UT-BATTELLE

Scale-Up of Microporous Inorganic Hydrogen-Separation Membranes

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Presented at

DOE Hydrogen Program Annual Review
Crystal City, VA

May 17 2006

Project #PD12

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Project Overview

Budget

- FY05 $1M
- FY06 $1M
- The Project was initiated in December 2004
- Project duration – 3 years

Partners and Collaborators

- The Southern Company
- *Eastman Gasification Services Company*
- Pall Corporation
- National Energy Technology Laboratory (NETL)
- University of North Dakota Energy and Environmental Research Center

Sponsors

Office of Fossil Energy
Gasification
Coal Fuels

Barriers Addressed

- Cost – Technology is already commercialized in other membrane types
- Impurities – H_2S and other impurities do not impact H_2 permeance
- Durability – ORNL technology is versatile. Membranes can be made from materials stable in environment
- Flux – Microporous membranes have very high fluxes.

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).

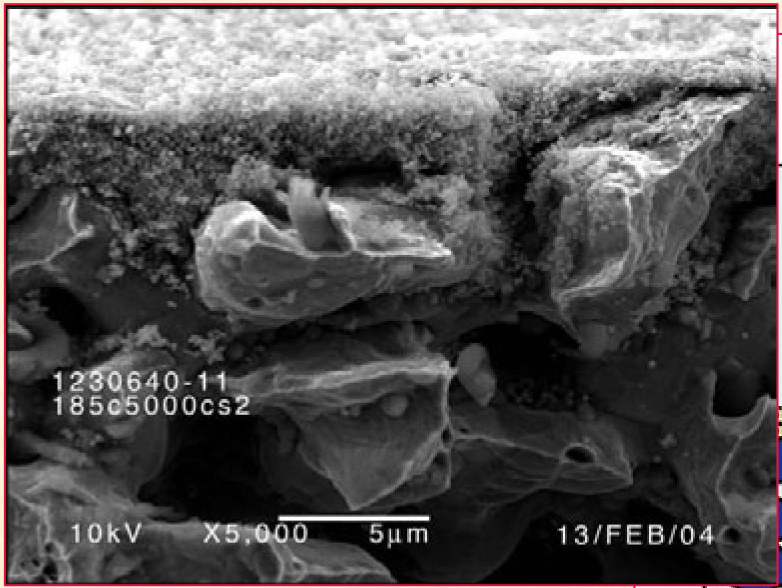
Approach

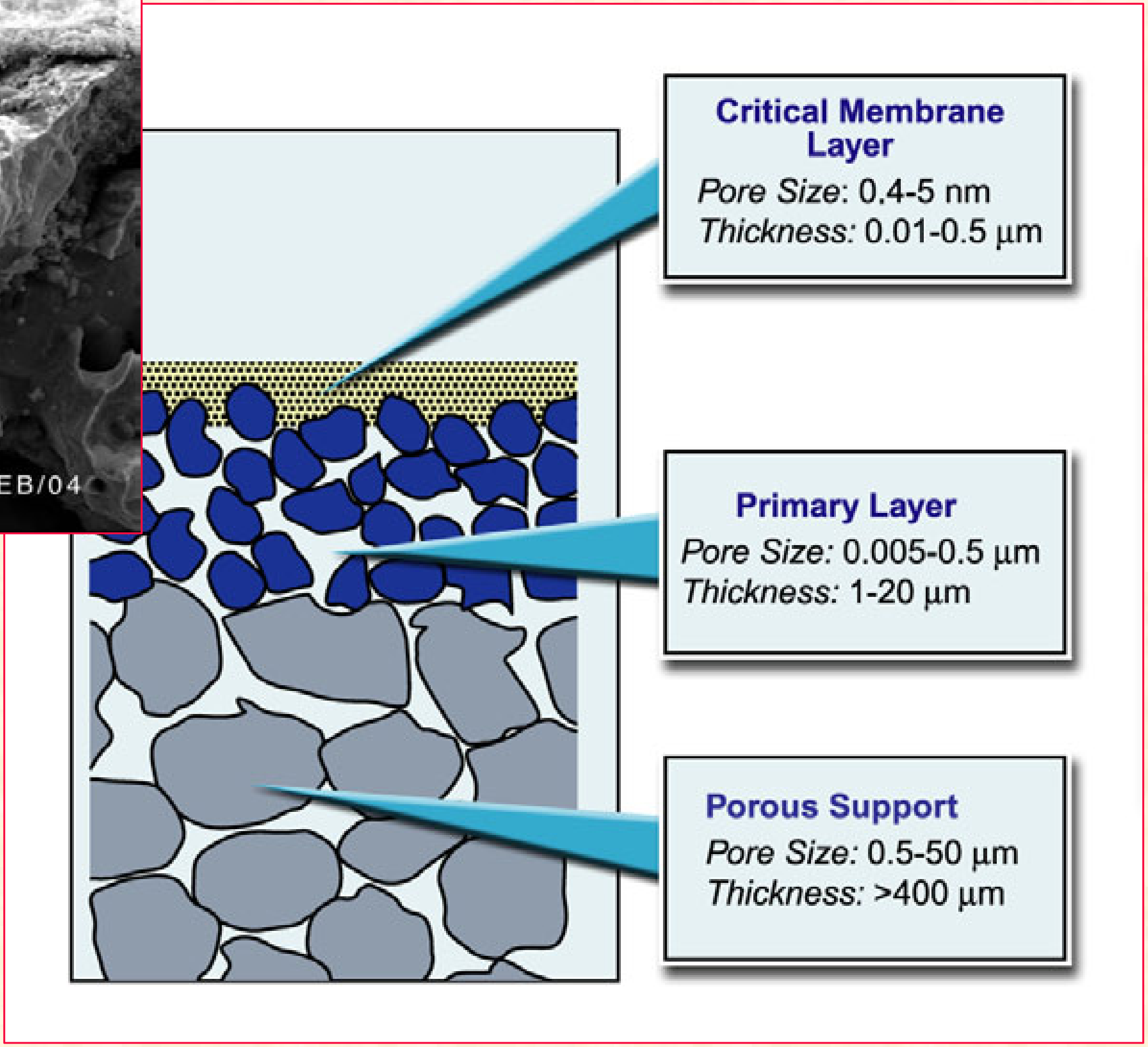
- Determine operating conditions and performance criteria for membranes (e.g. temperature, pressure, contaminant gas concentrations, hydrogen purity required, carbon dioxide removal, etc.).
- Test candidate membrane materials for compatibility in operating environment.
- Utilize technology developed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

ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

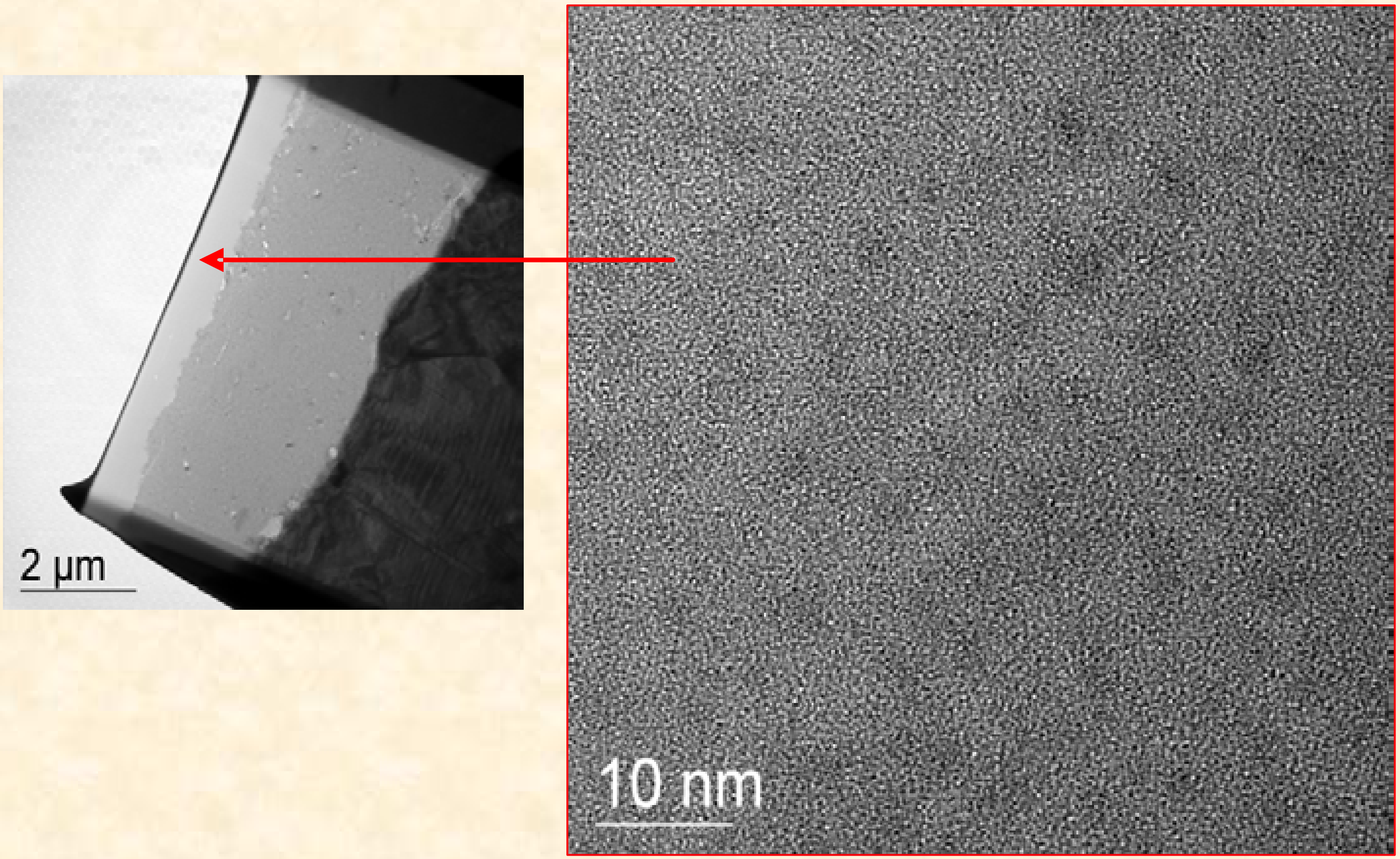
- Pore diameters of 0.5 nm – 20,000 nm; for H_2, pore diameters of <1 nm are preferred
- Tubular support structure and layer made of variety of metals and ceramics
- Excellent mechanical, thermal, and chemical stability
- Membrane layer(s) applied to inside of support tube
- Membrane layer thickness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





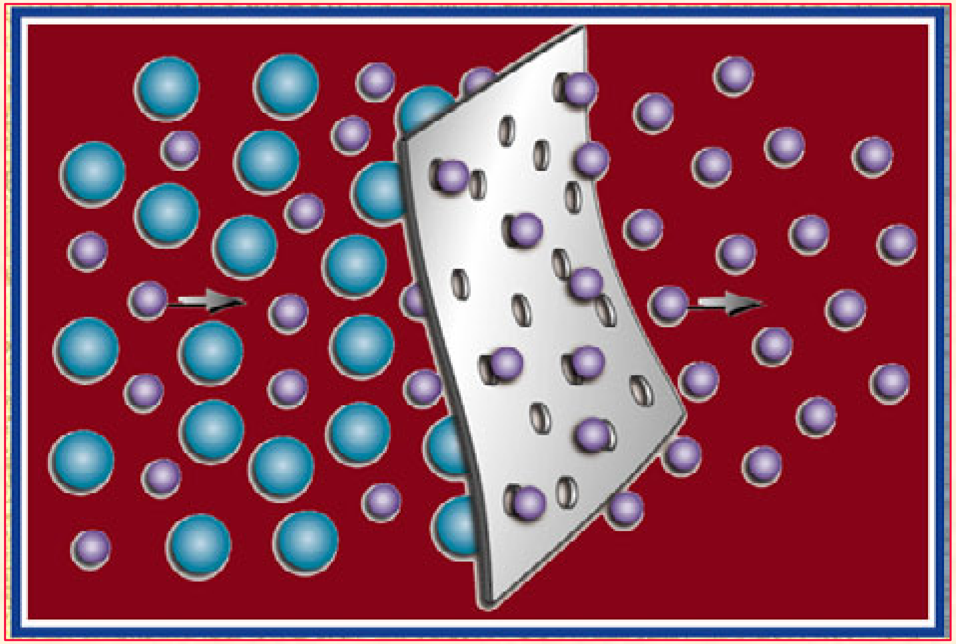
In Distinct Contrast To Palladium Or Ion Transport Membranes, These Are Porous



Membranes are descriptively nanoporous with pore sizes <2 nm, but IUPAC nomenclature is "microporous”

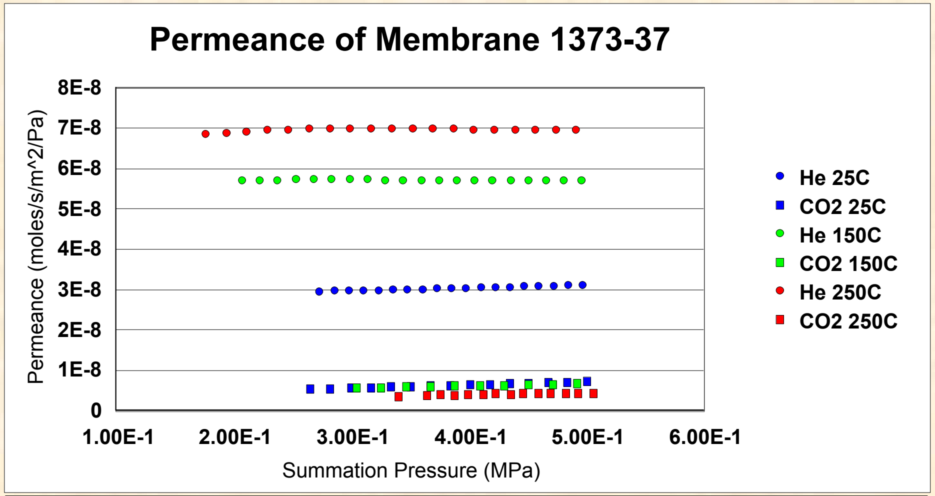
How Do They Work?

- 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



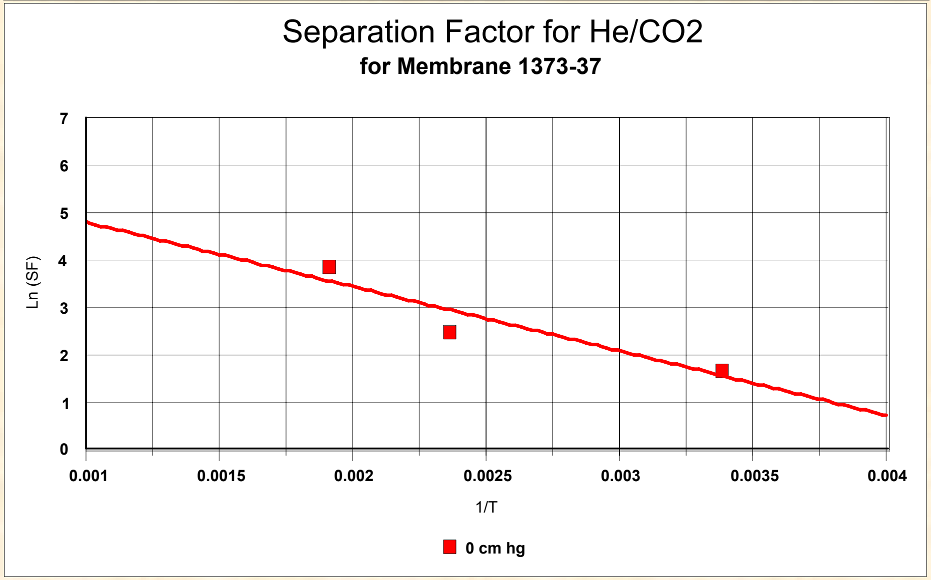
High Operating Temperatures Result in Both Higher Permeances and Higher Separation Factors

As the temperature is increased, the permeance of helium (also hydrogen) increases faster than CO_2. This phenomenon results in larger separation factors as temperatures are increased.



- Variation of permeance with temperature suggests a thermally activated diffusion process
- Lighter gases are affected more than heavier gases

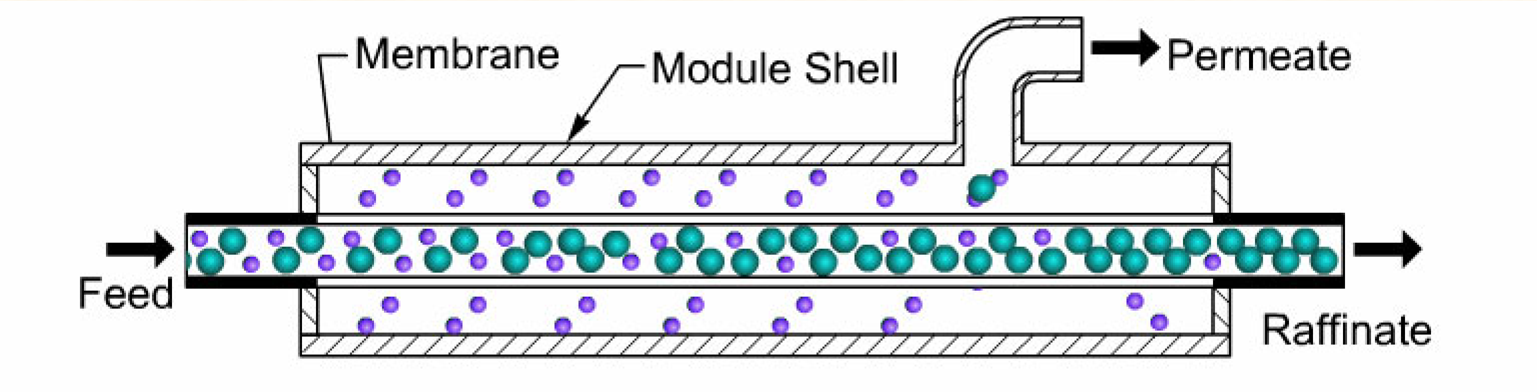
N.B.: Multiply permeances on chart by 927 for slpm/cm²/psi



Separation Factor for He/CO_2 – 48.3 at 250°C

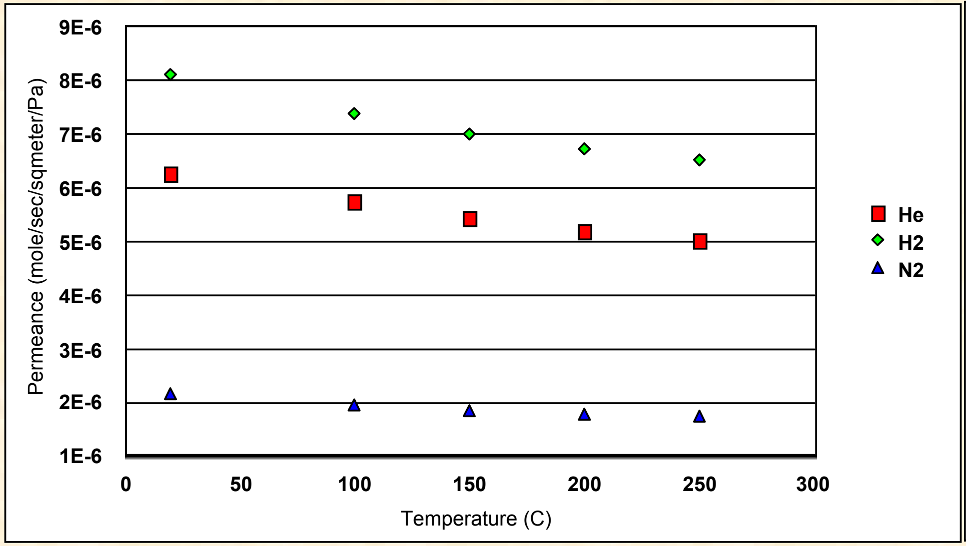
Permeance and Separation Factor are the Two Most Critical Attributes of Microporous Membranes

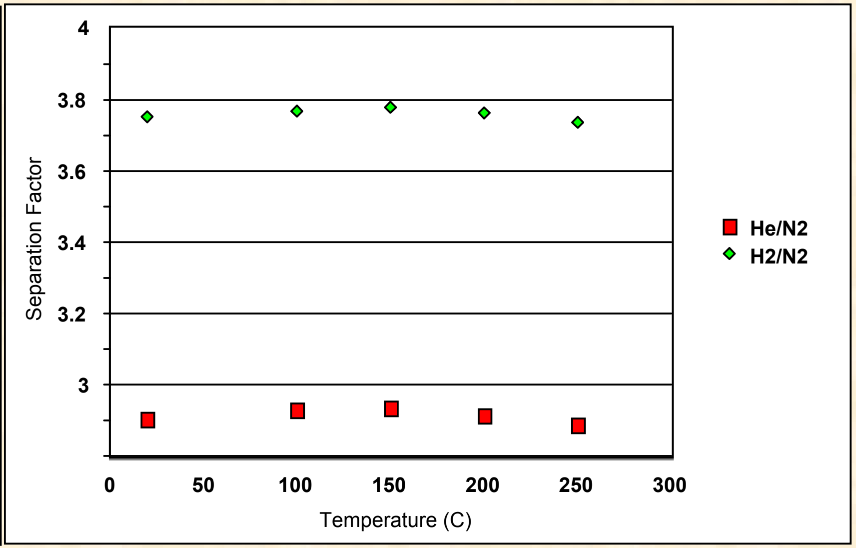
95%



- *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)

Metal Supported 70 Å Alumina Membrane Achieves Knudsen Separation





<u>Theoretical Separation Factors</u>

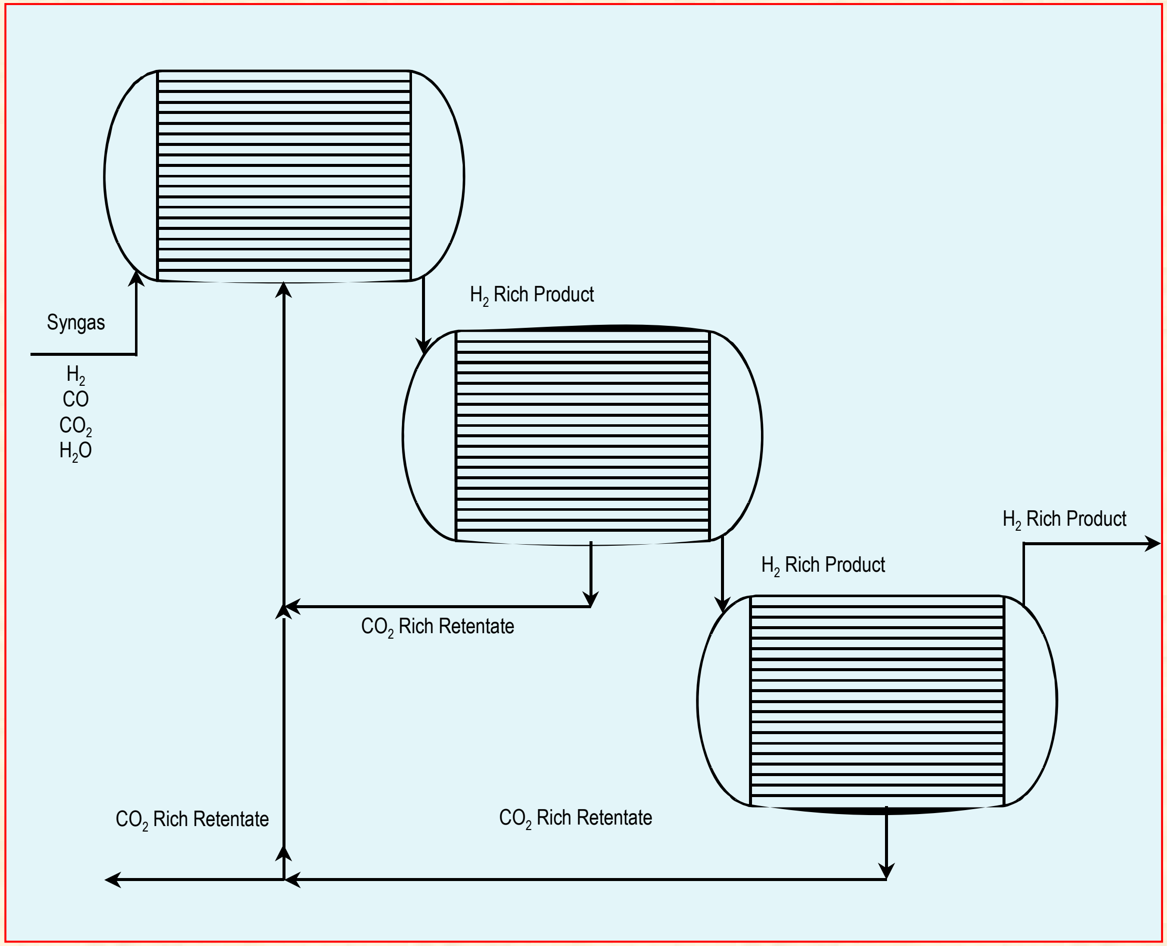
H_2/N_2	3.74
He/N_2	2.65

A Multi-Stage Hydrogen Separation Device Yields High Purity Hydrogen But With Recovery and Cost Penalties

	O_2 blown and shifted*		
	Stage 1	**Stage 2**	**Stage 3**
Membrane Type	**Knudsen**	**Knudsen**	**Nanoporous**
Partial P H_2 PSI	78.75	72.4	66
Permeate P (PSI)	72.4	66	20
Area needed M^2	0.17	0.17	1.13
Length (M)	1	1	1
Number of tubes needed	5	5	33
Separation Factor	4.69	4.69	10.00
%H_2 at Outlet	71.63	92.21	99.16

For PSDF slip stream at 30 lb/h gas flow; synthesis gas with 35% hydrogen; total pressure 225 psi

Hydrogen Separation Devices May Include a Series-Staged Configuration



Where do we go from here?

High Recoveries and Purities can be Achieved with High CO_2 Removal

Calculations were made to simulate the effects of a steadily declining concentration of hydrogen along the length of the tube as a result of some hydrogen being removed in each successive section by dividing the 1-meter long tube into 10 sections, each 0.1 m long.

%cut/H_2 Recovery	50.00%	75.00%	86.00%
%CO_2 in Permeate	3.77%	5.42%	9.50%
Hydrogen Purity	96.23%	94.58%	90.50%
% of CO_2 rejected	98.04%	95.70%	90.97%

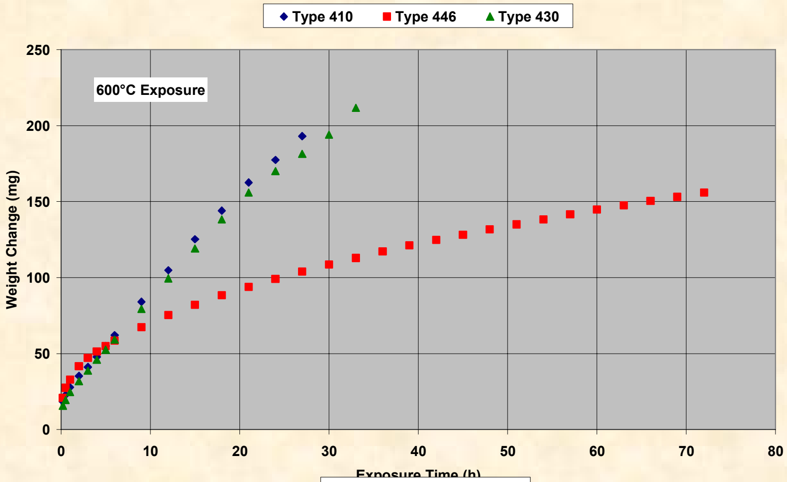
Based on membrane 1373-37 having ideal selectivity of 48.3 for He/CO_2

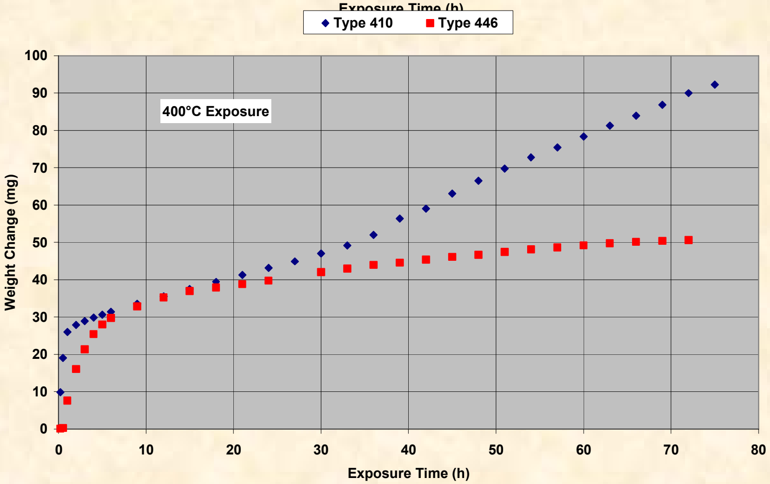
The Environmental Compatibility of Candidate Support Tube Alloy Compositions Are Being Systematically Assessed

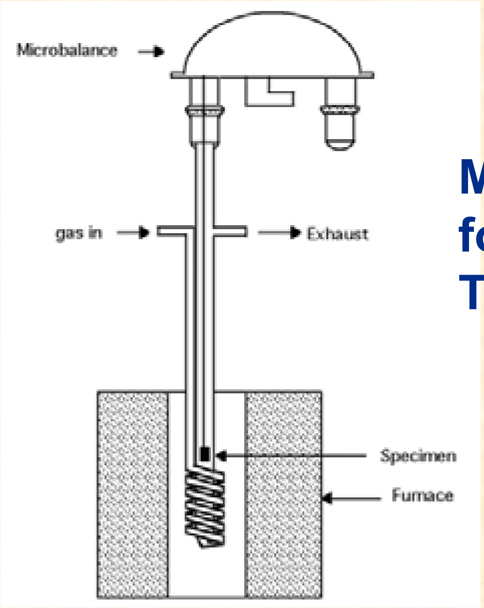
- Three alloy types - austenitic (Fe-Cr-Ni) and ferritic (Fe-Cr) steels; iron aluminide
- Simulated synthesis gas (H_2-H_2S-H_2O) composition - typical exit gas from gasifier and H_2-enriched (thermochemical analyses to characterize oxidizing and sulfidizing potentials)
- Gravimetric, chemical, and microstructural analyses
- Scoping tests
  - Three temperatures - 400, 600, 800°C
  - Dense alloys of candidate compositions, short times (100 h)
- Flow-through exposures at temperature appropriate for accelerated testing
  - Actual support tubes of most promising alloy compositions
  - Longer times (up to 3000 h)

Support Samples Were Studied for Stability in H_2S

Weight gain after exposure to H_2S







Microbalance for Exposure Tests

446 Samples after Exposure

800°C

400°C

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, NETL, UNDEERC

Several Materials and Performance Test Locations Have Been Identified

- Confirmatory materials compatibility tests (flow-through testing) at ORNL (Corrosion Science and Technology Group); January through September 2006
- Laboratory separation using simulated synthesis gas (ORNL); February through August 2006
- Separations testing of hydrogen from synthesis gas using nine-inch long membranes at UNDEERC (Mike Swanson); May through December 2006
- Separations testing of hydrogen from synthesis gas using one-to-three inch long membranes at NETL (Rich Killmeyer); Schedule TBD
- Pilot-scale separations testing of hydrogen from synthesis gas using one-meter long membranes at PSDF (Frank Morton); October 2006-September 2007
- *Pilot-scale separations testing of hydrogen from synthesis gas with one-meter to eight-feet long membranes at EGSC (David Denton); Schedule TBD but tentatively January-November 2007*

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

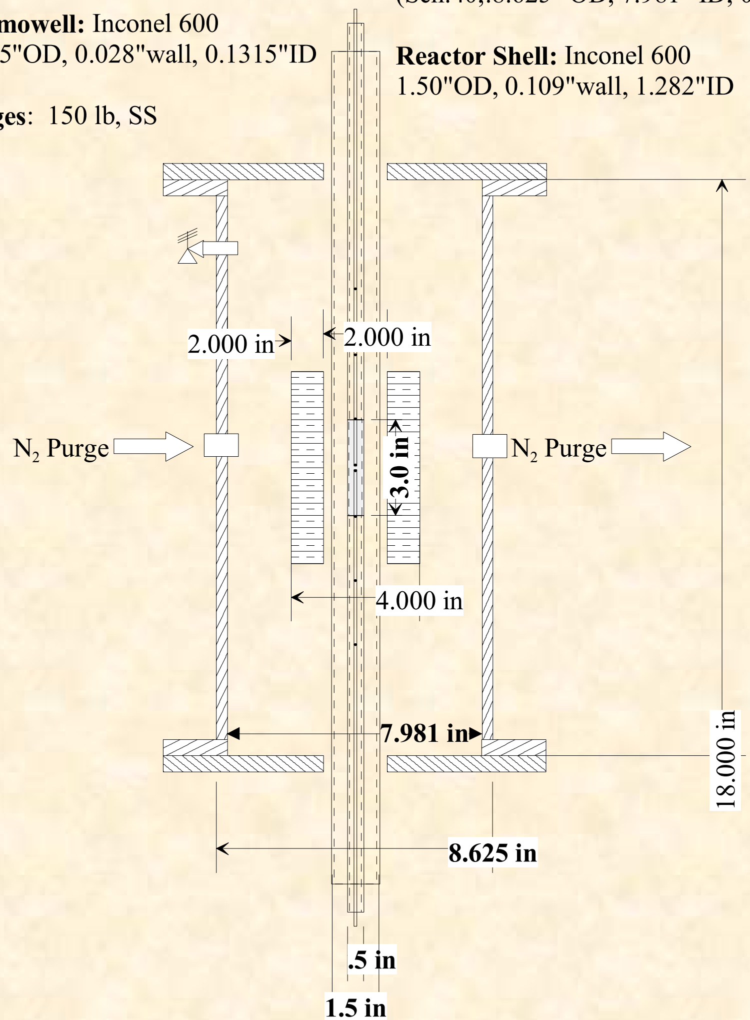
Membrane: 0.5" to 0.25" OD tubes
0.194" min ID (0.25"OD,0.028"wall)

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 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

UNDEERC Has Bench System and Transport Reactor Testing Capabilities

Bench System Properties

- **Synthesis gas flow: 8 scfm (606 moles/hr) maximum**
- **Total P (psi), 150 psig**

Transport Reactor

- **Syngas flow: 400 scfm**

Membrane Properties

	Nanoporous Membrane	Knudsen Membrane
H_2 Permeance (mole/sec/sqmeter/Pa)	1.50E-07*	7.15E-06
Pore Size (Angstroms)	6-8	70

* Measured at 400°C

	% H_2 by volume	Partial P H_2 (PSI)	Delta P (PSI)	Hydrogen Moles/Hr	Area Needed (M^2)		# of 1-meter Tubes Needed	
					Nanoporous	Knudsen	Nanoporous	Knudsen
To Treat Max Flow*	40%	60	40	242.7	1.63	0.034	47.5	1

* Bench system @ 8 scfm

The Wilsonville Slipstream Test System will be Used

Slip Stream Properties

- 30 lbs (556 moles) of synthesis gas per hour
- Average molecular weight of synthesis gas, 24.5
- Total P (PSI), 225

Membrane Properties

	Nanoporous Membrane	Knudsen Membrane
H_2 Permeance (mole/sec/m^2/Pa)	1.50E-07*	7.15E-06
Pore Size (Angstroms)	6-8	70

* Measured at 400°C

	% H_2 by volume	Partial P H_2 (PSI)	Delta P (PSI)	Moles/Hr	Area Needed (M^2) Nanoporous	Area Needed (M^2) Knudsen	# of 1-meter Tubes Needed Nanoporous	# of 1-meter Tubes Needed Knudsen
O_2 blown and shifted	35%	78.75	58.75	194.6	0.89	0.02	25.9	0.5
Air blown and shifted	20%	45	25	111.2	1.19	0.03	34.8	0.7
O_2 blown - no shift	20%	45	25	111.2	1.19	0.03	34.8	0.7
Air blown - no shift	10%	22.5	2.5	55.6	5.97	0.13	174.1	3.7

Project Summary

- One-meter long support tubes were fabricated from 316L stainless steel and sintered to obtain proper strength and porosity. 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
- The primary (initial) membrane layers have been applied
- Materials Compatibility Task underway. Results will confirm materials selection
- The necessary equipment has been acquired to apply the membrane separative layers to one-meter long support tubes
- Membranes are currently being fabricated for testing at ORNL, NETL, and UNDEERC

Response to Reviewers' Comments

- Is 95% purity good enough, given competing technologies that are being developed? *For use in gas turbine, 95% hydrogen with over 90% capture of CO_2 is more than adequate. For use in PEM fuel cells, microporous membranes could be staged or coupled with a small PSA unit.*
- Project plan needs to be revisited once collaborators are in place. *Project plan has been revised and further revision will be completed once system analysis is completed.*
- Project should bring analyst in early on to help identify economic viability and areas that should be focused on in the design of the system. *System analysis is being completed by NETL subcontractor.*
- It is recommended to improve the hydrogen selectivity of the membranes before scale-up. *Improvements to supports (uniform pore size, surface roughness) and reduction of oversized pores being done in parallel through Advanced Research Materials Program.*