ADVANCED HYDROGEN TRANSPORT MEMBRANES FOR VISION 21 FOSSIL FUEL PLANTS

Presented by

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#PD11

Overview

Timeline

- Project start date: October 1, 2000
- Project end date: September 30, 2005
- 85% percent complete

Budget

• Total project funding:	$2,800,000
– DOE share:	$2,240,000
– Contractor share:	$ 560,000
• Funding received in FY04:	$ 377,765
• Funding for FY05:	$ 736,244

Barriers Addressed

- Reducing hydrogen cost
- Hydrogen production from diverse pathways
- Hydrogen of sufficient purity for fuel cells

Technical Targets

- High hydrogen flux at temperatures compatible with water-gas shift catalysis
- Compatibility with simultaneous carbon dioxide sequestration
- Stable to syngas conditions

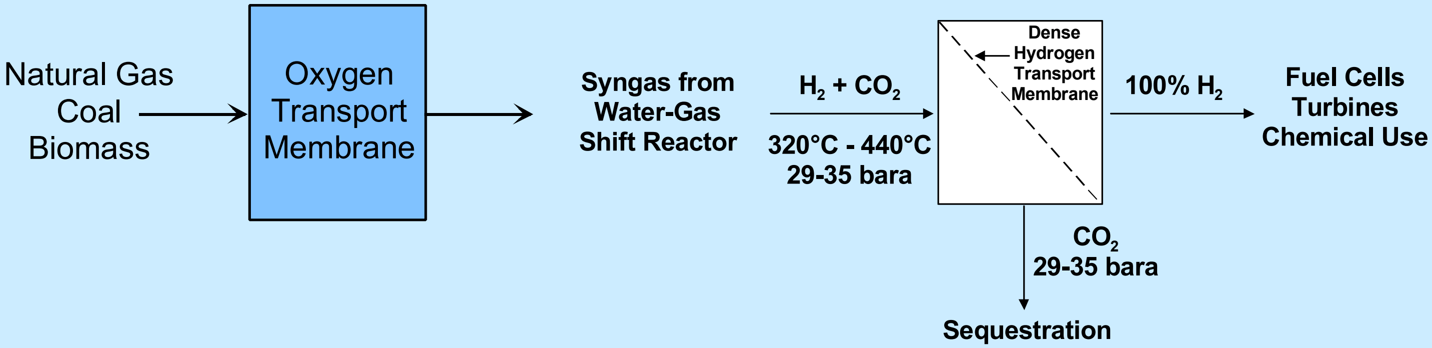
Partners

- CoorsTek
- Sűd Chemie
- Noram Engineering
- ANL

Objectives

- Identify low-cost high-performance hydrogen transport membranes
- Operate using representative synthesis mixtures
- Verify performance under high-pressure differentials comparable with simultaneous carbon dioxide sequestration
- Address sweep gas / no sweep gas issue on membrane permeate side
- Long-term performance
- Cost issues

Overall Scheme for Converting Hydrocarbon Feedstock to Hydrogen with Simultaneous Carbon Dioxide Sequestration


Natural Gas
Coal
Biomass

Oxygen Transport Membrane

Syngas from Water-Gas Shift Reactor

$H_2 + CO_2$

320°C - 440°C
29-35 bara

Dense Hydrogen Transport Membrane

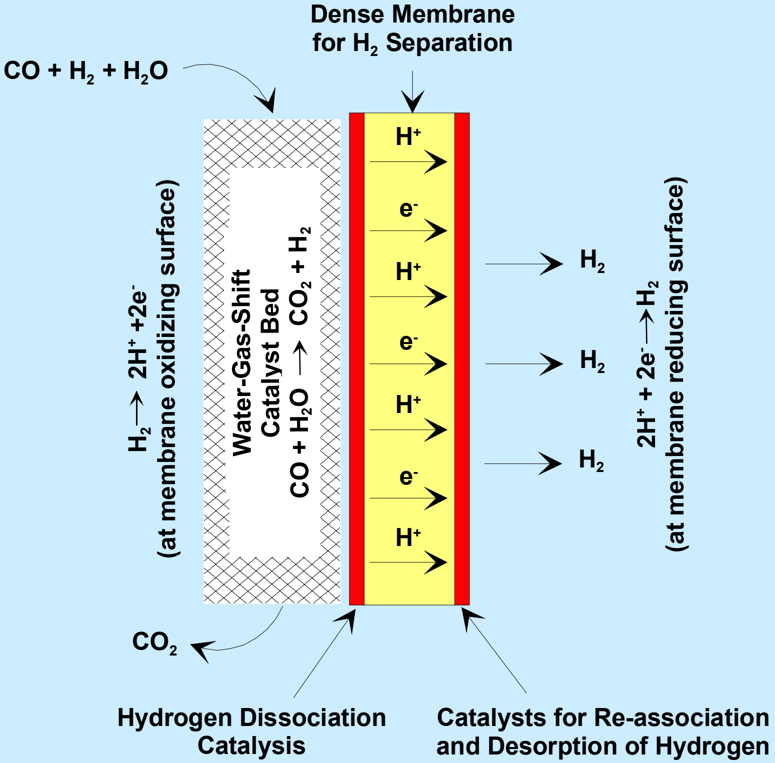
100% H_2

Fuel Cells
Turbines
Chemical Use

CO_2
29-35 bara

Sequestration

Integration of Water-Gas Shift Catalysts with Hydrogen Transport Membranes for Separation of Hydrogen from Carbon Dioxide



Dense Membrane for H_2 Separation

$CO + H_2 + H_2O$

$H_2 \longrightarrow 2H^+ + 2e^-$ (at membrane oxidizing surface)

Water-Gas-Shift Catalyst Bed

$CO + H_2O \longrightarrow CO_2 + H_2$

H^+

e^-

H^+

e^-

H^+

e^-

H^+

H_2

H_2

H_2

$2H^+ + 2e^- \longrightarrow H_2$ (at membrane reducing surface)

CO_2

Hydrogen Dissociation Catalysis

Catalysts for Re-association and Desorption of Hydrogen

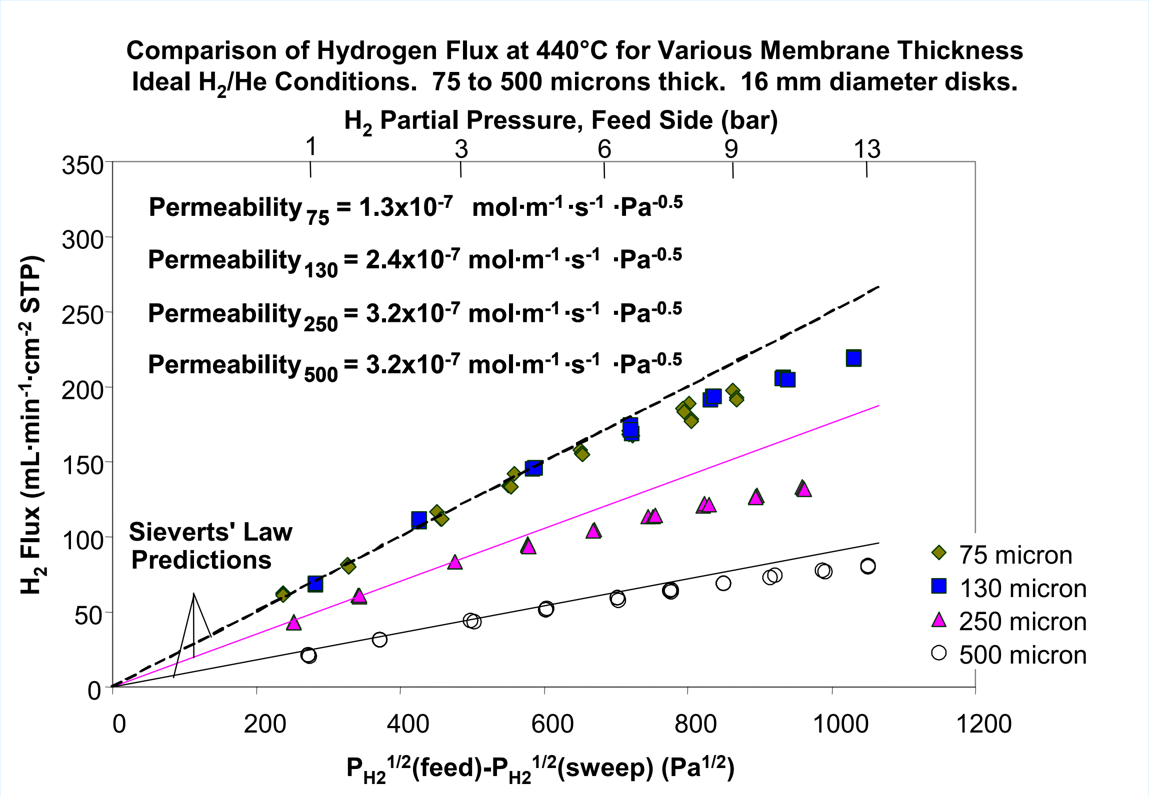
Eltron H_2 Separation Membrane Characteristics

Membrane Category	Temperature Range (°C)	Maximum Permeation Rate ($mL \cdot min^{-1} \cdot cm^{-2}$)
Single Phase Ceramic	**700 to 950**	**≈ 0.01**
Ceramic/Ceramic	**700 to 950**	**≈ 0.1**
High-Temperature Cermet With Non H_2-Permeable Metal (Ni)	**700 to 950**	**≈ 1**
High-Temperature Cermet with H_2-Permeable Metal (Pd)	**400 to 800**	**≈ 4**
Thin Film Palladium on Porous Support	**320 to 600**	**>50**
Intermediate-Temperature Composite	**320 to 440**	**>400**

High-Pressure Differential Hydrogen Separation Units

- Tests to 69 bar (1000 psi) differential pressure at 320-440°C
- Tests with high pressure WGS mixture

Pressure Differential Hydrogen Flux Measurements under Ideal 40% H_2/He Conditions as a Function of Membrane Thickness



Comparison of Hydrogen Flux at 440°C for Various Membrane Thickness
Ideal H_2/He Conditions. 75 to 500 microns thick. 16 mm diameter disks.

$\text{Permeability}_{75} = 1.3\times10^{-7}$ mol·m^{-1}·s^{-1} ·Pa$^{-0.5}$

$\text{Permeability}_{130} = 2.4\times10^{-7}$ mol·m^{-1}·s^{-1} ·Pa$^{-0.5}$

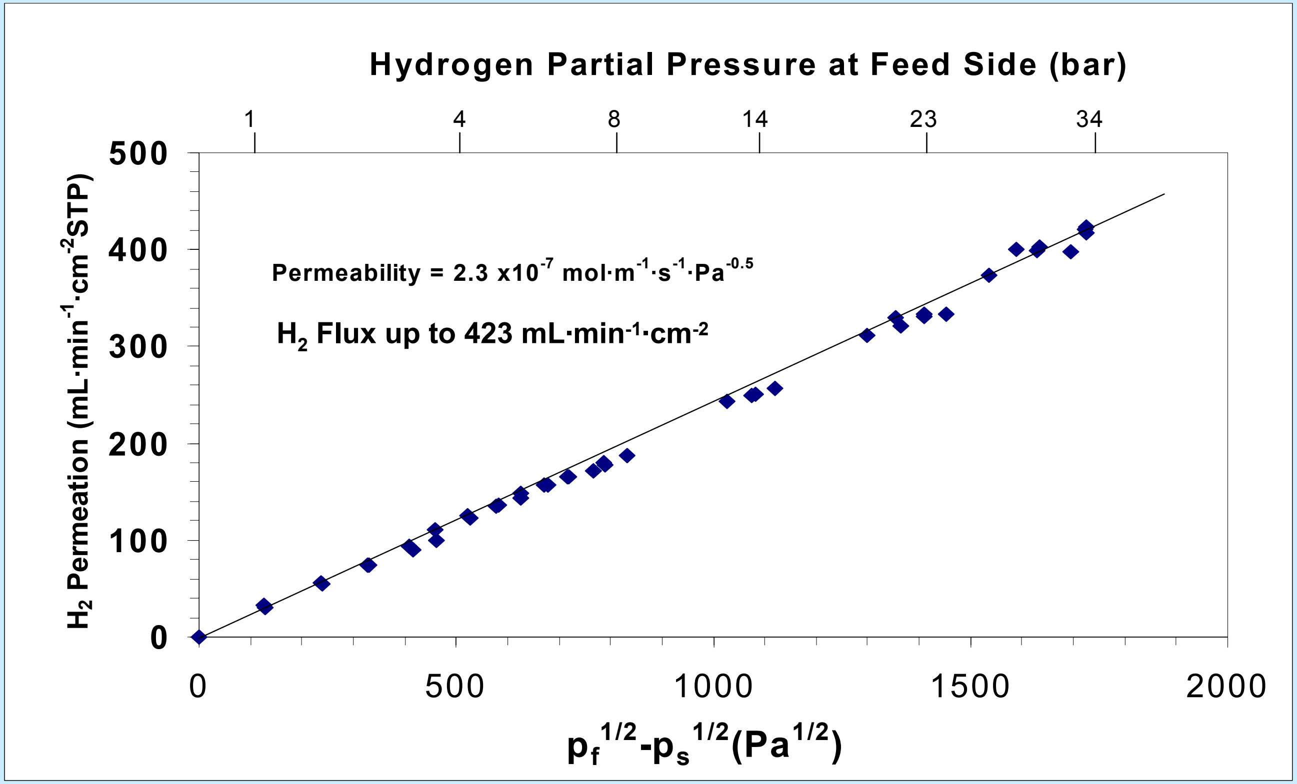
$\text{Permeability}_{250} = 3.2\times10^{-7}$ mol·m^{-1}·s^{-1} ·Pa$^{-0.5}$

$\text{Permeability}_{500} = 3.2\times10^{-7}$ mol·m^{-1}·s^{-1} ·Pa$^{-0.5}$

Sieverts' Law Predictions

- **Bulk diffusion is rate limiting for 250 and 500 micron thick membranes.**
- **Flux identical for 75 and 130 micron thick membranes. Bulk diffusion is not rate limiting.**
- **Gas phase diffusion limited.**

Hydrogen Flux at High Pressure Differential

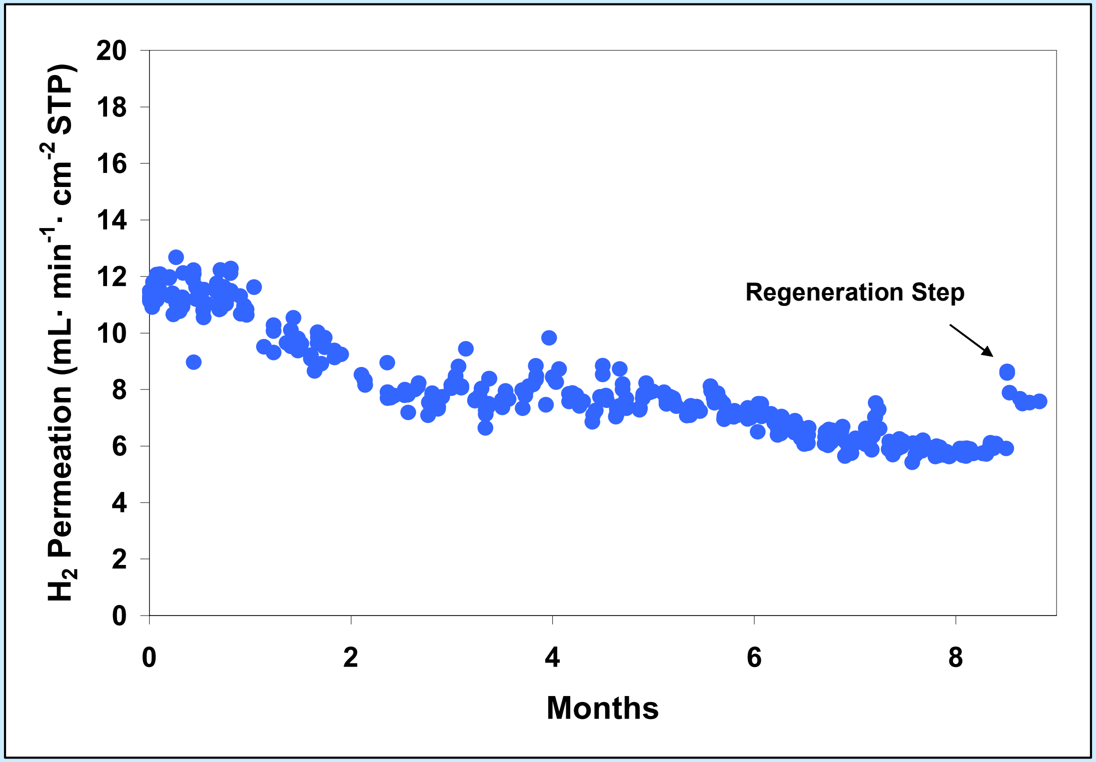


- Permeability of 2.3x10^{-7} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$ and hydrogen flux of 423 mL·min^{-1}·cm^{-2} (STP) achieved at 440°C (713K) under ideal hydrogen-helium mixture up to 33 bar (476 psi) differential pressure and partial pressure of hydrogen of 34 bar (488 psi).

Long-Term Ambient Pressure Performance

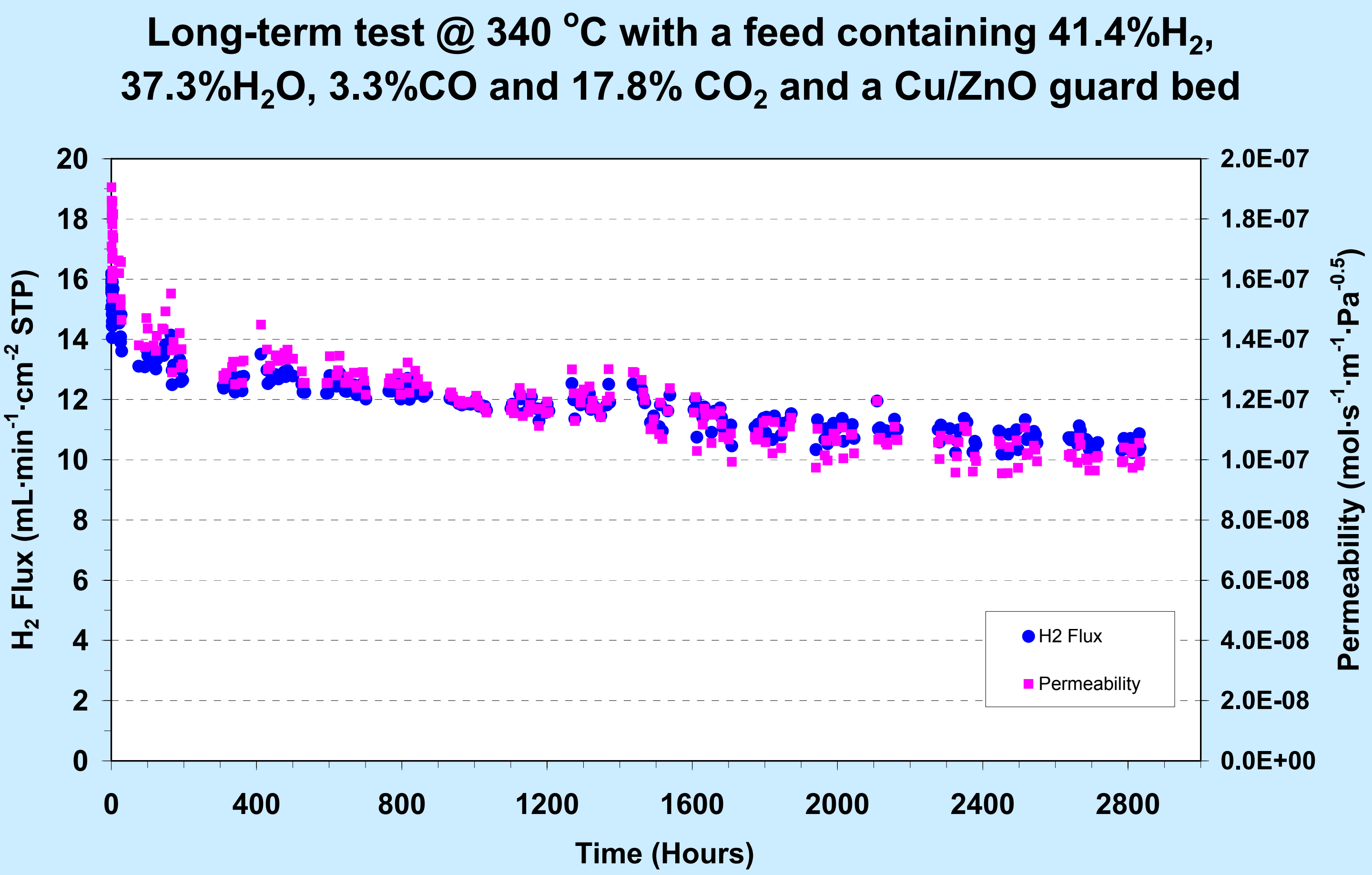
Performance of Hydrogen Transport Membrane

(80% H2 / 20% He Feed at 320°C)

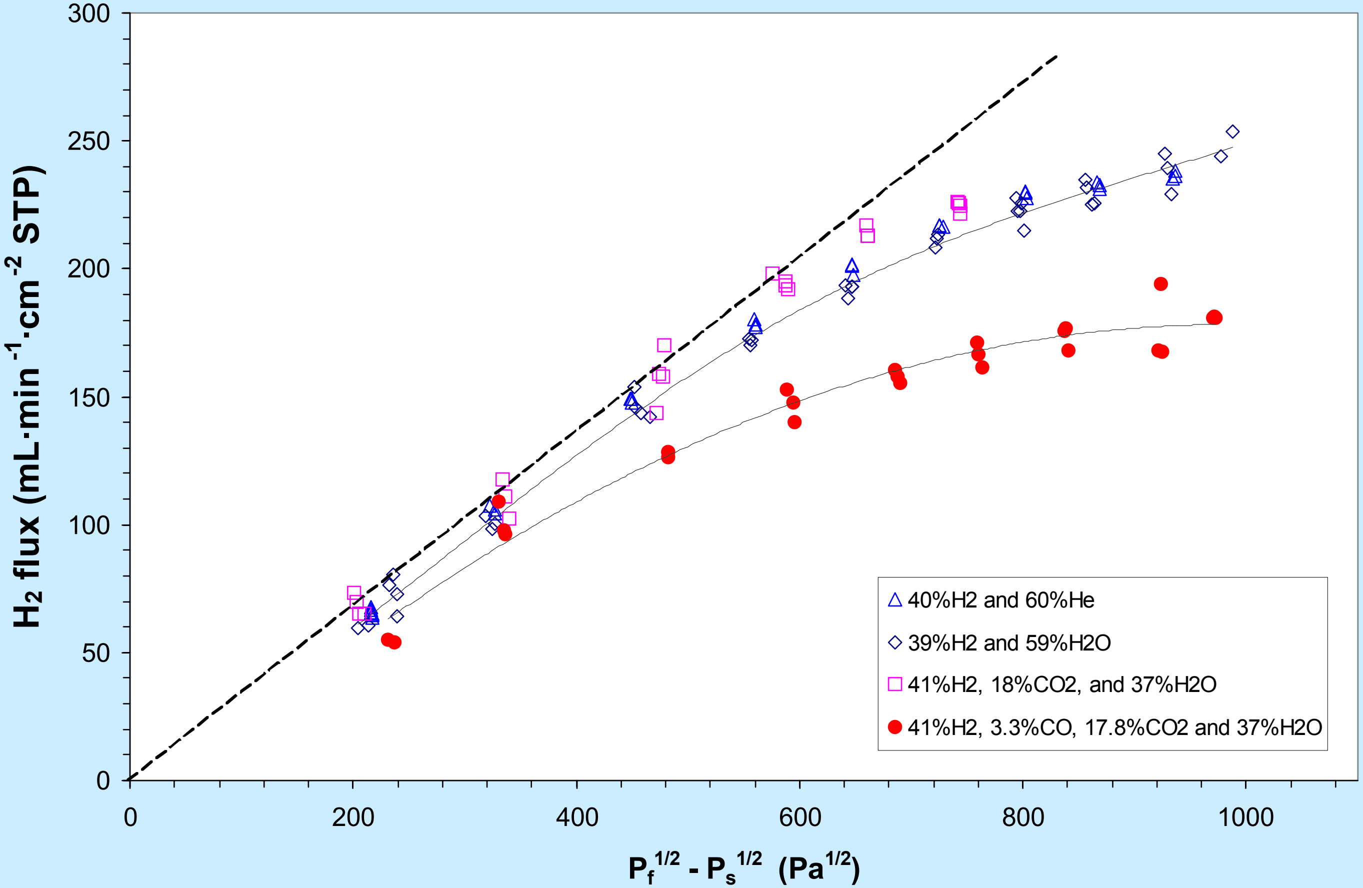


- No guard bed used to adsorb impurities.

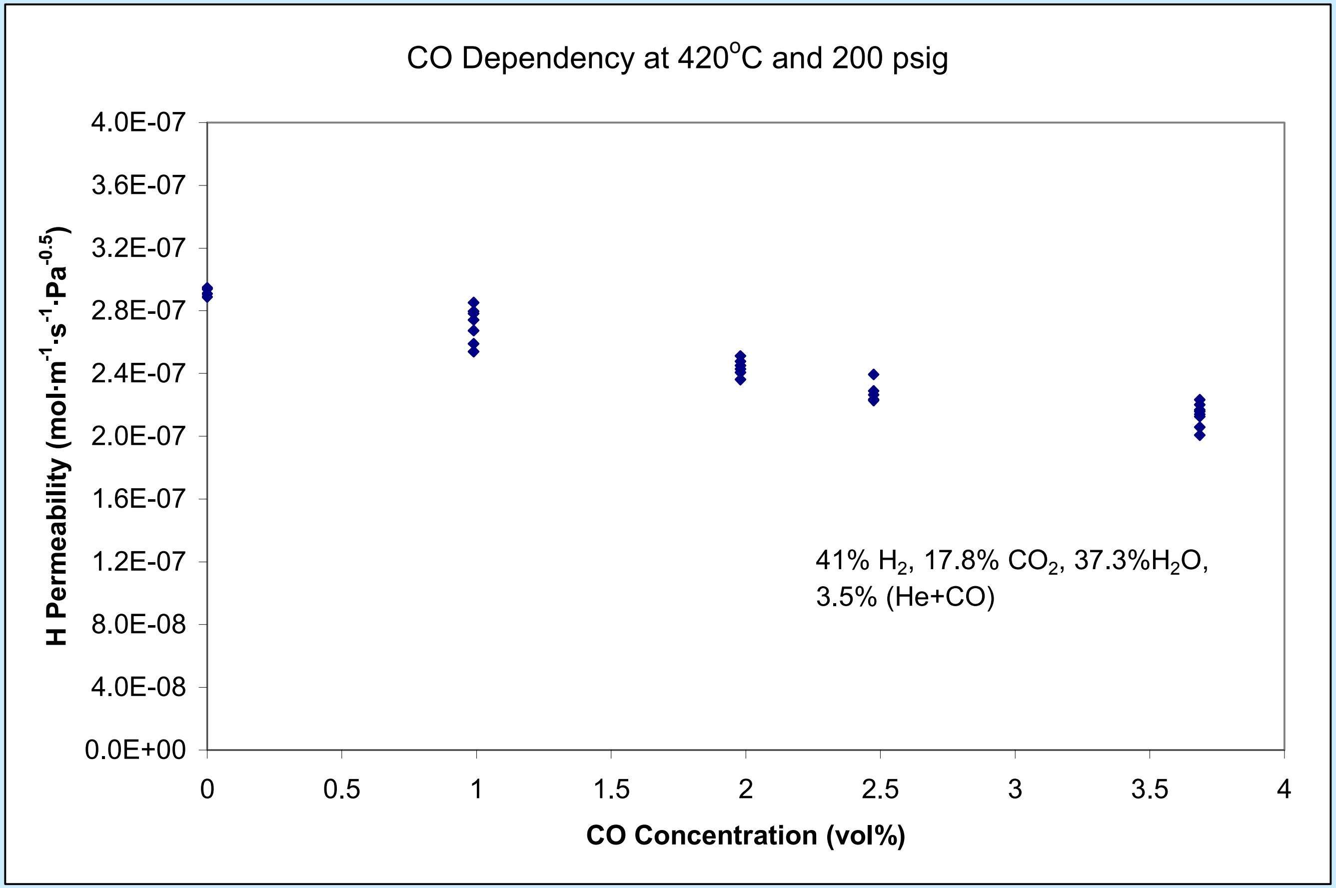
Long-Term Results



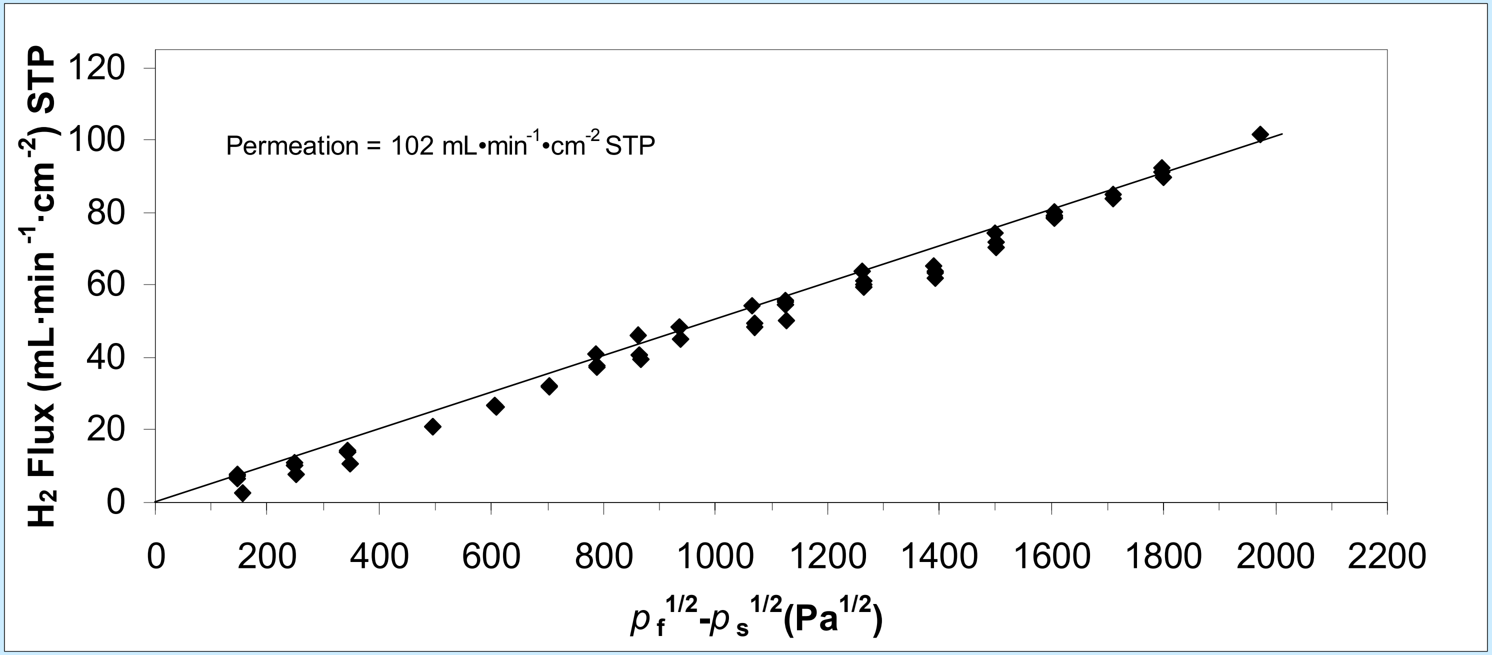
Membrane Performance upon Going from Ideal to Syngas Conditions



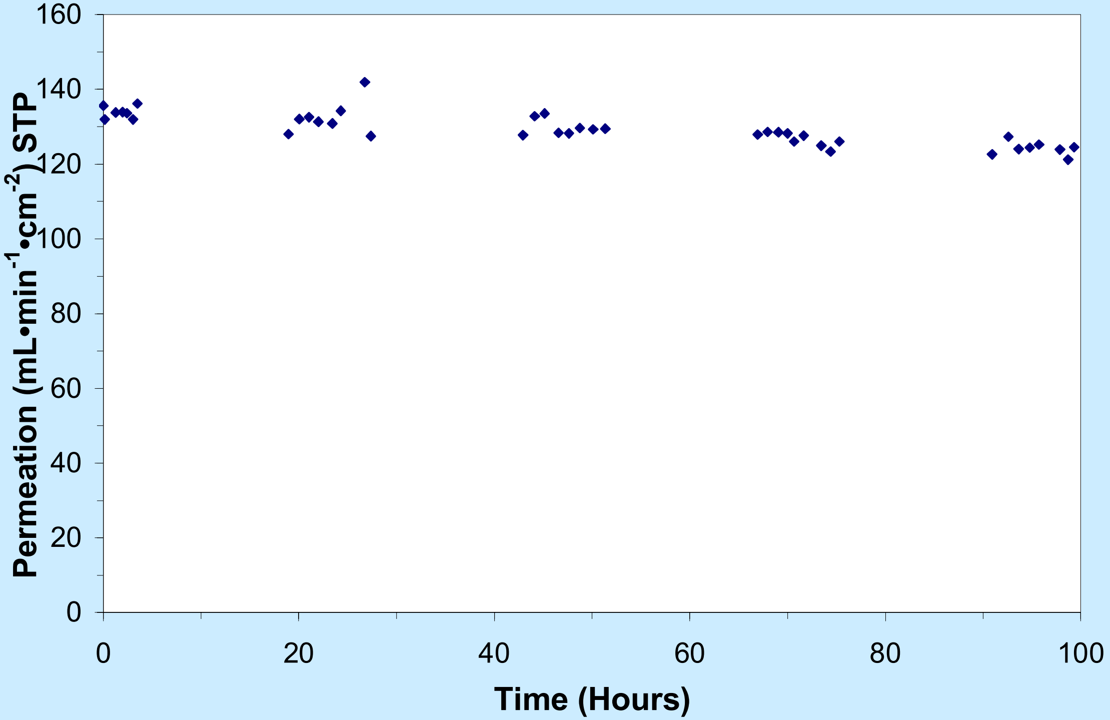
Dependency of Membrane Performance on Carbon Monoxide Fraction



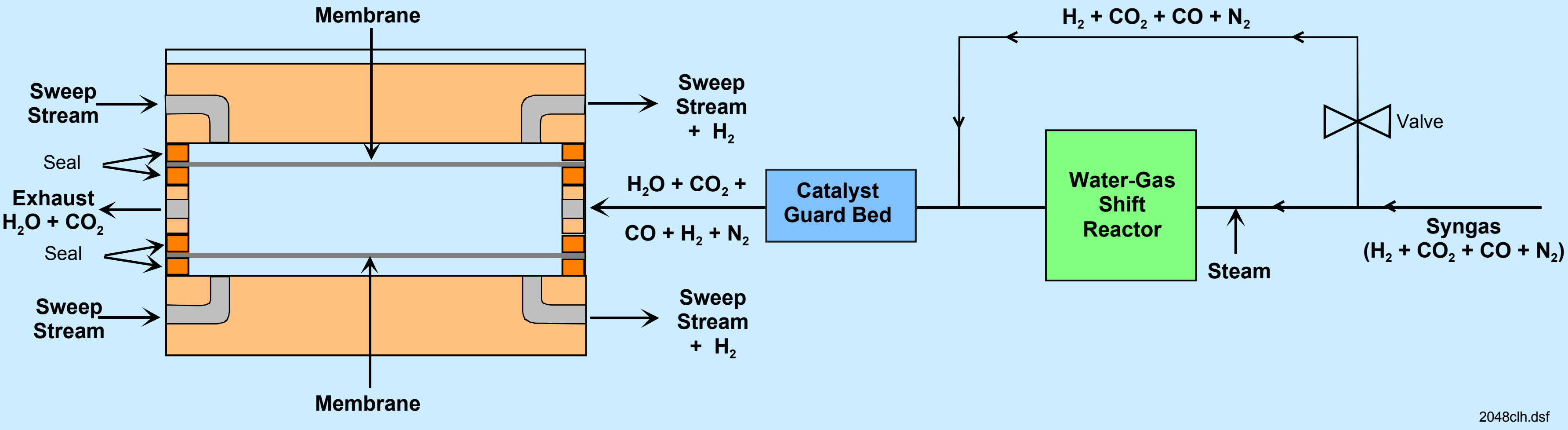
Performance of a 250-Micron Hydrogen Transport Membrane up to 1000 psi Pressure Differential at 420°C



Membrane Performance under Pressure (300 psig); 40% Hydrogen; No Sweep Gas. Hydrogen Pressure on Permeate Side 15 psia.



Cross-Sectional Schematic of Stacked Hydrogen Separation Membrane Unit



Membrane

Sweep Stream

Seal

Exhaust $H_2O + CO_2$

Seal

Sweep Stream

Membrane

Sweep Stream + H_2

Sweep Stream + H_2

$H_2O + CO_2 + CO + H_2 + N_2$

Catalyst Guard Bed

$H_2 + CO_2 + CO + N_2$

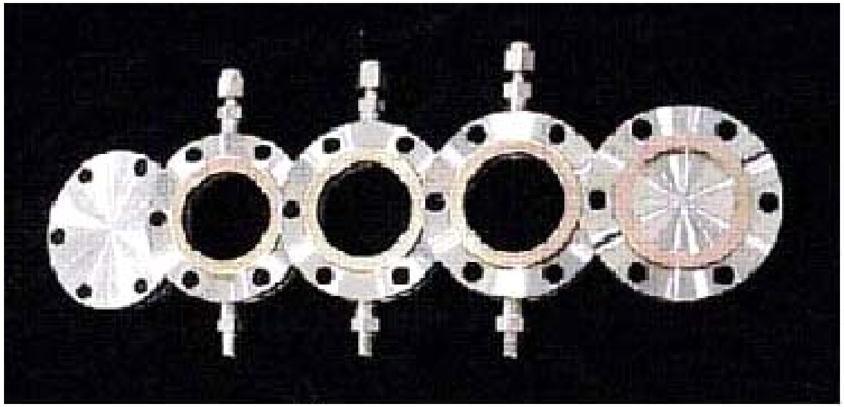
Valve

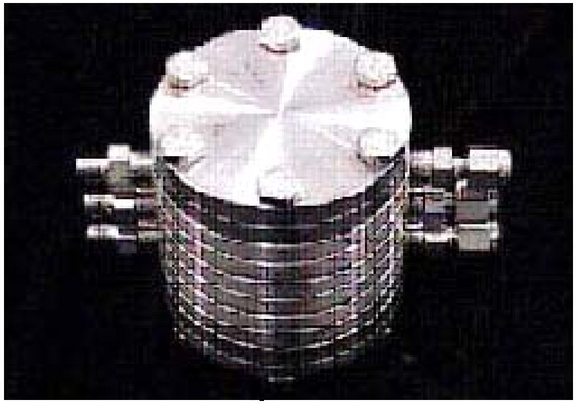
Water-Gas Shift Reactor

Steam

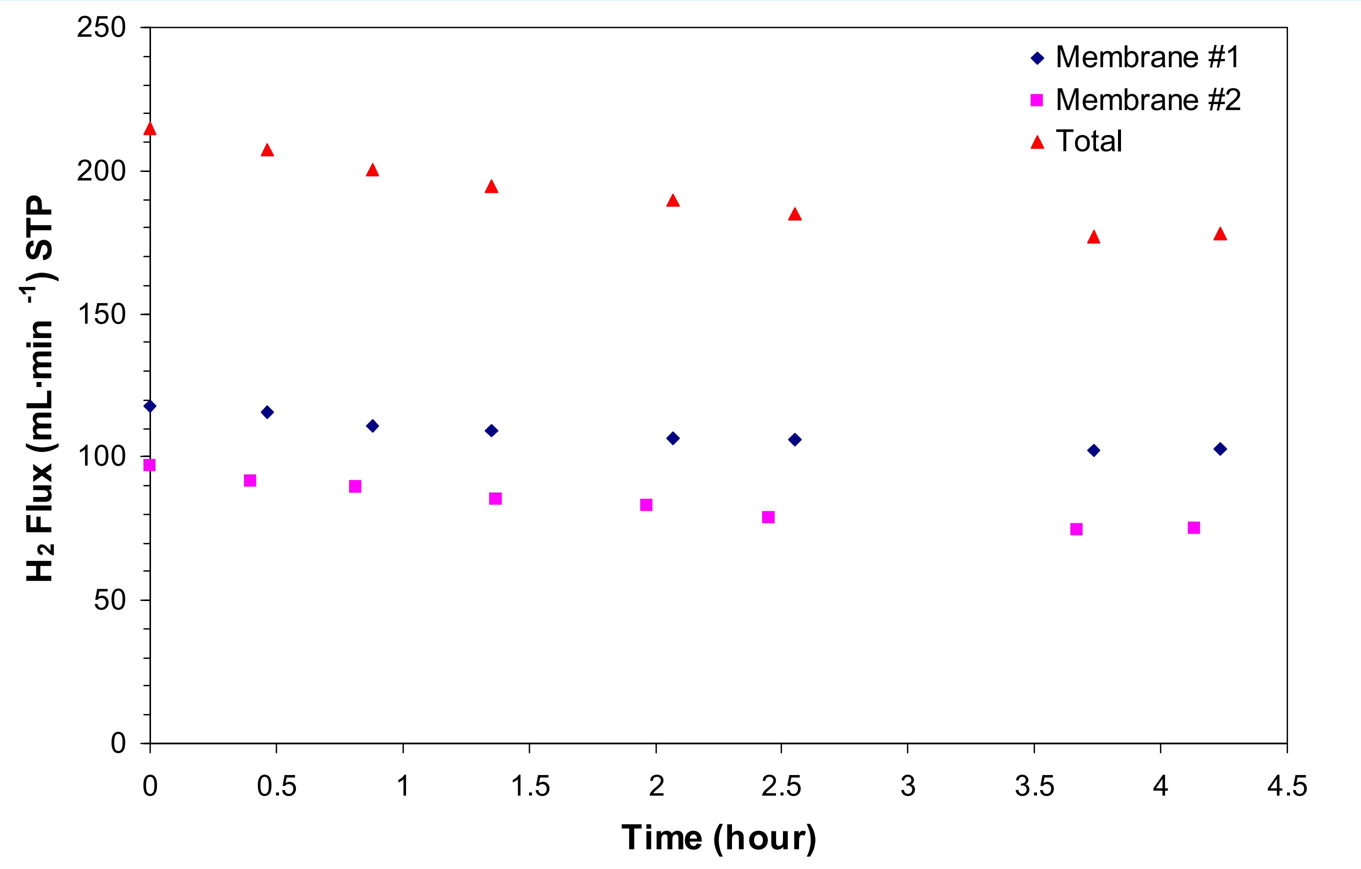
Syngas ($H_2 + CO_2 + CO + N_2$)

2048clh.dsf





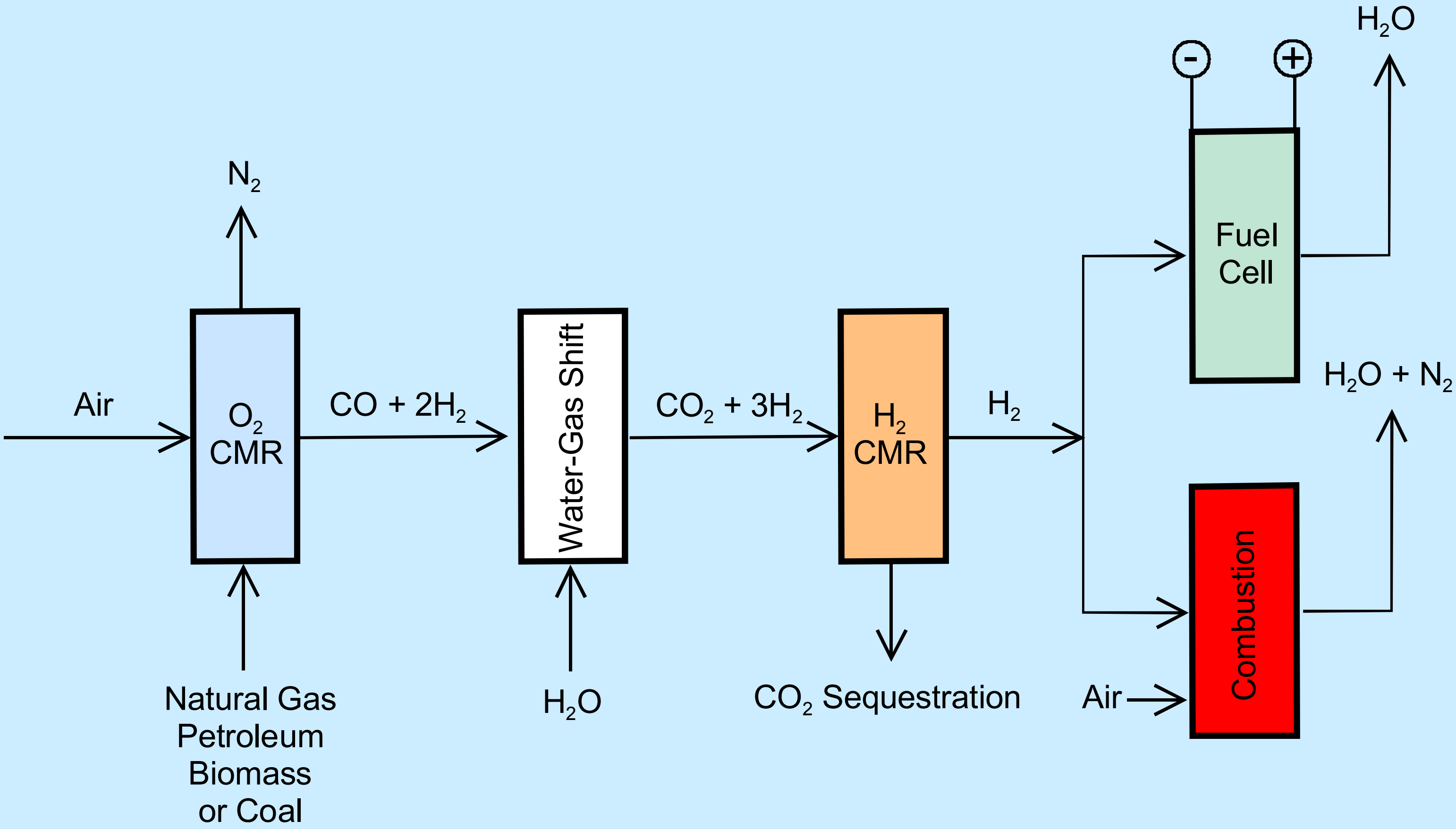
Performance of Two Membrane Stack at Ambient Pressure



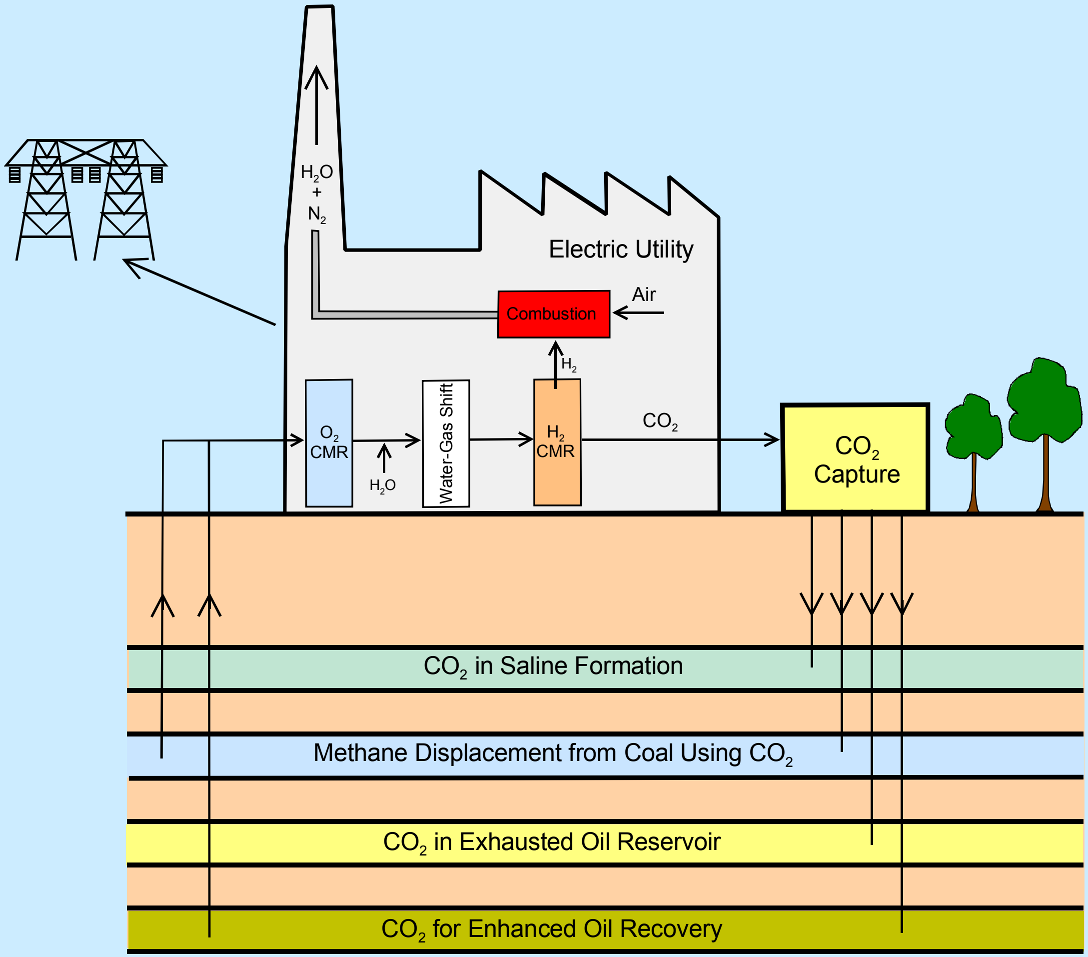
Relative Costs of H_2 Production Using Membrane Technologies

- H2 separation membranes could reduce purification cost by ~30% relative to Pressure Swing Absorption (PSA). (S. Lasher et al., Hydrogen Technical Analysis, *Proc. 2002 DOE Hydrogen Program Review*)
- Eltron H2 separation membranes are ~200 times cheaper than analogous Pd membranes and permeate 10x faster.
- Estimated H2 cost using combined oxygen and hydrogen transport membrane technologies is $4/MMBtu or $0.55/kg. (Hydrogen Production Facilities: Plant Performance and Cost Comparison, Final Report for Contract No. DE-AM26-99FT40465, Parsons)

Membranes for Hydrogen Supply



Concept for Emission-Free Electric Utility



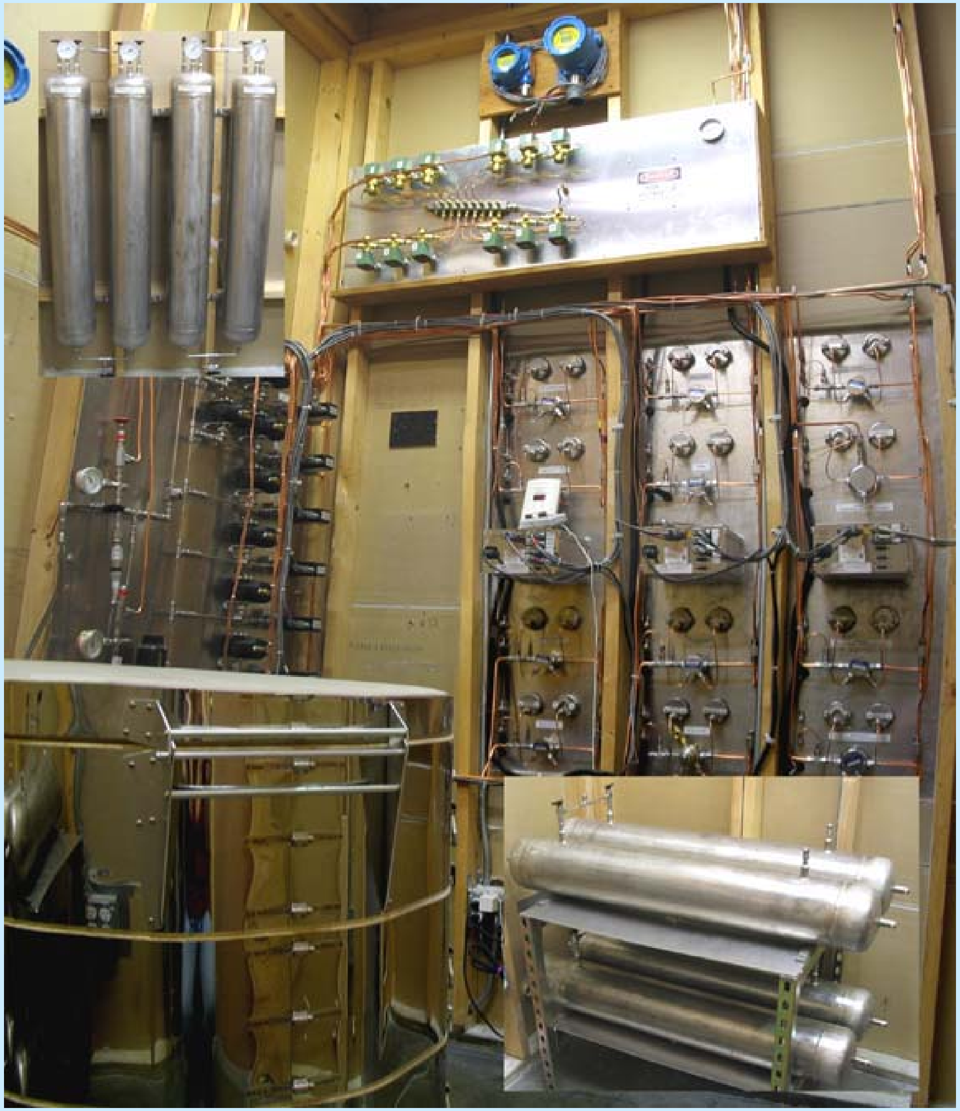
Future Work

- Remainder of FY 2005
  - Complete build and performance verification of 1.3 lb/day membrane separation unit
- FY 2006
  - Build and test 5 lb/day PDU
  - Integrate with coal gasifier slip stream

Participants:

Eltron Research Inc.
CoorsTek
Emery Energy
Noram Engineering and Constructors
Praxair

Hardware for Performance Testing of 1.3 lb/day Hydrogen Separation Unit



Acknowledgements

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Publications and Presentations

• *Hydrogen and Oxygen Transport Membranes for Spontaneous Conversion of Coal to Hydrogen*	29th International Conference on Coal Utilization and Fuel Systems, Clearwater, FL, April 2004	A.F. Sammells M.V. Mundschau S.E. Roark T.F. Barton
• *Simultaneous Hydrocarbon Reforming, Carbon Dioxide Sequestration and Hydrogen Separation Using Dense Inorganic Membranes*	Annual Carbon Capture and Sequestration Conference, Alexandria, VA, May 2004	M.V. Mundschau X. Xie C.R. Evenson A.F. Sammells
• *Oxygen and Hydrogen Transport Membranes for Combined Hydrocarbon Reforming and Hydrogen Separation*	8th International Conference on Inorganic Membranes, Cincinnati, OH, July 2004	A.F. Sammells M.V. Mundschau X. Xie

Publications and Presentations (cont.)

Dense Membranes for Separation of H_2 from CO_2 in High-Pressure Water-Gas Shift Reactors	7th International Conference on Greenhouse Gas Control Technology, Vancouver, BC, Sept. 2004	M.V. Mundschau X. Xie A.F. Sammells
Advanced Membranes for the Spontaneous Conversion of Coal to Hydrogen	21st Annual International Pittsburgh Coal Conference, Osaka, Japan, Sept. 2004	A.F. Sammells M.V. Mundschau X. Xie C.R. Evenson
Advances in Hydrogen Separation Membrane Technology for the Separation of CO_2 and the Purification of Hydrogen Produced from Coal	30th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, April 2005	M.V. Mundschau X. Xie A.F. Sammells

Hydrogen Safety

The most significant hydrogen hazards associated with this project are:

- Carbon monoxide poisoning
- Hydrogen leakage
- Hydrogen feed explosion

Hydrogen Safety

Our approach to dealing with these hazards is:

- Continuous monitoring for reducing gases
- Operation of hydrogen separation units in contained, well-ventilated conditions
- Hydrogen membrane hardware has incorporated rupture disks vented to the outside