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Thermal/Chemical Degradation of Inorganic Membrane Materials

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7B.4 Thermal/Chemical Degradation of Inorganic Membrane Materials

CONTRACT INFORMATION

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Period of Performance August 24, 1992 to May 19, 1995
Schedule and Milestones

FY95 Program Schedule

Task	S	O	N	D	J	F	M	A	M	J	J	A	S
Experimental Testing													
Final Technical Report (Draft and Approved)													

OBJECTIVES

The overall objective of this program is to evaluate the long-term thermal and chemical degradation of inorganic membranes that are being developed to separate gaseous products produced by the gasification or combustion of coal in fixed-, fluidized-, and entrained-bed gasifiers, direct coal-fired turbines, and pressurized-fluidized-bed combustors. The evaluation is accomplished by a review of available information in the literature, performing bench-scale experiments, and observing changes developed in membrane samples during exposure to a hot gas stream from an operating coal gasifier.

BACKGROUND INFORMATION

Coal represents a major source of fossil fuels in the U.S. During gasification of coal, hydrogen is produced as one of the gaseous components in the product gas stream (coal gas). Hydrogen has many uses as a feedstock in the chemical industry and is also the most desirable fuel for fuel cells. The fraction of hydrogen in the coal gas mixture can be enhanced by the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). The forward reaction is favored when hydrogen is removed from the gas mixture. Inorganic membranes are capable of separating H_2 from such gas mixtures at elevated temperatures and pressures. Several impurities, such as H_2S , NH_3 , and trace metal compounds,

are also generated during the coal gasification process and they must be removed from the coal gas to protect power generation equipment and meet environmental standards. Inorganic membranes are potentially capable of assisting in the removal of H₂S and NH₃. Hence, membrane materials must be identified that possess the required characteristics of permeability, selectivity, and durability for use under conditions expected in hot coal gas streams.

Many studies have examined the performance of ceramic and metal membranes in relatively clean gaseous environments. But, the coal gas at high temperatures can be an aggressive threat not only to the efficient operation but also to the long term survival of inorganic membranes. These gas streams contain several components, such as H₂O, CO, H₂S, and alkali vapor, that can react with membranes made of materials such as Al₂O₃, SiO₂, Pd, and Pt in the temperature range of interest (450° to 1000°C). Residual fly ash particulate matter, if present after passage through cyclones or filters, contains components such as alkali salts that can react with membrane materials at high temperatures to form different phases. Thus, several thermal and chemical degradation mechanisms could unfavorably alter the properties of inorganic membranes during exposure to high temperature coal gas streams.

PROJECT DESCRIPTION

The program is divided into the following tasks: (1) development of evaluation methodology, (2) evaluation of potential long-term degradation mechanisms, (3) submission of a topical report and a plan for experimental testing, and (4) experimental testing.

Tasks 1-3 were completed in 1994. The results of the evaluation of potential long-degradation mechanisms were presented at the Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC Review Meeting (Krishnan et al., 1994)

RESULTS

An evaluation of potential degradation mechanisms, using existing theories and data available in the literature, was published earlier (Krishnan et al., 1993 a; 1993 b; 1994). This evaluation was based on a literature search of computerized data bases that identified several

hundred citations. A critical review of relevant technical articles revealed the following most likely degradation mechanisms in hot coal gas environments:

- Hydrothermal sintering
- Reaction with H₂S
- Reaction with ash particles
- Interaction with alkali components
- Deposition of carbon in the pores of the membrane.

The effects of these mechanisms on the characteristics of several metal and ceramic membranes were experimentally evaluated.

Several candidate membrane materials were selected in consultation with the DOE program manager. Suppliers and manufacturers who were possible sources for different membrane materials were contacted to obtain 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:

- Alumina membranes (Membralox) with a separation layer pore size of 40 Å, supplied by U.S. Filter Corporation
- Alumina membranes modified by Media and Process Technology, Inc. to form a gas separation layer of amorphous silica
- Vycor porous glass membranes (mainly SiO₂) with a pore size of 40 Å, supplied by Corning, Inc.
- Vycor porous glass membranes modified in Professor Gavalas' Laboratory at the California Institute of Technology by depositing an amorphous silica inside the pores
- Platinum foils provided by Bend Research, Inc.
- Palladium foils supplied by Aldrich Chemical Company.

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

- Characterization of changes in physical and chemical properties of the membranes exposed to simulated hot coal gas streams under well-defined conditions in the temperature range 450° to 1000°C and pressures up to 20 atm
- Measurement of the permeation performance of membranes under simulated coal gas conditions
- 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.

Before and after exposure, the membrane samples were characterized by (1) B. E. T. analysis for determination of surface area and pore size distribution, (2) Auger electron spectroscopy for identifying the elemental composition on the surface layers, (3) scanning electron microscopy to indicate changes in morphology, and (4) dynamic flow-weighted pore size distribution analysis. Permeation experiments were also performed to determine pure component permeation as well as mixed-gas permeation rates.

Results of the Exposure Tests

The pore size of the unmodified Vycor membrane samples increased significantly in simulated coal gas streams at high temperatures and pressures (Table 1). 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 (Figure 1). The effect of gasifier ash at 450° and 550°C was negligible, presumably due to slow reaction kinetics between the two solid phases.

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.

Table 1. Surface Area And Mean Pore Size of Exposed Vycor Membrane Samples

Temperature (°C)	Pressure (psig)	Duration (hours)	Surface Area (m ² /g)	Mean Pore Size (Å)
As-received	0	0	190	40
1000	0	24	2	1000
800	0	76	33	117
650	0	113	141	45
550	0	410	150	44
550	270	500	103	60
450	300	1000	99	60
550 (ash coat)	0	410	161	44
550 (ash coat)	270	500	110	58
450 (ash coat)	300	1000	105	57

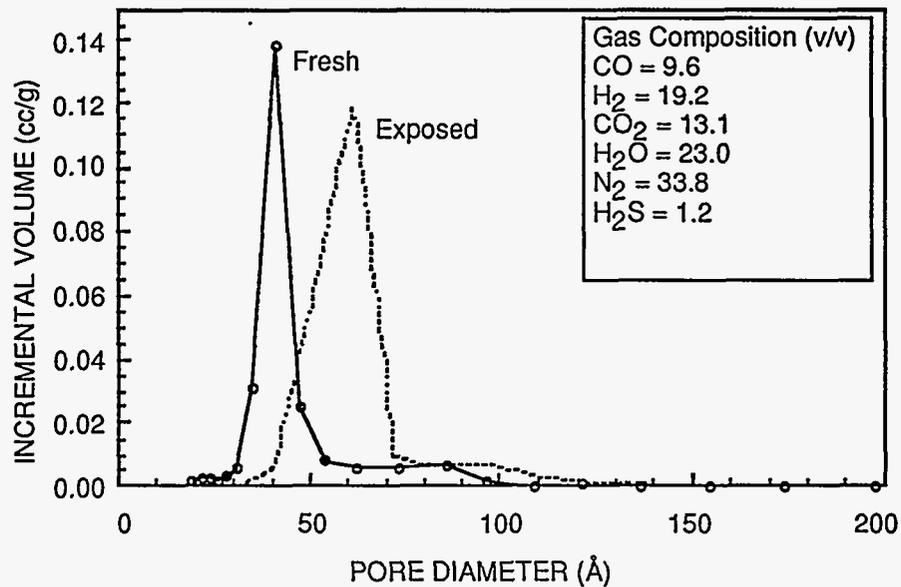


Figure 1. Pore Enlargement in Vycor Membranes During Exposure at 450°C and 20 atm Pressure for 1020 h

The alumina membrane samples are made of several layers of differing pore size (asymmetric) and the pore volume of the microporous layer is only a small fraction of the total pore volume. Hence, the B. E. T. method could not be used to determine its pore size distribution accurately. However, more than 90% of the surface area of the membrane is due to the particles in the microporous layer. Thus, changes in the surface area, as determined by the B. E. T. analysis, would reflect

the changes in the pore size distribution of the microporous layer. The surface area of the alumina samples decreased significantly at the tested conditions, indicating coarsening of the 40 Å layer (Table 2). 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.

Table 2. Surface Area Of Exposed Alumina Membrane Samples

Temperature (°C)	Pressure (psig)	Duration (hours)	Surface Area (m ² /gm)
As-received	0	0	2.1
1000	0	24	1.3
800	0	76	0.4
650	0	113	0.9
550	0	410	0.4
550	270	500	0.9
450	300	1000	1.0
550 (ash coat)	0	410	0.8
550 (ash coat)	270	500	1.4
450 (ash coat)	300	1000	1.5

Alumina membrane samples also released a significant amount of sodium vapor ($\sim 10^{-7}$ atm) at temperatures exceeding 700°C . Evolved sodium vapor actually crystallized the Vycor and quartz materials placed nearby in the same reactor indicating that it is a serious threat to the silica layer in modified-alumina membranes.

In the later stages of the project, a dynamic pore size measurement (DPSM) technique was used to measure the pore size distribution of asymmetric membranes. This technique, originally developed at the Oak Ridge National Laboratory, provides a pore size distribution based on changes in gas permeation rate when membrane pores are blocked with a liquid film (Fain, 1989). The Kelvin equation correlates the pressure at which a vapor will condense as a liquid film in a pore:

$$\ln(P_0/P) = 2\gamma V/(rRT) \text{ or } r = (2\gamma V/RT) \cdot \ln(P/P_0)$$

where, P and P_0 are, respectively, the partial and saturation 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. At a constant temperature, increasing the partial pressure of the vapor will allow increasingly larger pores to be blocked by the condensate film. The observed changes in the permeate flow as a function of the partial pressure of the vapor can be correlated to a flow-weighted pore size distribution of the membrane. The advantage of this technique is that it could measure accurately the pore size distribution of a thin microporous layer incorporated on supporting thick, macroporous layers. DPSM analysis indicated that the mean size of alumina membrane microporous layer increased from 40 to 65 Å when exposed to a simulated coal gas at 550°C and 20 atm for 500 h (Figure 2).

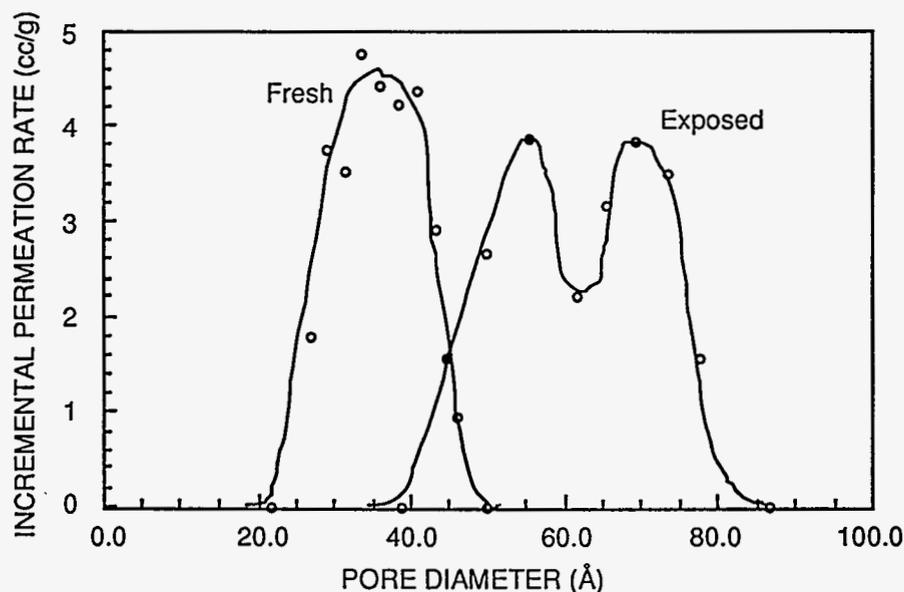


Figure 2. Pore Size Distribution in Membralox Alumina Membranes during Exposure to a simulated Coal Gas at 550°C and 20 atm pressure for 500 h (Gas Composition was similar to that shown in Figure 1)

H_2S present in the hot coal gas could result in the chemisorption of S atoms on Pt and Pd surfaces and possible bulk sulfide formation. Such poisoning could reduce the H_2 permeability of the

metals. The extent of sulfur poisoning on Pt foils exposed to simulated coal gas streams containing 1.2% H_2S depended on both temperature and pressure. Whereas at 1 atm, the sulfur layer was

less than 10 Å at 1000°C, it increased to 50Å at 450°C. However, Pt samples exposed at 450°C and 20 atm pressure had extensive surface sulfide coatings, more than 200 Å thick. Thus, the extent of sulfidation increased with decreasing temperature and increasing pressure. Pre-coating of Pt foils by a gasifier ash did not significantly affect the extent of surface sulfidation. Palladium foils melted at temperatures above 650°C and deformed extensively below that temperature due to PdS formation by reaction with H₂S present in the simulated coal gas. Thus, Pd is not suitable as a membrane material in direct contact with coal gas.

Membrane Permeation Tests

The permeation performance of several modified-alumina and modified-Vycor membranes (tubular) was evaluated at high temperature and high pressure especially in the presence of steam. Initial experiments with modified membranes produced results different from those reported by the suppliers, possibly as a result of changes that might have occurred during a 3-month storage of the membranes at ambient conditions in the

laboratory prior to testing. In later experiments, two additional modified-alumina membranes and one modified-Vycor membrane were procured and they exhibited permeation characteristics under dry conditions consistent with those reported by the suppliers. All three modified-membrane samples degraded in a few hours in the presence of a feedgas containing about 20% steam in the temperature range 450° to 600°C and at 100 psig total pressure.

Pure component permeation tests with a modified-alumina membrane were first conducted with He and N₂ gases at temperatures up to 600°C. As shown in Table 3, the N₂ permeance decreased with increasing temperature from 0.08 m³/(m²·h·atm) at 25°C to 0.03 m³/(m²·h·atm) at 600°C. However, He permeance increased from 0.25 to 7.7 m³/(m²·h·atm) as temperature was increased from 25° to 600°C. As a result, the pure component He/N₂ selectivity increased from 3 to 227 under dry gas conditions. These results were consistent with those obtained by Media and Process Technologies, Inc. with this membrane.

Table 3. Permeation Results With a Modified-Alumina Membrane

Temperature (°C)	Steam (%)	Permeance m ³ /(m ² ·h·atm)		Selectivity P _{He} /P _{N₂}
		Helium	Nitrogen	
Pure Component 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 adding steam.

² 5 h after adding steam.

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

Because of the large stage cut of 80% in this experiment, the calculated permeances and selectivity values during mixed gas tests were significantly lower than the true values.

The effect of steam on the membrane performance was determined at 600°C by adding ~20% steam to the feed gas. The permeate and raffinate gas compositions were monitored for about 5 h. Initially, the results were found to be comparable with those obtained under dry gas conditions. However, both the nitrogen and CO₂ concentrations in the permeate were found to increase 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 m³/(m²·h·atm) respectively with a corresponding He/N₂ selectivity of 8.3. Subsequent pure component permeation measurements at 25°C indicated a substantial increase in permeation rates as compared to the earlier measurements. The helium and nitrogen permeances were found to have increased to 1.5 and 0.62 m³/(m²·hr·atm) respectively with a pure component selectivity of only 2.4. These results confirmed that the size-selective layer made of silica had been altered during exposure to steam.

The He/N₂ selectivity of another modified-alumina membrane was initially 250, but it also decreased to 4 after less than 30 h exposure to a gas mixture containing 20% steam at 100 psig total pressure in the temperature range 450° to 600°C (Figure 3). During this exposure period, pure-component helium permeance at 450°C decreased from 9.5 to 5.5 cm³/(cm²·min·atm), whereas nitrogen permeance increased from 0.05 to 1.6 cm³/(cm²·min·atm).

The DPSM test performed on the modified-alumina membrane before and after exposure showed that the pore diameter of the separation layer in the unexposed membrane was below the detection limit (<15Å) of the technique. Although, the selectivity of the exposed modified-alumina membrane had decreased substantially compared to that of the fresh membrane, the pore size distribution of the exposed membrane was still too small to be measured accurately by the DPSM technique. The present results confirm that for a porous membrane to be used for gas separation in industrial applications, the pore size of the separation layer must be substantially smaller than 15Å.

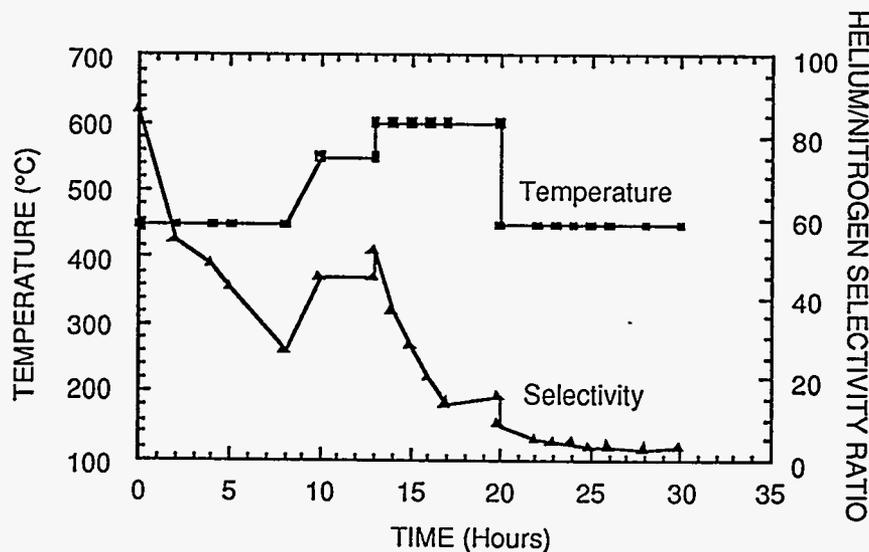


Figure 3. The He/N₂ selectivity of a Modified-Membralox Membrane as a function of Time and Temperature (Gas Composition: N₂ = 8.0%; CO₂ = 8.7%; H₂O = 16.7%; He = Balance)

The He/N₂ permeance ratio of the modified-Vycor membrane also decreased from 160 to 3.5 upon exposure to a gas mixture containing 20% steam at 100 psig total pressure and 450°C for less than 15 hours (Figure 4). During this exposure test, the pure component helium permeance

remained constant at 0.45 cm³/(cm²·min·atm), whereas, that of nitrogen increased from 0.005 to 0.14 cm³/(cm²·min·atm). Thus, degradation of both alumina and silica membranes resulted in a substantial increase in nitrogen permeance indicative of coarsening of the size-selective pores.

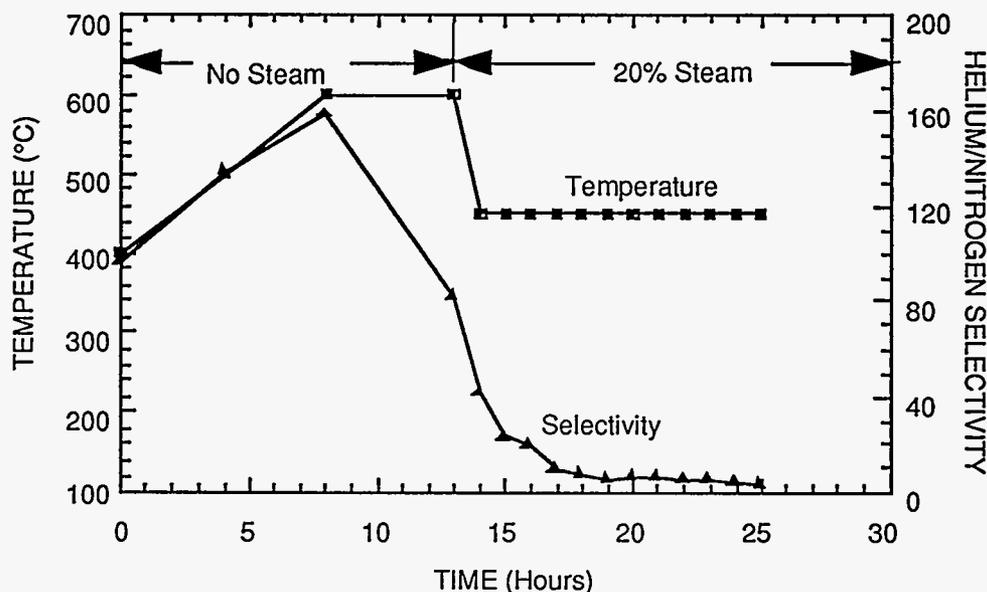


Figure 4. The He/N₂ selectivity of a Modified-Vycor Membrane as a function of Time and Temperature (Gas Composition: N₂ = 40%; He = 40%; H₂O = 20%)

Both the alumina and Vycor membranes were modified by depositing a thin SiO₂ layer to reduce the pore size. The results indicate that a gas mixture containing ~ 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 SiO₂ layer, reducing the gas selectivities to those expected from unmodified alumina and Vycor membranes.

Two different experiments were carried out to determine the permeation characteristics of 25-μm thick Pt foils. In the first experiment, a fresh Pt foil was exposed to a simulated coal gas at 700°C and the permeance of H₂ present in the coal gas was monitored as a function of time. Periodically, the coal gas flow was interrupted and the permeance of H₂ was also determined with pure H₂ as feed gas. Due to burnout of graphite ferrules and seals, the maximum duration of this experi-

ment was 24 h. The H₂ permeance decreased from 0.02 to 0.01 cm³/(cm²·min·atm) during the initial 4-h exposure to the simulated coal gas (Table 4). At longer exposures, the H₂ permeation rate appeared to remain stable.

In the second experiment, a Pt foil was exposed to a simulated coal gas at 550°C and 270 psig for 500 h and then the H₂ permeance was determined using pure H₂ as feed gas at 115 psig pressure and 700°C. The H₂ permeance increased from an initial value of 0.006 to 0.02 cm³/(cm²·min·atm), after about 1 h, and then remained stable (Figure 5). This behavior may be explained by the removal of an adsorbed sulfur layer formed at 550°C by reaction with the pure H₂ feed gas at 700°C. Both types of experiments confirm that sulfur atoms are reversibly adsorbed on the surface of a Pt foil at 700°C and they could reduce the H₂ permeability of Pt membranes.

Table 4. Hydrogen Permeation Through Platinum Foil at 700°C

Cumulative Exposure Time (h)	Feed Gas	Feed Pressure (psig)	Hydrogen Permeance $\text{cm}^3/(\text{cm}^2 \cdot \text{min} \cdot \text{atm})$
1	Coal gas	150	0.022
1.5	Hydrogen	80	0.020
2	Hydrogen (dry)	80	0.020
3	Coal gas	250	0.022
18	Coal gas	250	0.016
19	Hydrogen (dry)	80	0.010

Notes: Platinum foil thickness: 25 μm
 Coal gas composition: $\text{H}_2 = 19.3\%$; $\text{CO} = 9.6\%$; $\text{CO}_2 = 13.1\%$; $\text{N}_2 = 33.8\%$; $\text{H}_2\text{O} = 23.0\%$; $\text{H}_2\text{S} = 1.2\%$
 Pressure on the permeate side = 0 psig

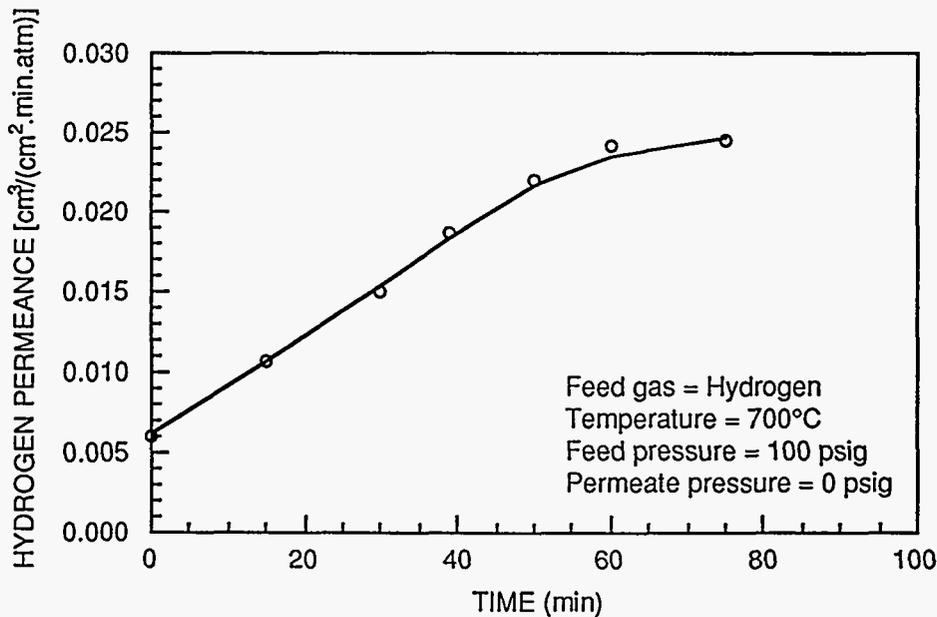


Figure 5. Hydrogen Permeation Through a Platinum Membrane After Exposure to a Simulated Coal Gas at 550°C, 270 psig for 500 h.

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). During the run in which an Illinois #6 coal was gasified, the particulate loadings at locations 1 and 2 were about 100 and 50 ppmw, respectively.

During this exposure testing, all specimens accumulated a substantial amount of a black deposit. The deposit was mainly soot (~98 wt%) with small amount of ash material mixed in it.

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. At the primary cyclone outlet, most of the platinum samples were sheared off the support plates because of the abrasive dust. However, at the secondary cyclone outlet location, fragments of two platinum samples were recovered. All Vycor membrane samples had turned black, apparently due to deposition and absorption of tar vapors. Similarly, the 40 Å microporous layer of the alumina membrane had also turned black. 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.

B. E. T. analysis indicated that the mean pore size of the Vycor membrane increased from about 40 Å to about 78 Å with a corresponding decrease in the surface area from 190 to 85 m²/g. DPSM test indicated that the modified-alumina membrane tube suffered loss of microporosity and a reduction in permeation rate. These results indicate coarsening of the pores along with pore blockage by absorbed tar or fly ash deposits.

Platinum samples retrieved from the gasifier had sulfur, sodium, and iron impurities on the surface, as determined by Auger-electron spectroscopy measurements. The presence of sulfur atoms was expected due to the H₂S present in the coal gas. The cause of iron impurity on the sample is not apparent. Discussions with the GE-CRD staff suggested that iron impurity 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 tested inorganic membranes degrade significantly on exposure to coal gas conditions. The enlargement of pores, even during the relatively short time, 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.

CONCLUSIONS & RECOMMENDATIONS

The experimental tests conducted on the 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 H₂ selectivity 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 a reduction in the hydrogen permeation rate due to surface sulfidation by H₂S in the coal gas. The extent of sulfidation increases as the temperature is decreased. Thus, Pt is suitable as an H₂ transfer membrane only at high temperatures (>700°C) because both inherent diffusion rate through the metal and sulfur poisoning of the surface reduce the hydrogen permeation rate at low temperatures. Other major gaseous components of the coal gas stream do not appear to have a significant effect on Pt membranes. Fly ash, if present, may erode the soft metal and hence Pt membranes may be used only downstream of high temperature barrier filters. Palladium membranes are degraded extensively by H₂S 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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