

Scale-Up of Microporous Inorganic Hydrogen-Separation Membranes

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Project Overview

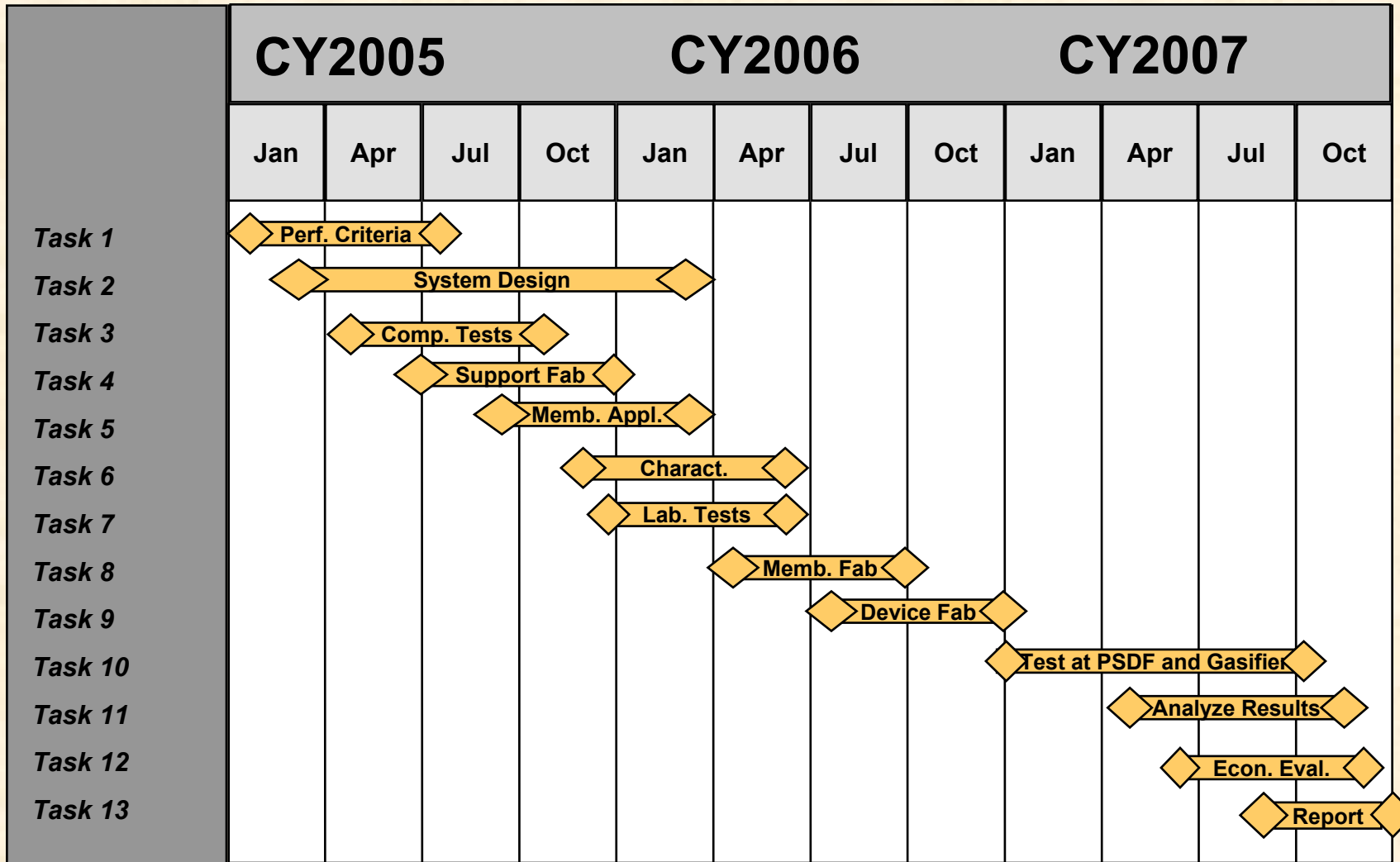
Budget

- FY05 \$1M
- The Project was initiated in December 2004
- No Funding was received in FY04

Potential Partners and Collaborators

- The Southern Company
- Commercial Gasification System Operator
- Pall Industrial Membranes
- National Energy Technology Laboratory (NETL)

Project Schedule



Objectives

The purpose of this project is to pursue further development of the Oak Ridge National Laboratory (ORNL) microporous inorganic hydrogen-separation membrane fabrication technology to produce industrial size (one-meter-long) tubular membrane elements and to demonstrate, at the pilot scale, the efficacy of membrane systems to separate and purify hydrogen from coal-derived synthesis gas (raw, clean, and/or shifted).

Approach

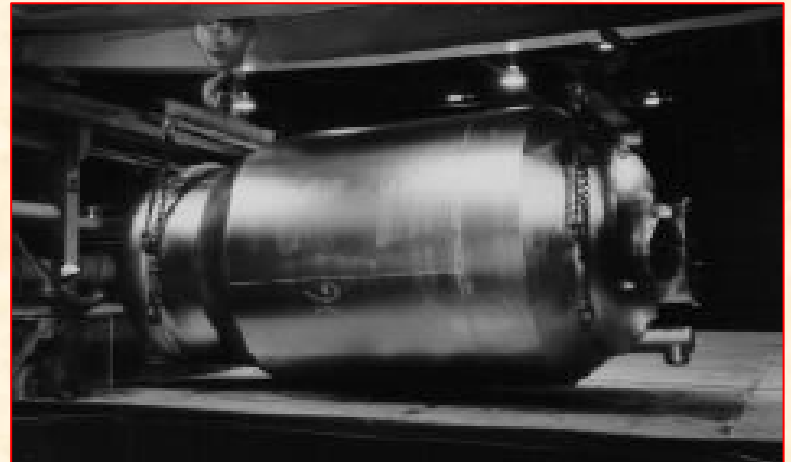
- **Determine operating conditions for membranes (e.g. temperature, pressure, contaminant gas concentrations, etc.).**
- **Test candidate membrane materials for compatibility in operating environment.**
- **Utilize technology developed through FE Advanced Research Materials Program to fabricate 1-meter long membranes for hydrogen purification.**
- **Assemble membranes in module for testing in gasifier facilities.**

The Project was Initiated in December 2004

- First activity was a meeting at Southern Company's Power Systems Development Facility (PSDF) in Wilsonville, AL to present information on the project and enlist PSDF as a collaborator
- Preparation of the Project Plan was begun
- First draft of the Project Plan was completed in January 2005
- Internal scheduling of project was accomplished at ORNL
- Contacts were made with a coal gasification system operator and with Pall Industrial Membranes to determine interest in participating in project
- Pall will be a participant on some significant level
 - Details, i.e., CRADA or other contract vehicle, regarding collaboration are being discussed
 - In their first task, Pall will attach end fittings using their electron beam welding process for 75–100 porous metal support tubes (two end fittings for each support tube)

ORNL Microporous Inorganic Membrane Technology Has an R&D Foundation of >50 Years

- FE has sponsored the development of several components based on inorganic membranes
- H₂ separation membranes have been principally supported by the Advanced Research Materials Program
- The President's Hydrogen Initiative is the principal focus of our inorganic membrane R&D
- Legacy classified technology issues impose the requirement for classification and nonproliferation reviews prior to release and use; however, this same legacy classified technology provided:

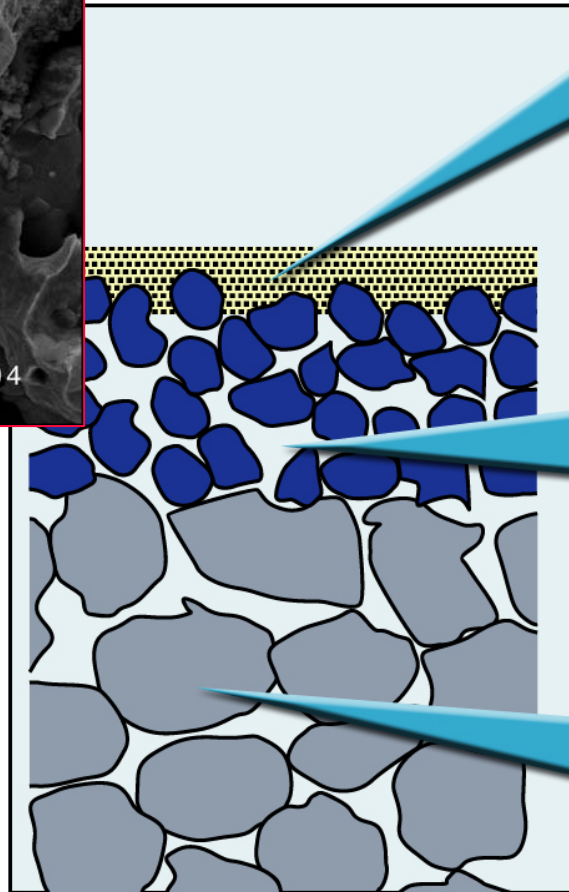
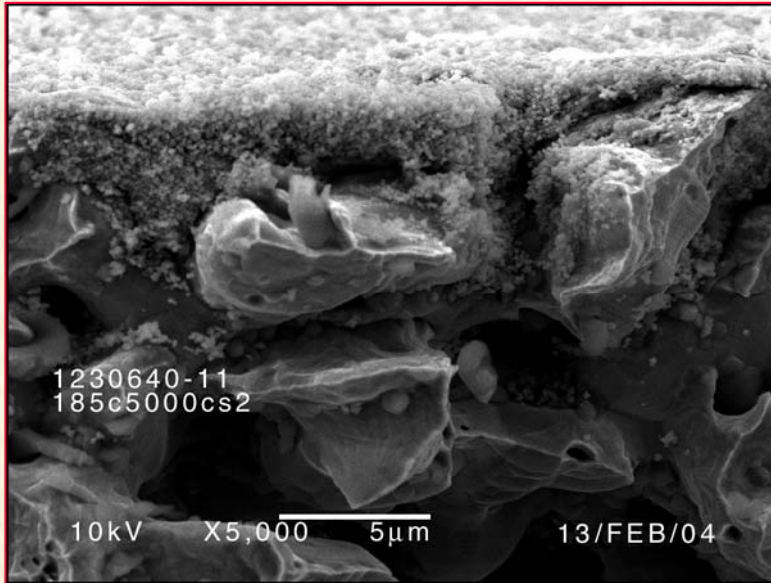


ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

- Pore diameters of 0.5 nm – 20,000 nm; for H₂, pore diameters of <1 nm are preferred
- Tubular support structure and layer made of variety of metals and ceramics
- Excellent mechanical, thermal, and chemical stability
- Membrane layer(s) applied to inside of support tube
- Membrane layer thickness of 2 μm or less yields high gas flows at low pressure drop; small pores result in high selectivity
- Proven scalability



A Thin Separation Layer Allows High Flow of Gases Through Small Pore Membranes



Critical Membrane Layer

Pore Size: 0.4-5 nm
Thickness: 0.01-0.5 μ m

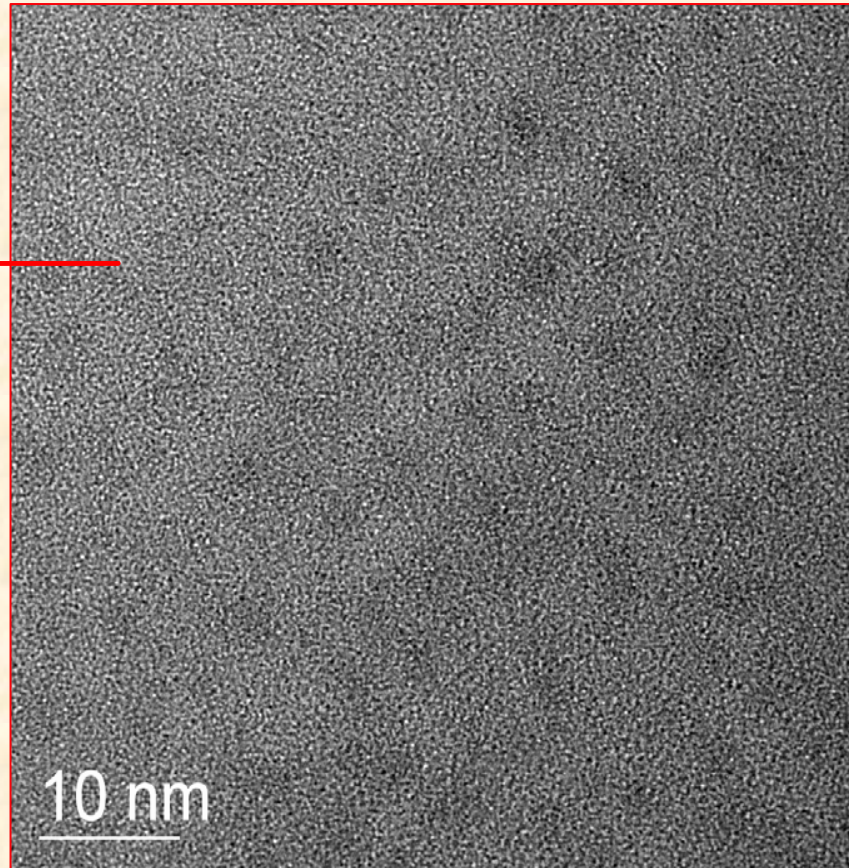
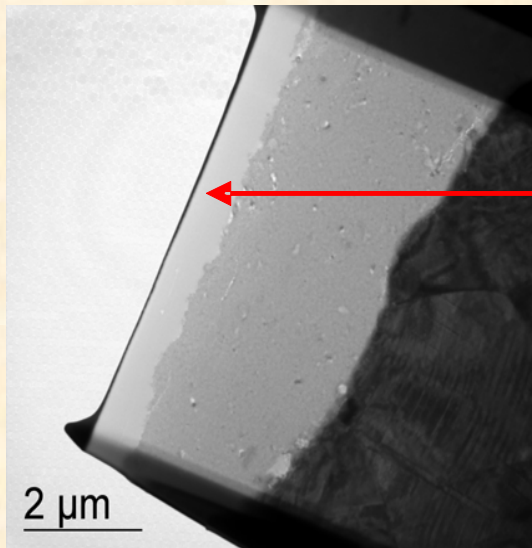
Primary Layer

Pore Size: 0.005-0.5 μ m
Thickness: 1-20 μ m

Porous Support

Pore Size: 0.5-50 μ m
Thickness: >400 μ m

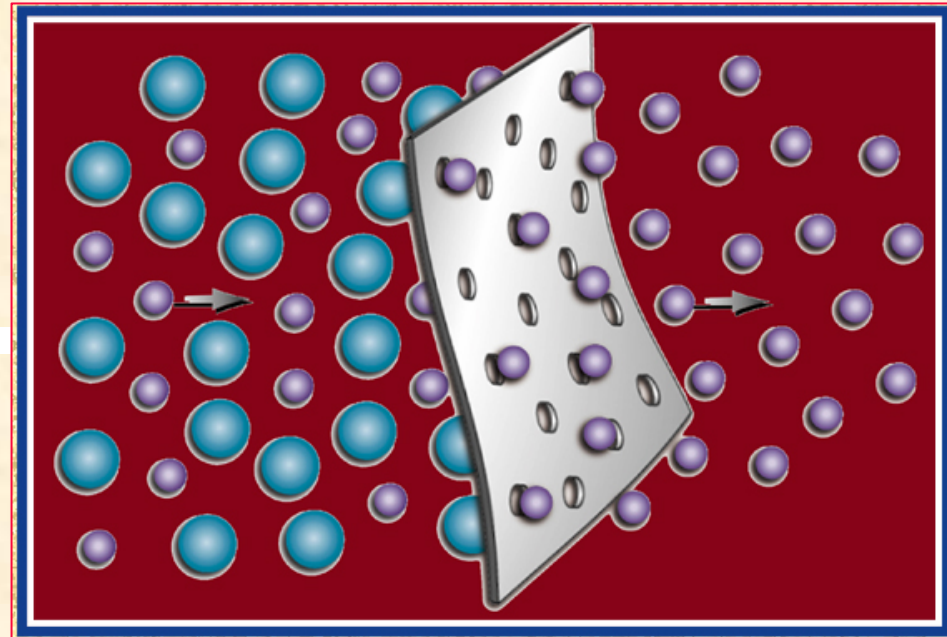
In Distinct Contrast To Palladium Or Ion Transport Membranes, These Are Porous



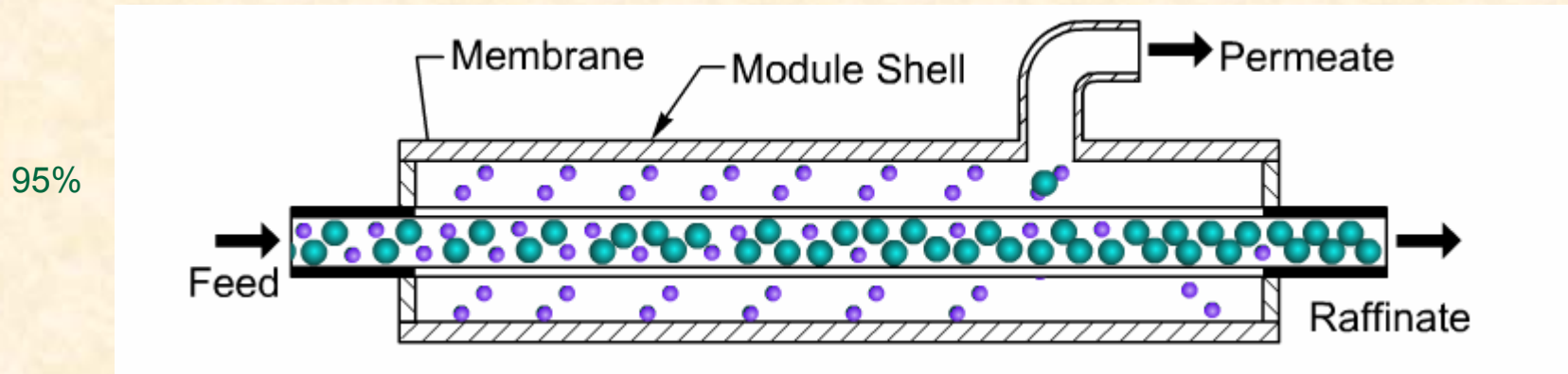
Membranes are descriptively nanoporous with pore sizes < 2 nm, but IUPAC nomenclature is 'microporous' (I didn't make the rules)

How Do They Work?

- Transport through porous membranes is via molecular diffusion
- The process is pressure driven and has a significant temperature relationship
- Separation may occur by Knudsen diffusion, molecular sieving, surface flow or a combination of these transport mechanisms
- Implications are
 - High flux and high purity
 - Less than 100% selectivity



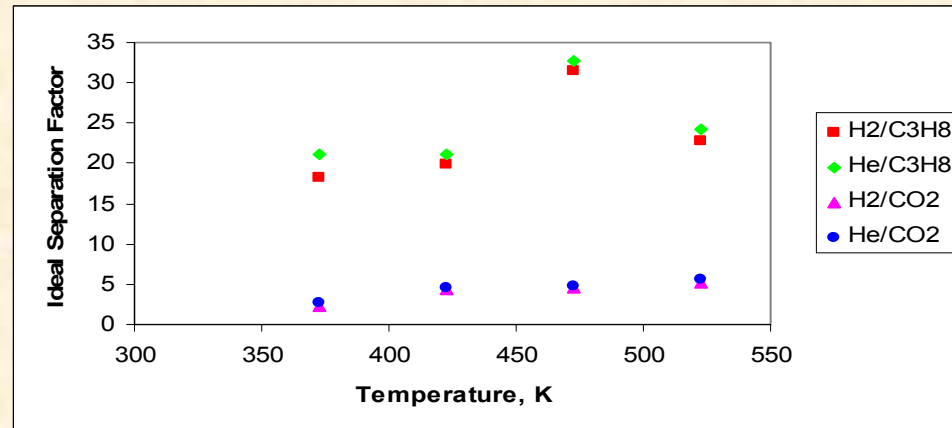
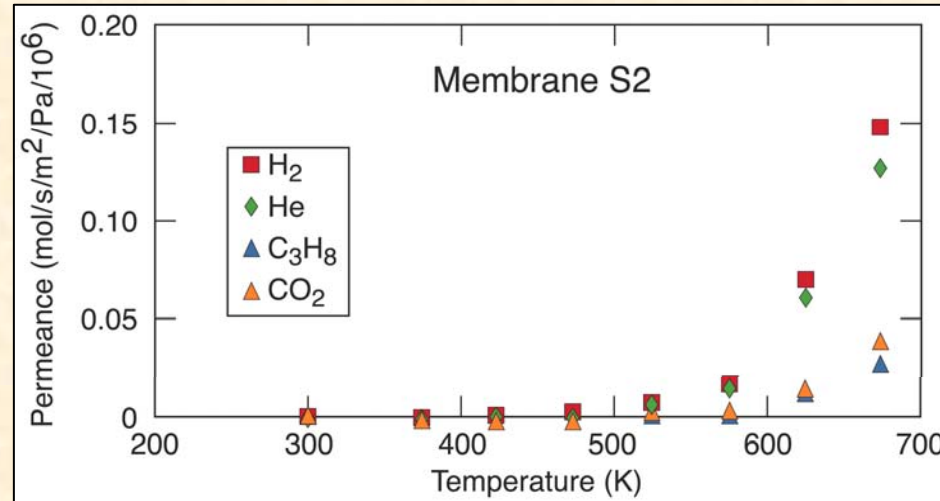
Permeance and Separation Factor are the Two Most Critical Attributes of Microporous Membranes



- *Permeance*: volumetric flow rate per unit of surface area per unit of transmembrane pressure (ΔP) at a particular temperature
- *Separation factor*: ratio of the flow of two gases in a binary gas mixture; indicator of selectivity of the membrane (*Separation factor depicted in figure is 19 and yields 95% hydrogen purity*)
- Design that achieves an appropriate balance of permeance and separation factor is key
- Both permeate gas flow and purity are affected by the “cut” (fraction of total gas flow that goes through the membrane)

High Operating Temperatures Result in Both Higher Permeances and Higher Separation Factors

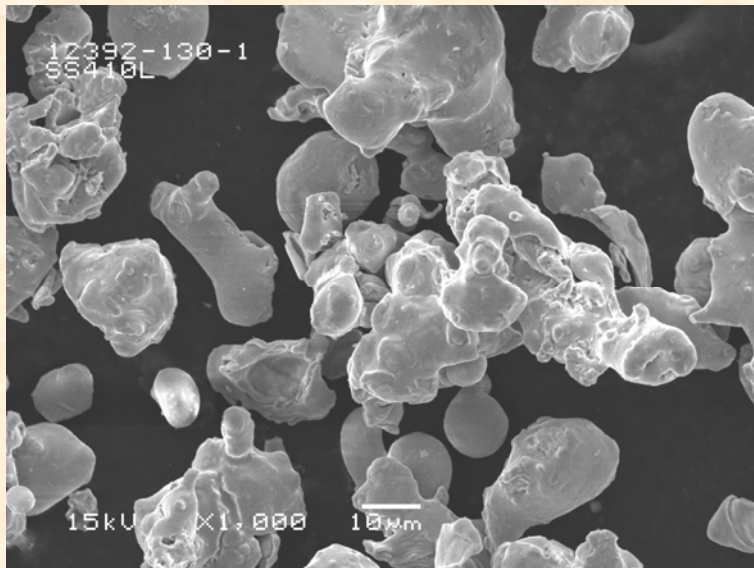
As the temperature is increased, the permeance of hydrogen and helium increase faster than CO₂ and propane. This phenomenon results in larger separation factors as temperatures are increased.



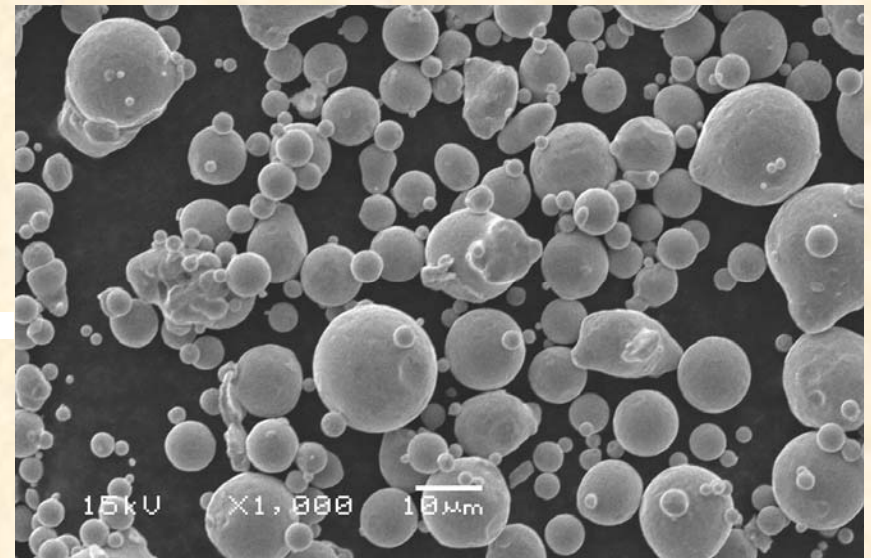
Several of the Project Plan Tasks Have Been Initiated

- Technology Status Report
- Establishment of Performance Criteria for PSDF and Commercial Gasification Operator
 - Meeting at PSDF
 - Meeting and Discussions with Commercial Gasification Operator
- Materials Compatibility and Selection
 - Evaluation of Historical Data
 - Development of Testing Plan
 - Flow-through Tests
- Fabrication of One-Meter Porous Support Tubes
- Equipment Acquisition for Membrane Application
- Performance Testing
 - NETL
 - PSDF

Gas Atomized Powder is More Spherical



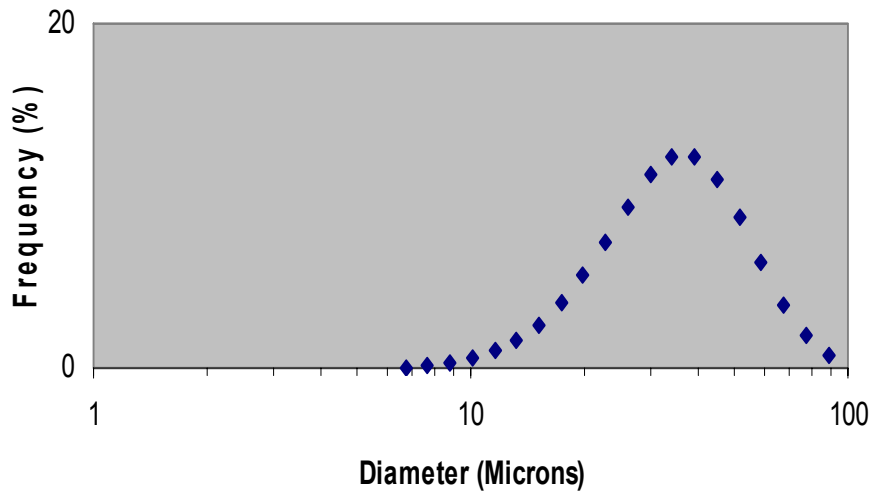
**Water Atomized 410
Stainless Steel Powder**



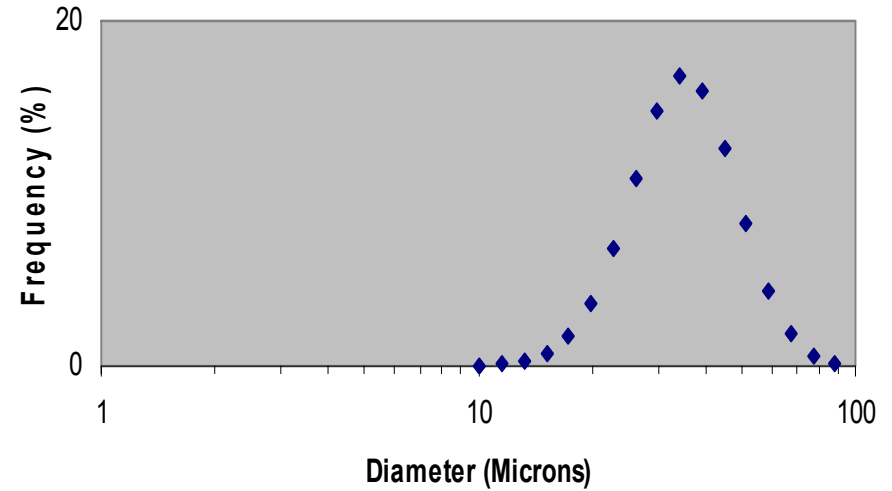
**Gas Atomized 410
Stainless Steel Powder**

Ames Laboratory Can Fabricate Spherical Particles With a Very Narrow Size Distribution

Particle Size Distribution of Water Atomized Powder



Particle Size Distribution of Gas Atomized Powder from Ames



Support Tube Materials Compatibility and Selection are Under Way

- Historical data indicate that materials compatibility is generally governed by resistance to sulfidation from H_2S
- Voluminous data are available on materials compatibility with coal gasification environments
- At temperatures below 250 °C most 300 and 400 series stainless steels are stable in a sulfidizing environment
- 400 series stainless steels have much less nickel content and some versions, particularly type 446, are stable in these environments at temperatures up to 500 °C
- Several specialty steels have also performed reasonably well, but do not offer particular advantages over the standard alloys
- Above 500 °C iron aluminide will be the best choice for the material of construction of the support tubes. Iron aluminide is an alumina former and alumina is very stable to H_2S at high temperatures

Plans are Being Developed for Materials Compatibility Testing

- 304L, 316L, 410, and 434 stainless steel powders have been procured
- Porous tubes have been fabricated and sintered from the 304L, 316L, and 410 powders
- Powder and sintered porous tubes made from iron aluminide are available as a result of our project on the development of hot gas filters.
- Design begun for construction of a small module containing several tubes made from each material
- Discussions with PSDF on the possibility of installing this module in a slip stream where gases would flow through the pores for up to 60 days.
- The porous tubes would be evaluated for strength and flow properties both before and after exposure.

Porous Support Tube Fabrication Has Been Initiated

- One-meter long support tubes were fabricated from 316L stainless steel and sintered to obtain proper strength and porosity
- 316L stainless steel was chosen for initiation of this task because of its availability in the desired particle size
- This task is conducted in parallel with the materials selection task to permit resolution of fabrication issues encountered when scaling up to longer support tubes
- Results from the materials selection task will determine the best material to be used in a gasifier
- The long tubes will be employed in a later task to verify the membrane application techniques
- The necessary equipment has been acquired to apply the membrane separative layers to one-meter long support tubes

The NETL Tubular Membrane Testing System Offers Good Testing Capability for the ORNL Membranes

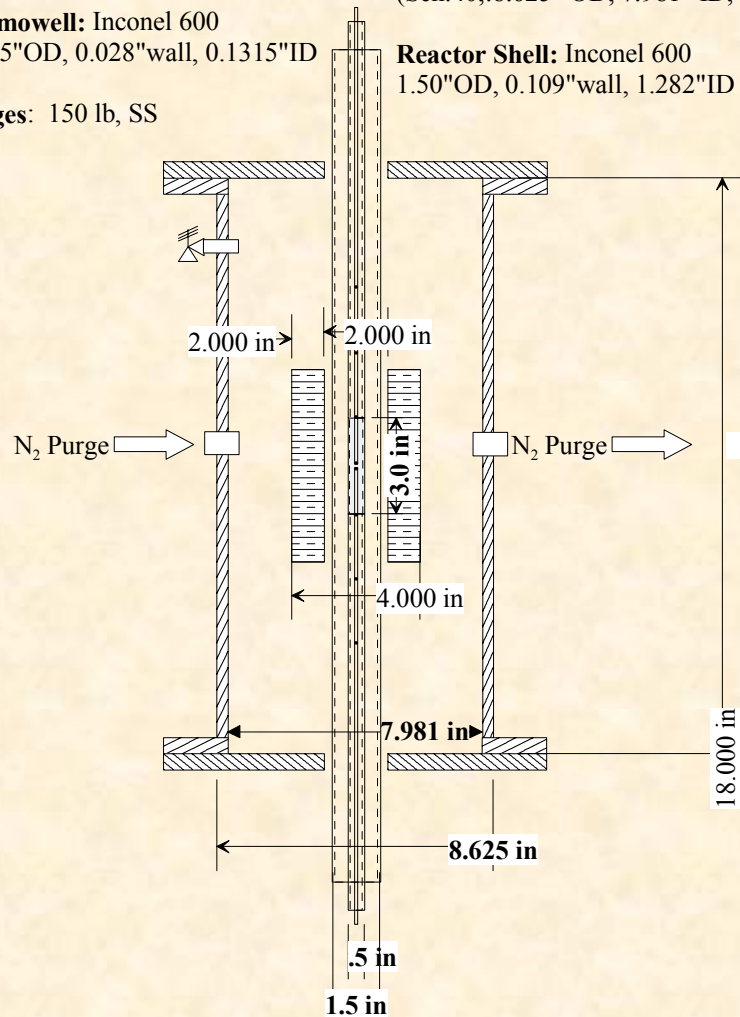
Membrane: 0.5" to 0.25" OD tubes
0.194" min ID (0.25"OD,0.028"wall)

Thermowell: Inconel 600
0.1875"OD, 0.028"wall, 0.1315"ID

Flanges: 150 lb, SS

Vessel: Stainless Steel
Nominal Pipe Size of 8"
(Sch.40,:8.625" OD, 7.981" ID, 0.322" wall)

Reactor Shell: Inconel 600
1.50"OD, 0.109"wall, 1.282"ID



Test System Features

- Membranes seal into system outside of heating zone.
- Hydrogen flux is determined by measuring the hydrogen concentration in a sweep gas using gas chromatography.
- NETL can evaluate performance in presence of H₂S and CO.
- NETL has ability to test at pressures of over 400 psi.
- NETL test system can accommodate ORNL 0.5" o.d. membranes for evaluation

Future Work over Next Year

- **Complete compatibility tests to determine which materials will be stable in the different gasifier environments.**
- **Fabricate 1-meter long support tubes from compatible materials**
- **Extend membrane application technology to 1-meter long tubes**
- **Complete separation tests on membranes made from compatible materials at ORNL and NETL**

Project Safety

The most significant hazard is the use of hydrogen in our membrane test systems

Our approach to ensuring safe operation includes:

- Project has undergone “Integrated Safety Management Pre-Planning and Work Control” (Research Hazard Analysis and Control)
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI’s and cognizant managers
- The RSS is reviewed/revised yearly, or sooner if a change in the work results in a need for modification.
- Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D including periodic safety reviews of installed systems
- Results of Work Control Process requires:
 - Monitoring hydrogen concentration at ceiling above test system. Alarm sounds at 50% LEL.
 - Personnel be present at all times when using hydrogen.
 - Evacuation of gas lines of air or purging with inert gas prior to introduction of hydrogen
 - Exhaust of gas lines containing hydrogen using eductors instead of electrically driven vacuum pumps.
 - Flammable gas storage in labs should be minimized. Either cylinders should be stored outside with gas piped in or small cylinders of flammable gases should be used in labs.