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GAS SEPARATIONS USING INORGANIC MEMBRANES*

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B. Z. Egan
S. P. N. Singh

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

D. E. Fain
G. J. Kidd
G. E. Roettger
D. E. White

Quality and Technical Support Division
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, TN 37831

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1. FWP NUMBER: FEAA326

   CONTRACTOR: Martin Marietta Energy Systems, Inc.
   Oak Ridge National Laboratory
   P. O. Box 2008
   Oak Ridge, TN 37831

   CONTRACTOR PROJECT MANAGER: R. R. Judkins

   PRINCIPAL INVESTIGATORS: B. Z. Egan
   D. E. Fain
   G. J. Kidd
   G. E. Roettger
   S. P. N. Singh
   D. E. White

   METC PROJECT MANAGER: Lisa A. Jarr

   PERIOD OF PERFORMANCE: April 3, 1988 to September 30, 1990

2. SCHEDULE/MILESTONES:

Program Schedule (Quarters)

	FY 1989				FY 1990			
	1	2	3	4	1	2	3	4
Assess R&D status of inorganic membranes	----	----	----					
Develop performance targets		----	----					
Complete draft report on R&D status review				*				
Develop and test membranes	----	----	----	----	----	----	----	----
Measure membrane performance			----	----	----	----	----	----
Prepare report on results and recommendations							----	----

3. OBJECTIVES:

The objective of this project is to explore the applicability of inorganic membranes for gas separations in hostile process environments encountered in fossil energy conversion processes such as coal gasification. The program will apply porous membrane technology to develop inorganic membranes and test them for the separation of various gases. The program could lead to the development of processes that would significantly reduce gas cleanup and separation costs.

4. <u>BACKGROUND</u>:

Developments in membrane technology have led to major improvements in both performance and economics in gas processing applications. The development of membranes with high selectivity and flux capabilities has led to the commercial-scale use of membranes to separate gaseous components from gas mixtures. For example, modular membrane separation systems are now commercially available for hydrogen purification and recovery in ammonia plants, separation of oxygen and nitrogen from air, sweetening of sour natural gas, and recovery of carbon dioxide from wellhead gas in enhanced oil recovery operations. However, the membranes used in these systems are thin-film composites of polymeric organic materials that have limited thermal stability and are susceptible to abrasion and chemical attack in harsh environments. Therefore, these membranes have not found applications in separation processes where hot, reactive gases are encountered. Inorganic membranes generally have better chemical and thermal stability and should much more effectively withstand such hostile environments.

Hydrogen is an important and valuable raw material that has numerous uses in the chemical and fuel industries. Synthesis gas produced in coal gasification processes may contain hydrogen, carbon monoxide, nitrogen, water, carbon dioxide, hydrogen sulfide, and other gases, depending on the particular gasification process. If technology could be developed to separate the H_2 from the raw gas at high temperatures, it would significantly lower the cost of H_2 separation. The proposed inorganic membrane separation process is being developed to achieve this goal.

Commercially, at present, bulk removal of acid gases from raw process gas such as synthesis gas is carried out using solvent scrubbing processes at temperatures below 100°C. A typical entrained-bed gasification-combined cycle (IGCC) process requires cooling the product gases to about 40°C to permit removal of CO_2, H_2S, and other contaminant gases. The cleaned fuel gas (carbon monoxide and hydrogen) must then be reheated to 300-325°C for downstream combustion in a gas turbine to generate power. The efficiency of the process could be increased substantially if the contaminant gases could be separated at the higher downstream operating temperature. Briefly stated, the gas cooling and the gas cleanup system would be replaced with a membrane separation system operating under conditions closer to the exit gas conditions.

Although the permeability of several gases in various inorganic materials has been studied, there has been no large-scale application of inorganic membrane separations of gases except for uranium enrichment. Gas permeabilities of metals such as tungsten, molybdenum, iron, copper, nickel, silver, palladium, and alloys of these metals have been studied. Ceramics and porous metals have also been tested as supports for deposition of metal films of vanadium and aluminum, as well as for membrane coatings of zirconium oxide, nickel oxide, and titanium oxide. Inorganic polymeric membranes, such as polyphosphazenes, and organic-inorganic membranes containing heteropoly acids and salts have been prepared.

Several porous inorganic materials that could be used as membranes are commercially available in the form of disks, tubes, and monoliths. However, the minimum pore diameter is in the range of 30-40 Å. While some gas separations can be achieved with these materials, it is generally accepted that smaller pore diameters or other membrane modifications will be needed for efficient gas separations.

Table 1 shows the effect of membrane pore diameter on the calculated separation factors for binary mixtures of hydrogen with nitrogen, carbon dioxide, and sulfur dioxide. At larger pore sizes, the primary transport mechanism is free-molecule or Knudsen flow, and the separation factor can be estimated from the square root of the ratio of the molecular weights. However, as the pore size decreases, some molecular screening can occur. At some point, if the membrane has no pores greater than the diameter of the larger molecule, then the membrane will not be permeable to that molecule and the separation factor will approach infinity. Of course, in practice there will be a distribution of pore sizes and other transport mechanisms may be operative. Also, as the pore size decreases, the membrane porosity may decrease, resulting in a lower gas flow through the membrane. So these two factors must be balanced before a practical, efficient membrane can be developed. Nevertheless, the potential advantage of smaller pore sizes is illustrated. Development of improved inorganic membranes with these properties could provide significant advantages for gas separations.

Table 1. Calculated Gas Separation Factors Based on Molecular Size for Membranes with Various Pore Diameters.

Pore diameter	Separation factor		
(Å)	H_2/N_2	H_2/CO_2	H_2/SO_2
100	3.76	4.72	5.72
10	4.15	5.47	6.94
5	5.74	9.46	16.1
4	12.1	1210	∞

5. PROJECT DESCRIPTION:

This R&D program consists of developing, fabricating, and testing inorganic membrane separation systems for the recovery of H_2 and the separation of coal gasification gases. Major parts of the program include (1) assessment of the status of R&D activity related to gas separations using inorganic membranes; (2) identification and selection of candidate membrane materials, based on the chemistry of the separation environment and the availability and cost of the materials; (3) fabrication and characterization of candidate membranes using specialized techniques available at the Oak Ridge Gaseous Diffusion Plant; and (4) evaluation of the separations capability of the fabricated membranes in terms of permeabilities and fluxes of gases. The program is jointly funded by the Gas Stream Cleanup Program and the AR&TD Fossil Energy Materials Program.

6. RESULTS/ACCOMPLISHMENTS:

Accomplishments can be summarized as follows:

- Literature searches of several data bases were completed to compile information on the status of R&D on inorganic membranes for gas separations.
- A survey was made of commercially available porous inorganic materials and their characteristics.
- A commercially available tubular alumina membrane was evaluated in terms of mean pore size, pore size distribution, and gas permeabilities of nitrogen, helium, and carbon dioxide.
- Several tubular alumina membranes were fabricated and characterized by pore size distribution measurements. Membranes with mean pore radii of 15 to 20 Å were prepared.
- The design of a test apparatus for measuring the gas permeabilities of membranes at high temperatures and pressures was completed. Construction of the apparatus is nearing completion.

STATUS OF INORGANIC MEMBRANE TECHNOLOGY

An indication of the status of inorganic membrane technology can be gained from a survey of commercially available porous inorganic materials. Table 2 lists some of the companies that market porous materials, the composition of the materials, pore sizes, and the configurations available. Some of the materials (ceramics, metals, and glass) are available only as prototypes or in developmental quantities. They are available in tubes, disks, monoliths, and rods. The minimum pore size is in the range of 30 to 40 Å (diameter). This limits their applicability primarily to filtration. Some gas separations can be achieved with these

Table 2. Commercial Porous Inorganic Membranes.

Company	Membrane/Support Material	Pore Size (Diameter)	Configuration
Alcan/Anotec	Alumina/alumina	0.025-0.2 μm	D
Alcoa	Alumina/alumina	40 Å-5 μm	M, T
Asahi Glass	Glass	40 Å-10 μm	D, T
Bolt Technical Ceramics	Alumina Silicon carbide	1-40 μm	T
CARRE	Zirconia/ss, carbon	40 Å-0.1 μm	T
Ceram Filtre	Silicon carbide	0.15-8 μm	T, M
CeraMem	Alumina/silica Zirconia	0.1 μm	M, T
Coors	Ceramics	0.5-108 μm	-
Corning	Glass	40 Å	T
	Cordierite, mullite	2.6-4.9 μm	M
DuPont	Alumina, mullite Silica, cordierite	0.06-1.0 μm	T
Fuji Filters	Glass	40 Å-1.2 μm	T
GFT	Carbon	40 Å-1.0 μm	T
Mott	SS, Ni, Ag, et al	0.5-100 μm	D, T, R
NGK	Alumina/alumina Silicon carbide/SiC	0.2-13 μm	T
Norton	Alumina/alumina	0.2-1.0 μm	T, M
Osmonics	Silver Ceramic	0.2.5 μm -	D -
Pall	SS, Ni, et al.	0.5 μm	T
Poretics	Silver Ceramic (Al, Si)	0.2-5 μm 0.3-25 μm	D D
PTI Technologies	SS	0.5-2.0 μm	-
Schott Glass	Glass	100 Å-0.1 μm	T
SepTech/PPG	Glass	60-300 Å	F
SFEC	Zirconia/carbon	40 Å-0.1 μm	T
TDK	Zirconia/alumina	100 Å	T
Toyobo	Glass	200 Å	T
Union Carbide	Zirconia/carbon	30 Å	T

*D = disk; T = tube; M = monolith; R = rod; F = hollow fiber.

materials, primarily by Knudsen diffusion. However, smaller pore sizes or other membrane modifications will probably be needed for efficient gas separations. Of course, it is necessary to maintain high gas permeability while reducing the pore size. Generally, this means developing a very thin membrane. Research and development activities are continuing in this direction, but commercial inorganic membranes for gas separations are not yet readily available.

Several universities have established research centers or programs to carry out membrane R&D. Many have financial support from industry. Some of those which include inorganic membrane studies are listed in Table 3. Various aspects being addressed by these centers include preparation and characterization of inorganic polymers, ceramics, and metals; membrane applications; modeling and simulation; membrane reactor development; transport mechanisms; and membrane catalysis.

Table 3. Academic Inorganic Membrane Research.

University	Center/Program
University of Cincinnati	Center of Excellence for Membrane Technology
University of Texas	Separations Research Program
University of Wisconsin	Water Chemistry Program
Rutgers (State University of New Jersey)	Center for Ceramic Research
Syracuse University	Center for Membrane Engineering and Science
Worcester Polytechnic Institute	Center for Inorganic Membrane Studies

Inorganic membranes are being investigated worldwide for separating gases on a laboratory scale. Membrane materials include metals, ceramics, and glass. Metals, particularly palladium and palladium alloys, have been used to separate hydrogen isotopes from each other and hydrogen from various other gases. Metallic oxides, ceramics, and porous glass membranes have been utilized to separate a variety of gases, although again many of the studies involve the separation of hydrogen from other gases. This is understandable because the pore diameters of most of the membranes are greater than 20 Å, and the primary transport mechanism is Knudsen diffusion, which is dependent on the relative molecular weights of the gases.

The most prevalent membrane materials are alumina, silica, zirconia, and glass. Membrane preparation methods are based on sol-gel, slipcasting, anodic oxidation (metallic oxides), and phase separation/leaching (porous glass) techniques. Isotope separation is still the only large-scale application of inorganic membranes for separating gases.

MEMBRANE FABRICATION AND TESTING

Several materials such as alumina, silica, zirconia, and titania have been identified as potential membrane media. Our primary effort has been directed toward preparing tubular alumina membranes about 1 cm in diameter and 20 cm long. Development work has been directed toward reducing the pore size and minimizing leak flow (flow through larger pores and cracks). Membranes are characterized primarily by pore size and pore size distribution to guide the development effort.

Some significant changes were made in instrumentation and operation of the pore size distribution test apparatus at ORGDP. In addition, new software was developed to process more acquired experimental data and to extend the data analysis to smaller pore sizes. The improved apparatus and software were used to measure the pore size distribution of a commercial alumina membrane (Figure 1).

Significant improvements were made in fabricating alumina membranes. The average pore radius of the membranes was reduced from about 150 Å for the initial membranes to 15-20 Å for present membranes (Figure 2). In addition, a relatively high leak flow detected in some of the earlier membranes has been reduced to about 0.4%. Leak flow is considered to be flow through excessively large pores and faults or cracks in the membrane. It was determined by microscopic examination of the membranes that the high leak flow was caused by small cracks that were formed at the ends of the tubes as a result of the handling and testing procedures. Metal ferrules were attached to the ends of the tubes with an epoxy compound to facilitate the handling and testing and to alleviate the cracking problem. This method is satisfactory at lower temperatures, but the epoxy compound will not survive high temperatures, so a different approach will be needed for tests at higher temperatures.

The design of a test apparatus for measuring the gas permeabilities of membranes at high temperatures (up to 500^{o}C) and pressures (up to 4 MPa) was completed. Gases will be supplied from cylinders through high-pressure regulators and an associated manifold. Pressures will be controlled by pressure control valves, and gas flows will be measured with differential-pressure transmitters. The gases will be preheated in a tube furnace, which will also house the membrane enclosed in an outer tube. Temperatures will be measured with thermocouples. Exit gases will be cooled with heat exchangers and analyzed by gas chromatography. Construction of the apparatus is nearing completion.

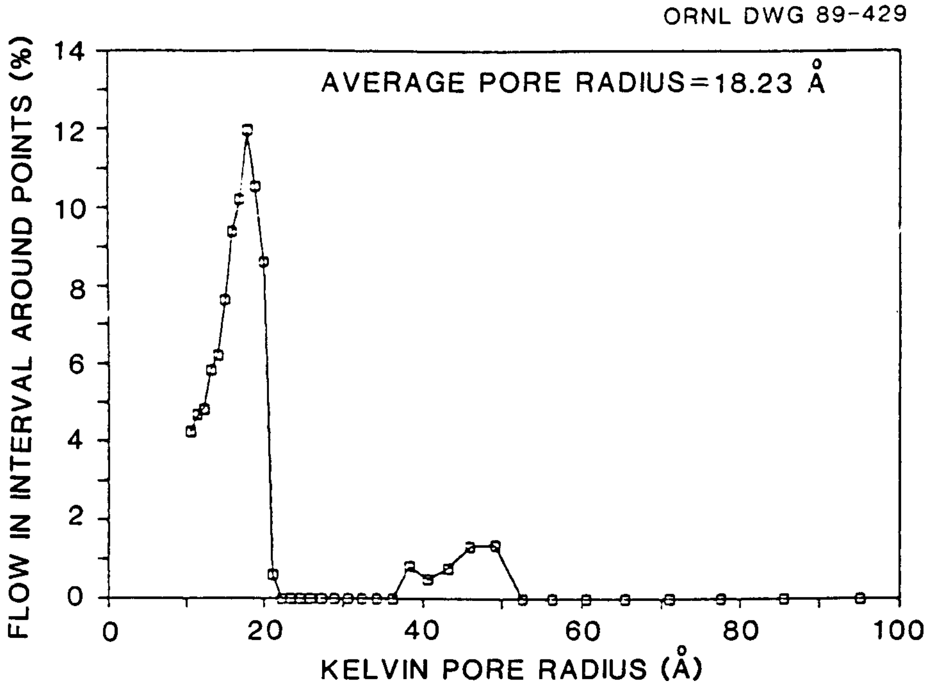

Fig. 1. A DYNAMIC PORE SIZE DISTRIBUTION FOR A COMMERCIAL ALUMINA MEMBRANE

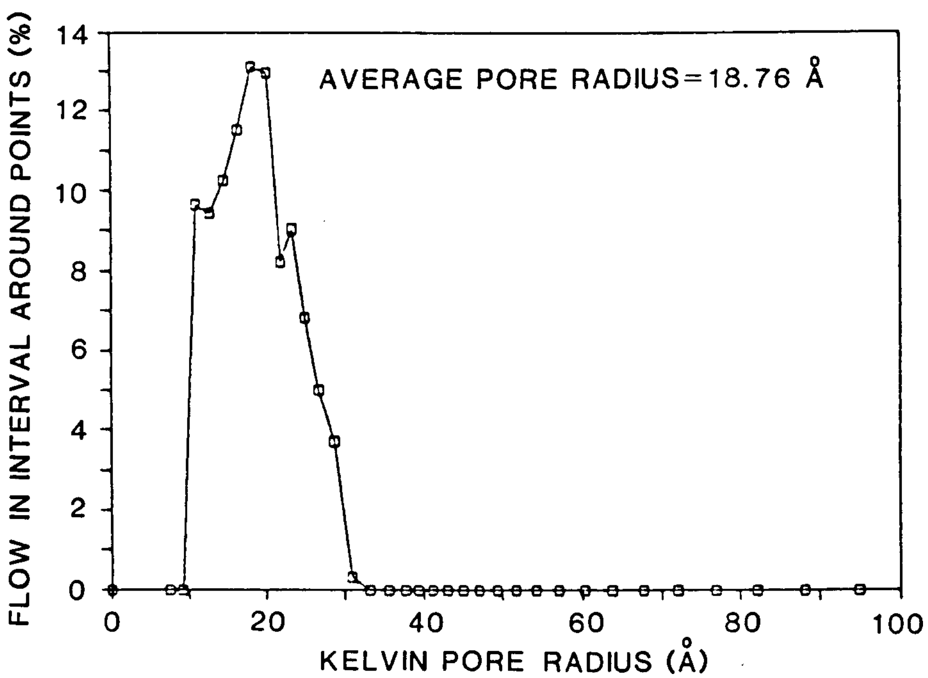

Fig. 2. A DYNAMIC PORE SIZE DISTRIBUTION FOR AN ORGDP EXPERIMENTAL MEMBRANE

7. <u>FUTURE WORK</u>:

Information on inorganic membrane R&D will be compiled and summarized in a report that will assess the status of inorganic membrane R&D applied to gas separations.

Membrane development is an iterative process involving membrane fabrication followed by membrane characterization; information from the characterization is then used to fabricate improved membranes. Present efforts are directed toward fabricating membranes with smaller pores. Once a suitable membrane is developed through the iterative process, the membrane will be tested further. Initial tests of membrane permeabilities will be made with pure gases at room temperature and low pressures. Results from the tests with pure gases will be used to select a membrane for further testing with mixed gases.

The apparatus for measuring gas permeabilities at higher temperatures and pressures will be completed, and test procedures will be developed. Selected membranes will be tested to separate gases from a simulated coal gasification product gas. Other potential membrane materials will be evaluated.