# Scale-Up of Microporous Inorganic Hydrogen-Separation Membranes

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# Project Overview

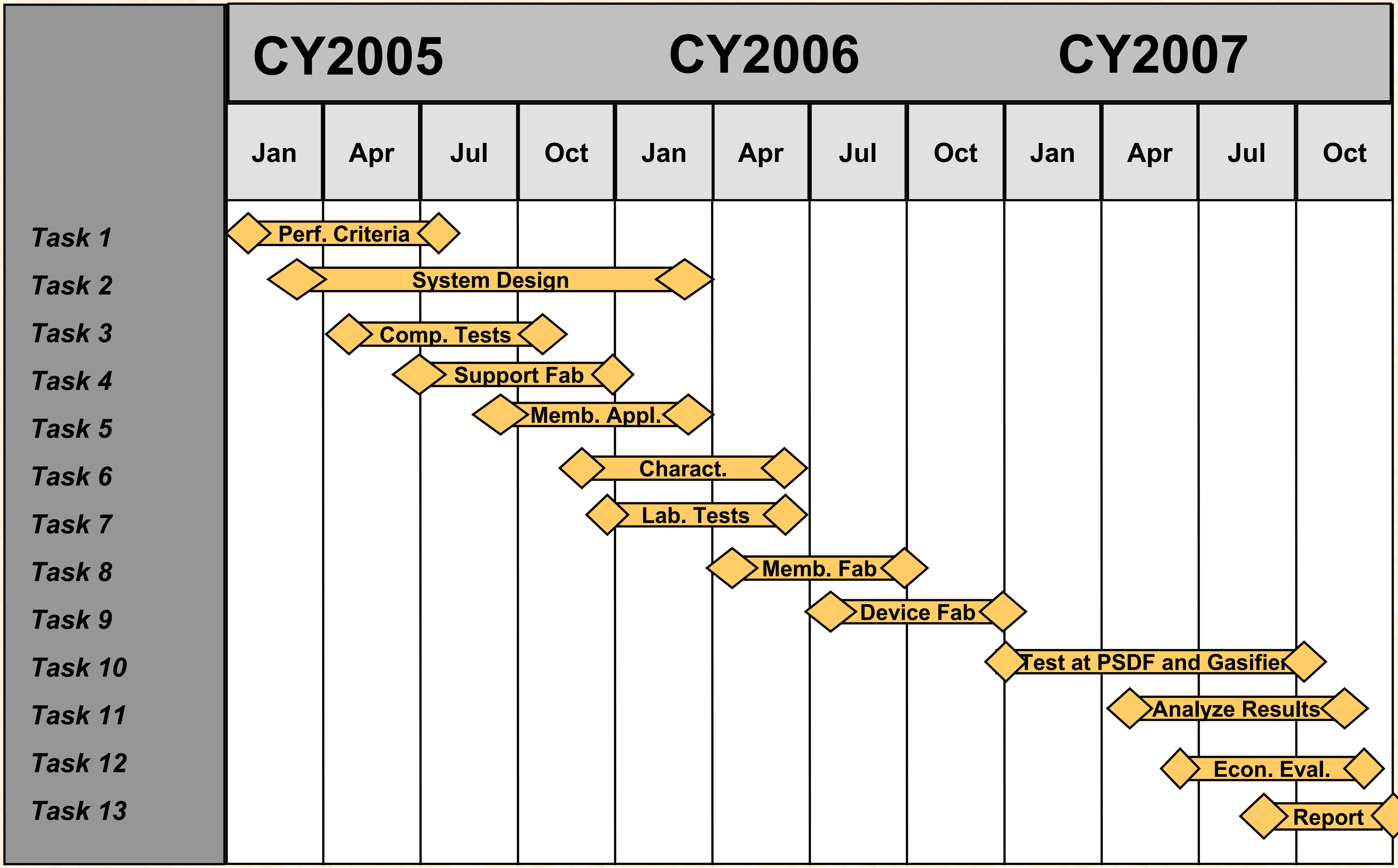
## Budget

- 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

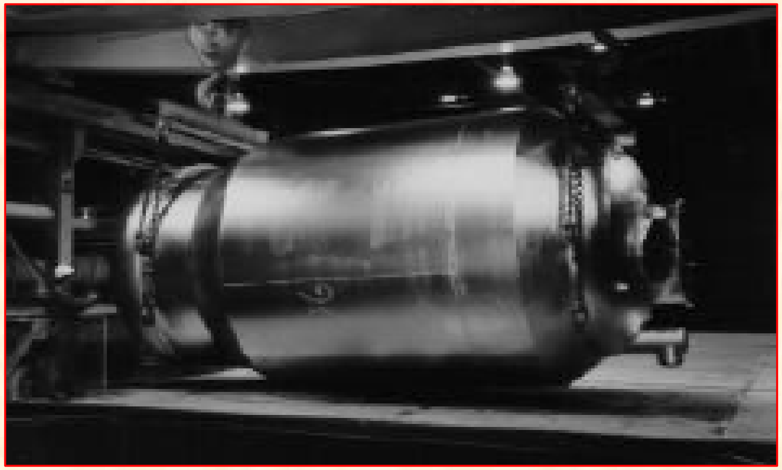
- Determine operating conditions for membranes (e.g. temperature, pressure, contaminant gas concentrations, etc.).
- Test candidate membrane materials for compatibility in operating environment.
- Utilize technology developed through FE Advanced Research Materials Program to fabricate 1-meter long membranes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

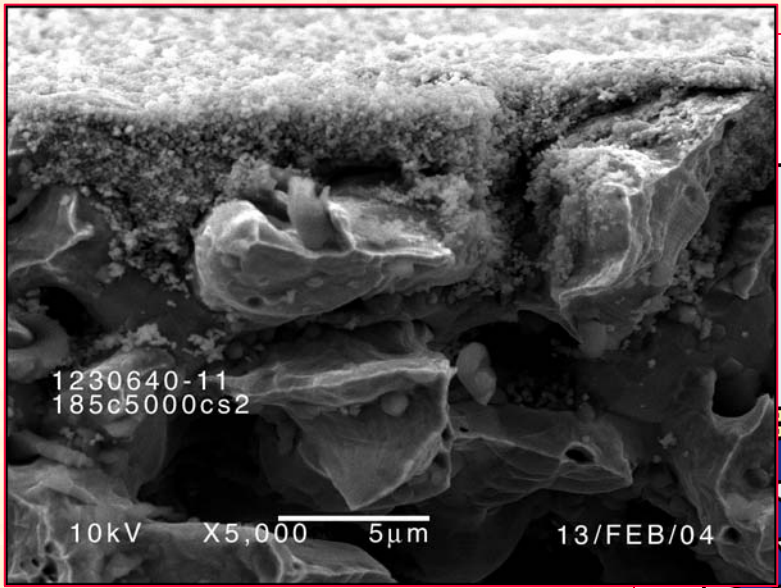
- FE has sponsored the development of several components based on inorganic membranes
- $H_2$ separation membranes have been principally supported by the Advanced Research Materials Program
- The President's Hydrogen Initiative is the principal focus of our inorganic membrane R&D
- Legacy classified technology issues impose the requirement for classification and nonproliferation reviews prior to release and use; however, this same legacy classified technology provided:

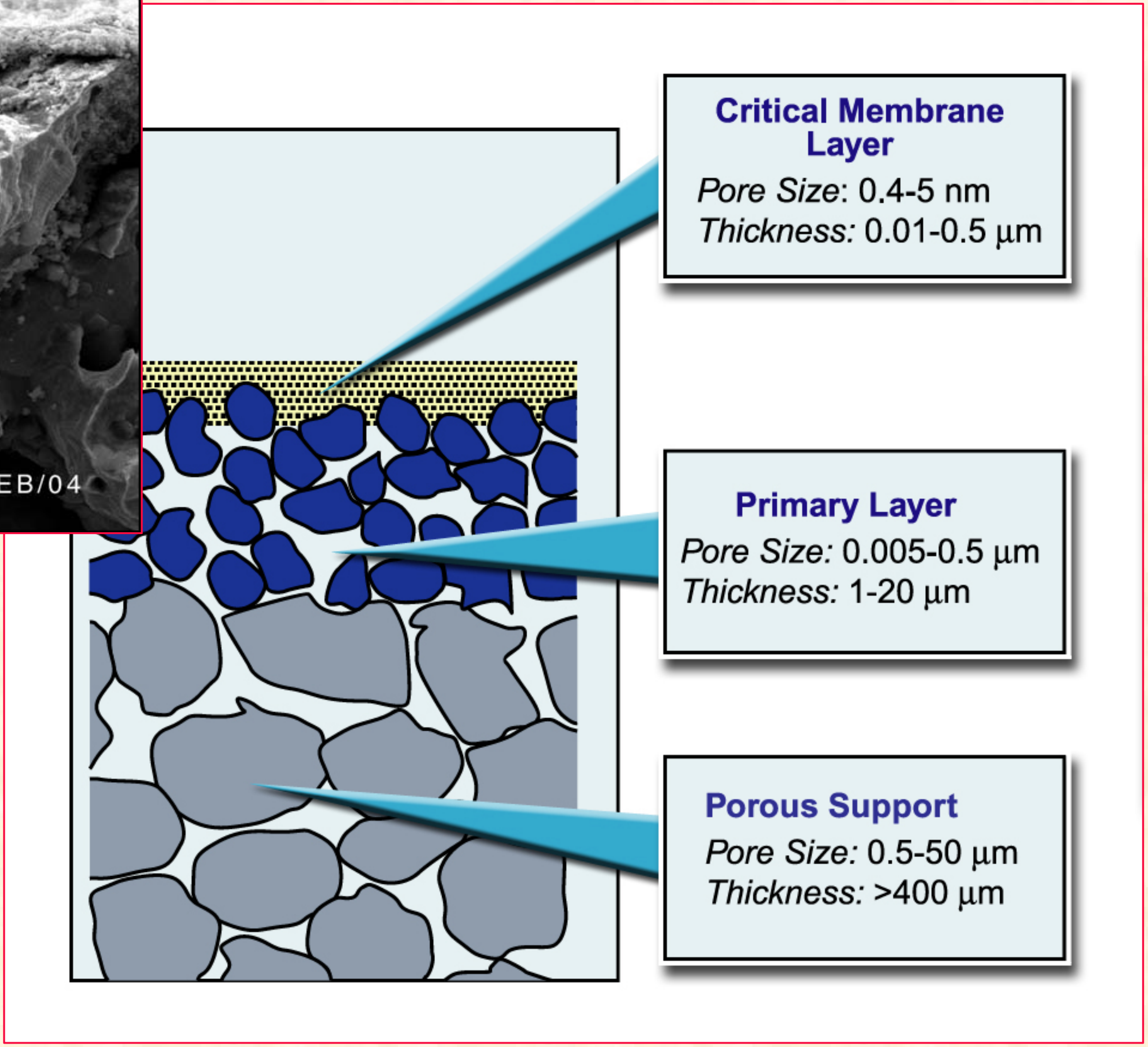


# ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

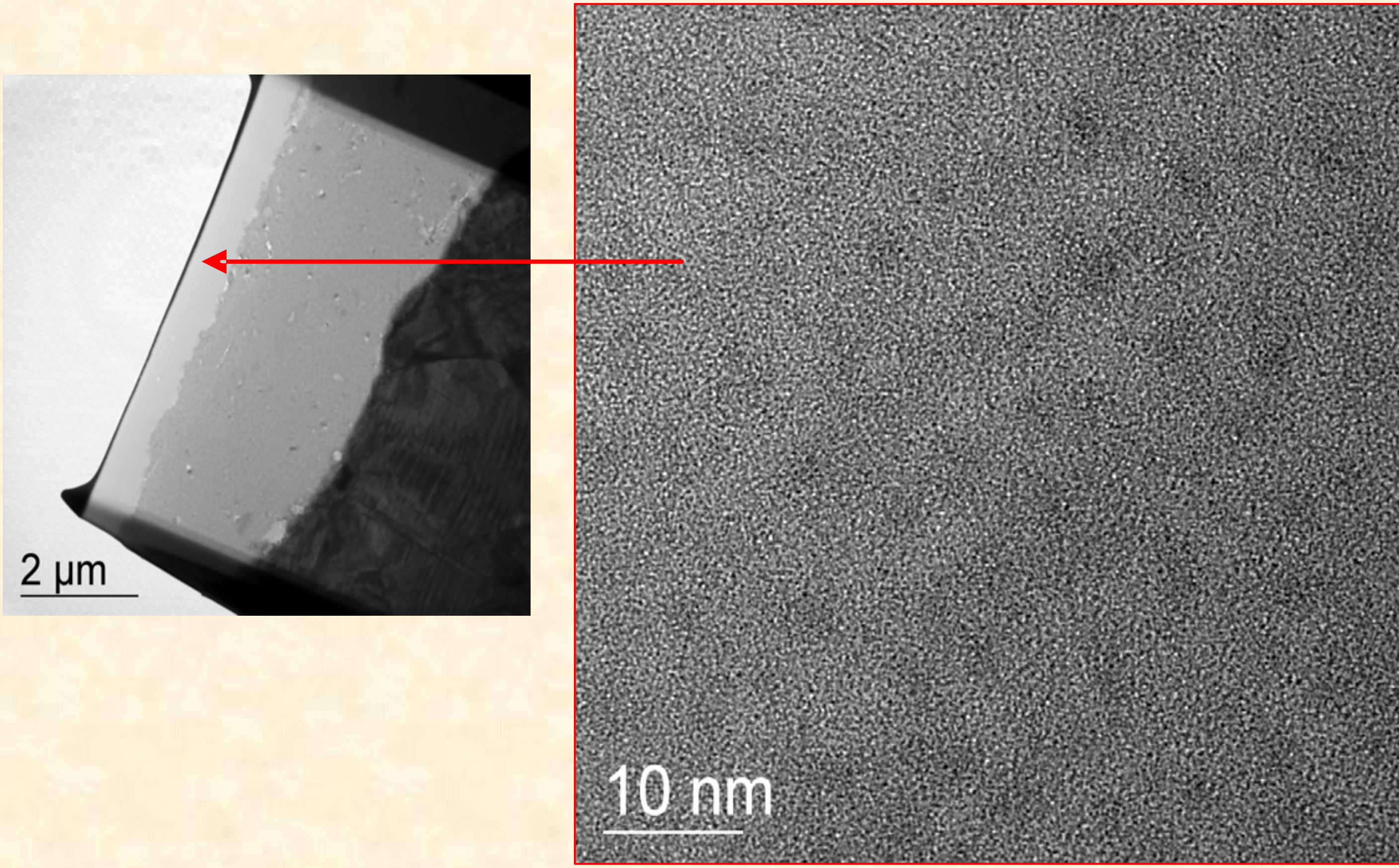
- Pore diameters of 0.5 nm – 20,000 nm; for $H_2$, pore diameters of <1 nm are preferred
- Tubular support structure and layer made of variety of metals and ceramics
- Excellent mechanical, thermal, and chemical stability
- Membrane layer(s) applied to inside of support tube
- Membrane layer thickness 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



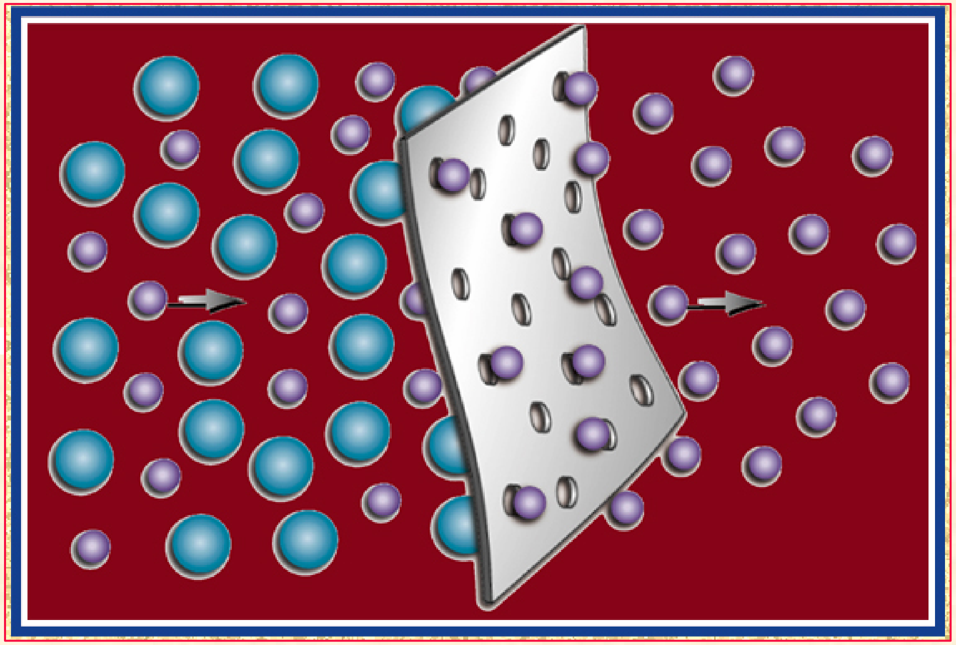
# In Distinct Contrast To Palladium Or Ion Transport Membranes, These Are Porous




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

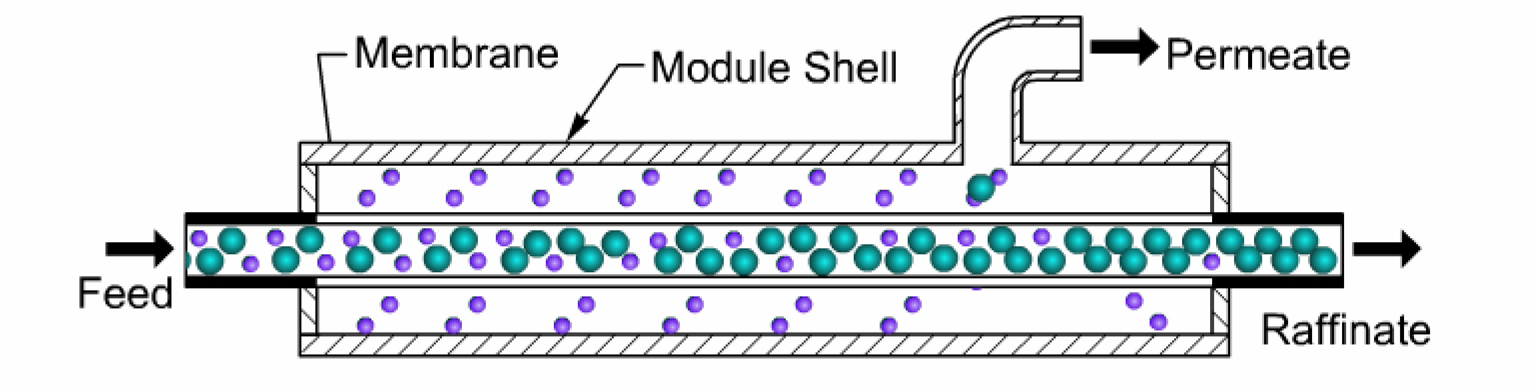
# How Do They Work?

- 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

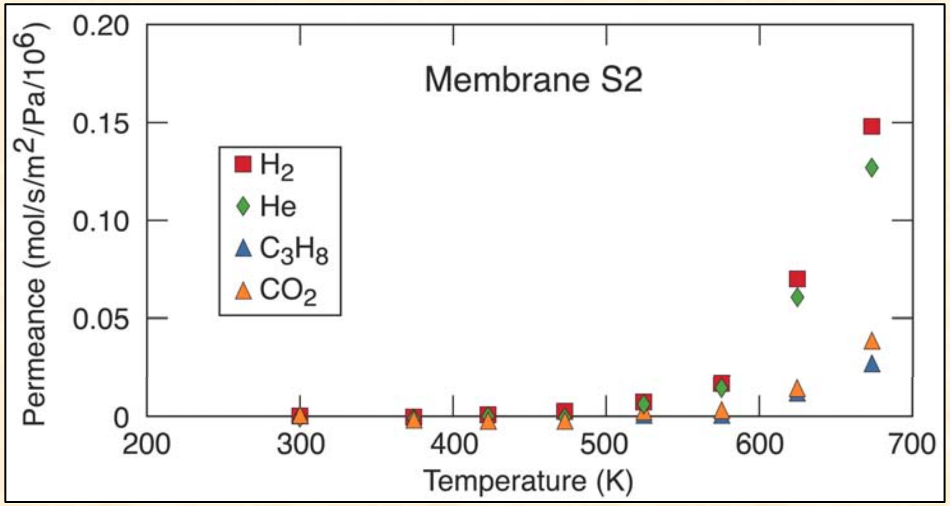
95%

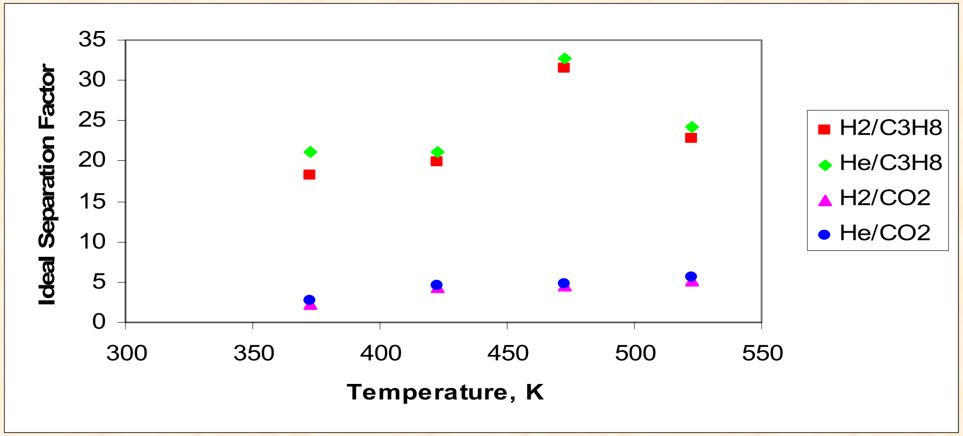



- *Permeance*: volumetric flow rate per unit of surface area per unit of transmembrane pressure (ΔP) at a particular temperature
- *Separation factor*: ratio of the flow of two gases in a binary gas mixture; indicator of selectivity of the membrane *(Separation factor depicted in figure is 19 and yields 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 $CO_2$ and propane. This phenomenon results in larger separation factors as temperatures are increased.

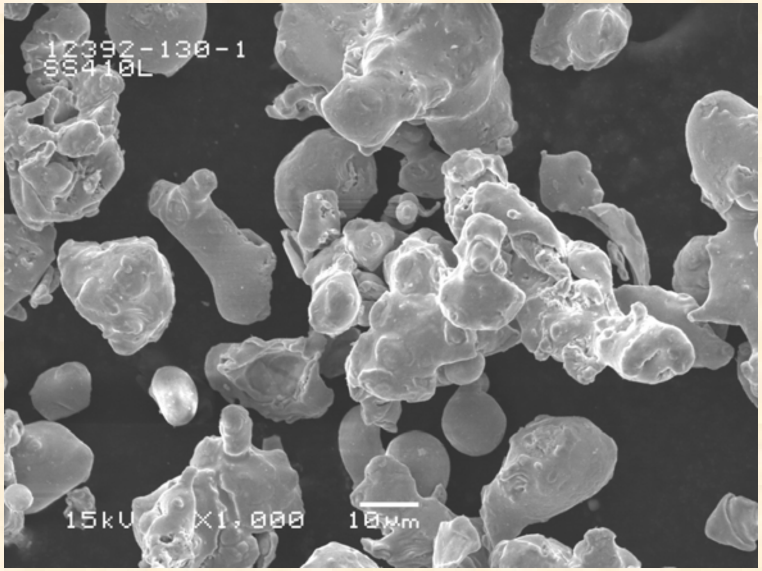


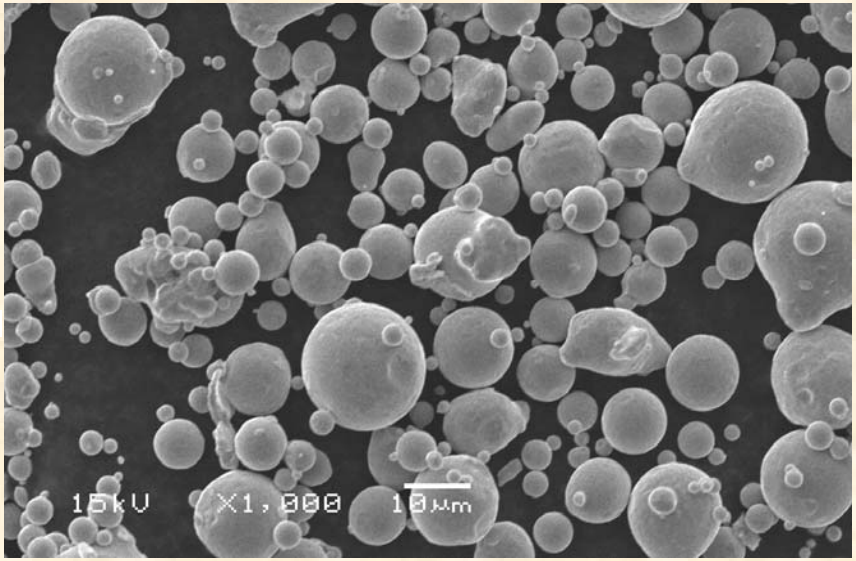
# Several of the Project Plan Tasks Have Been Initiated

- 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

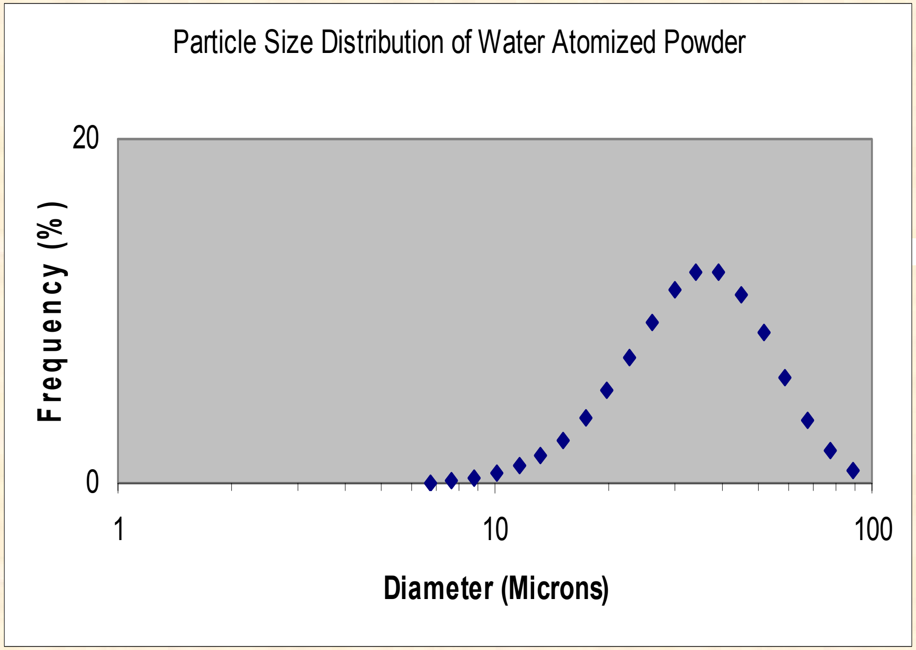


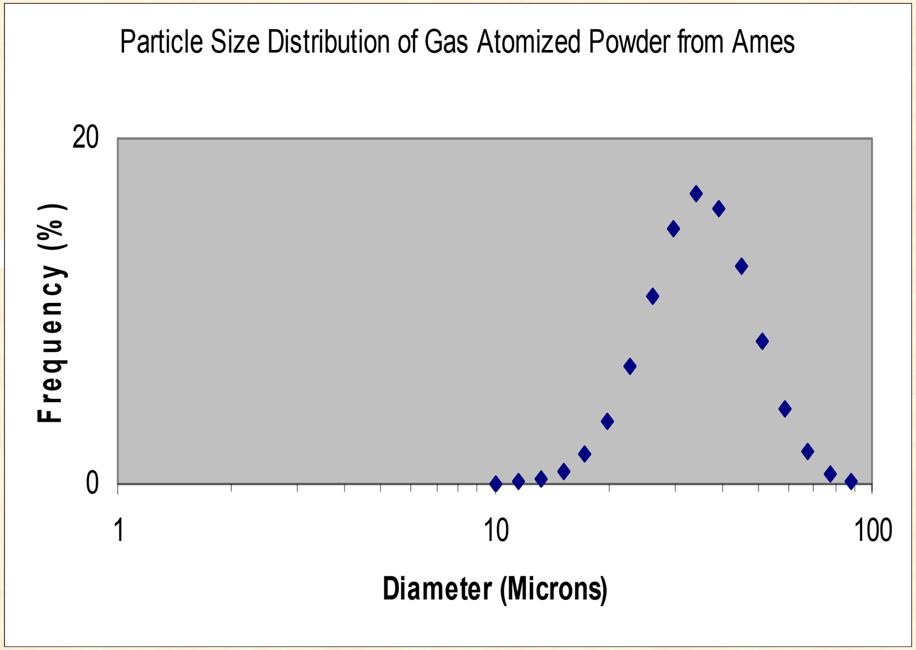

**Water Atomized 410 Stainless Steel Powder**




**Gas Atomized 410 Stainless Steel Powder**

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



# 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

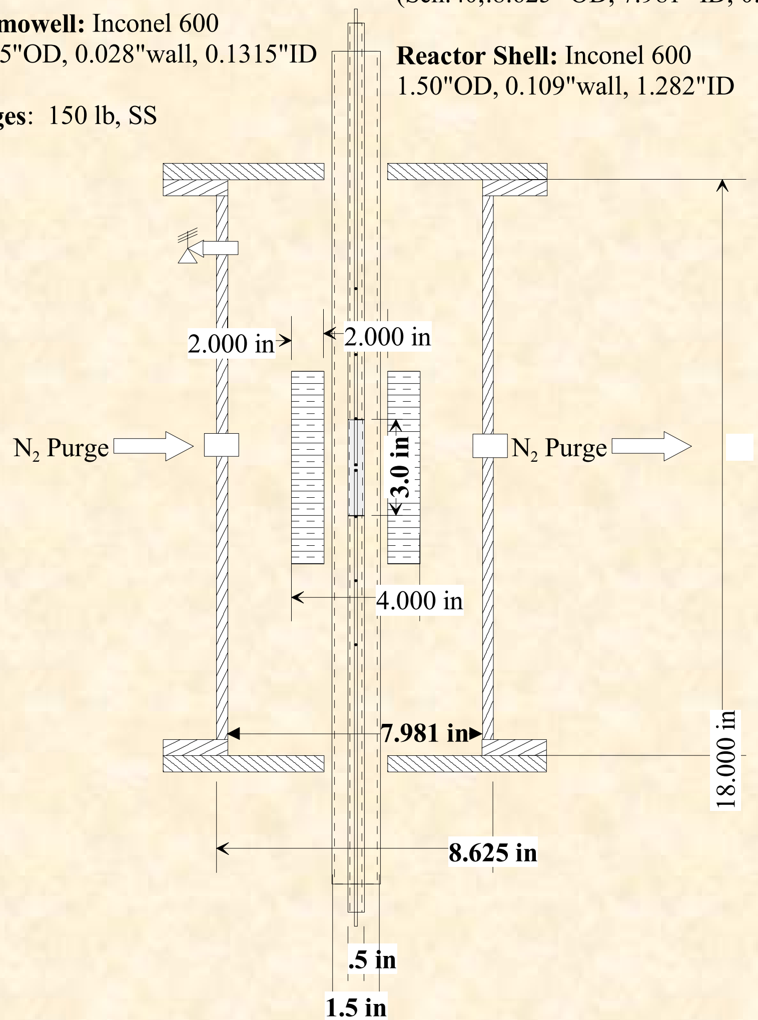
**Membrane:** 0.5" to 0.25" OD tubes
0.194" min ID (0.25"OD,0.028"wall)

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

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

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

**Flanges**: 150 lb, SS




## 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 $H_2S$ 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.