DEVELOPMENT OF INORGANIC MEMBRANES FOR GAS SEPARATION*

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ABSTRACT

Hydrogen for commercial coal liquefaction processes may be provided by a coal gasification plant operated to maximize hydrogen production. Hydrogen is a major chemical requirement for coal liquefaction, and the use of liquefaction by-products such as mineral ash residue as feed to the gasifier can improve the overall process efficiency and economics. Also, recovery of hydrogen from gaseous streams in the coal liquefaction plant can have a significant impact on coal liquefaction process economics. In these hydrogen production scenarios, there is a need to improve the quality of the hydrogen produced by separating the other impurity gases from it. The DOE-Fossil Energy AR&TD Materials Program is presently developing inorganic membranes for gas separation, including the recovery of valuable resources such as hydrogen from hot-gas streams. This project was initiated in 1988 and is developing inorganic membranes using classified technology developed over the last 45-50 years at the Oak Ridge Gaseous Diffusion Plant for uranium enrichment for nuclear power applications. Significant technical advances have been made on this project and declassification of the technology appears imminent. A summary of efforts to produce alumina membranes with mean pore radii $< 5 \text{ \AA}$ is presented as well as a status report on declassification of this important technology.

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**Oak Ridge Gaseous Diffusion Plant

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OBJECTIVES

The objective of this project is to explore the applicability of inorganic membranes to separate gases at high temperatures and pressures and/or in hostile process environments encountered in fossil energy conversion processes such as coal gasification. The overall program will develop porous inorganic membranes and apply porous membrane technology to the separation of gases present in coal gasification processes. Successful completion of the program could lead to the development of processes that would improve the economics of fossil energy conversion processes by significantly reducing gas cleanup and separation costs.

BACKGROUND INFORMATION

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 membrane technology could be developed to separate these gases under gasifier exit gas conditions, it would significantly improve process efficiency and economics. Inorganic membranes could potentially be used for this purpose.

Polymeric membranes have been used on a commercial scale to separate various gases, such as hydrogen and ammonia, oxygen and nitrogen, and carbon dioxide and methane. These membranes have limited thermal stability and are susceptible to abrasion and chemical attack. Consequently, they cannot be utilized in many separation processes.

Until recently, inorganic membranes have been used primarily for microfiltration and ultrafiltration. There has been no large-scale application of porous inorganic membrane to separations of gases except for uranium enrichment. However, gas permeabilities of porous metals, glasses, and ceramics have been studied. These materials are stable to much higher temperatures than polymeric membranes, and the limitation is usually set by the seals and module materials and not by the membrane itself.

Several porous inorganic materials that could be used as membranes are commercially available, but the minimum pore diameter is in the range of 20 to 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.

PROJECT DESCRIPTION

This R&D program consists of developing, fabricating, and testing inorganic membrane systems for the separation and recovery 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; (3) fabrication and physical characterization of candidate membranes using specialized techniques available at the Oak Ridge Gaseous Diffusion Plant (ORGDP); and (4) evaluation of the separations capability of the fabricated membranes in terms of permeabilities and fluxes of gases.

Previously, the literature on inorganic membrane R&D related to separating gases of interest was reviewed and assessed. The performance targets for the membrane separation process were determined, based on the coal gasification process operating temperatures and pressures and gas flux requirements. Potential membrane materials were selected, based on thermal and chemical stability, availability and cost of raw materials, and effects on gas transport mechanisms.

Present work is directed toward fabricating improved membranes and testing them on a laboratory scale for separating gases of interest. The technical approach is to develop and fabricate membranes with small pores (less than 20 Å) and a narrow pore size distribution to take advantage of gas transport mechanisms other than, or in addition to, simple Knudsen diffusion, thereby providing better gas selectivity.

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RESULTS

Status of Membrane Technology

Information on inorganic membrane R&D related to gas separation was compiled and published in a report entitled, "Using Inorganic Membranes to Separate Gases: R&D Status Review." This report described the preparation, properties, and utilization of inorganic membranes. The information was evaluated in terms of limitations, needs, and prospects for future development.

Metallic membranes have been used primarily for separating hydrogen isotopes and for removing hydrogen from other gases. Many of the studies are directed toward the separation of hydrogen, deuterium, and tritium isotopes. One application is the removal of tritium from radioactive effluents from nuclear fuel reprocessing plants; another is separation of the hydrogen isotopes produced in a fusion reactor. Palladium is usually alloyed with silver to improve the physical and mechanical properties of the membrane material.

The separation of several gases with porous glass membranes has been demonstrated. Some of the gases that have been separated using porous glass membranes include hydrogen, helium, argon, nitrogen, oxygen, carbon dioxide, carbon monoxide, and light hydrocarbons. Many of the applications of porous glass for gas separations have come from Japan.

The most frequently used materials for metallic oxide membranes are alumina and silica. Some membranes contain mixtures of these along with other oxides such as zirconia or titania. Alumina is also frequently used as the support for other membrane materials. Most of the metallic oxide membranes are made by sol-gel/slipcasting or anodic oxidation techniques. Other preparation techniques include chemical vapor deposition, sputtering, precipitation/compaction, and phase leaching. Membranes with pore sizes ranging from a few angstroms to nearly a micrometer have been prepared. The permeation behavior of several gases has been studied using alumina or

alumina-containing membranes. These gases include hydrogen, nitrogen, helium, argon, oxygen, carbon dioxide, sulfur dioxide, hydrogen sulfide, water, alcohols, and light hydrocarbons.

Membrane Test System

The design and construction of a test apparatus for measuring the gas permeabilities of membranes at high temperatures (up to 500°C) and pressures (up to 4 MPa) was completed. A flow diagram of the apparatus is shown in Fig. 1. Gases are supplied from cylinders through high-pressure regulators and an associated manifold. Pressures are controlled by pressure control valves, and gas flows are measured with differential pressure transmitters. The gases are preheated in a tubular furnace, which will also house the membrane enclosed in an outer tube. Temperatures are measured with thermocouples. Exit gases are cooled with heat exchangers and analyzed by gas chromatography. Shutoff valves are operated by air-controlled actuators, supplied through solenoid-operated valves. The recorder/controllers, thermocouple readouts, and valve switches are installed in a separate instrument cabinet.

Membrane Fabrication and Characterization

Efforts to produce the optimum membrane are continuing. Over 100 tubular alumina membranes, having a diameter of about 0.9 cm, have been fabricated. Significant improvements were made in fabricating alumina membranes. The average pore radius of the membranes was reduced to less than 10 Å. The pore size distributions of several experimental alumina membranes were measured using the ORGDP dynamic pore size measurement technique. An example of the pore size distribution of a membrane prepared using our established preparation method is shown in Fig. 2. Several additional treatments have been used to improve the pore size distribution (i.e., either to reduce the large-pore-size tail or to shift the whole distribution to smaller pore sizes). The improvement after such treatment can be seen in the example in Fig. 3. The mean pore

radius of the improved membrane is less than 9 Å, with essentially no pores with a radius larger than 20 Å. Efforts to prepare membranes with still smaller pores are continuing.

Hydrostatic tests were made on six of the tubular membranes to determine their burst strength at room temperature. The burst strength at 1000°F is expected to be about 90% of the value determined at room temperature. The burst strength values ranged from 800 to 1600 psig, with a mean value of about 1300 psig.

Gas Permeability Measurements

Gas permeability measurements were completed on two series of membranes fabricated at ORGDP. The first set consisted of seven different membranes, made from alumina, having different pore radii ranging from about 7 to 18 Å. The permeabilities of the membranes were measured at room temperature using helium, nitrogen, and carbon dioxide. The second set consisted of six different membranes made from another material having different pore sizes ranging from approximately 9 to 22 Å in pore radius. The permeabilities of the second set of membranes were also measured, using air and sulfur hexafluoride in addition to helium, nitrogen, and carbon dioxide.

Typical results for one of the alumina membranes are shown in Fig. 4, in which the permeability-versus-pressure summation (sum of the feed and permeate pressures) is plotted. The permeability of the gases does not vary appreciably with pressure for the gases and pressure ranges that were tested. In general, the order of permeability is $\text{He} \gg \text{air} \geq \text{N}_2 \geq \text{CO}_2 > \text{SF}_6$. The data are summarized in Fig. 5, in which the calculated separation factors (ratio of permeabilities) for helium/nitrogen and helium/carbon dioxide are plotted versus the average pore size for the different alumina membranes. Also shown in Fig. 5 are the calculated ideal separation factors, assuming a Knudsen gas transport mechanism (i.e., relative gas flows are inversely proportional to the square root of the molecular weights). Permeability measurements for nitrogen,

helium, and carbon dioxide were made at higher pressures using the Oak Ridge National Laboratory test system on an alumina membrane obtained from ORGDP. Measurements were made at room temperature in the pressure range of 15 to 150 psi (Fig. 6). Nitrogen and helium permeabilities of a second membrane sample were measured up to a feed gas pressure of 589 psi (Fig. 7).

In general, the relative gas permeabilities correlate qualitatively with a Knudsen flow mechanism. However, it is apparent that other gas transport mechanisms play a role, particularly in the case of carbon dioxide. The enhanced permeability of carbon dioxide, probably due to membrane interaction, reduces the helium/carbon dioxide separation factor. The helium/nitrogen separation factor is also reduced somewhat as the membrane pore size decreases (Fig. 5) and as the pressure increases (Fig. 7). These data reinforce the need to develop membranes with smaller pores to take advantage of other gas transport mechanisms, such as molecular screening, to improve the separation factors for the gases of interest.

FUTURE WORK

Significant progress has been made in decreasing the pore size of our fabricated membranes, and we are continuing our effort to develop membranes with still smaller pores. The goal is to develop membranes with a mean pore radius below 5 Å.

Other efforts are directed toward developing better alumina-metal seals so that gas permeability measurements can be made at high temperatures. The permeability and separation of gas mixtures containing hydrogen, carbon monoxide, nitrogen, carbon dioxide, and methane will be determined for selected membranes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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Figure 1. Test Apparatus for Gas Permeability Measurements

Figure 2. Pore Size Distribution for a Membrane Fabricated at ORGDP

Figure 3. Pore Size Distribution of an Improved Membrane After Additional Treatment

Figure 4. Gas Permeabilities of an Alumina Membrane Fabricated at ORGDP (Mean Pore Radius, 18 Å)

Figure 5. Separation Factors for Helium/Carbon Dioxide and Helium/Nitrogen for a Series of Alumina Membranes with Different Pore Sizes

Figure 6. Gas Permeabilities of a Fabricated Alumina Membrane at Intermediate Pressures

Figure 7. Helium and Nitrogen Permeabilities of a Fabricated Alumina Membrane at High Pressure

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