Development of Porous Inorganic Membranes for Gas Separations

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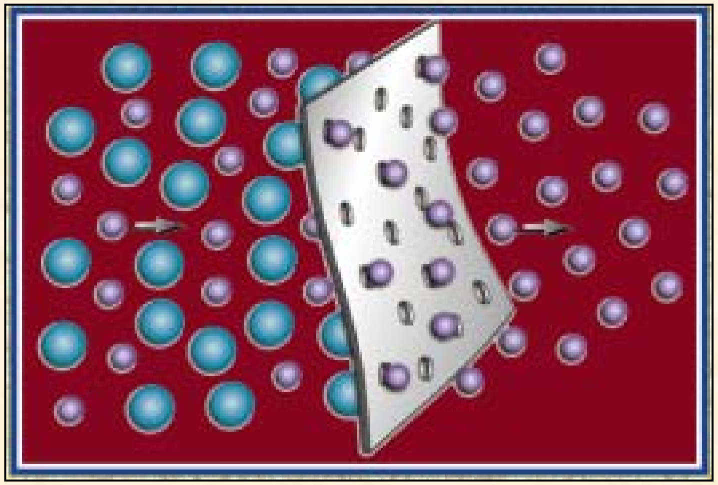
The Technology is Based on Oak Ridge Developed Microporous Membranes

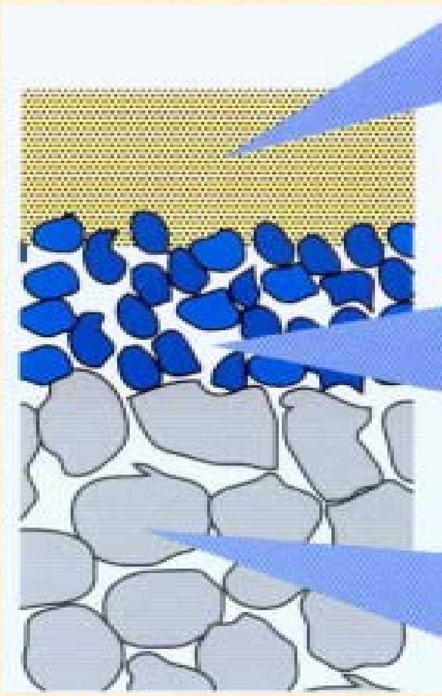
- Porous gas separation membranes
- Microporous is the IUPAC nomenclature, but membranes are actually nanoporous
- Transport is via molecular diffusion
- Separation may occur by:
  - Molecular sieving
  - Knudsen diffusion
  - Surface flow
- Technology is also applicable to:
  - Filtration
  - Ultra-filtration
  - Reverse osmosis



ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

- Pore diameters of 0.5 nm to 20,000 nm
- Support structure and layer made of variety of metals and ceramics
- Mechanical, thermal, and chemical stability
- Membrane layer thickness of 2µm or less yielding a high permeance at low pressure drop
- Proven scalability

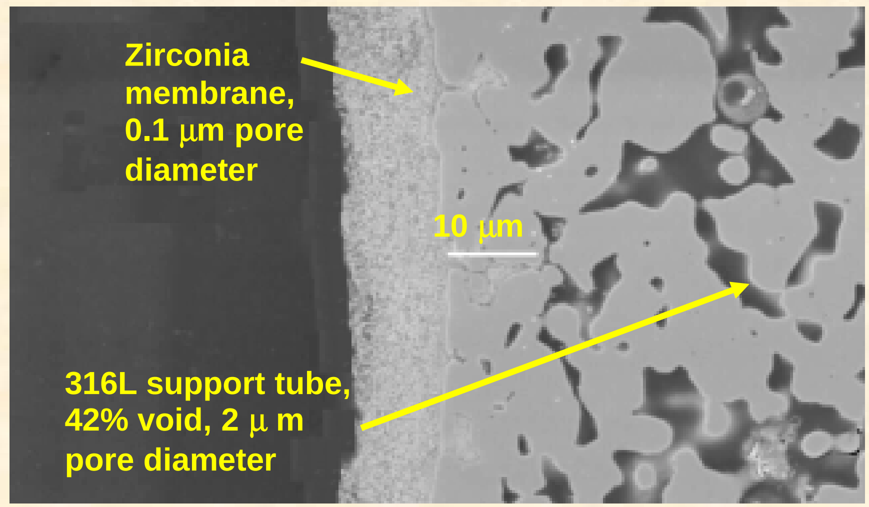
Separation Occurs at the Critical Separation Layer



Critical membrane Layer
Pore Size: 0.4-5nm
Thickness: 0.01-0.5 µm

Primary Layer
Pore Size: 0.005-0.5 µm
Thickness: 1-20 µm

Porous Support
Pore Size: 0.5-50 µm
Thickness: >400 µm



Fossil Energy Has Been the Principal Supporter of Oak Ridge Membrane Development

- DOE-FE, through the ORNL Fossil Energy Program, has been a long-term supporter of inorganic membrane development
- Advanced Research Materials Program
  - High temperature (to 600°C) hydrogen separation membrane
- Coal combustion and gasification
  - Improved iron aluminide hot gas filters
- Office of Natural Gas and Petroleum Technologies
  - Hydrogen separation membrane for refinery purge gases
- Technology transfer through funds-in CRADAs with Pall Corporation and Coors Technical Ceramics

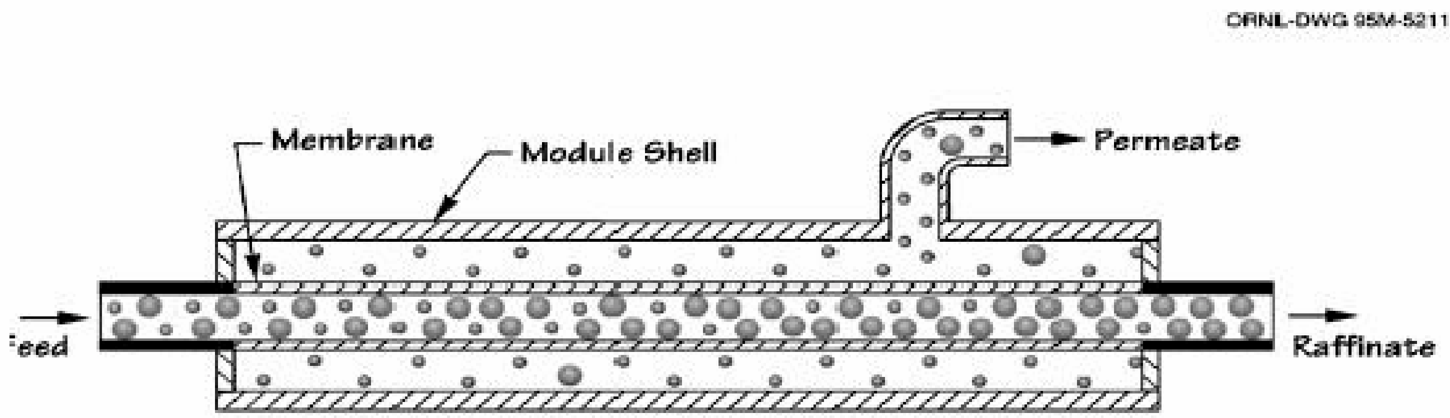
High-Temperature Separation Primarily Applies to Hydrogen Production

- Natural gas reformate
  - Mixture of H_2, CO, CO_2, CH_4, and H_2O
- Coal-derived synthesis gas
  - Mixture of H_2, CO, CO_2, and, H_2O plus, usually, contaminant gases
- This is a pressure driven approach that results in some pressure reduction of hydrogen while maintaining CO_2 at high pressure
- He has been determined to be an excellent surrogate for hydrogen in the performance evaluation of membranes
- In these separations, CO_2 is rejected, i.e., not transported through the membrane

Significant Progress Has Been Made in Hydrogen Separation Membranes

- Five angstrom pore diameter membranes
- Very high permeance (0.14 cc/min/cm^2/cm Hg at ~500°C)
- Several performance criteria have been met
  - 90 % of hydrogen at 90 % purity
  - >4.2 MPa burst pressure
  - 600°C temperature capability
  - Metal/Alloy, Ceramic, or Intermetallic Support Structure
  - Metal/Alloy, Ceramic, or Carbon Membrane

Conceptual Systems for the Use of Inorganic Membranes are Quite Simple



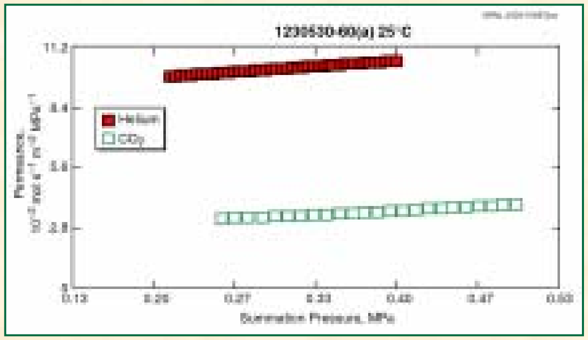
Separation Module Using Molecular Sieve Membrane to Separate Gases

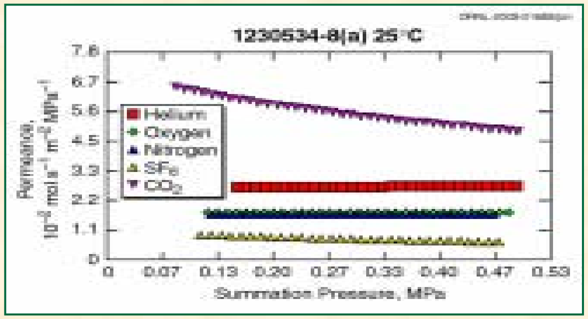
Permeance and Separation Factor are Critical Membrane Attributes

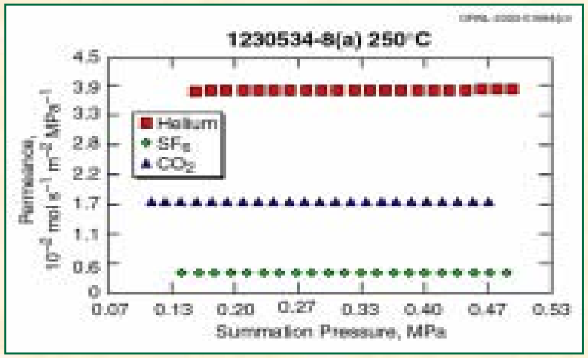
- Permeance is the volumetric flow per unit of time per unit of membrane surface area per unit of pressure difference between the feed stream and product stream
- Permeability is the product of permeance times membrane thickness
- Separation factor is the ratio of flow rate of gases in a binary gas mixture and is indicative of the separation effectiveness of a membrane
- Permeance and separation factor exhibit a positive temperature dependence
- Very high permeance and separation factors are desirable

Membrane Performance Depends Strongly on Process Conditions and Defects

- Top figure illustrates permeance dependence on pressure for a membrane with minor defects
- Middle figure illustrates permeance dependence on pressure for a defect-free membrane at low, 25°C, temperature
- Bottom figure illustrates permeance dependence on pressure for a defect-free membrane at high, 250°C, temperature

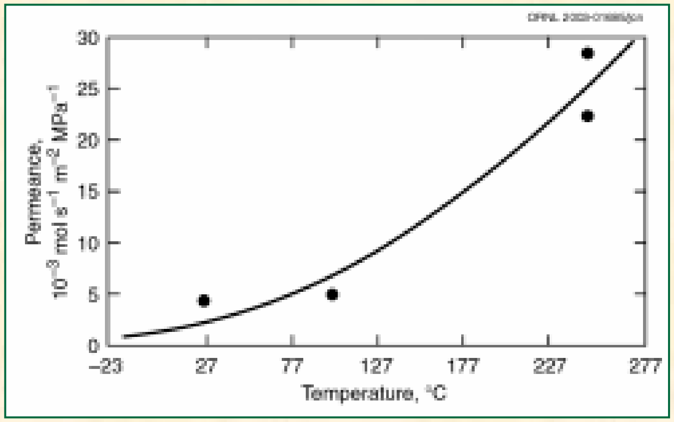


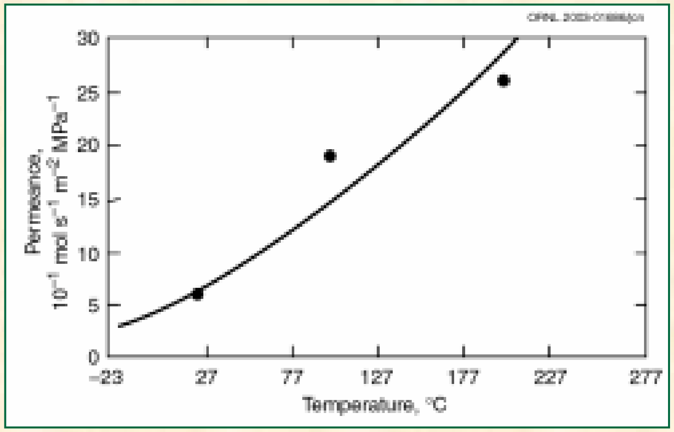




Permeance is Significantly Influenced by Process Temperature

- Temperature dependence is opposite in sign to Knudsen and surface diffusion processes
- Results of helium permeance through an alumina membrane are shown in top figure
- Results of hydrogen permeance through a silicon-modified alumina membrane are shown in the bottom figure
- These data exhibit the signature of thermally activated processes





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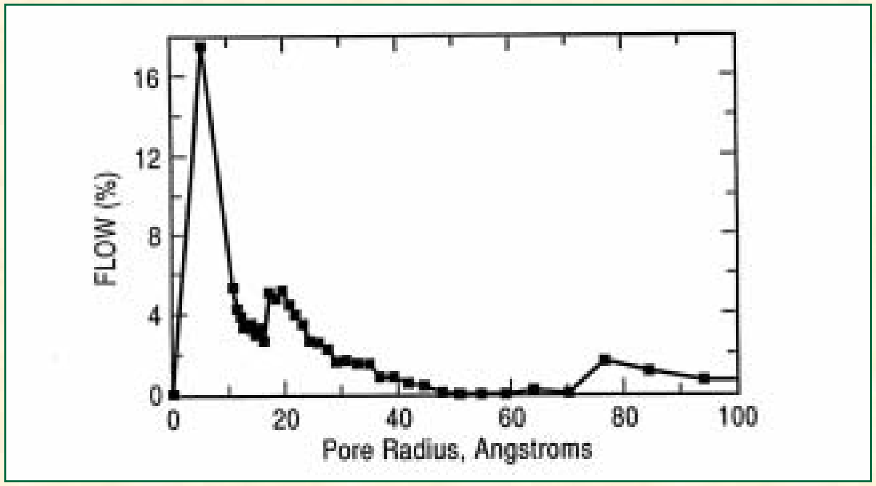
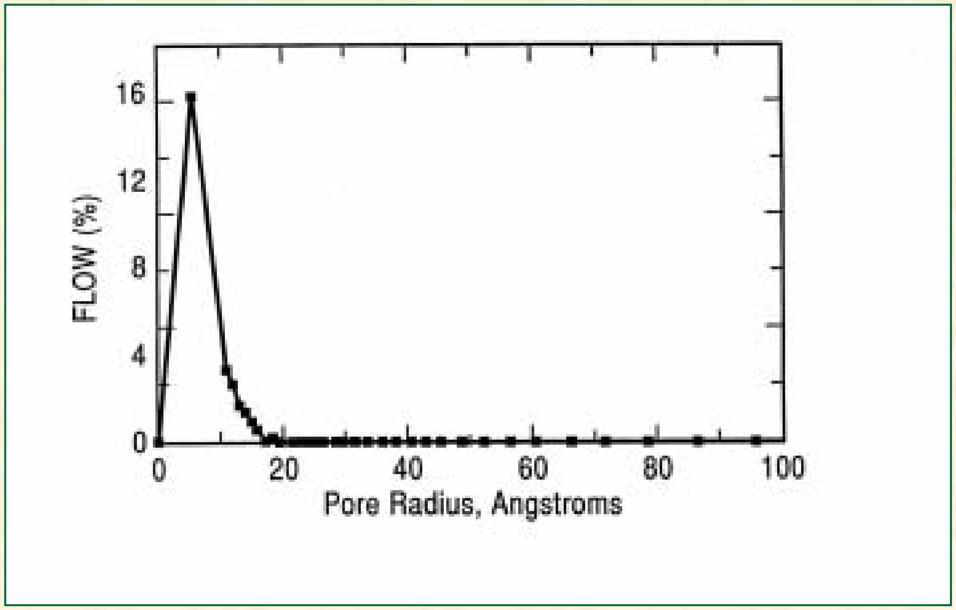
Large Pores Were Common Early in Development

- Pore size distribution indicated some large pores, although most pores were within the desired range
- Leaks limit the efficacy of gas separations
- High efficiency, high flux membranes require excellent control of pore size and pore size distribution

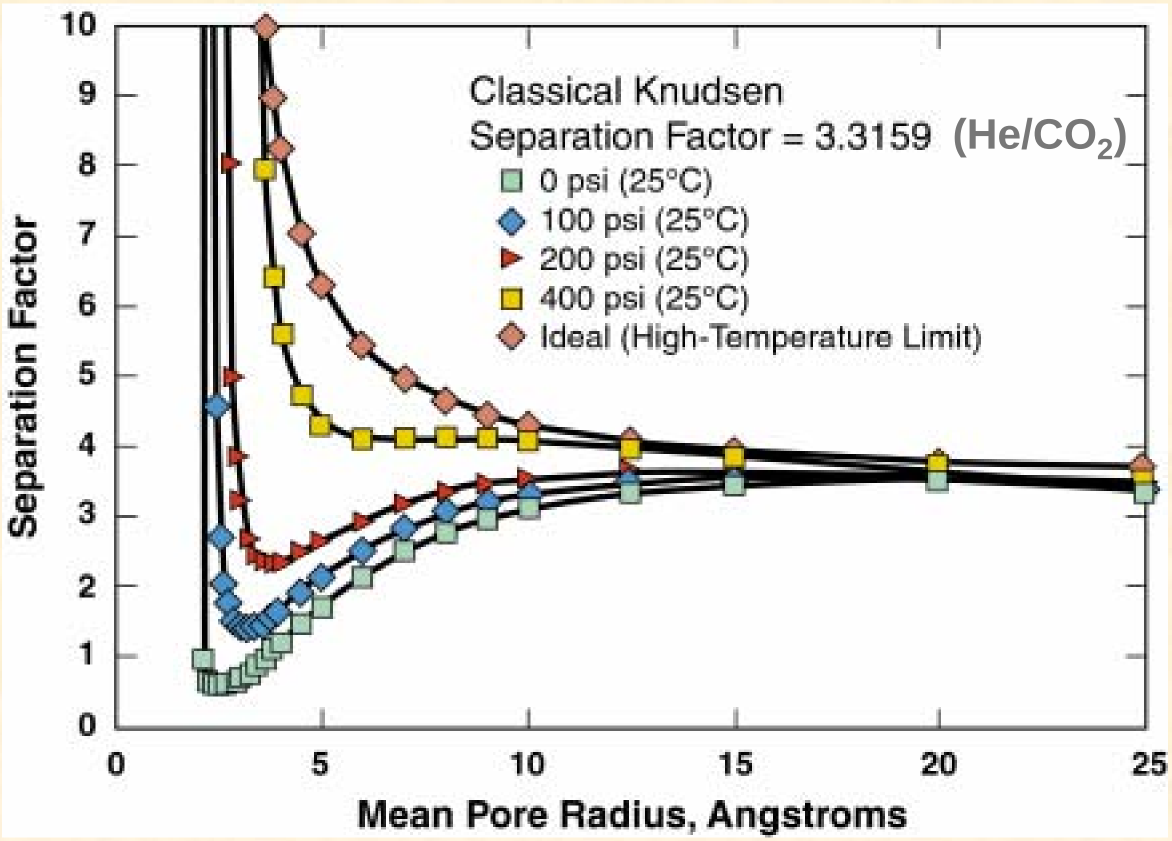


Pore Sizes Within the Desired Range and Distribution can now be Achieved

- Improvements in fabrication process
- Methods for repairing defects

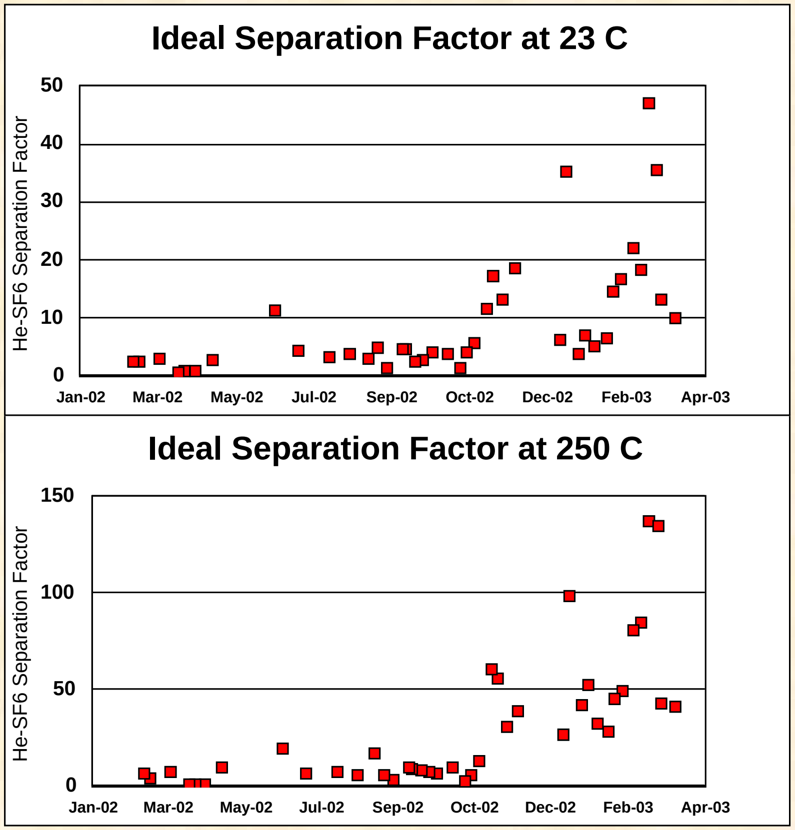


Model Calculations on Separation Behavior Have Been Confirmed Experimentally



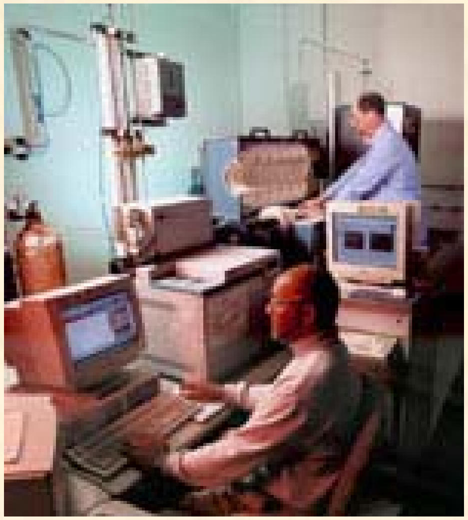
Dramatic Improvements in Separation Factors Have Been Made In FY 2002-2003

- He - SF6 separation factors up to ~140
- Single-stage purification (>99%) of H2 is possible
- Positive dependency of separation factor on temperature
- Data gives strong indication that flux of H2 increases rapidly with increasing temperature



The Efficacy of ORNL Membranes Has Been Demonstrated for Several Gas Pairs

- He-CO_2 ideal separation factors of 2.7–25.7 at 250°C and 44.7–64.6 at 600°C
- He-CF_4 ideal separation factors of 8.4–75.0 at 250°C and 9.3–70.0 at 600°C
- He–SF_6 ideal separation factors of 9.5–165.9 at 250°C
- He–Ar ideal separation factors of 4.4–6.0 at 250°C and 9.8 at 600°C



* Ideal separation factors refer to calculated values (ratios of pure gas permeances)

Parsons' H_2 Separation Device Designs Based on ORNL Membranes Imply a Very Compact System

- Synthesis gas inlet temperatures 207–513°C
- Separation device operated at 300–761°C
- Tubular membranes 12.7 mm id; 15.875 mm od; by 3 m long
- 11,800 tubular membranes in each of three vessels
- Hydrogen mass flow rate of 15,969–16,585 kg/h depending on temperature

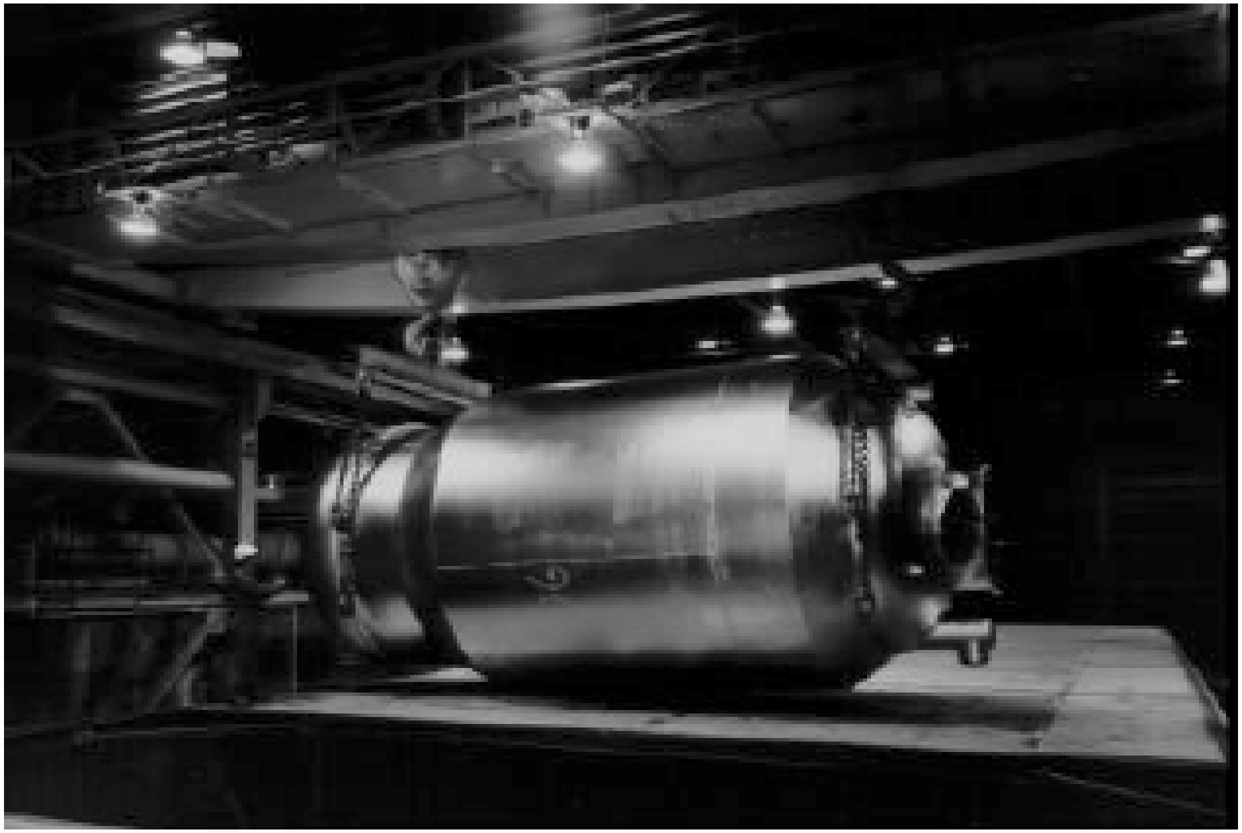
[For ~1,400 m^3/d (~50,000 ft^3/d), 20 tubular membranes 25 mm diameter about 1 meter long would be required.]

Some Membranes Have Been Approved for Commercial Production by Pall Corporation

- 316L stainless steel filters
- Nickel on nickel HEPA-like filters
- Titania on alumina ultrafilter
- Inconel 600 filters
- 310 stainless steel filters
- 304L stainless steel filters
- Hastelloy X filters
- Nickel depth filter
- Zirconia on stainless steel ultrafilter
- Zirconia on Hastelloy ultrafilter
- Any 300 series stainless steel, Monel, Inconel, and Hastelloy filters
- Titania filter
- Others pending

Photograph of an industrial system based on Pall's AccuSep™ inorganic membranes

Large Vessels Have Been Built for Gas Separations



The Oak Ridge Inorganic Membrane Technology Offers Great Potential for Important Gas Separations

- Most advanced porous inorganic membrane technology in the world
- Significant R&D required to adapt membranes to specific gas separations
- Several separation mechanisms possible
- Very high flux achievable
- Applicable over a wide temperature range
- Single-stage or multiple-stage systems
- No known materials limitations
- Environmental stability dependent only on material