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Using Inorganic Membranes to Separate Gases: R&D Status Review

B. Zane Egan

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**USING INORGANIC MEMBRANES TO SEPARATE GASES:
R&D STATUS REVIEW**

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Chemical Technology Division**

Date Published - November 1989

**Prepared for the
Morgantown Energy Technology Center**

**Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400**

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ABSTRACT

This report describes the preparation, properties, and utilization of inorganic membranes, primarily emphasizing the research and development aspects related to the separation of gases. Included are definitions, a brief historical background, a comparison of inorganic and polymeric membranes, a discussion of separation mechanisms, descriptions of various preparation or fabrication methods, studies and applications of inorganic membranes related to gas separations, and compilation of information on commercially available porous materials. The information is evaluated in terms of limitations, needs, and prospects for future development.

The major types of gas transport through porous membranes are discussed in terms of viscous flow, free-molecule (Knudsen) flow, surface diffusion, capillary condensation, surface adsorption, ion exchange, and molecular sieving. Membrane preparation and fabrication techniques include: extrusion, powder suspension, molten salt inclusion, phase separation and leaching, nuclear track etching, dynamic deposition, anodic oxidation, pyrolysis, particle dispersion/slipcasting, and thin film deposition. Metallic, porous glass, ceramic, and metallic oxide membranes for separating various gases are tabulated. The needs for improved membrane materials, metal-to-nonmetal seals which will withstand high temperatures and pressures, and better membrane characterization techniques are discussed. There are 199 references cited.

1. INTRODUCTION

1.1 INFORMATION SOURCES

Information for this report was obtained from computer searches of various literature data bases, including Metals Abstracts, Ceramic Abstracts, and Chemical Abstracts. Other information sources were the North American Membrane Society meetings; Membrane Technology/Planning conferences; Membrane and Separation Technology News; North American Membrane Society (NAMS) Quarterly; workshops; special reports from Business Communications Co., Inc.,¹ Technical Insights, Inc.,² and SRI International; and personal contacts with the people and organizations whose work involves inorganic membranes.

1.2 SCOPE

This report describes the preparation, properties, and utilization of inorganic membranes, primarily emphasizing the research and development aspects related to the separation of gases. It required some definitions, a brief historical background, a comparison of inorganic and polymeric membranes, a discussion of separation mechanisms, descriptions of various preparation or fabrication methods, studies and applications of inorganic membranes related to gas separations, and compilation of information on commercially available porous materials. Finally, the information was evaluated in terms of limitations, needs, and prospects.

1.3 DEFINITIONS

It is difficult to define a membrane without describing what it does. Papers have been devoted to this topic alone.³ A synthetic

membrane can be defined as a semi-permeable barrier between two phases through which differential transport can occur. Differential transport occurs when the membrane restricts the transport of different species in some specific way. The transport process is a non-equilibrium process, and separation of chemical species results from differences in transport rates through the membrane.

A membrane can be organic or inorganic, homogeneous or heterogeneous, symmetric or asymmetric, charged (either positive or negative) or uncharged, dense or porous, solid or liquid (or even gases). Inorganic membranes include metals, metal oxides, ceramics, glasses, salts, and for the purposes of this report, carbon, and inorganic polymers.

Membranes are frequently identified or characterized according to the pore size or the size of the materials they are used to separate. Reverse osmosis (also called hyperfiltration) or gas separation membranes separate materials on the molecular level and have pore sizes* less than about 50 nm; ultrafiltration membranes have pore sizes in the range of 2 to 100 nm; microfiltration membranes have pore sizes in the range of 100 to 5000 nm and membranes with pores >5000 nm are particulate filters. Inorganic membranes have been used primarily for microfiltration and ultrafiltration.

1.4 BACKGROUND

1.4.1 Chronological Development. Early inorganic membranes were developed about fifty years ago. Corning Glass developed a

*1 nm = 1 nanometer = 10^{-9} m = 10^{-3} μ m = 10 angstroms = 10 Å

homogeneous porous glass (Vycor) with 20 to 40 Å pores in the 1940s. Also in the 1940s, membranes were developed in the Manhattan Project to enrich uranium by separating uranium isotopes as UF_6 . This was the first large-scale membrane gas separation process. Over the years, the Department of Energy has encouraged and supported significant improvements in the gaseous diffusion process, including a $\$1.5 \times 10^9$ cascade improvement program at the Oak Ridge Gaseous Diffusion Plant. Since much of this technology remains classified for security reasons, it has not been directly transferred to commercial applications. However, membrane research and development has continued for many years at the Oak Ridge Gaseous Diffusion Plant and efforts are underway to transfer some of the technology to industry. Membranes developed by the French for isotope enrichment were described in the late 1950s and early 1960s, and formed the basis for some of the present commercial inorganic membranes.

In the mid-1960s, dynamically-formed membranes, formed by depositing zirconia or titania from a suspension onto porous carbon tubular supports, were developed at Oak Ridge National Laboratory for separating electrolytes from aqueous solutions. These formed the basis for the Ucarsep^R membranes introduced by Union Carbide in the 1970s. These membranes consisted of a thin layer of zirconia on the inside of tubular carbon. This technology was later licensed by the French (Societe de Fabrication d'Elements Catalytiques, SFEC), who modified it and called their membranes Carbosep^R.

In the 1980s, more applications of inorganic membranes were identified, and there was increased commercial activity as well as

increased research and development. Norton began marketing tubular, two-layer, asymmetric, composite alumina membranes with pore sizes in the 0.2 to 1 μm range. Ceraver produced a three-layer alumina membrane with pore sizes ranging from 40 Å to 5 μm . These were later produced in monolith configurations containing several channels to obtain a higher surface area/volume ratio. Alcoa acquired Ceraver and began marketing their products; Millipore is now the sole distributor of the Norton Ceraflo^R products.

In 1986, the Anotec subsidiary of Alcan produced an asymmetric alumina membrane with pore sizes of 0.02 and 0.2 μm , having a very narrow pore size distribution, by anodic oxidation of aluminum. Although these were the first commercial membranes of this type, similar membranes were evaluated in the 1950s for uranium enrichment in France⁴ and Sweden.⁵ GFT (Gesellschaft für Trenntechnik-Le Carbone Lorraine) recently introduced carbon composite membranes, available in pore sizes from 40 Å to 1.0 μm . In the past five years, several companies have produced developmental quantities of membranes from various materials in different configurations (see Sect. 6).

Until recently, inorganic membranes were used primarily for microfiltration or ultrafiltration. As mentioned earlier, there has been no large-scale application of porous inorganic membrane separations of gases except for uranium enrichment, even though the permeability of several gases in various inorganic materials has been studied. 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, and 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. Other membrane materials include silicon nitride, zeolites, and mixtures of metals and salts.

1.4.2 Inorganic vs. Polymeric Membranes. Most commercial membrane development has focused on polymeric membranes, beginning some forty years ago. One of the primary driving forces for the development was the perceived critical need to desalt sea water. The development started with ion exchange membranes, since the objective was to remove salts. Development evolved toward the use of reverse osmosis membranes using cellulose acetate, and then eventually asymmetric "skin" membranes, made from various polymers such as aromatic polyamides, polysulfone, nylon, polytetrafluoroethylene, polypropylene, and silicones were developed. For practical applications of the membranes, it was necessary to assemble them into modules. Modules have evolved from plate-and-frame configurations to spiral-wound to hollow fibers. The commercial utilization of polymeric membranes for gas separations took place over the past ten years, starting with the introduction of the Prism^R membranes by Monsanto in 1979.

The efficiency of polymeric membranes decreases with time due to fouling, compaction, biological and chemical degradation, and thermal instability. Because of this limited thermal stability and susceptibility to abrasion and chemical attack, polymeric membranes

have not found applications in separation processes where hot, reactive gases are encountered. The biggest advantages of inorganic membranes over polymeric membranes are derived from their chemical and thermal stability. Most of the polymeric membranes are limited to a maximum temperature of about 100°C. Some hybrid membranes having polymer membranes coated onto inorganic supports are stable to higher temperatures (200 to 250°C).

Inorganic membranes, especially ceramics, are stable to much higher temperatures, and the limitation is usually set by the seals and module materials and not the membrane itself. The principal disadvantages of inorganic membranes are perceived to be brittleness and high cost. The brittleness depends on the choice of membrane material and the physical characteristics of the fabricated membrane. The higher cost can be offset somewhat by longer membrane life, improved fabrication methods, and improved economics of scaleup in manufacturing.

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 3 to 4 nm. 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.

2. MECHANISMS OF GAS TRANSPORT THROUGH MEMBRANES

Transport of gases through a polymeric membrane is usually described by a "solution/diffusion" mechanism.⁶ A gas molecule is

adsorbed on one side of the membrane, dissolves in the membrane, diffuses through the membrane, and desorbs on the other side. Gas permeability rates, and ultimately separation factors, are functions of the solubility and diffusivity of the particular gaseous components in the specific membrane material. Various modifications have been proposed and mathematical models presented in the literature to quantitatively describe the transport of gases through polymeric membranes. These will not be discussed in this report.

The major types of gas transport through porous membrane materials are viscous flow, free-molecule (Knudsen) flow, surface diffusion, capillary condensation, surface adsorption, ion exchange, and molecular sieving.⁷⁻¹² The Knudsen number, defined as the ratio of the mean free path of the gas molecules (average distance between collisions) to the pore radius, is useful in describing the different kinds of transport. If the Knudsen number is $\ll 1$, viscous flow predominates, and the gas flux through the pore is described by the expression:¹⁰

$$G_{\text{vis}} = \frac{r^2(P_1^2 - P_2^2)}{16L\mu RT}$$

where r = pore radius
 P_1 = partial pressure of gas on feed side
 P_2 = partial pressure of gas on permeate side
 L = pore length
 μ = gas viscosity
 R = gas constant
 T = absolute temperature
 G_{vis} = viscous flow

This essentially describes the bulk flow of gases and no significant separation of a gas mixture occurs.

2.1 KNUDSEN DIFFUSION

If the pore is much smaller than the mean free path of the gas molecules (Knudsen number >10), then Knudsen or free-molecule diffusion occurs, and the gas flux is described by the expression:

$$G_{\text{mol}} = \frac{8r(P_1 - P_2)}{3L(2\pi MRT)^{1/2}}$$

M = molecular weight
 G_{mol} = molecular flow

The viscous flow, G_{vis} , and the molecular flow, G_{mol} , are usually expressed in mol/cm²/s. For Knudsen flow, the separation factor for binary gas mixtures can be estimated from the square root of the ratio of the molecular weights. The smaller molecules with a higher velocity move through the pores faster. Examples of some calculated separation factors for several gas pairs, based on Knudsen flow through a porous material are shown in Table 1. These are ideal separation factors. Actual separation factors also depend on the molar composition (mol fraction) of the gases in the feed and permeate. Other factors, such as back-diffusion, tend to reduce the separation factors.

2.2 MOLECULAR SIEVING

As the pore size decreases and approaches the size of a gas molecule, some molecular sieving or screening can occur. Separation factors greater than 10 should be achievable¹³ as the pores become smaller than about 0.5 nm. If the membrane has pore sizes between the diameters of the smaller and larger gas molecules, then only the

smaller molecule can permeate, and the separation factor would approach infinity.

Table 1. Calculated separation factors based on Knudsen flow for selected binary gas mixtures

Gas pair	Separation factor
H ₂ /N ₂	3.73
H ₂ /CO	3.73
H ₂ /H ₂ S	4.11
H ₂ /CO ₂	4.67
H ₂ /SO ₂	5.64
N ₂ /O ₂	1.07
²³⁵ UF ₆ / ²³⁸ UF ₆	1.004

In practice, there will generally be a distribution of pore sizes, and the gas permeabilities can best be described by a combination of transport mechanisms. Also, pore sizes on the order of crystal spacings becomes a more complex concept. Are these pores, crystal spacings, or crystal defects? As membrane pore sizes approach crystal dimensions, the gas transport may involve gas interaction with the crystal lattice. From a practical standpoint, as the pore size decreases, the membrane porosity is expected to decrease also, resulting in a lower gas flow through the membrane. So the pore size and porosity must be balanced to produce a practical, efficient membrane.

2.3 ADSORPTION

Gas adsorption on the surface of the pore wall may result in surface flow or surface diffusion and it also effectively decreases the pore size. This affects the total gas flux through the membrane, depending primarily on the pore size and the thickness of the adsorbed layer, and becoming more significant as the pores become smaller. Surface flow generally increases the gas flux over that expected for free-molecule flow alone. Adsorption and surface diffusion have been used to explain, for example, the separation by porous glass membranes of gases having the same molecular weight.¹⁴⁻¹⁶

2.4 CAPILLARY CONDENSATION

Capillary condensation occurs when the combination of sufficiently small pores and multilayer adsorption of a gas due to a high relative pressure results in the pore becoming filled or partially filled with a condensed phase. Then condensate flow and/or vaporization of the condensate may affect the apparent gas flow or flux through the pore. If the pores are completely filled by condensate, then other gases may be excluded (assuming they are insoluble in the condensate) and prevented from flowing through the pores of the membrane, thereby enhancing the separation.

2.5 OTHER TRANSPORT MECHANISMS

Other gas transport mechanisms such as ion exchange, solution/diffusion, and solid diffusion involve interaction between the gas and the membrane. Solution/diffusion is more often used to describe gas transport across a polymeric membrane. However, it is

possible for gases to dissolve in an inorganic membrane, diffuse through the membrane, and be released as permeate. The gases may also interact through ion-exchange processes with the membrane matrix. These transport mechanisms may operate especially in "facilitated transport" and "molten salt" membranes. Membrane interactions can also be used to explain the permeability of hydrogen through certain metals.

3. PREPARATION OF INORGANIC MEMBRANES

Several methods can be used to prepare porous membranes from inorganic materials, and the choice of method depends upon the desired membrane material and the pore size. Since many membranes are a multilayered, composite material, different methods may also be used to prepare the support material and the separating layer. Preparation and fabrication techniques include: (1) extrusion; (2) powder suspension; (3) molten salt inclusion; (4) phase separation and leaching; (5) nuclear track etching; (6) dynamic deposition; (7) anodic oxidation; (8) pyrolysis; (9) particle dispersion/slipcasting; and (10) thin film deposition. The primary methods which have been used to prepare commercial membranes are phase separation and leaching, anodic oxidation, particle dispersion/slipcasting, and pyrolysis. These methods will be described in more detail than the others.

3.1 EXTRUSION

Powdered materials are mixed with solvents and binders to form a paste which is forced through dies to form a "green" body, usually a tube. The tube is then heated to remove solvent and binder, and then

may be sintered to consolidate the powder into a stable, porous material. Extrusion is used to prepare some membrane support materials, and for the fabrication of membranes with larger pore sizes (>100 nm).

3.2 POWDER SUSPENSION

Powder of appropriate particle size is suspended in a solvent, along with organic binders and surfactants, and deposited as a thin layer on a porous support, forming a thin, filter-cake layer. Drying and further thermal treatment are used to stabilize the final product.

3.3 MOLTEN SALT INCLUSION¹⁷⁻¹⁸

A continuous thin layer of a molten salt is immobilized in the pores of a rigid, porous support. The dry salt can be melted in the support, or the support can be soaked in the molten salt. The support can be either ceramic or metallic. Salts are chosen to have the appropriate melting point and generally are involved in reversible oxidation-reduction reactions with the gases to be separated.

3.4 PHASE SEPARATION AND LEACHING

Phase separation (transition) and leaching is a technique used primarily to prepare porous glass,¹⁹⁻³⁰ but the concept may also be used to form porous metals.³¹ A borosilicate glass is heated to 550 to 600°C and allowed to separate into two phases: an acid-insoluble, silica-rich phase and an acid-soluble, borate phase. The borate phase is then removed by acid (e.g., HCl + ethylene glycol) leaching, leaving a porous silica-rich phase. This technique can be used to produce either porous glass tubes or hollow glass fibers. Porous glass having pore sizes <2 nm can be produced this way.

3.5 NUCLEAR TRACK ETCHING³²⁻³⁴

When a particle from a radioactive source passes through a material, a characteristic "track" is made in the material. The material in the track can be leached away, leaving a hole. This technique has been used primarily to form uniform pores in thin polymeric films to produce filters, e.g., Nucleopore.^R However, this technique can also be applied to some inorganic materials. Mica foils have been irradiated with heavy ions from an accelerator, cleaned with potassium dichromate/sulfuric acid, and etched with HF. Porous mica has been produced with pore sizes ranging from 6 to 6×10^5 nm with a narrow pore size distribution and an effective porosity between 5 and 40%.

3.6 DYNAMIC DEPOSITION³⁵⁻⁴⁰

Membranes can be formed in situ by precipitation of a metallic oxide, followed by filtration to produce a colloidal layer on a porous support. Zirconia is the most widely used membrane material, and it is usually formed on porous stainless steel or carbon tubes. Modifiers such as polyacrylic acid may be added. Silica membranes on ceramic supports may also be made this way. These membranes are usually formed from an aqueous solution, and they tend to crack and separate from the support when they are dried. Consequently, they are not generally used for gas separations.

3.7 ANODIC OXIDATION^{4,5, 41-49}

This method is used to produce the commercial Anapore membranes. A thin, high-purity aluminum sheet is anodically oxidized on one side

in an acid electrolyte. The electrolyte may contain sulfuric, phosphoric, chromic, or oxalic acid, or mixtures of these. The unoxidized metal remaining on the other side is then removed by dissolution in a strong acid, leaving the porous metallic oxide membrane. The membranes are stabilized by a hydrothermal treatment.

Impurities in the starting sheet may result in defects in the membrane. Pore size is controlled by electrolyte composition and voltage. The current and anodizing time control the thickness. The membranes are asymmetric with a thick layer of larger pores, and a thin layer of smaller pores connected to the larger pores. Membranes with pore sizes ranging from 10 to 200 nm have been produced.

3.8 PYROLYSIS⁵⁰⁻⁵⁴

Polymers are coated onto porous supports, and then degraded by controlled pyrolysis to produce a membrane. Silica membranes can be produced from silicone rubber, while carbon membranes can be produced from thermosetting polymers such as polyacrylonitrile.

This technique is used by GFT to produce their commercial porous carbon composite membranes. The support is formed by the pyrolysis of an appropriate polymer tube in a controlled environment. One or two layers are added to the support. For medium size pores, an organic solution of phenolic resins is deposited on the support, followed by controlled pyrolysis. To produce smaller pores, a film is produced by in situ polymerization, followed by stepped pyrolysis. Surface properties, pore sizes, and morphology are controlled by additives and the degree and type of pyrolysis. Film thickness is 100 to 1000 nm

with a porosity of 65 to 75%. Pore sizes of these membranes range from 4 to 1000 nm.

3.9 THIN-FILM DEPOSITION⁵⁵⁻⁵⁹

Various techniques are available to produce thin films on a substrate. Some of these techniques are also applicable to the preparation of inorganic membranes. Chemical vapor deposition, plasma deposition, sputtering, ion plating, and metal plating can be used to coat a porous support in ways to control the pore size. Deposition of various materials can be used to reduce the pore size of the support and to modify the surface characteristics of the support. As examples, one side of a porous polycarbonate membrane was coated with a thin layer of titania by sputtering; and SiCl_4 in the gas phase was introduced into a flame to form fine SiO_2 particles which were deposited on a target to give a porous glass membrane. Porous silicon nitride has been coated with alumina by chemical vapor deposition. Thin metal films of gold and palladium have been formed by plasma deposition.

3.10 PARTICLE DISPERSION/SLIPCASTING

Composite ceramic membranes can be prepared by slipcasting from a dispersion of particles. In slipcasting, particles are deposited from a suspension onto a porous support in one or more layers by dipping or casting. The particle dispersion can be prepared by precipitation, crystallization, and/or sol-gel processes. The slip containing the particles, along with organic binders and/or viscosity modifiers, flows into the pores of the dry support by capillary action

(pressure differential). The solvent is removed and the particles are retained to form a layer. The layer is then stabilized by drying and thermal treatment to form a membrane.

Slipcasting is probably the most widely used technique for preparing metallic oxide and ceramic membranes.⁶⁰⁻⁸⁰ Membranes of alumina, zirconia, titania, and silica have been prepared by this method. When preparing membranes with small pores by this method, it is necessary to prepare a stable slip (suspension) of very small particles. A sol-gel technique is frequently used for this purpose.^{61,66,68,81-87} This technique has also been studied extensively as a process to produce nuclear fuels. Steps in the sol-gel process usually include hydrolysis, peptization, gel formation, drying, and thermal treatment. Metal alkoxides and esters (e.g., aluminum butoxide, titanium isopropoxide, tetramethyl orthosilicate) and metal chlorides (e.g., titanium tetrachloride, zirconium tetrachloride) are hydrolyzed to form a precipitate. Mixtures of these materials may also be used. Organic binders such as polyvinyl alcohol, methyl cellulose, or hydroxyethyl cellulose, are added to the slip to increase the strength of the unfired membrane. Plasticizers such as glycerols, glycols, and sorbitol are added to prevent cracking of the membrane during thermal treatment. The precipitate is peptized (dispersed) with acid (e.g., hydrochloric, nitric, or perchloric) to produce a stable sol. The sol is contacted with the support, reaching a concentration at which a gel layer is formed. The gel layer is then carefully dried, calcined, and further heat-treated to produce a stable membrane. The drying and calcining are carried out slowly to

prevent membrane cracking. Some cracks and defects can be repaired by repeating the casting procedure.

Membrane thickness is controlled by dipping time, slip concentration, and the pore size of the support. The pore size depends primarily on the particle size of the sol. The time and temperature of the thermal treatment affects pore size, porosity, and sometimes phase composition. Membranes prepared by this method have pore sizes ranging from about 2 nm to several thousand nm, with a porosity up to 55%.

In a variation of the slipcasting method, a porous support is filled with a volatile solvent such as acetone, then coated with a suspension of ZrO_2 . The excess suspension is drained off, the membrane is heated to remove the volatile liquid, and the zirconia fills the voids. Further heat treatment and washing stabilizes the membrane.

3.11 OTHERS

Polyphosphazenes have nitrogen/phosphorous backbones rather than a carbon backbone, although the side groups attached to the phosphorous are organic. Phosphazene polymers are derived from cyclic hexachloro or hexafluoro trimers. They are cast into membranes by the same knife casting techniques used to produce organic polymeric membranes. These inorganic/organic membranes have a higher thermal stability than the organic polymeric membranes.⁸⁸⁻⁹⁰

Metals, heteropoly acids, and heteropoly salts have been mixed with polymers to produce polymer blend membranes.⁹¹⁻⁹³ Porous supports of alumina and glass have been coated with polymer films⁹⁴⁻⁹⁵ and in some cases the pores have been filled by in situ polymerization.⁹⁶

4. MEMBRANE RESEARCH

4.1 MEMBRANE CENTERS

In addition to the research and development activities of various companies, several universities have established research centers or programs to carry out membrane R&D. Many have financial support from industry. Some of these which include inorganic membrane studies are listed in Table 2. Various aspects being addressed by these centers include (1) preparation and characterization of inorganic polymers, ceramics, and metals; (2) membrane applications; (3) modeling and simulation; (4) membrane reactor development; (5) transport mechanisms; and (6) membrane catalysis.

Table 2. Academic inorganic membrane research

University	Principal investigators	Center/program
University of Cincinnati	S.T. Hwang	Center of Excellence for Membrane Technology
University of Texas	J.R. Fair W.J. Koros	Separations Research Program
University of Wisconsin	M.A. Anderson	Water Chemistry Program
Rutgers (State University of New Jersey)	L.C. Klein	Center for Ceramic Research
Syracuse University	J. Fendler A. Stern I. Cabasso	Center for Membrane Engineering and Science
Worcester Polytechnic Institute	Y.H. Ma	Center for Inorganic Membrane Studies

The Center of Excellence for Membrane Technology at the University of Cincinnati was started by a grant from Standard Oil of

Ohio. Research includes studies on a continuous membrane column for gas separations; developing optimal cascades for gas separations; transport mechanisms of condensible vapors through porous materials, especially porous glass; modeling membrane gas separators; preparation of silica membranes by pyrolysis of silicone rubber; and preparation of hybrid membranes by in situ polymerization.

Membrane research directed by M. A. Anderson at the University of Wisconsin is directed toward producing ceramic membranes. The research has focused on the preparation of alumina and titania membranes, primarily using sol-gel techniques, and also preparing clay and alumina membrane supports.⁶⁶⁻⁶⁷ Parametric studies have been used to determine the solution variables that control the characteristics of the final membranes. Membranes with pore diameters of 18 to 50 Å have been produced.

At the Rutgers Center for Ceramics Research, L. C. Klein et al. have been investigating the preparation of silica membranes, again using sol-gel techniques.⁸²⁻⁸³ They have produced a silica membrane by casting a solution containing tetraethyl orthosilicate, ethanol, and water onto tetrabromoethane. Atmospheric moisture reacted with the solution, forming a thin sheet, which was then dried. Membranes having pore sizes from 5 μm to 65 μm were produced.

The Center for Membrane Engineering and Science was established at Syracuse University in 1987. Much of the research is directed toward polymeric membranes; however, one of the stated objectives is to develop ceramic and other inorganic membranes. Other research is directed toward transport mechanisms, membrane characterization, and

new applications. Stated areas of interest include (1) the preparation and characterization of oxides used in sol-gel procedures; (2) investigation of colloid chemistry related to metal oxide gelation; and (3) inorganic polymers and metal barriers.

The Center for Inorganic Membrane Studies at Worcester Polytechnic Institute is directed by Y. H. Ma. The center was established in 1988 with initial support from Alcoa and Texaco. Areas of investigation include (1) inorganic membrane synthesis, (2) reactive membrane studies, (3) fouling and transport studies, (4) characterization of membrane degradation, (5) biotechnology applications, and (6) NMR spectroscopic studies. A High Temperature Aerosol Decomposition (HTAD) process was developed to synthesize hollow spheres. Transport studies on catalytic membranes to dehydrogenate ethylbenzene are being conducted. Magnetic Resonance Velocity Imaging (MRVI) is used to study flow patterns in inorganic membrane reactors.

4.2 University and Government Research

Membrane-related research is also being carried out at the University of Washington, North Carolina State University, the University of Massachusetts, and Virginia Polytechnic Institute and State University. Research on dynamically formed membranes, started at Oak Ridge National Laboratory, has been continued at Clemson University, partly in collaboration with Conservation and Resource Recovery Engineering (CARRE). The Department of Energy is supporting programs at Alcoa, SRI International, Oak Ridge National Laboratory, and Oak Ridge Gaseous Diffusion Plant to develop and test inorganic membranes for high temperature gas separations, particularly for

applications in coal gasification processes. CeraMem is developing ceramic membranes for gas separations under the DOE Small Business Innovation Research program.

Polyphosphazene membranes have been developed and are being evaluated at the Idaho National Engineering Laboratories. Initial studies involved diffusion measurements of alcohols in poly[bis(trifluoroethoxy)]phosphazene.⁸⁹ The studies were extended to measurements of gas permeabilities of poly[bis(phenoxy)]phosphazene.⁸⁸ Similar membranes are being developed and evaluated in Italy by Separem S.p.A., in collaboration with E. Drioli at the University of Calabria.⁹⁰

4.3 Worldwide Membrane Research

Research on ceramic membranes in Europe is concentrated in France and the Netherlands. Most of the French technology evolved from the Commissariat a l'Energie Atomique. Research has been focused on development of sol-gel and slipcasting techniques to prepare ceramic membranes, primarily of alumina and zirconia. Various aspects of membrane development are under study by L. Cot, C. Guizard, A. Larbot, et al.,^{68,69,74,78,79,81,86,97} at the Ecole Nationale Supérieure de Chimie de Montpellier, Laboratoire de Physicochimie des Matériaux. Similar studies are carried out at Twente University of Technology, Enschede, The Netherlands, by A. J. Burggraaf, K. Keizer, et al.⁶⁰⁻⁶⁵ Research on tubular alumina membranes for ultrafiltration and gas separations is also carried out at the Netherlands Energy Research Foundation ECN by R. A. Terpstra, et al.,⁶⁴ in collaboration with Twente University.

A Basic Research in Industrial Technology for Europe (BRITE) program has been established to encourage collaboration between industrial and academic organizations across Europe. The United Kingdom Atomic Energy Agency (UKAEA) Harwell, Permutit, and Morgan Matroc in the United Kingdom; Enichem and Eniricerche in Italy; and ECN in Holland are collaborating in a project on "New Techniques for the Separation of Liquids and Gases Using Improved Inorganic Membranes."⁹⁸

In Israel, membrane research at the Atomic Energy Commission, Nuclear Research Center-Negev, has developed a molecular sieve carbon membrane by pyrolysis of polymeric hollow fibers.^{53,54,99} The membrane has been evaluated for the separation of various gases.

In addition to the research at the various Japanese companies which market membranes, research on inorganic membranes is also carried out at several universities. Research on porous glass is performed at the National Chemical Laboratory for Industry.¹⁰⁰⁻¹⁰⁵ Other membrane research is being done at Yokohama National University (glass and ceramics),¹⁰⁶⁻⁷ Tohoku University (hybrid membranes and anodic alumina),^{57,94,95,108} University of Tokyo (metal alloys),¹⁰⁹ and Hiroshima University (water/alcohol separations).¹¹⁰⁻¹³

5. SEPARATING GASES WITH INORGANIC MEMBRANES

Isotope separation is still the only large-scale application of porous inorganic membranes for separating gases. However, as indicated above, 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. Porous glass membranes have received a lot of attention, particularly in Japan, for separating gases. Metallic oxides and ceramics have been utilized to separate a larger variety of gases. Many of these studies involve the separation of hydrogen from other gases, and rely primarily on a Knudsen diffusion transport mechanism, which is dependent on the relative molecular weights of the gases. However, other transport mechanisms, such as surface adsorption and diffusion, frequently play a significant role.

5.1 METALLIC MEMBRANES

Metallic membranes have been investigated worldwide, primarily for separating hydrogen isotopes (Table 3) and for separating hydrogen from other gases (Table 4). Many of the studies have evolved from an interest in the extent and effect of hydrogen permeation of structural metals. Others are directed specifically toward the problem of separating hydrogen, deuterium, and tritium isotopes. One application is the removal of tritium from radioactive effluent from nuclear fuel reprocessing plants. Another is separation of the hydrogen isotopes produced in a fusion reactor.

Most commonly, palladium alloys are used to separate the gaseous hydrogen isotopes. Palladium is usually alloyed with silver (typically 20 to 25%) to improve the physical and mechanical properties of the material. To reduce cost, membranes have been made from niobium, tantalum, and vanadium, each coated with a palladium alloy. Alloys of palladium and yttrium have also been used.¹²³ Even with the alloys, some hydrogen embrittlement occurs at higher temperatures (300 to 750°C) and pressures (5 bars).¹⁴⁵ In addition to

palladium, an iron (α -Fe) membrane has been used to separate hydrogen isotopes from a mixture with steam.¹³⁴

Table 3. Metallic membranes for separating hydrogen isotopes

Material	Gases	Location	Reference
Pd alloy	H ₂ /HT, H ₂ /D ₂ , H ₂ /HD/D ₂	Japan	114-116
Pd alloy	H ₂ /T ₂	Japan	117
Pd alloy	H ₂ /D ₂ /T ₂	Japan	115, 118
Pd, Pd alloy	H ₂ /D ₂	Japan	109, 119
Pd-Ag alloy	H ₂ /T ₂	Japan	120
Pd alloy	H ₂ /D ₂ /T ₂	U.K.	121, 122
Pd-Y alloy	H ₂ /D ₂	U.K.	123
Pd-Ag, Pd-Y	H ₂ /D ₂ /T ₂	U.K.	124, 125
Pd alloy	H ₂ /T ₂	Fed. Rep. Ger.	126
Pd alloy	H ₂ /DT/D ₂	U.S.S.R.	127-131
Pd-Ag	T ₂	U.S.	132
Fe	H ₂ /D ₂ /T ₂	U.S.S.R.	133
α -Fe	H ₂ /D ₂ /T ₂	Fed. Rep. Ger.	134
Ni-Al alloy	H ₂ /HT	Japan	135
Transition metals	H isotopes	U.S.	136

Metallic membranes have also been used to separate hydrogen from several other gases. Palladium membranes have been used to separate hydrogen produced from the steam conversion of methane to carbon monoxide, carbon dioxide, and hydrogen on a nickel catalyst.¹⁴² Vanadium, niobium and tantalum foils coated with Pd and Pd-Ni and Pd-

Cu alloys have been used in Germany to separate hydrogen from mixtures containing methane, nitrogen, carbon monoxide and carbon dioxide.¹⁴³⁻⁶

Table 4. Metallic membranes for gas separations

Material	Gases	Location	Reference
Pd alloys	H ₂ , CO, N ₂ , CO ₂	U.S.S.R.	137, 138
Pd-Ru alloy	H ₂ , N ₂	U.S.S.R.	139
Metallic, Metallic/oxide	H ₂ /NH ₃ /N ₂	U.S.S.R.	140, 141
Pd	H ₂ /CH ₄	Fed. Rep. Ger.	142
Ti-Ni, Pd, Nb, Ta, V	H ₂ /CH ₄ H ₂ /CO H ₂ /CO ₂ H ₂ /N ₂	Fed. Rep. Ger.	143-145
(Pd-Cu, Pd-Ag)/ Ta-Nb alloy	H ₂	Fed. Rep. Ger.	146
Pd-Ag	H ₂ /HI H ₂ /He	Fr	147, 148
Pd-(Ag, Ni)	H ₂ /C ₂ H ₄	U.S.	149, 150
Ti-Zr alloy	H ₂	U.S.	151
Cu, Ni alloys	H ₂ /N ₂	Japan	152
Pd alloy	H ₂ /air	Japan	153
Pd/Nafion	H ₂ /N ₂	Japan	92, 93
Pd, Pt, Ni/plastic	H ₂	Japan	154
Pd/porous glass	H ₂ /N ₂	Japan	155
Pd, Pt/alumina	H ₂ /N ₂	Japan	57, 156

In Russian studies, an alloy of Pd containing 2 to 10% Ru was used to separate hydrogen from a hydrogen-nitrogen mixture at 300 to 600°C and 10 to 70 bar.¹³⁹ Pd-Ag-In alloys were used to separate hydrogen from mixtures containing carbon monoxide, carbon dioxide, and nitrogen.¹³⁰ Pd-Ag-In-Y alloys have also been fabricated into seamless pipes and the hydrogen permeability measured.¹²⁷ Hydrogen was recovered from a mixture with ammonia and nitrogen using a metallic membrane after thermal dissociation of the ammonia.¹⁴⁰

In Japan, composite membranes for separating gases were made by sputtering Pt/Pd (80/20 weight ratio) onto an anodic alumina film treated with a palladium solution.⁵⁷ A palladium membrane was also formed on a porous glass support by dipping the surface-activated porous glass into a palladium coating solution.¹⁵⁵ This membrane was used to separate hydrogen from a mixture with nitrogen. Membranes of palladium on an alumina support were prepared using a similar procedure.^{57,156}

Several "hybrid" membranes have been prepared by incorporating metals into non-metallic substrates. Norita has incorporated Pd, Pt, or Ni powders in a plastic membrane to improve the selectivity for hydrogen.¹⁵⁴ Pd, Pt or Rh have also been incorporated in Nafion membranes by an ion-exchange/reduction procedure.⁹²⁻⁹³ Ishikawa, et al., prepared a membrane from a mixture containing epoxy resin and a La-Ni-Al alloy powder coated with copper.¹⁵²

Inorganic anisotropic hollow fibers have been described in which metals such as Pt, Pd, Ag, and Ni are incorporated into polymeric fibers and sintered to produce a membrane useful for hydrogen separation.⁹¹

Union Carbide demonstrated the commercial application of palladium membranes for large-scale hydrogen production some 25 years ago.¹⁵⁷ Plants with capacities ranging from 0.5 to 4.2 million cubic feet (1.4 to $12 \times 10^4 \text{ m}^3$) of hydrogen per day were built. Operating temperature was 575 to 750°F (300 to 400°C).

5.2 POROUS GLASS MEMBRANES

Porous glass membranes have been around over fifty years, and most of them are produced by a phase separation/leaching process. Glasses with pore sizes ranging from a few angstroms to several thousand nanometers have been produced.

Several studies, particularly earlier ones,^{14,15,158} on porous glass were concerned primarily with gas transport mechanisms through "capillary pores," using porous glass as a model, rather than with specific gas separations. It was found that even though pore sizes were 4 nm or larger, some of the gases were not separated according to molecular weight. Indeed, pentane isomers showed different diffusion behavior.¹⁴ Obviously, transport mechanisms other than Knudsen flow, including adsorption and surface diffusion, can occur in porous glass membranes. The effects of temperature were also established several years ago.

The separation of several gases with porous glass membranes has been demonstrated (Table 5). Kammermeyer and coworkers^{15,158} studied the behavior of light hydrocarbons, $\text{H}_2\text{-D}_2$, $\text{O}_2\text{-CO}_2$, and He-N_2 mixtures in porous Vycor at temperatures up to 600 K (327°C). The behavior of pentane isomers and inert gases was reported by Wright, et al.¹⁴ Significant efforts were made to quantitatively describe the results of these experiments.

Table 5. Porous glass membranes for separating gases

Material/support	Pore size (Å)	Gases	Location ^a	Ref.
Glass	40	H ₂ , D ₂ , CO ₂ , CH ₄ , C ₂ H ₆ , C ₃ H ₈	U.S.	15
Glass	40	O ₂ /CO ₂ He/N ₂ CO ₂ /C ₃ H ₈ N ₂ /C ₂ H ₄	U.S.	158
Glass	40	He, Ar, CO ₂ , C ₂ H ₆ , C ₃ H ₈	U.S.	14
Glass	-	Ar, Kr, N ₂ , O ₂ , CH ₄ , C ₂ H ₆	U.K.	159
Glass	31, 58 110, 200	H ₂ /CO	J	102
Glass	45	H ₂ /H ₂ S	J	104, 105, 161
Glass	-	H ₂ /CO	J	101, 160
Glass	-	He/CO ₂	J	100
Glass	15-30	H ₂ /He/N ₂	J	21
Glass	-	H ₂ , He, CO ₂ , CH ₄	J	162
Glass	40	He, Ar, O ₂	J	103
Glass (hollow fiber)	40-300	H ₂ /N ₂	J	22, 23
Glass (hollow fiber)	10-3000	H ₂ -CO/H ₂ O	J	163, 164
Glass/ceramic	-	CO ₂ /CH ₄	J	106
Glass/ceramic	78-640	N ₂ , CO ₂ , CH ₄	J	107
Glass/alumina	30-160	H ₂ /N ₂	J	20
Glass (surface modified)	-	CO ₂ , Freon 22, Freon 114	J	165
Silicone/glass	-	He, Ar, N ₂ , CO ₂ , H ₂ , O ₂ , CO, C ₂ H ₄	U.S.	96

^aU.S. = United States; U.K. = United Kingdom; J = Japan

In 1976, transient-state separation factors for several binary gas mixtures, including N_2-O_2 and N_2-Ar , were calculated for Vycor glass membranes and compared to microporous carbon by Ash, et al.¹⁵⁹ Some fractionation was observed, although it turned out that the microporous carbon membranes were of more interest.

Many of the applications of porous glass for gas separations have come from Japan. Mixtures of hydrogen and carbon monoxide were separated with different kinds of porous glass membranes¹⁰¹ and by the combination of porous glass membranes.¹⁶⁰ Shindo, et al.,¹⁰⁰ studied the separation of $He-CO_2$ mixtures at temperatures up to $700^\circ C$. They also measured the permeabilities of He , H_2 , CO , N_2 , O_2 , Ar , and CO_2 through porous Vycor glass in the temperature range from 300 K to 950 K (27 to $677^\circ C$).¹⁶ Mathematical expressions were derived to describe the behavior, including the interaction of the gases with the glass surface and the effect on gas transport. A numerical simulation of the separation of gas mixtures containing H_2 , CH_4 , CO , and CO_2 was also carried out.¹⁶⁶ Experimental separation of a ternary mixture of helium, oxygen, and argon was demonstrated using cocurrent flow at 407 K ($134^\circ C$) and a feed pressure of 120 kPa to 220 kPa.¹⁰³ The permeabilities of H_2 , He , and N_2 through a specially prepared porous glass with 15 to 30 Å pores have also been reported.²¹

The possibility of using porous glass (and also alumina) for the separation and production of hydrogen by the catalytic decomposition of H_2S has been examined by Kameyama, et al.^{104,105,165} Membranes were operated up to $800^\circ C$. The removal of hydrogen through the membrane doubled the yield, compared to the equilibrium value.

However, the alumina membrane had 30 to 50 times higher permeability than the Vycor glass. It is of interest that several other membranes were evaluated, including porous nickel, porous nickel coated with alumina, and porous nickel coated with Teflon.

Hollow porous glass fiber membranes have been prepared^{22,23} and bundled into modules.¹⁶³⁻⁴ The permeabilities of hydrogen and nitrogen have been measured, and the use of these membranes for separating CO-H₂ from steam reforming processes has been suggested.

Composite membranes have been prepared by coating ceramic or alumina support tubes with a thin porous glass or silica membrane.^{20,106-7} These membranes have been used to separate mixtures of CO₂-CH₄ and H₂-N₂.

The surface of porous glass membranes can be modified by heating with alcohols in an autoclave.¹⁶⁵ The surface modification can increase gas transport. The permeabilities of carbon dioxide and some Freons through such surface-modified membranes have been reported.

Porous Vycor glass has been used as a support for a silicone polymer coating to produce a hybrid membrane.⁹⁶ The coating is formed by in situ polymerization in the pores of the Vycor glass tube. The gas selectivity of this membrane is determined by the polymer rather than by the porous glass. The permeabilities of He, H₂, N₂, CO, O₂, Ar, C₂H₄, and CO₂ have been measured.

5.3 CERAMIC AND METALLIC OXIDE MEMBRANES

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. Other membrane materials which have been used (Table 6) include porous carbon, supported molten salts, and polyphosphazenes. These are included in this discussion because they are in many ways more closely related to the inorganic membranes than to the polymeric organic membranes.

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 tenths to nearly a thousand nanometers have been prepared.

The early work in Great Britain, France, and Sweden related to barriers for gaseous diffusion for uranium isotope enrichment led the way toward developing inorganic membranes for other gas separations. Even though the first large enrichment plant was built in the United States, most of the technical details related to U.S. barrier development still remain classified as restricted data. The Japanese have built upon the earlier technology and are aggressively pursuing gas separation applications.

As seen in Table 6, the permeation behavior of several gases has been studied using alumina membranes. These gases include hydrogen,

Table 6. Ceramic and metallic oxide membranes for separating gases

Material/support	Pore size (Å)	Gases	Location ^a	Ref.
Al ₂ O ₃ -MgO/Al ₂ O ₃	70	N ₂ /gases	Fr	70, 80
ZrO ₂ /CaO	-	H ₂ /O ₂	Fr	167-169
ZrO ₂ -CeO ₂ -Y ₂ O ₃	-	H ₂ /O ₂	Fr	170
Al ₂ O ₃	150	H ₂ /CO ₂	J	171, 172
Al ₂ O ₃	-	H ₂ /N ₂ H ₂ /CH ₄	J	173
Al ₂ O ₃ -TiO ₂	-	H ₂ /N ₂	J	174
Al ₂ O ₃ -TiO ₂ -SiO ₂	-	H ₂ /N ₂ H ₂ /CH ₄	J	175
SiO ₂ /Al ₂ O ₃	80	H ₂ /N ₂	J	71
Al ₂ O ₃	40-100	H ₂ , He, CH ₄ , O ₂ , N ₂ , CO ₂	J	72
Al ₂ O ₃ -Pd/Al ₂ O ₃	-	H ₂ /N ₂	J	156
Pd/Al ₂ O ₃	-	H ₂ /N ₂	J	57
Al ₂ O ₃	1000-1020	H ₂ /H ₂ S	J	104, 105
Inorganic	-	Kr/air	J	176
Al ₂ O ₃ -SiO ₂ /clay	10	N ₂ /H ₂ O	J	177, 178
Al ₂ O ₃ /mullite	200	H ₂ /N ₂	J	58
SiO ₂ (glass)/Al ₂ O ₃	30-50	CH ₄ /CO ₂	J	179
Al ₂ O ₃ /Si ₃ N ₄	130	H ₂ /N ₂	J	59
Pb ₃ O ₄ -TiO ₂	-	H ₂ /Ar	J	180
Al ₂ O ₃ , SiO ₂ -Al ₂ O ₃ , ZrO ₂ , C, Zeolite, (+catalyst)	-	H ₂ /H ₂ S	J	181
Zeolite/Al ₂ O ₃	-	O ₂ /N ₂	J	182

Table 6. Ceramic and metallic oxide membranes for separating gases
(continued)

Material/support	Pore size (Å)	Gases	Location ^a	Ref.
Al ₂ O ₃ (anodic)	100	H ₂ /He, H ₂ /N ₂ , H ₂ /CO ₂	J	183
Al ₂ O ₃ (anodic)	80-500	H ₂ , He, N ₂ , CO ₂ , C ₂ H ₆ , C ₃ H ₈	J	108, 184
SiO ₂ /Al ₂ O ₃	-	H ₂ O/EtOH	J	110, 111
Al ₂ O ₃	5-20	H ₂ O/EtOH H ₂ O/MeOH H ₂ O/isoPrOH	J	112, 113 185, 186
Al ₂ O ₃ /Al ₂ O ₃	<20	hexane/air, water/air	J	187
SnO ₂	-	O ₂ /H ₂ O	J	56
Al ₂ O ₃ /Ni	-	UF ₆ (U isotopes)	J	188
Metal oxides, salts, alumina, teflon, nickel	<200	U isotopes	Fr	4
Ni/PTFE	600-4000	UF ₆ (U isotopes)	Fr	9
Alumina, nickel	100-1200	U isotopes	Swe	5
Al ₂ O ₃	30	H ₂ /N ₂	Neth	65
Al ₂ O ₃	30	H ₂ , He, N ₂ , CO ₂	Neth	189
Al ₂ O ₃	50	H ₂ , He, N ₂ , CO ₂	Neth	64
Al ₂ O ₃	40	He, N ₂ , CO ₂	U.S.	190
Al ₂ O ₃	28	H ₂ , He, N ₂ , CO ₂ Ar, O ₂ , SO ₂	U.S.	191
SiO ₂	-	He, N ₂ , CO ₂	U.S.	85
ZnCl ₂	-	H ₂ /N ₂ /NH ₃	U.S.	18
Alkali salts/metal, ceramic	-	O ₂ /N ₂	U.S.	17

Table 6. Ceramic and metallic oxide membranes for separating gases
(continued)

Material/support	Pore size (Å)	Gases	Location ^a	Ref.
SiO ₂ , Al ₂ O ₃	-	He, N ₂ , Kr, CO ₂ C ₂ H ₆	Gre	192
C	-	H ₂ , D ₂ , He, Ne, Ar, Xe, Kr, N ₂ , CO	U.K.	159
C	-	UF ₆ (U isotopes)	U.K.	159
C (mol sieve)	3-5	He, N ₂ , O ₂ , CO ₂ , SF ₆	Israel	53, 54, 99
Polyphosphazenes	-	He, Ar, N ₂ , O ₂ , CO, CO ₂ , SO ₂ , H ₂ S, CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀	U.S.	88
Polyphosphazenes	-	N ₂ , O ₂ , CO ₂	Italy	90
Siloxane/Al ₂ O ₃	-	H ₂ , He, N ₂ , O ₂ , CO ₂	J	94, 95 44,

^aFr = France; J = Japan; Swe = Sweden; Neth = Netherlands; U.S. = United States;
U.K. = United Kingdom; Gre = Greece

nitrogen, carbon dioxide, helium, argon, oxygen, hydrogen sulfide, sulfur dioxide, water, alcohols, and light hydrocarbons. Several of these studies are discussed below.

Thin films of alumina with 4 to 10 nm pores were prepared by casting an alumina suspension onto a glass plate, and the permeabilities of hydrogen, helium, methane, oxygen, nitrogen, and carbon dioxide were determined. The order of permeation coefficients was CO₂ > H₂ > CH₄ > He = O₂ > N₂.⁷²

The addition of silica to an Al₂O₃-TiO₂ membrane was used to

change the characteristics of the membrane. This appeared to improve the separation of H_2-N_2 and H_2-CH_4 mixtures,^{71,175} when compared to an alumina membrane.

An alumina membrane coated onto a porous clay pipe was considered for removal of water vapor from a gas stream. Pore sizes <1 nm were claimed for the membrane.¹⁷⁷⁻⁸

An alumina membrane was prepared by vapor deposition of $AlCl_3-H_2O$ onto a sintered mullite support.⁵⁸ The membrane was used to increase the hydrogen concentration in the permeate stream from a H_2-N_2 feed mixture.

A glass membrane was prepared by coating an alumina support using a $Si(EtO)_4-B_2O_3$ solution, followed by sintering and acid leaching. It showed some separation of a methane-carbon dioxide mixture.¹⁷⁹

Zeolite membranes have also been deposited on the surface of alumina and used to separate oxygen and nitrogen.¹⁸² The separation factor was 3.3.

A porous silicon nitride tube was used as a support for an alumina membrane formed by chemical vapor deposition.⁵⁹ It was used to separate hydrogen from a hydrogen-nitrogen mixture.

In a unique application, porous, inorganic, sintered membranes were evaluated for the removal of radioactive krypton from the off-gas of a fuel reprocessing plant.¹⁷⁶

A very broad patent¹⁸¹ describes the separation of hydrogen from the catalytic decomposition of hydrogen sulfide, and suggests other potential reaction process applications. The membrane layer can be

alumina, silica-alumina, zirconia, zeolite, porous glass, or carbon. Porous supports include alumina, silica-alumina, mullite, cordierite, zirconia, or carbon. Catalysts such as molybdenum sulfide, platinum, or palladium are uniformly distributed in the membrane.

Alumina membranes were prepared by anodic oxidation, and the permeabilities of several gases were measured.^{108,183} Separation factors of 1.22, 3.69, and 4.95 were reported for H₂/He, H₂/N₂, and H₂/CO₂, respectively, indicating that a Knudsen flow transport mechanism was primarily involved. These results are in contrast to studies of other membranes, both alumina and porous glass, which indicate a significant contribution from surface flow. The difference is postulated to be due to the much smaller surface area of the anodic membranes.

Alumina membranes, and alumina membranes stabilized with silica, have been used to separate gaseous alcohol-water mixtures.^{110-113,185,186} Separation factors of 5, 8, and 10 for methanol/water, ethanol/water and isopropanol/water, respectively, were reported. It was suggested that capillary condensation and molecular sieving played significant roles in the transport mechanisms.

Several types of membranes (barriers) have been evaluated for uranium enrichment in Great Britain,¹⁵⁹ France,^{4,9} Sweden⁵ and Japan.¹⁸⁸ The behavior of other gases in these membranes has also been studied. The commercial alumina membranes produced by Ceraver and marketed by Alcoa have been evaluated for gas separations,^{190,191} and several applications are being pursued. The order of permeabilities was found to be CO₂ > SO₂ > H₂ > He > N₂ > O₂ > Ar. Similar developmental membranes have been prepared in the Netherlands

and are also being evaluated for gas separations.^{64,65,189} In both cases, the multilayered membranes are prepared using slipcasting techniques. Surface diffusion of CO₂ is significant, and can be increased even more by modification of the membrane with MgO. Also, finely dispersed silver has been used to achieve O₂ surface diffusion.

Pez, et al.,^{17,18} at Air Products and Chemicals, Inc., have developed "molten salt" membranes in which a molten salt is immobilized in a porous support. The salt is capable of reversible oxidation-reduction reactions to selectively separate gases. The support can be ceramic or metallic. One example uses an alkali metal nitrate/nitrite system to separate oxygen from air (nitrogen) by transporting the oxygen through the membrane. Another example uses zinc chloride to transport ammonia through the membrane.

Hollow-fiber, molecular-sieve carbon membranes have been developed in Israel.^{53,54,99} Separation factors have been reported for O₂/N₂ (7-10); He/N₂ (22); He/O₂ (>20); N₂/SF₆ (>24); and H₂/CH₄ (700).

Polyphosphazene membranes were developed for separations at the Idaho National Engineering Laboratory.^{88,89} Although the polymers have organic side groups, the polymer backbone is composed of phosphorous and nitrogen, giving the polymers better thermal and chemical stability than pure organic polymers. The membranes have been evaluated with several gases. Transport of carbon dioxide, hydrogen sulfide, and sulfur dioxide was found to be sorption controlled, while the transport of light hydrocarbons and atmospheric gases was diffusion controlled (related to molecular size). Similar membranes have been further developed in Italy.⁹⁰

A hybrid composite membrane was prepared by fixing siloxane polymers on porous anodic alumina supports.^{94,95} The membranes were usable up to 200°C. The gas permeabilities of the membrane were determined by the characteristics of the polymer, rather than by the alumina.

The behavior of several gases on inorganic membranes, and other aspects of alumina membranes have been summarized in papers by Hsieh¹⁹³ and by Hsieh, Bhave and Fleming.¹⁹⁴

6. COMMERCIAL INORGANIC MEMBRANES

An indication of the status of inorganic membrane technology can be gained from a survey of commercially available porous inorganic materials. Table 7 lists some of the companies that market porous materials, the composition of the materials, pore sizes, and the configurations available. Some of the ceramic and glass materials are available only as prototypes or in developmental quantities. The most prevalent membrane materials are alumina, zirconia, and glass. Membranes are available in tubes, disks, monoliths, hollow fibers, and rods.

6.1 POROUS METALS

Porous metal membranes made of stainless steel, silver, nickel, Monel, Inconel, Hastelloy, gold, platinum, and other metals are available with pore sizes of 0.5 to 100 μm from Mott Metallurgical Corporation. Membrane elements with diameters ranging from 3/8 to 4 in. (0.9 to 10 cm) and lengths up to 72 in. (183 cm) are available. Porous metal tubes are also available from Pall Corporation.

Table 7. Commercial porous inorganic membranes

Company	Membrane/support material	Pore size	Configuration ^a
Alcan/Anotec	Alumina/alumina	0.02-0.2 μm	D
Alcoa	Alumina/alumina Zirconia/alumina	40 Å-5 μm 500-1000 Å	M, T
Asahi Glass	Glass	40 Å-10 μm	D, T
Bolt Technical Ceramics	Alumina Silicon carbide	1-40 μm	T
CARRE/DuPont	Zirconia/ss, carbon	40 Å-0.1 μm	T
Ceram Filtre	Silicon carbide	0.15-8 μm	T, M
CeraMem	Alumina/cordierite Zirconia/alumina/ cordierite	0.1-0.2 μm 200-300 Å	M
Coors	Ceramic	0.5-108 μm	-
Corning	Glass Cordierite, mullite	40 Å 2.6-4.9 μm	T 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
NCK	Alumina/alumina Silicon carbide/SiC	0.2-13 μm	T, M
Norton/Millipore	Alumina/alumina	0.2-1.0 μm	T
Osmonics	Silver Ceramic	0.2-5 μm 0.3-25 μm	D D, T
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

^aD=disk, T=tube, M=monolith, R=rod, F=hollow fiber.

Porous silver disk membranes with pore sizes of 0.2 to 5 μm are marketed by Poretics, who also markets porous ceramic disks. In the Poretics membrane, the silver particles are deposited in sheet form, then molecularly bonded to give a homogeneous material that is 50 μm thick. The silver membranes are packaged in disc sizes from 13 to 293 mm. Their ceramic discs are packaged in disc sizes from 10 to 30 mm (1/8 in. thick) and 1/2 in. to 2 in. (1/4 in. thick) with pore sizes ranging from 0.1 to 12 μm . Porous silver and porous ceramic disks are also marketed by Osmonics, Inc.

6.2 POROUS GLASS

The primary producers of porous glass are Asahi Glass, Corning Glass Works, Fuji Filters, Schott Glass, SepTech/PPG, and Toyobo. Most are supplied as tubes or capillaries with pore sizes as small as 4 nm. SepTech/PPG also produces hollow fibers of porous glass. They are evaluating developmental porous glass hollow fibers, said to have pores smaller than 2 nm, in collaboration with the Gas Research Institute and SRI International, for separating gases.

Corning "Vycor" porous glass is available as tubing, rod, and sheet. It is stable up to about 800°C, with a maximum operating temperature of about 500°C. The standard pore size is 40 Å, and average pore diameters up to 160 Å can be produced. Corning also produces honeycomb monoliths made of mullite, cordierite, and mixtures of mullite-cordierite by an extrusion process. These are designed primarily for catalyst supports. Mean pore sizes range from 2.6 to 4.9 μm . They are stable up to 1410°C.

Asahi Glass produces porous glass tubes and sheets, as well as complete modules. Pore sizes range from 40 to 100,000 Å. Tubes are 2.7 or 10 mm in diameter and 450 mm long.

6.3 ANODIC ALUMINA

Alcan/Anotec produces alumina membrane filtration disks by anodic oxidation. They are marketed under the tradenames Anopore, Anotop, and Anodisc. They are available in 0.2 μm and 0.02 μm pore sizes, and are packaged in 10 mm, 25 mm, and 47 mm disk sizes. The membranes are 45 or 60 μm thick. The membrane consists of a honeycomb of parallel pores at right angles to the surface. The 0.2 μm membrane has a symmetrical structure, while the 0.02 μm membrane is asymmetrical.

6.4 POROUS CERAMICS

DuPont has developed a unique ceramic monolith, consisting of hollow ceramic tubes spirally wound to form a self-supporting unit.¹⁹⁵ The composition of the materials can be alumina, mullite, cordierite, or combinations of these. Pore diameters range from 0.06 to 1.0 μm ; pore volume is 25 to 50%. The tube size ranges are 0.06 to 0.18 in. OD; 0.02 to 0.08 in. ID. The membrane is made by coating a continuous combustible core with a paste of the inorganic material, fabricating the coated core into a spiral wound unit, and firing the coated core to burn off the core and sinter the coating. DuPont recently acquired CARRE, Inc. (Conservation and Resource Recovery Engineering), which markets primarily dynamic membrane systems.

The Alcoa Membralox^R membranes are available as tubes or multichannel monoliths.¹⁹⁶ The tubes are 7 or 15 mm ID and 750 mm

long. The monoliths are 850 mm long and have up to 19 channels with diameters of 4 or 6 mm. Modules with 37 smaller channels are planned. The membranes are three-layered, asymmetric structures consisting of alpha and gamma alumina. Membranes with pore diameters from 0.2 to 5 μm are made of alpha alumina; membranes with smaller pores (40-1000 Å) contain gamma alumina. The support is alpha alumina with a pore size of 15 μm . Similar materials with pore sizes larger than 0.1 μm are marketed by NGK Insulators, Ltd., in Japan. Alcoa also produces an alumina-supported zirconia membrane with pore sizes of 500 and 1000 Å; membranes with smaller pore sizes are under development.

The Norton Ceraflo^R membranes are marketed by Millipore Corporation. These are also asymmetrical alumina structures. The standard tube size is 3 mm ID. Available pore sizes are 0.2, 0.45, and 1.0 μm .

Membranes consisting of a zirconia coating on either stainless steel, carbon, or alumina are produced by CARRE, SFEC, TDK, and Union Carbide.

6.5 POROUS CARBON

Porous carbon membranes made by a controlled pyrolysis technique are produced by GFT, a German company owned by Le Carbone-Lorraine of France. These are carbon-carbon composite membranes in tubular form. Standard tubes are 6 mm ID. Pore sizes range from 40 Å to 1.0 μm . Capillary hollow fibers and oxide-coated membranes with pore sizes <20 Å are under development.

6.6 OTHERS

CeraMem membranes are still developmental. Development quantities of an alpha alumina membrane supported on cordierite is available in a 1 in. diameter by 1 ft long module with a membrane area of 1.2 to 1.5 ft². A membrane with pore sizes of 200-300 Å was produced by adding a zirconia coating.

7. LIMITATIONS, NEEDS, AND PROSPECTS

Inorganic membranes have been used primarily for microfiltration and ultrafiltration. They have advantages over polymeric membranes where higher temperatures are required and where harsh chemical environments are encountered. They can be sterilized and cleaned more easily, making them especially useful for food processing, pharmaceutical, medical, and biotechnology applications. There are many other applications, such as wastewater treatment, that are being explored.

Inorganic membranes are more expensive, but they also have a higher life expectancy. They have higher structural stability toward compaction and swelling, but they are more brittle. Present inorganic membranes have a lower surface area to volume ratio than the hollow fiber polymeric membranes.

As stated earlier, the applications of porous inorganic membranes to large-scale gas separations have been limited to uranium isotope enrichment. Although gaseous diffusion plants are still operating, gaseous diffusion technology for isotope enrichment has been largely superseded by centrifuge and atomic vapor laser isotope enrichment processes. Consequently, isotope enrichment no longer

provides the incentive for inorganic membrane development. In some cases it may have even discouraged other gas separation applications because of the large size required for such plants. However, it should be remembered that uranium enrichment necessitated the separation of gases having a mass difference of less than 1%.

7.1 DEVELOPING IMPROVED MEMBRANES

Assuming a Knudsen flow transport mechanism, the ideal separation factors are less than ten for gases of general interest (Table 1). For example, the separation factor for N_2/O_2 is 1.07. For comparison, separation factors for N_2/O_2 are 3 to 5 for polymeric membranes. This indicates the necessity for taking advantage of other gas transport mechanisms to improve separation factors for inorganic membranes. One approach is to develop membranes with smaller pores. Present commercial membranes (primarily glass and alumina) have pores in the 3 to 4 nm range. Development of membranes with smaller pores which retain high gas permeability is needed, and efforts are focused in that direction at several laboratories. Methods for doing this include chemical vapor deposition, incorporation of molecular sieves into the membranes, and other techniques using organic solvents or supercritical conditions to prepare the membranes. The use of organic solvents and supercritical conditions are aimed at reducing cracking and defect formation during the drying and sintering steps. Another approach is to modify the membrane through incorporation of catalysts, either dispersed throughout the membrane or as an ultrathin layer. This approach has been discussed recently in an excellent review.¹⁹⁷ This technique has been especially useful where catalytic

hydrogenation and dehydrogenation reactions are involved. This application would also benefit from the development of improved, thin, inexpensive inorganic membranes with small, uniform pores.

7.2 MEMBRANE CHARACTERIZATION

As pore sizes of membranes are decreased, it becomes even more important to eliminate any cracks, pinholes, or leaks. Membrane characterization and defect detection become necessary, both for quality control of fabricated membranes and to point the way toward improved membranes. Precise gas transport measurements are imperative. Other necessary measurements include (1) pore size, (2) pore size distribution, (3) surface area, (4) porosity, and (5) particle size distributions. These measurements require a combination of electron microscopy, various adsorption methods, liquid permeability measurements, small-angle x-ray scattering, and related experimental techniques. Still other techniques may be required as better membranes are produced, particularly for membranes with pores smaller than 2 nm.

7.3 MATERIALS

Inorganic membrane materials appropriate for gas separations are currently limited to certain metals, alumina, and silica, although membranes have been produced from several other materials such as zirconia and titania. Each of these membrane materials have chemical and/or physical limitations, and other materials will continually need to be developed. The maximum operating temperature for glass is about 800°C, and it is susceptible to chemical attack, for example, by alkaline conditions or hydrogen fluoride. Alumina has a limited

useful pH range and may undergo attack from alkali metals at high temperature. Zirconia may undergo undesirable phase transitions and require stabilizers.

Thermal stability is one factor in choosing membrane materials. Many metallic oxides, carbides, borides, and nitrides have good thermal stability. Melting points can act as a guide in selecting potential membrane materials, even though the sintering temperature and maximum operating temperature may be considerably lower than the melting point. Also, the pore size and structure of fabricated membranes may change as the membrane is heated and different materials will behave differently. Table 8 lists several metal oxides and carbides with high melting points¹⁹⁸ that might be considered for high temperature membranes. Other factors to be considered in choosing new membrane materials are availability, cost, reactivity, adaptability to fabrication methods, and crystalline phase stability during thermal cycling. Therefore, membrane materials will have to be tailored for specific needs; no single membrane material will be the best for all applications.

7.4 SEALS

In many cases, the membranes themselves are not the limiting factors in their use. At higher temperatures and pressures, the seals required to assemble the membrane into useful module configurations becomes most important. Seals must be compatible with both the membrane material and the structural component, and they must be able to withstand both the chemical environment and temperature cycling encountered in process applications. Research and development on

joining metals and ceramics is proceeding, but additional research and development will be required in this area as various types of membranes are developed for different industrial applications.

Table 8. Some inorganic oxides and carbides with high melting points

Material	Melting point (°C)
TiO ₂ (rutile)	1857
BaO	2013
Al ₂ O ₃ (gamma)	2018
Al ₂ O ₃ (alpha)	2054
V ₂ O ₃	2067
MgO-Al ₂ O ₃ (spinel)	2135
Cr ₂ O ₃	2330
Y ₂ O ₃	2420
BeO (alpha)	2508
SrO	2665
ZrO ₂	2677
MgO	2825
UO ₂	2827
HfO ₂	2910
CaO	2927
ThO ₂	3220
CaC ₂	2300
B ₄ C	2470
UC	2525
MoC	2692
SiC	>2700
WC	2785
VC	2830
TiC	3017
C	>3500
HfC	4160

7.5 INORGANIC MEMBRANE MARKET

Future development of inorganic membranes will depend to a large extent on the potential market. As stated earlier, the primary applications of inorganic membranes have been and continue to be in microfiltration (MF) and ultrafiltration (UF). Out of a total world

inorganic membrane market estimated¹ at \$31 million in 1989, \$28 million was in UF and MF. It has been projected¹ that by 1999 the total will reach \$432 million, with \$320 million in UF and MF; and \$80 million in gas separations, of which \$50 million will be for hydrogen separation, primarily in refineries, and the remaining \$30 million for coal gasification, light hydrocarbon separations, flue gas separations, etc. Sales of all inorganic membranes for gas separation and pervaporation have been projected¹ to be about 500,000 ft² in 1999.

7.6 APPLICATIONS TO COAL CONVERSION PROCESSES

Potential applications of membranes to various coal gas cleanup processes were recently evaluated¹⁹⁹ for several coal conversion processes, including (1) the Integrated Gasification Combined Cycle (IGCC), (2) Molten Carbonate Fuel Cell (MCFC), and (3) Direct Coal-Fueled Turbine (DCFT), as well as for (4) oxygen enrichment and (5) hydrogen production. This study reenforced the need to develop inorganic membranes which could separate gases by mechanisms other than Knudsen diffusion. Then gases having comparable molecular weights could be more readily separated. It is also preferable in many processes to retain the lower-molecular-weight gases, such as hydrogen, on the high pressure side of the membrane while allowing contaminant gases such as hydrogen sulfide or carbon dioxide to permeate through the membrane. Such separations will require a more reactive membrane which does not rely on Knudsen diffusion alone for gas transport. Consequently, present inorganic membranes are not as readily adaptable to the IGCC, MCFC and DCFT cleanup processes, but

are more appropriate for hydrogen recovery. Development of catalytic membranes and modified membranes which do not depend on Knudsen diffusion to effect gas separation could potentially remedy some of these problems.

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