect the permeability apparatus to the tube and sweep side gas plumbing lines.

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Figure IV-2. Shell and tube test apparatus for permeation tests.

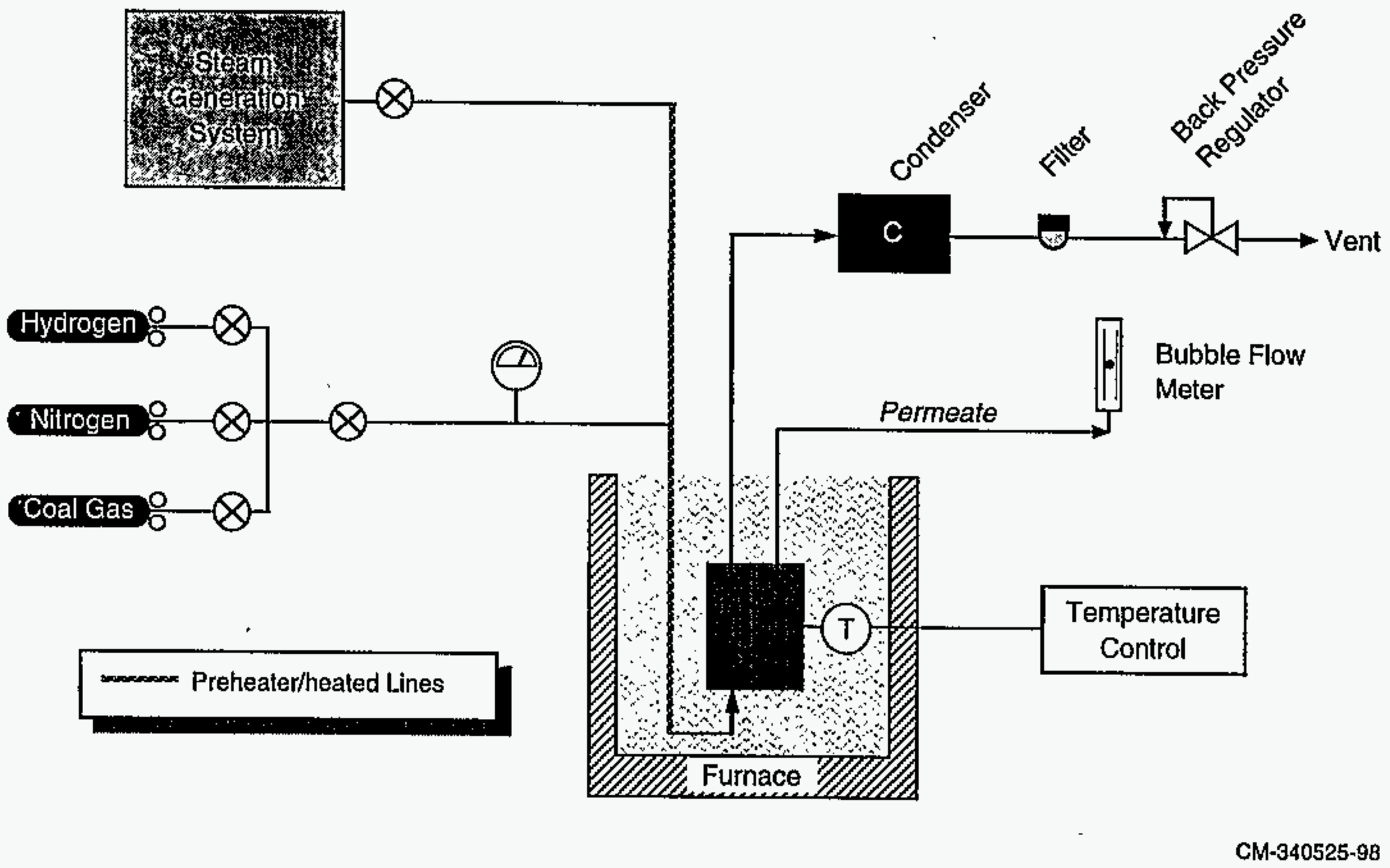

Figure IV-3. Schematic of disc membrane test system.

stainless steel frit that provided mechanical support for the foil while allowing passage of permeate gas. Before determining the hydrogen permeation rate, the membrane module was leak tested by pressurizing the feed side of the heated module with nitrogen.

MODIFIED ALUMINA MEMBRANE TESTS

Pure component and mixed gas permeation tests were conducted with four alumina membranes (Si521, Si522, Si547, and Si550) modified by MPT by depositing a nanoporous silica layer on the gamma-alumina microporous layer. The results of tests on each membrane are discussed below.

Si521 Modified Membrane

Permeation tests were conducted with a simulated coal gas feed (mixture 1, Table III-2). The membrane separation characteristics were determined at 25°C and 100°C respectively with 100 psig pressure on the feed side of the membrane and without added steam. The permeate side was at atmospheric pressure with no sweep gas. The H_2/N_2 selectivity was fabout 1.4 at 25°C and about 2.4 at 100°C, with nitrogen permeance of about 0.02 m^3/m^2-h-atm.

The membrane was exposed to a simulated coal gas containing 30% (v/v) steam at 100 psig in the temperature range 300° to 500°C. At 300°C, the observed H_2/N_2 selectivity was about 6.4 with a N_2 permeance of 0.01 m^3/m^2-h-atm. At 550°C, the H_2/N_2 selectivity was about 5.2 with a N_2 permeance of 0.02 m^3/m^2-h-atm. Table IV-1 summarizes the mixed gas permeation results obtained with Si521 membrane at different temperatures. After the mixed gas testing at 550°C in the presence of steam, the pure component N_2 permeance at 25°C had increased significantly from the original value of 0.02 m^3/m^2-h-atm to 0.04 m^3/m^2-h-atm.

Si522 Modified Membrane

Pure component permeance data were first obtained with nitrogen and helium at temperatures from 25° to 600°C. As shown in Table IV-2, the nitrogen permeance decreased with increasing temperature, whereas helium permeance increased with increasing temperature. As a result of these changes, the pure component He/N_2 selectivity increased from 3 at 25°C to 39 at 600°C.

Table IV-1
PERMEATION RESULTS -- Si521 MEMBRANE MIXED GAS TESTS

Temperature (°C)	Permeance m^3/m^2-h-atm N_2	H_2	H_2/N_2 Selectivity
25	0.019	0.027	1.4
110	0.016	0.038	2.4
300	0.011	0.069	6.4
550	0.017	0.09	5.2
25*	0.044	—	—

* After exposure to coal gas at 300 and 550°C in presence of 30% steam in coal gas at 100 psig feed pressure for 10 h.

Table IV-2
PURE COMPONENT PERMEABILITIES OF NITROGEN AND HELIUM WITH Si522 MEMBRANE AT THE BEGINNING AND AT THE END OF THE TEST PERIOD

	N_2 Permeance (m^3/m^2-h-atm)		He Permeance (m^3/m^2-h-atm)		He/N_2 Selectivity	
Temperature (°C)	Initial	End[1]	Initial	End[1]	Initial	End[1]
25	0.045	0.11	0.14	0.21	3.1	1.9
140	0.038	0.089	0.3	0.25	7.9	2.8
300	0.031	0.073	0.71	0.41	22.9	5.6
450	0.03	0.065	0.92	0.65	30.7	10
600	0.027	0.055	1.06	0.46	39.3	8.4

[1] After exposure for 20 h in the presence of steam at 500°C.

Mixed gas permeation tests were conducted next with a feed gas containing 9.7% N_2, 10.4% CO_2 and balance helium. At 600°C and 100 psig feed pressure, the He/N_2 selectivity was about 12.3 with helium and nitrogen permeances of 0.36 and 0.03 m^3/m^2-h-atm respectively. At 520°C with 20% steam in the feed gas, the He/N_2 selectivity was 13.7, with helium and nitrogen permeances of 0.47 and 0.03 m^3/m^2-h-atm respectively. With 30% steam at the same temperature, the He/N_2 selectivity decreased to 8.5 with helium and nitrogen permeances of 0.49 and 0.06 m^3/m^2-h-atm respectively. After the exposure to steam, a mixed gas permeation test with no steam at 600°C showed an increase in the helium and nitrogen permeances (0.45 and 0.05 m^3/m^2-h-atm respectively) and a decrease in helium to nitrogen selectivity (9.6).

A mixed gas permeation test was then conducted using coal gas with 30% steam as a feed gas at 100 psig feed pressure and 500°C. The observed H_2/N_2 selectivity was about 3.1 with nitrogen permeance of 0.07 m^3/m^2-h-atm. Finally, pure component permeation experiments were repeated with helium and nitrogen to determine the change in membrane performance as a result of exposure to high temperature and steam in the mixed gas permeation tests. Table IV-2 summarizes the results, which indicate an increase in the nitrogen permeability and a decrease in the helium permeability. As a result, pure component He/N_2 selectivity decreased substantially compared to initial values. The cumulative membrane exposure to temperatures greater than 500°C was about 35 h with about 20 of those h were in the presence of steam at 500°C.

The observed helium permeabilities with both Si521 and Si522 membranes were substantially lower than those measured by MPT with the same membranes prior to shipping. The expected H_2/N_2 selectivity based upon information provided by MPT, was about 4.4 at 24°C with a nitrogen permeance of 0.04 m^3/m^2-h-atm for the Si521 membrane. In comparison, the present results indicate that at 25°C, the H_2/N_2 selectivity was 1.4 and the nitrogen permeance was 0.02 m^3/m^2-h-atm for the same membrane. Similar decreases in selectivity and permeance were also observed with the Si522 membrane. These differences may be attributable to a ten-week storage in the laboratory before testing at SRI during which period absorption of moisture may have altered the silica layer.

Si547 Modified Membrane

Pure component permeation tests were first conducted with helium and nitrogen gases at temperatures up to 600°C. As shown in Table IV-3, the nitrogen permeance decreased with increasing temperature from 0.08 m^3/m^2-h-atm at 25°C to 0.034m^3/m^2-h-atm at 600°C. However, helium permeance increased from 0.25 to 7.7 m^3/m^2-h-atm as the temperature was increased from 25° to 600°C. As a result, the pure component He/N_2 selectivity increased from 3 to 227. These results were consistent with those obtained by MPT with this membrane.

Table IV-3
PERMEATION RESULTS — SI547 MEMBRANE

Temperature (°C)	Steam (%)	Permeance m^3/m^2-h-atm Helium	Permeance m^3/m^2-h-atm Nitrogen	Selectivity P_{He}/P_{N_2}
Pure Component Permeation Tests				
25	—	0.25	0.079	3.2
150	—	1.7	0.049	34.7
300	—	3.8	0.044	86.4
450	—	5.7	0.038	150.0
600	—	7.7	0.034	226.5
Mixed Gas Tests				
300	0	2.3	0.05	45.8
600	0	2.5	0.045	58.3
600[1]	20	2.2	0.035	63.0
600[2]	20	2.8	0.34	8.3
Pure Component Permeation Test after Mixed Gas Tests				
25[3]	—	1.5	0.62	2.4

[1] 1 h after starting steam

[2] 5 h after starting steam

[3] After 5 h exposure to 20% steam at 600°C, 100 psig total pressure

Following testing with pure gases, mixed gas permeation tests were performed with a feed gas containing 9.7% N_2, 10.4% CO_2 and balance helium. At 300°C and 100 psig feed pressure, the He/N_2 selectivity was calculated to be about 45.8 with helium and nitrogen permeances of 2.3 and 0.05 m^3/m^2-h-atm respectively. Because of the large stage cut of 80% in this experiment, the calculated helium permeability and selectivity values are significantly lower than the true values. At 600°C and 100 psig feed pressure, the He/N_2 selectivity was calculated to be about 58 with helium and nitrogen permeances of 2.5 and 0.045 m^3/m^2-h-atm respectively.

The effect of steam on the membrane performance was determined at 600°C by exposing to a feed gas containing 20% steam. The permeate and residual gas compositions were monitored for about 5 h. Initially, the results were comparable with those obtained under dry conditions with calculated helium and nitrogen permeances of

2.2 and 0.04 m^3/m^2-h-atm and He/N_2 selectivity of 63. However, both the nitrogen and CO_2 concentrations increased steadily in the permeate gas after about 2 h. After about 4 h, the helium and nitrogen permeances increased to 2.8 and 0.34 m^3/m^2-h-atm respectively with a corresponding He/N_2 selectivity of 8.3. Subsequent pure component permeation measurements at 25°C indicated that the helium and nitrogen permeances were to 1.5 and 0.62 m^3/m^2-h-atm respectively corresponding to a pure component selectivity of only 2.4. These results represent a substantial increase in permeation rates as compared to the earlier measurements, confirming the alteration of the size-selective layer made of silica during exposure to steam.

The DPSM technique was used to determine the pore size distribution of the Si547 membrane after the mixed gas permeation tests in the presence of steam. Although the selectivity of the exposed Si547 membrane had decreased substantially compared to the fresh membrane, the pore size distribution of the exposed membrane was still too small to be measured adequately by the DPSM system. The smallest pore diameter that can reasonably be measured by a DPSM system is about 1.5 nm. The present results confirm that for a porous membrane to be gas species-selective, the pore size of the gas separation layer must be substantially smaller than 1.5 nm. Analysis of similar freshly prepared membranes by MPT also indicated that the pore size distribution of the gas separation layer of modified alumina membranes was too low to be measured by a DPSM system [Lin et al., 1994].

Si550 Modified Membrane

Pure component permeation tests were first conducted with helium and nitrogen gases at temperatures up to 600°C. As shown in Table IV-4, the nitrogen permeances were in the range of 0.02 to 0.04 m^3/m^2-h-atm, whereas, helium permeance was found to increase from 0.07 to 10.2 m^3/m^2-h-atm as the temperature was increased from 25° to 600°C. As a result, the pure component He/N_2 selectivity increased from 2.4 to 251 as the temperature was increased from 25° to 600°C. These results were consistent with those obtained by MPT with this membrane.

Table IV-4
PURE COMPONENT PERMEATION RESULTS — SI550 MEMBRANE

Temperature (°C)	Permeance m^3/m^2-h-atm Nitrogen	Permeance m^3/m^2-h-atm Helium	Helium/Nitrogen Selectivity
25	0.03	0.073	2.44
110	0.025	0.32	13.0
300	0.024	3.75	158.0
450	0.029	5.73	200.1
600	0.041	10.17	250.77
600[1]	0.27	2.82	10.43
450[2]	0.16	1.46	9.0
450[3]	0.94	3.33	3.54
25[4]	0.26	0.58	2.22

[1] After exposure to 20% steam at 100 psig and 450° to 600°C for 17 h

[2] After an additional 3 h of exposure to 20% steam at 100 psig and 600°C

[3] After an additional 5 h of exposure to 20% steam at 100 psig and 450°C

[4] After an additional 5 h of exposure to 20% steam at 100 psig and 450°C

Mixed gas permeation tests were conducted next under dry conditions at 600° and 450°C with two different feed gas mixtures, one containing 9.7% N_2, 10.4% CO_2, and the balance helium, and the other containing 52.4% helium with the balance nitrogen. At 100 psig feed pressures, the He/N_2 selectivity under these dry conditions ranged from 64 to 86 with helium and nitrogen permeance in the range of 3 and 0.04 m^3/m^2-h-atm respectively. Because of the large stage cuts, the calculated helium permeance and He/N_2 selectivity values are lower than the pure component values.

In a test with the feed gas containing 20% steam at 450°C and 100 psig, the He/N_2 selectivity decreased steadily from 86 to 27 over a 10-h period (Table IV-5). The helium permeance decreased from 3.1 to 2.1 m^3/m^2-h-atm, whereas the nitrogen permeance increased from 0.04 to 0.08 m^3/m^2-h-atm. Additional 3 h of exposure at 550°C and 7 h of exposure at 600°C decreased the He/N_2 selectivity further to about 15.

The pure component nitrogen permeance at 450°C increased by a factor of 5 after a total of 20 h of exposure to 20% steam at 100 psig at a temperatures from 450° to 600°C (Table IV-4).

Table IV-5
MIXED GAS PERMEATION RESULTS — SI550 MEMBRANE

Temperature (°C)	Steam (%)	Total Exposure to Steam (hrs)	Permeance m^3/m^2-h-atm Nitrogen	Permeance m^3/m^2-h-atm Helium	Selectivity He/N_2
600	0	0	0.042	2.71	64
450	0	0	0.036	3.1	86.1
450	20	2	0.073	3.96	54.1
450	20	4	0.075	3.63	48.3
450	20	5	0.04	1.7	42.6
450	20	8	0.076	2.03	26.6
550	20	10	0.078	3.51	45.3
550	20	13	0.047	2.11	45.2
600	0	13	0.054	2.78	51.8
600	20	14	0.059	2.17	36.7
600	20	15	0.088	2.44	27.8
600	20	16	0.124	2.49	20.1
600	20	17	0.188	2.61	13.9
600	20	20	0.228	3.47	15.2
450	0	20	0.18	1.61	8.9
450	20	22	0.41	2.02	4.9
450	20	23	0.61	2.6	4.3
450	20	24	0.76	2.96	3.9
450	20	25	0.96	2.94	3.1
450	20	26	0.94	3.01	3.2
450	20	28	1.84	4.99	2.7
450	0	30	0.95	3.0	3.1

Further decrease in He/N_2 selectivity was observed when the membrane continued to be exposed to a mixed gas containing 42% He, 42% N_2, and 18% steam at 450°C and 100 psig. After 10 h of exposure, the He/N_2 selectivity decreased to about 3.1 with helium and nitrogen permeances of about 3 and 0.95 m^3/m^2-h-atm. The pure component He and N_2 permeances measured at 25°C after a total steam exposure of 30 h were about an order of magnitude higher than those found originally (Table IV-4). After exposure to steam, the He/N_2 selectivity decreased dramatically, for example from 200 to 4 at 450°C and 250 to 10 at 600°C.

MODIFIED VYCOR MEMBRANE TESTS

Pure component and mixed gas permeation tests were conducted with three modified Vycor membranes. Commercially available Vycor glass membranes with 40 Å pore size were modified to prepare these membranes. The pores were effectively constricted by depositing a thin, nonporous, SiO_2 layer within the membrane cross-section by chemical vapor deposition. Two techniques based upon alternating CVD were used to prepare these membranes. The results of tests for each membrane are discussed below.

Modified Vycor Membrane #1

At 25°C and a pressure difference of 100 psi across the membrane, the pure component N_2 flow was less than 0.1 cm^3/min. Under these conditions, the pure component helium flow was only 2.9 cc/min corresponding to a permeance of 0.027 cm^3/cm^2-min-atm. The temperature was then raised slowly to 150°C. Again, no pure component nitrogen flow could be measured, while helium permeance increased to about 0.14 cm^3/cm^2-min-atm. A mixed gas permeation test was conducted at this temperature with a feed gas containing 9.74% N_2, 10.4% CO_2 and balance helium. No CO_2 was detected in the permeate upon sampling by a gas chromatograph. Because of the very small gas permeation rate, a decreasing concentration of nitrogen was detected by the GC caused by the initial presence of nitrogen on the permeate side. Similar results were obtained upon raising the temperature slowly to 300°C, at which point the helium permeance increased to 0.24 cm^3/cm^2-min-atm.

However, upon slowly raising the temperature to 450°C, substantial concentrations of N_2 and CO_2 were detected by GC in the permeate sample. The calculated helium and nitrogen permeances were about 0.79 and 0.37 cm^3/cm^2-min-atm respectively with a He/N_2 selectivity of only 2.14. Pure component nitrogen flow tests confirmed that below 350°C no nitrogen flow (< 0.1 cm^3/min) could be detected, whereas, at 400°C and above a measurable nitrogen flow was observed. At first, a leak was suspected in the viton o-ring fittings which were at a temperature much lower than the porous membrane section. A nonporous quartz tube of identical length and diameter was then installed in the same membrane module with the same o-ring fittings. No measurable nitrogen or helium flow could be detected upon raising the membrane temperature to 650°C. The porous membrane tube was then reinstalled and it reproduced the same permeation behavior observed earlier. Thus, the nitrogen permeation breakthrough observed at about 400°C must be real. In the Caltech laboratory, the same membrane had hydrogen and nitrogen permeances of 0.3 and 0.0001 cm^3/cm^2-min-atm respectively at 500°C.

Modified Vycor Membrane #2

This membrane was first heated gradually in nitrogen to 500°C. Again, no nitrogen flow was observed below 400°C. At 400°C, a small flow rate of nitrogen was detected initially with a permeance of 0.04 cm^3/cm^2-min-atm, which increased to about 0.16 cm^3/cm^2-min-atm. Pure component helium permeances were measured as a function of temperature and were found to be about 0.4 cm^3/cm^2-min-atm at room temperature and about 0.6 cm^3/cm^2-min-atm at temperatures greater than 400°C. Between 400° to 600°C the permeance was actually found to decrease slightly from 0.64 to 0.6 cm^3/cm^2-min-atm.

Mixed gas permeation tests were next conducted with this membrane at room temperature and at 450°C using a mixed gas containing 9.74% N_2, 10.4% CO_2 and balance helium. The observed helium and nitrogen permeances in the room temperature tests were 0.36 and 0.025 cm^3/cm^2-min-atm respectively with helium to nitrogen selectivity of about 15. At 450°C, the observed helium and nitrogen permeances were 0.6 and 0.032 m^3/cm^2-min-atm respectively with a He/N_2 selectivity of about 19. The helium permeances observed in the mixed gas test were similar to those obtained in the pure component tests, whereas, the observed N_2 and CO_2 concentrations in the permeate in the mixed gas test at room temperature were somewhat surprising. A leak test was then conducted with a nonporous quartz tube as mentioned before, which again indicated no measurable pure component helium or nitrogen flow for temperatures up to 650°C. In the Caltech laboratory, the same membrane had hydrogen and nitrogen permeances of 0.65 and 0.0005 cm^3/cm^2-min-atm respectively at 500°C.

Both Membranes #1 and #2 had helium permeances similar to those measured in the Caltech laboratory. However, the performances differed significantly for nitrogen permeation. Membrane #1 appeared to be impermeable to nitrogen up to about 350°C with a sudden increase in nitrogen permeability at higher temperatures. No such sudden change in nitrogen behavior was observed with Membrane #2. However, a small nitrogen permeability was observed in the mixed gas test (which is more sensitive than a pure component test due to GC sampling), even at room temperature.

Modified Vycor Membrane #3

Table IV-6 shows pure component helium and nitrogen permeabilities measured during gradual heating of the membrane from 25 to 600°C over a three-day period. The He/N_2 was about 100 at temperatures greater than 300°C. Mixed gas permeation tests conducted at 100 psig using 50% He:50% N_2 feed gas at 400°, 500°, and 600°C indicated He/N_2 selectivities of 97, 134, and 158 respectively.

Table IV-6
PURE COMPONENT PERMEATION
RESULTS — MODIFIED VYCOR MEMBRANE #3

Temperature (°C)	Permeance cm³/cm²-min-atm		Helium to Nitrogen Selectivity
	Nitrogen	Helium	
25	0.0043	0.124	28.7
165	0.0059	0.443	74.6
300	0.005	0.484	96.9
400	0.0041	0.465	112.7
600	0.0046	0.447	97.4
450[1]	0.071	0.448	6.28
450[2]	0.141	0.477	3.39
600[2]	0.127	0.448	3.54
600[3]	0.142	0.441	3.12

[1] After exposure to 25% steam at 100 psig and 450°C for 6 h.

[2] After an additional 5 h of exposure to 25% steam at 100 psig and 450°C.

[3] After an additional 4 h of exposure to 25% steam at 100 psig and 600°C.

Continued permeation experiments at 100 psig and 450°C with a feed gas containing 40% He, 40% N_2, and 20% steam showed a decrease in the He/N_2 selectivity from about 80 to 6 in about 6 h (Table IV-7). During this period, nitrogen permeance increased continuously from 0.006 to 0.11 cm^3/cm^2-min-atm. An additional 6 h of exposure to the same feed gas at 450°C and 100 psig reduced the He/N_2 selectivity further from 6 to 3.5 with an increased nitrogen permeance of 0.16 cm^3/cm^2-min-atm. Pure component helium and nitrogen permeances measured after 6 and 12 h of steam exposures are also shown in Table IV-6.

The pore size and surface area measurements of the modified membrane after these permeation tests indicated coarsening of the Vycor membrane substrate pores from 40 to 46 Å with a reduction in the surface area from 189 to 163 m^2/g (Figures IV-4 and IV-5). Thus, even a small increase in the pore size of the parent Vycor material appears to cause a dramatic decrease in the selectivity of the modified membranes. Pure component hydrogen permeances were slightly greater than those of helium.

Table IV-7
MIXED GAS PERMEATION RESULTS — MODIFIED VYCOR MEMBRANE #3

Temperature (°C)	Steam (%)	Total Exposure to Steam (h)	Permeance m^3/m^2-h-atm Nitrogen	 Helium	Selectivity He/N_2
400	0	0	0.0056	0.542	96.8
500	0	0	0.0034	0.523	134.1
600	0	0	0.0032	0.507	158.4
600	0	0	0.0063	0.517	82.06
450	20	1	0.0127	0.53	41.73
450	20	2	0.0283	0.66	23.32
450	20	3	0.0373	0.744	19.95
450	20	4	0.0752	0.713	9.48
450	20	5	0.0981	0.66	6.73
450	20	6	0.1096	0.636	5.80
450	0	6	0.081	0.5	6.15
450	20	7	0.111	0.674	6.07
450	20	8	0.118	0.659	5.58
450	20	9	0.121	0.652	5.39
450	20	10	0.157	0.585	3.73
450	20	11	0.163	0.574	3.52

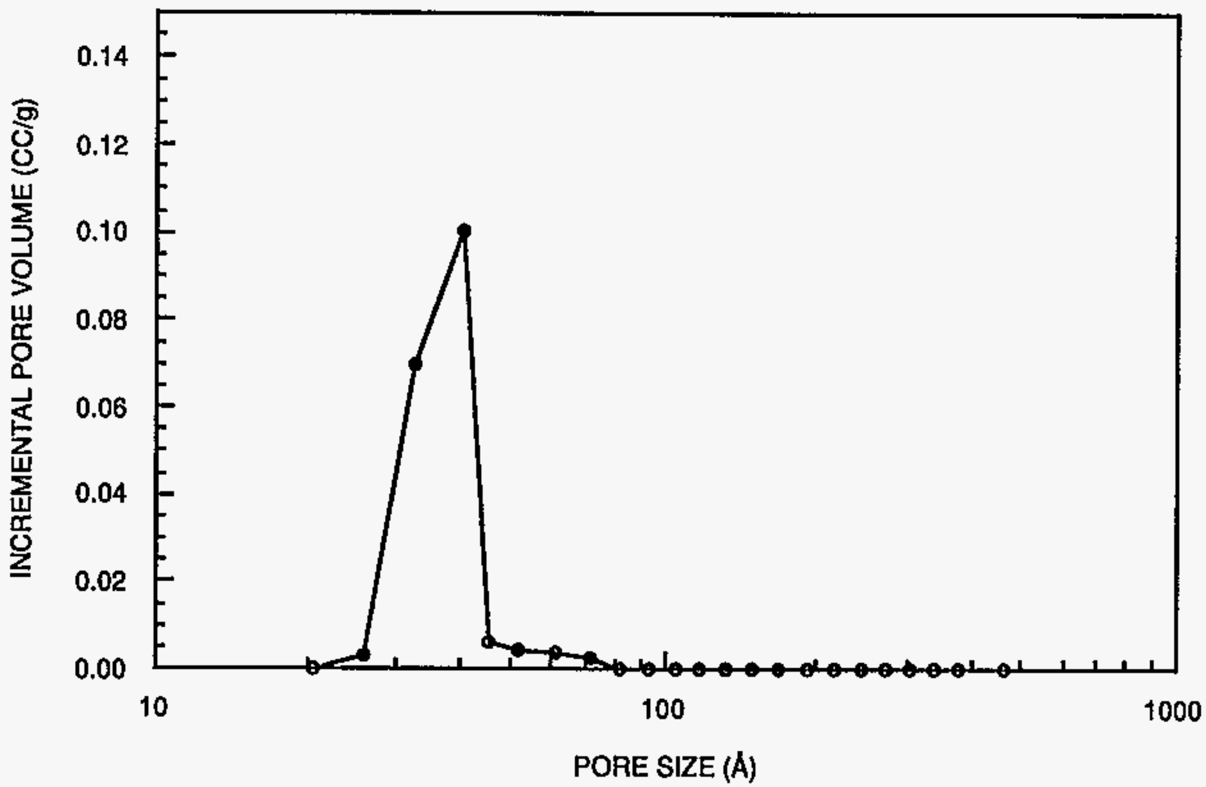

Figure IV-4. Pore size distribution of a modified Vycor membrane after heating to 600°C.

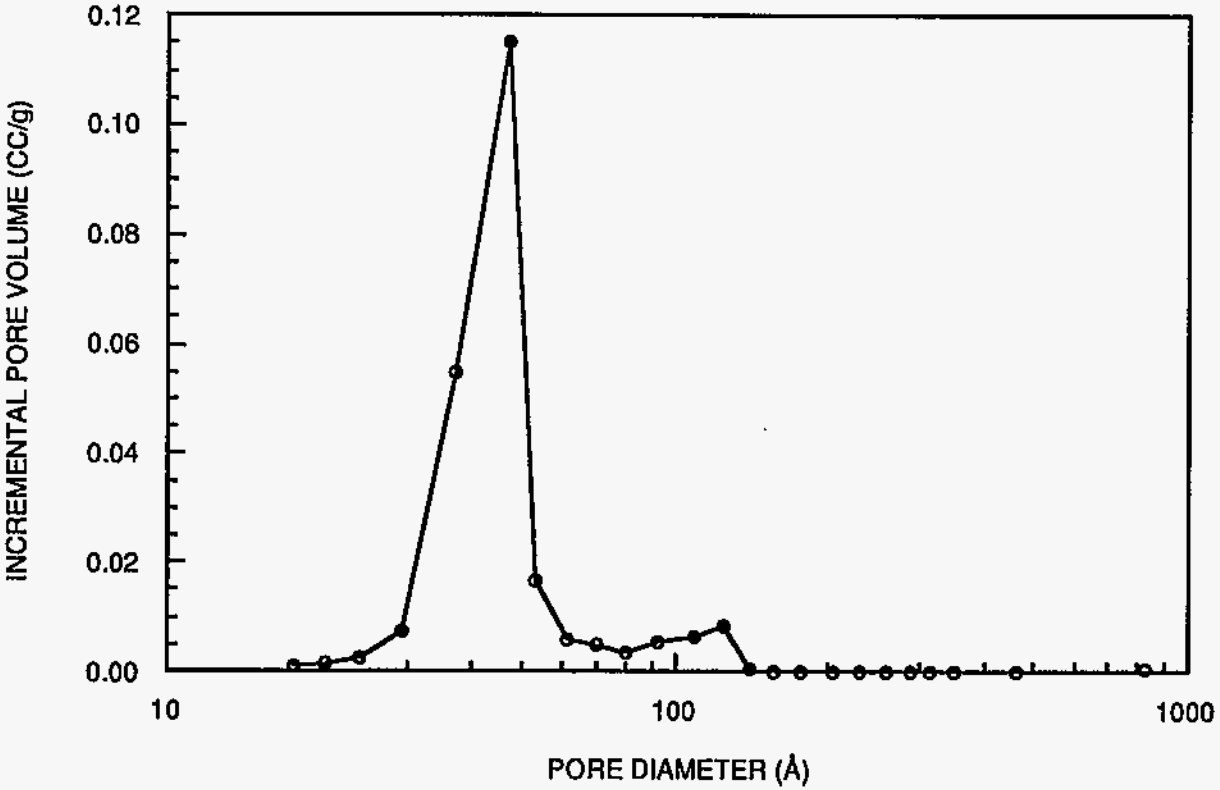

Figure IV-5. Pore size distribution of a modified Vycor membrane after exposure to steam at 600°C.

PLATINUM FOIL PERMEATION TESTS

Two different types of tests were performed to determine the permeation characteristics of 25 μm platinum foils. In the first test, fresh platinum foil was exposed to a simulated coal gas at 700°C and the rate of hydrogen permeation was determined. In the second test, a platinum foil was exposed to simulated coal gas at 550°C and 270 psig pressure for 500 h and subsequently, hydrogen permeance was determined using pure hydrogen as feed gas.

Unexposed Foil

Tables IV-8 and IV-9 show the data collected with two unexposed foils. Due to carbon burnout and the resultant leakage at the graphite ferrules and seals, this duration of this experiment was only 24 h. A simulated coal gas containing 20% hydrogen and 1.2% H_2S, and 20% steam was used in both tests. Initial pressure tests with nitrogen assured that the module was leak-free. The temperature was raised to 700°C in flowing nitrogen before adding steam and eventually switching to the simulated coal gas mixture. The initial hydrogen permeance was 0.02 cm^3/cm^2-min-atm. After about 5 h, the hydrogen permeance was measured to be about 0.014 cm^3/cm^2-min-atm, indicating about a 36% reduction. The hydrogen permeance at 700°C remained steady at 0.014 cm^3/cm^2-min-atm, indicating a stable hydrogen permeance was achieved during the last 17 h of this test.

500-h Exposed Foil

The hydrogen permeation rate through a platinum foil previously exposed to simulated coal gas containing 1.2% H_2S at 550°C and 270 psig for 500 h was determined as a function of time using pure hydrogen as feed gas at 115 psig pressure and 700°C. Figure IV-6 shows the calculated hydrogen permeances . Initially, the hydrogen permeance was only 0.006 cm^3/cm^2-min-atm, substantially less than that of the unexposed sample. However, in the pure hydrogen environment, the permeance increased slowly to 0.024 cm^3/cm^2-min-atm, in about 1 h and then leveled off. This behavior can be attributed to the removal of an adsorbed sulfur layer by reaction with the pure hydrogen feed gas. The results of these experiments show that hydrogen permeation decreases rapidly during the initial few h but may remain steady after this initial decrease. In the absence of H_2S in the coal gas stream, the adsorbed sulfur layer responsible for the degradation can be removed and the original permeation rate can be restored.

Table IV-8
HYDROGEN PERMEATION THROUGH A PLATINUM FOIL — UNEXPOSED FOIL #1

Exposure Time to Coal Gas (hrs)	Feed Pressure (psig)	Permeation Rate (cc/min)	Hydrogen Permeance cm^3/cm^2-min-atm
1	160	0.14	0.022
2	240	0.21	0.022
5	160	0.09	0.014
22	160	0.09	0.014

Temperature - 700°C
Hydrogen in coal gas - 25% (dry)
Hydrogen in coal gas with 25% steam - 18.8% (wet)
Platinum foil thickness - 25 µm

Table IV-9
HYDROGEN PERMEATION THROUGH A PLATINUM FOIL — UNEXPOSED FOIL #2

Exposure Time (h)	Feed Gas	Feed Pressure (psig)	Permeation Rate (cc/min)	H_2 Permeance cm^3/cm^2-min-atm
1	Coal gas with 25% steam	150	0.13	0.0217
1.5	Hydrogen with 25% steam	80	0.265	0.0192
2	Hydrogen (dry)	80	0.37	0.0202
3	Coal gas with 25% steam	250	0.216	0.0224
18	Coal gas with 25% steam	250	0.153	0.0159
19	Hydrogen (dry)	80	0.185	0.01

Temperature - 700°C
Hydrogen in coal gas - 25% (dry)
Hydrogen in coal gas with 25% steam - 18.8% (wet)
Platinum foil thickness - 25 µm

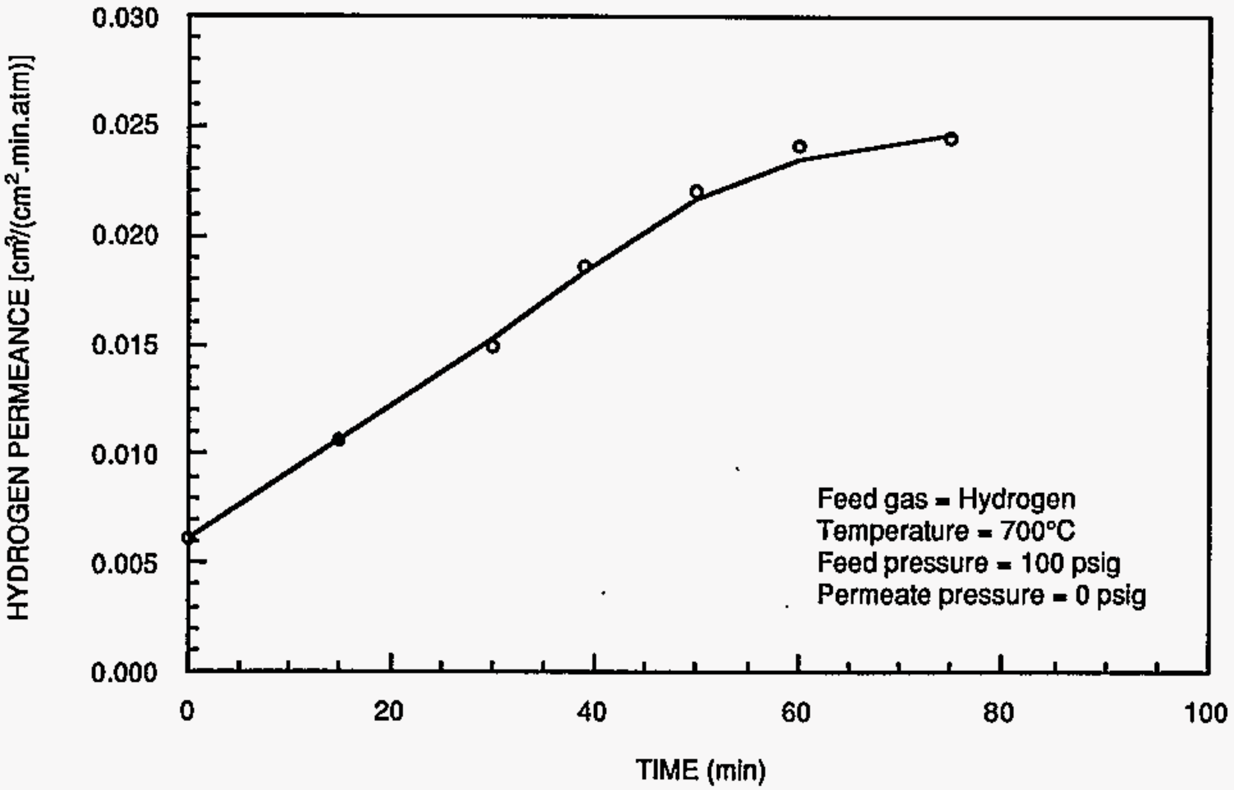

Figure IV-6. Hydrogen permeation through a platinum membrane after exposure to a simulated coal gas at 550°C and 270 psig for 500 h.

DISCUSSION

The results of the permeation testing indicate that modified alumina membranes degrade in a few hours in the presence of a feedgas containing 20% steam at 100 psig at temperatures exceeding 450°C. Wu et al. [1994] reported that silica modified alumina membranes have excellent thermal stability in dry N_2 streams, but degrade when the membranes were exposed at 600°C to a nitrogen gas stream containing 20% steam at 1 atm pressure. In the presence of steam, the permeances of both He and N_2 decreased. The activation energy for He permeance increased while that for N_2 decreased after the hydrothermal treatment. They hypothesized that the SiO_2 may have densified in the presence of steam resulting in a reduced porosity. During densification microcracks could have formed due to shrinkage. Because the nitrogen flow occurred through the relatively large opening of the microcracks, the activation energy for nitrogen flow could be low. But, diffusion of He through the dense silica layer would require higher activation energy than through micropores.

In the tests conducted in this program, the membranes were exposed to steam at elevated pressures that could accelerate the densification of SiO_2 layer and lead to extensive microcrack formation. The increased nitrogen permeation could indicate either pore coarsening or development of cracks in the gas separation layer of the membrane. DPSM showed no significant enlargement in pores in the range 1.5 to 50 nm in size. Hence, microcracks must have been developed resulting in increased N_2 and reduced He/N_2 selectivity.

Similarly, the He/N_2 permeance ratio of the modified Vycor membrane decreased from 160 to 3.5 upon exposure for 15 h at 100 psig and 450°C to a gas mixture containing 25% steam. Again, a significant increase in the nitrogen permeance was the main cause for the loss of selectivity. Long-term exposure studies show that pores 40 Å in size could grow to 60 Å in size at this temperature. The pores responsible for gas separation are significantly smaller than 40 Å and they were formed by deposition of an amorphous SiO_2 layer. Its small size make this layer thermodynamically unstable and prone to grain growth resulting in pore enlargement. As expected, these processes are accelerated in the presence of steam at elevated temperatures and pressures. In a relatively short time, changes in the pore size occur that result in gas selectivities similar to those expected from unmodified Vycor membranes. Continued exposure to coal gas streams may degrade the gas selectivity even further.

The results observed in this program contradicts the results reported by Kim and Gavalas [1995]. They reported that an exposure of modified Vycor membranes to a gas containing 70% N_2 and 30% steam at 500°C and 10 atm pressure for 21 days did not result in increased N_2 permeation although hydrogen transport decreased after the exposure. These results indicate that densification continues to occur in the SiO_2 layer during hydrothermal treatment. However, if microcraks occur because of atomic movement in the substrate Vycor during the exposure, then nitrogen flow across the membrane will increase. The enlargement of pores from the initial size of 40 to 60Å in the tests conducted at SRI suggests development of microcracks. It is likely that the membranes were pretreated differently at CalTech and SRI and it may account for the disparity in the behavior of the modified Vycor membranes.

The permeation of H_2 through platinum foils at 700°C decreases in the presence of H_2S, a common contaminant in hot coal gas streams. The permeation rate decreases further if the membrane is exposed to the H_2S-containing stream at temperatures lower than 700°C, but the poisoning effect is modest and reversible.

V. COAL GASIFIER EXPOSURE TEST

Conditions representative of coal gasifiers or combustors can be simulated only to a limited extent in a laboratory. Hence, the candidate inorganic membrane samples were exposed in a pressurized fixed-bed gasifier located at the General Electric Corporate Research and Development Center (GE-CRDC) at Schenectady.

FIXED BED GASIFIER FACILITY

Fixed-bed gasification involves counter-current contacting of lump coal with air or oxygen and steam. The coal is introduced at the top of the gasifier and, as it moves slowly downwards, enters first the devolatilization, then the gasification and finally combustion zones. Ash is withdrawn at the bottom through a rotating grate. The steam-to-air is adjusted to control temperatures in the combustion zone, so that the ash can be discharged as a lightly sintered product.

The GE gasifier vessel consists of a cylindrical shell that is 5 ft in diameter and 24 ft high with 1-inch thick walls and hemispherical end caps of 285 Grade C steel. The shell is protected from the high temperatures of the gasification process by two layers of castable refractory materials. The GE gasifier facility operates normally in the air-blown mode at about 300 psig and 480° to 540°C. High pressure air is supplied by one of two 800-hp, 3-stage inter-cooled and after-cooled Worthington compressors. The compressors can deliver 8 lbm/s of air at 300 psig. Steam is provided at 400 psig at saturated conditions (232°C) by a natural gas-fired steam generator capable of delivering up to 1.4 lbm/s. The product gas, which comes off the top of the fixed bed, is relatively cool compared to that of fluidized- and entrained-bed gasifiers, but it contains tars, oils, and fine unreacted coal.

The product gas is first passed through a single-stage primary cyclone equipped with a dust-removal lockhopper system to remove the bulk of the entrained fly ash, then through a zinc oxide-based sorbent bed (absorber) to remove hydrogen sulfide from the fuel gas. The fuel gas exiting the absorber is passed through a secondary cyclone prior to combustion in a gas turbine. Two sets of membrane samples were inserted in the ductwork for exposure studies. The first set was situated in the primary cyclone outlet gas stream upstream of the absorber unit. The second set was located at the secondary cyclone outlet gas stream downstream of the absorber. The membrane samples, mounted on stainless steel rods, were inserted in process piping "tees" with the membrane samples facing the gas flow. The membrane samples themselves were mounted on support plates that were welded in a spoke-wheel fashion to a stainless steel rod, which in turn was welded to a 4 inch stainless steel flange. The membrane samples were secured between the support plates and clamping plates by bolts as well as by a loop of stainless steel wire (Figure V1).

GASIFIER EXPOSURE CONDITIONS.

Two sets of membrane samples were exposed during a gasifier run conducted in March 1995. Illinois #6 bituminous coal was used as feedstock during this run at a feed rate of 1500 lbs/h producing coal gas at a nominal rate of 1.5 lbs/sec. The sulfur content of this coal was 1.66%. Short Vycor and alumina (Membralox) membrane samples were exposed at both locations along with platinum foil samples. At the secondary cyclone outlet location, a 10-inch long modified-alumina membrane sample, Si522, was also exposed to the gas stream. The overall duration of the exposure was 48 h, with an average gas stream pressure of 280 psig at the exposure locations. The exposure temperature at both locations was about 510°C during the steady-state periods. The samples at the primary cyclone exit were completely covered by a thick crusty layer of ash. The samples at the secondary cyclone outlet location were also coated with a substantial amount of ash, although the samples were recognizable as shown in the photographs (Figures V-2 and V-3). The particulate loading at the primary cyclone sampling location was approximately 100 ppmw, whereas that at the secondary cyclone location was 50 ppmw. Analysis of the primary cyclone ash indicated about 86 wt% unburnt carbon.

ANALYSIS OF EXPOSED MEMBRANE SAMPLES

Almost all membrane samples were broken, apparently due to impingement of abrasive dust at high gas velocities. All the Vycor membrane samples had turned black, apparently due to deposition and absorption of tar vapors. The 40 Å microporous layer of the alumina membrane had also turned black for a similar reason. At the primary cyclone outlet, most of the platinum samples were found to be sheared off from the support plates because of the abrasive dust. However, at the secondary cyclone outlet location, fragments of two platinum samples were recovered. All the recovered samples were washed ultrasonically in distilled water to remove embedded ash particles. The Vycor and alumina samples remained black, confirming absorption of organic and tar vapors.

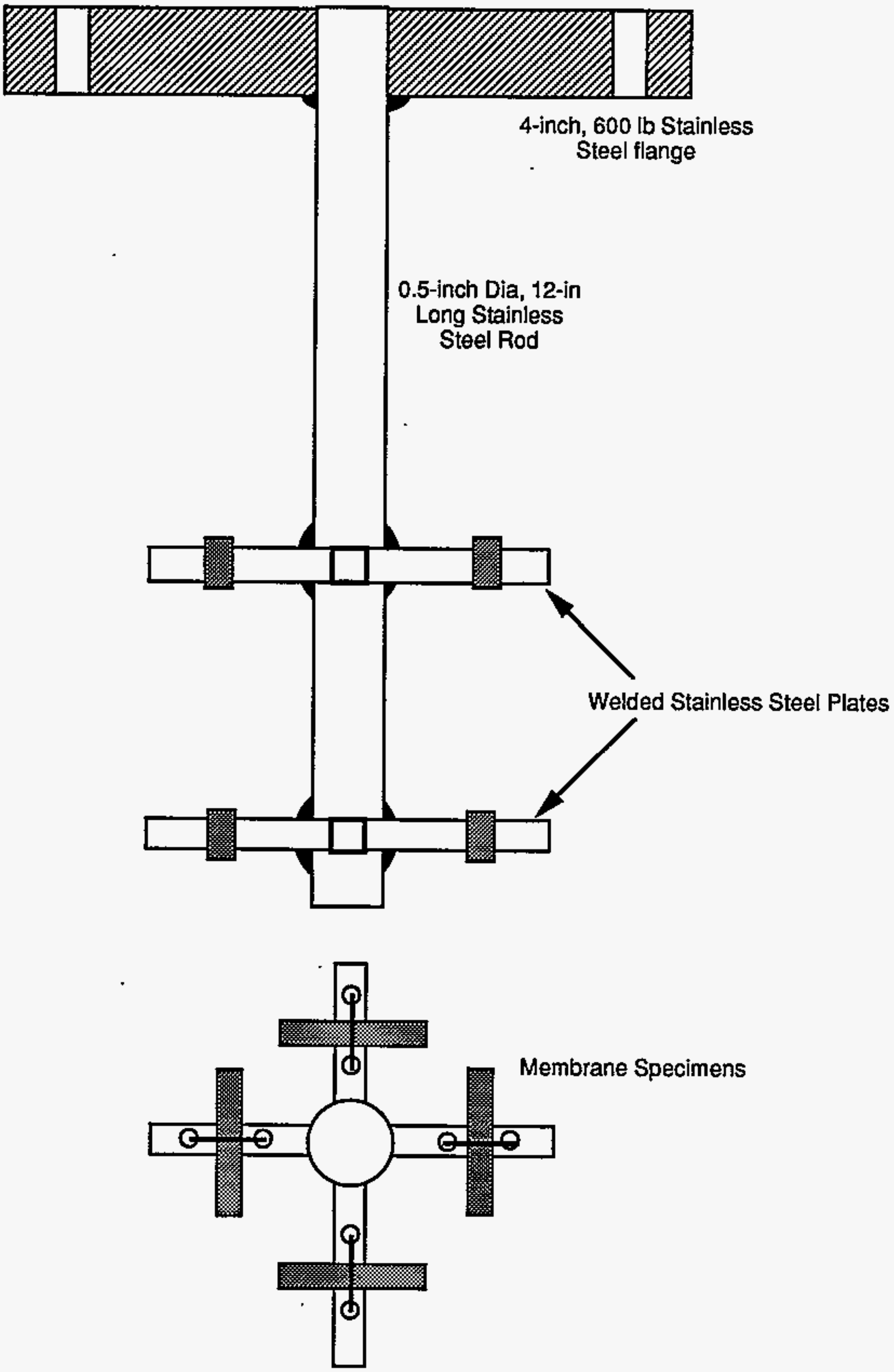

Figure V-1. Schematic diagram of the membrane mounting assembly for coal gasifier exposure.

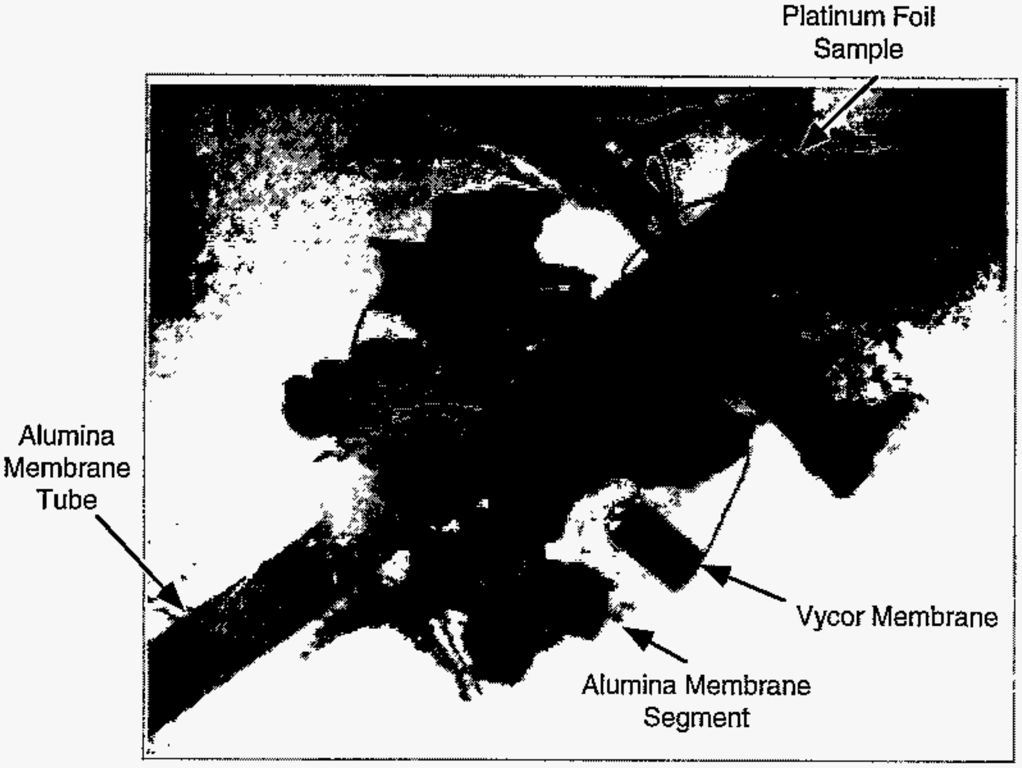

Figure V-2. Photograph of membrane samples exposed at the GE gasifier facility downstream of the secondary cyclone.

Figure V-3. Photograph of membrane samples exposed at the GE gasifier facility downstream of the primary cyclone.

BET analysis of the alumina membrane samples indicated that the surface areas were substantially reduced when compared with the unexposed samples. Samples at the primary cyclone outlet location had surface areas of 0.6 m^2/g, whereas those at the secondary cyclone outlet were about 0.9 m^2/g. These values correspond to a nearly 60% reduction in surface area. The dynamic pore size measurement of the exposed Si522 membrane failed to reveal any microporosity. The nitrogen flow rate through the membrane did not decrease significantly upon increasing the hexane vapor concentration almost to the saturation level (when all pores smaller than 50 nm would be blocked by a condensate layer) suggesting that the observed gas flow was primarily through cracks in the membrane. The pure nitrogen flow rate was also nearly four times lower than that for the Si547 membrane before exposure in the gasifier, suggesting blockage of micropores by ash or tar.

The Vycor membrane samples also showed significant reduction in the surface area and coarsening of the pores. A sample exposed at the primary cyclone outlet exhibited surface area reduction from 190 to 87.6 m^2/g with a mean pore size increasing from 40 to 62.8 Å. A sample exposed at the secondary cyclone outlet had a surface area of 77.7 m^2/g and a mean pore size of 64.7 Å. Such pore coarsening is significant, considering that it occurred in only 48 h of exposure.

Platinum samples retrieved from the gasifier had sulfur, sodium, and iron impurities on the surface, as determined by AES and EDAX measurements. The presence of sulfur atoms was expected due to the H_2S present in the coal gas. The cause of iron impurity on the sample is not apparent. Discussions with the GE-CRDC staff suggest that it may have come from the erosion of stainless steel pipes through which the coal gas was flowing before contacting the specimens.

The results from this short-term exposure in the product gas stream of an operating coal gasifier confirm that the inorganic membranes degrade significantly on exposure to coal gas conditions. The enlargement of pores, even during the relatively short run, raises concern whether porous inorganic membranes could operate effectively as a gas separation device in hot coal gas streams. The observed erosion of the metal foils indicates that they can be used only in a nearly particle-free gas stream, perhaps downstream of high temperature barrier filters.

VI. CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the literature review and the experimental results, the following conclusions are derived:

- Hydrothermal sintering is a serious degradation mechanism that leads to enlargement of the micropores in inorganic membranes such as silica and alumina. The increase in pore size leads to a decreased selectivity for separation of gaseous components in a gas mixture.

- Coarsening of pores from 40 to 70Å occurs in commercially available Vycor membranes at temperatures as low as 450°C in the presence of steam and at elevated pressures that are typical of IGCC conditions. A similar an increase in pore size (40 to 60 Å) occurs in a commercially available alumina membrane at 550°C and 20 atm pressure.

- Pure component and mixed gas He/N_2 selectivities of modified-Vycor and alumina membranes decreased drastically in less than 50 h in gas mixtures containing 20% steam at 450°C and 100 psig.

- Exposure to the hot coal gas stream from an operating fixed-bed gasifier for 50 h resulted in observable degradation of alumina and silica membranes.

- Palladium is not a suitable material for hydrogen separation from hot coal gas streams because of its rapid reaction with H_2S.

- The hydrogen permeability of platinum foil is decreased in the presence of H_2S. The formation of a sulfide layer is severe at 450°C, but an adsorbed layer persists even at 700°C.

- The physical and chemical degradation observed with many of the currently available oxide membranes may make them unsuitable for separation of gases in IGCC systems. Platinum foils could be used to separate hydrogen from hot coal gas streams at 700°C, if the relatively slow permeation rate is acceptable.

The following recommendation is made for further studies:

- Because alumina and silica membranes degrade mainly due to hydrothermal sintering, materials that are resistant to steam attack must be developed. The addition of other oxides, such as lanthanum or zirconium oxide, may impart hydrothermal resistance and may allow the membranes to maintain their gas-selective micropores.

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