

ADVANCED HYDROGEN TRANSPORT MEMBRANES FOR VISION 21 FOSSIL FUEL PLANTS

Presented by
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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

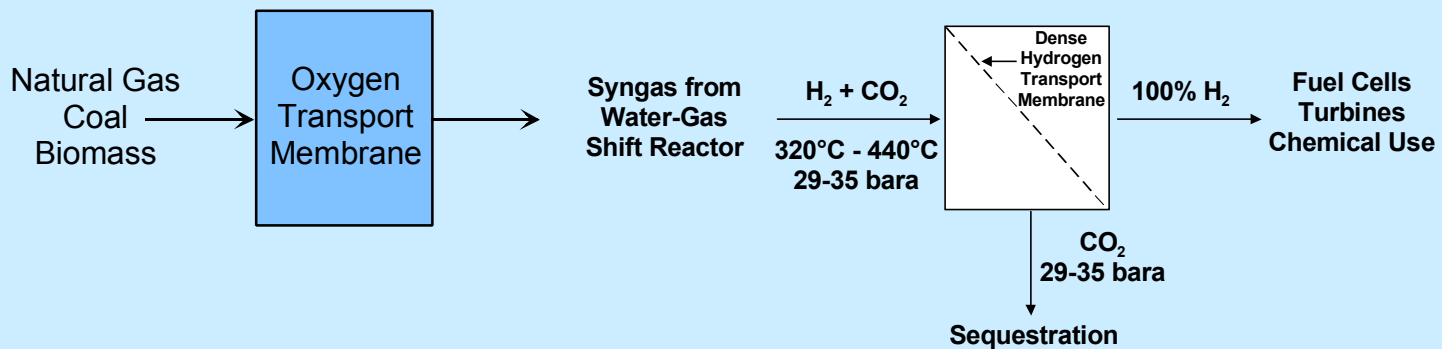
Partners

- CoorsTek
- Súd Chemie
- Noram Engineering
- ANL

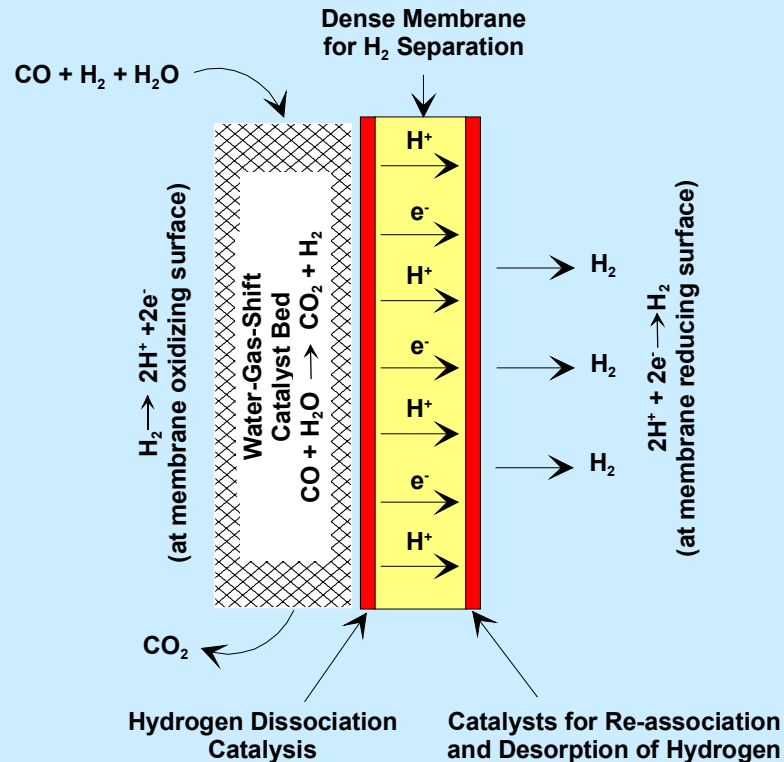
Objectives

- 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



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



Eltron H₂ Separation Membrane Characteristics

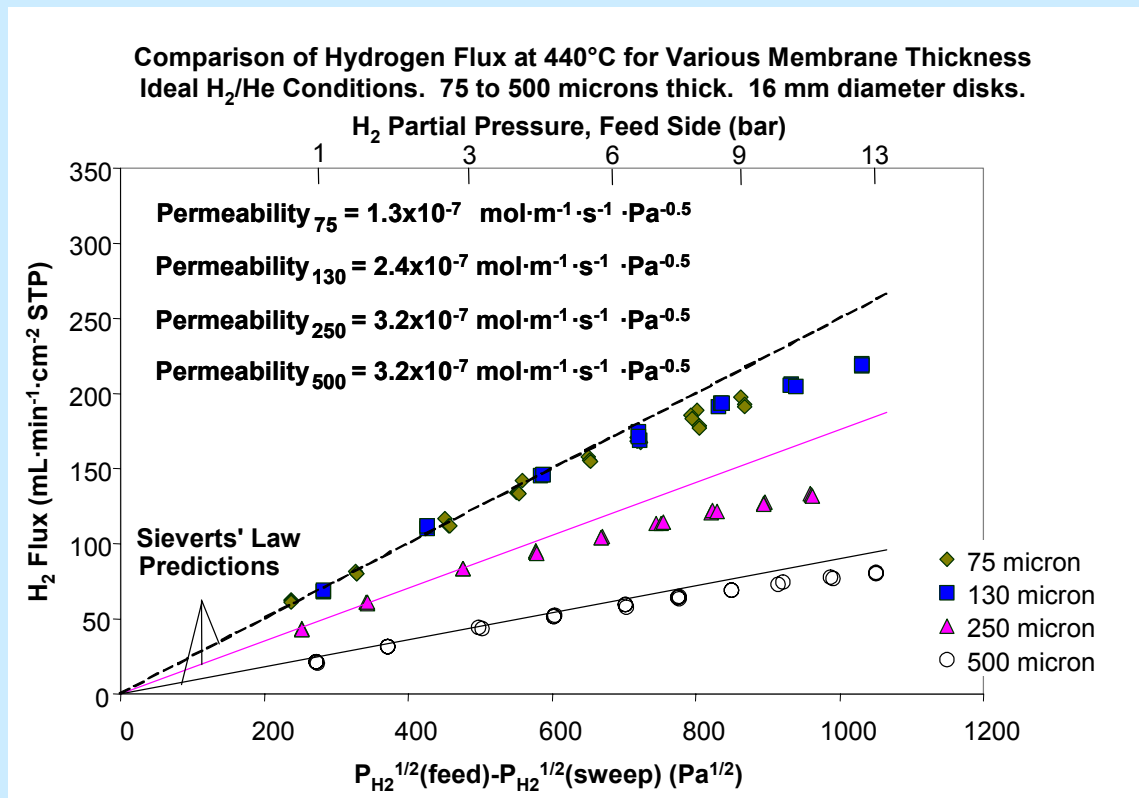
Membrane Category	Temperature Range (°C)	Maximum Permeation Rate (mL·min ⁻¹ ·cm ⁻²)
Single Phase Ceramic	700 to 950	≈ 0.01
Ceramic/Ceramic	700 to 950	≈ 0.1
High-Temperature Cermet With Non H₂-Permeable Metal (Ni)	700 to 950	≈ 1
High-Temperature Cermet with H₂-Permeable Metal (Pd)	400 to 800	≈ 4
Thin Film Palladium on Porous Support	320 to 600	>50
Intermediate-Temperature Composite	320 to 440	>400

High-Pressure Differential Hydrogen Separation Units



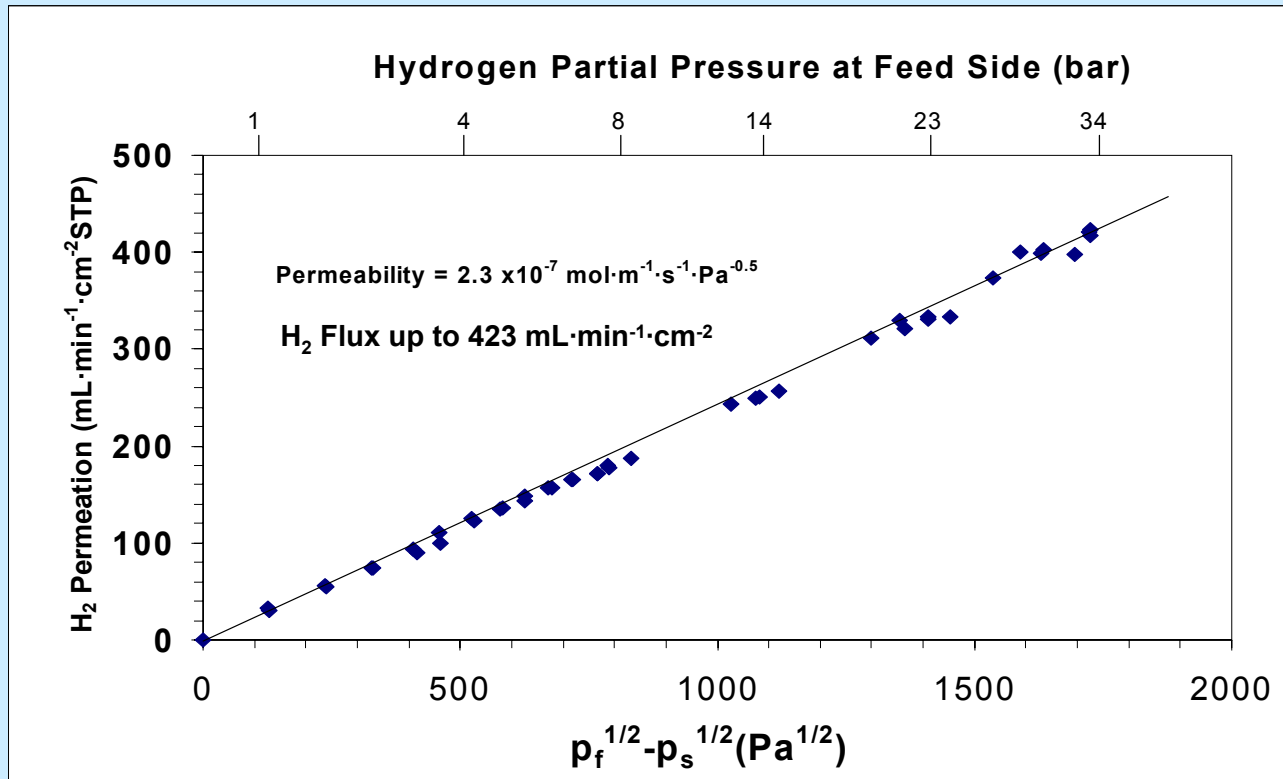
- Tests to 69 bar (1000 psi) differential pressure at 320-440°C
- Tests with high pressure WGS mixture

Pressure Differential Hydrogen Flux Measurements under Ideal 40% H₂/He Conditions as a Function of Membrane Thickness



- 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

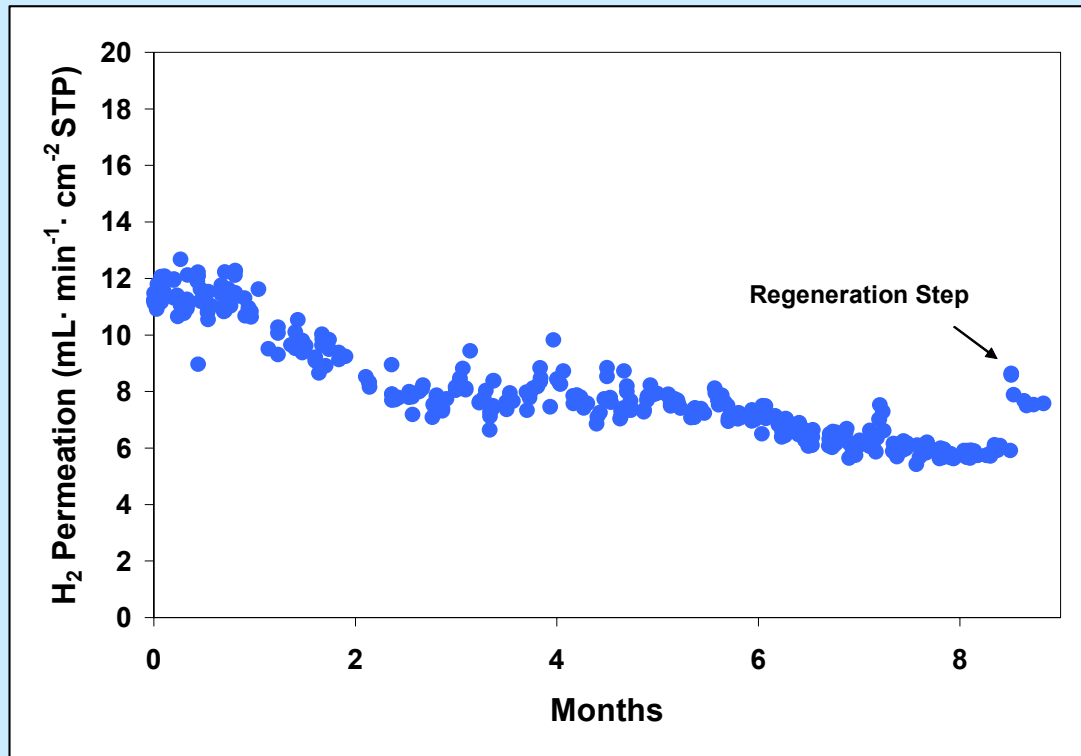


- Permeability of $2.3 \times 10^{-7} \text{ mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ and hydrogen flux of $423 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ (STP) achieved at 440°C (713K) under ideal hydrogen-helium mixture up to 33 bar (476 psi) differential pressure and partial pressure of hydrogen of 34 bar (488 psi).

Long-Term Ambient Pressure Performance

Performance of Hydrogen Transport Membrane

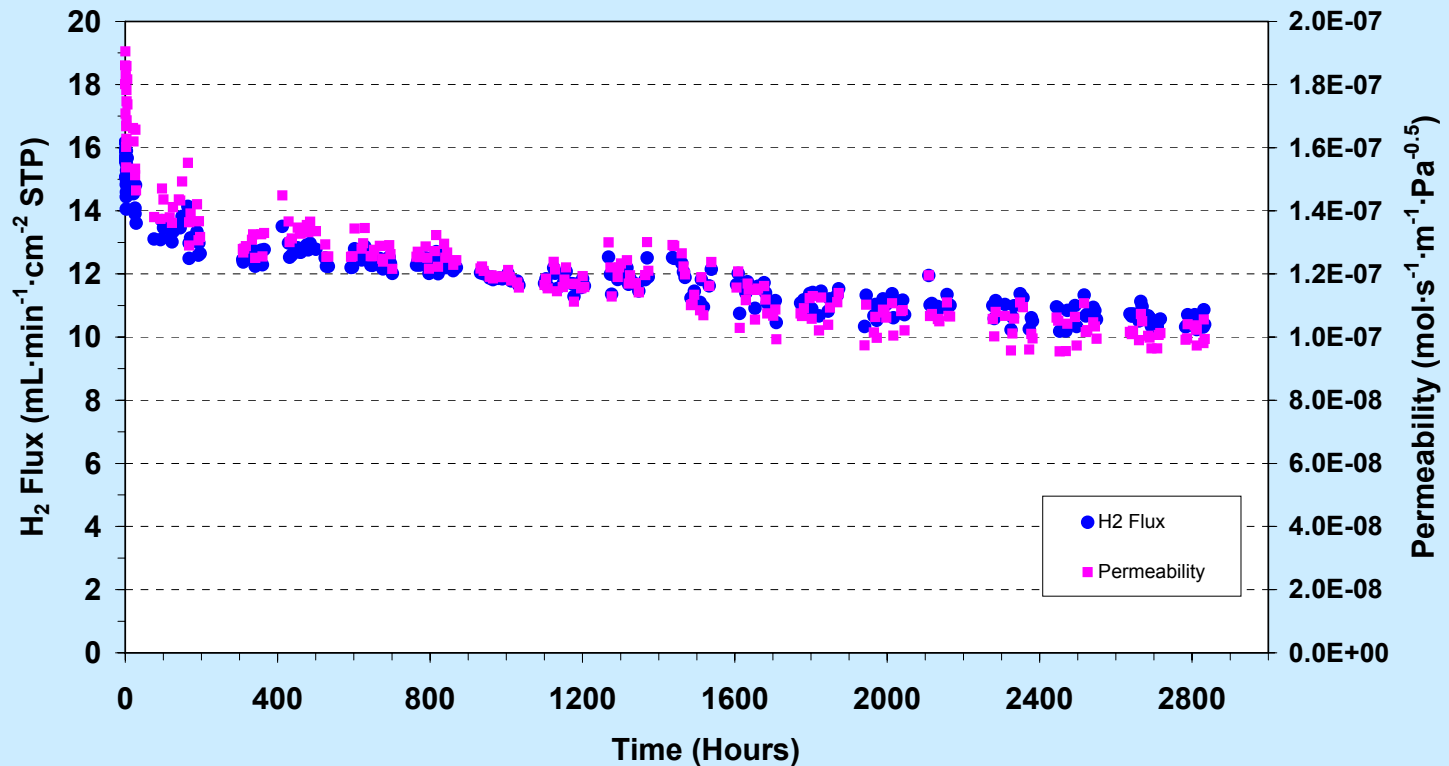
(80% H₂ / 20% He Feed at 320°C)



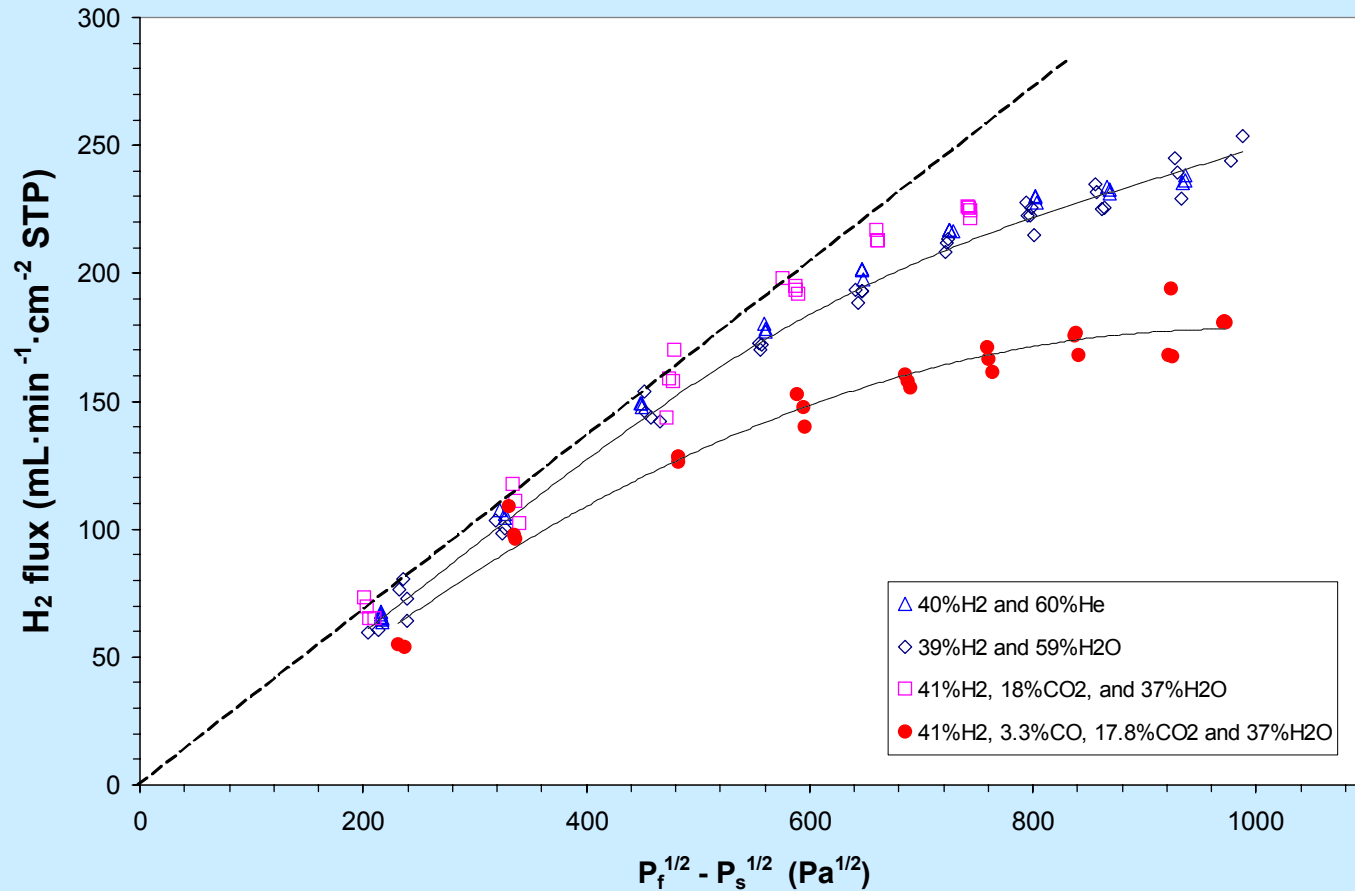
- No guard bed used to adsorb impurities.

Long-Term Results

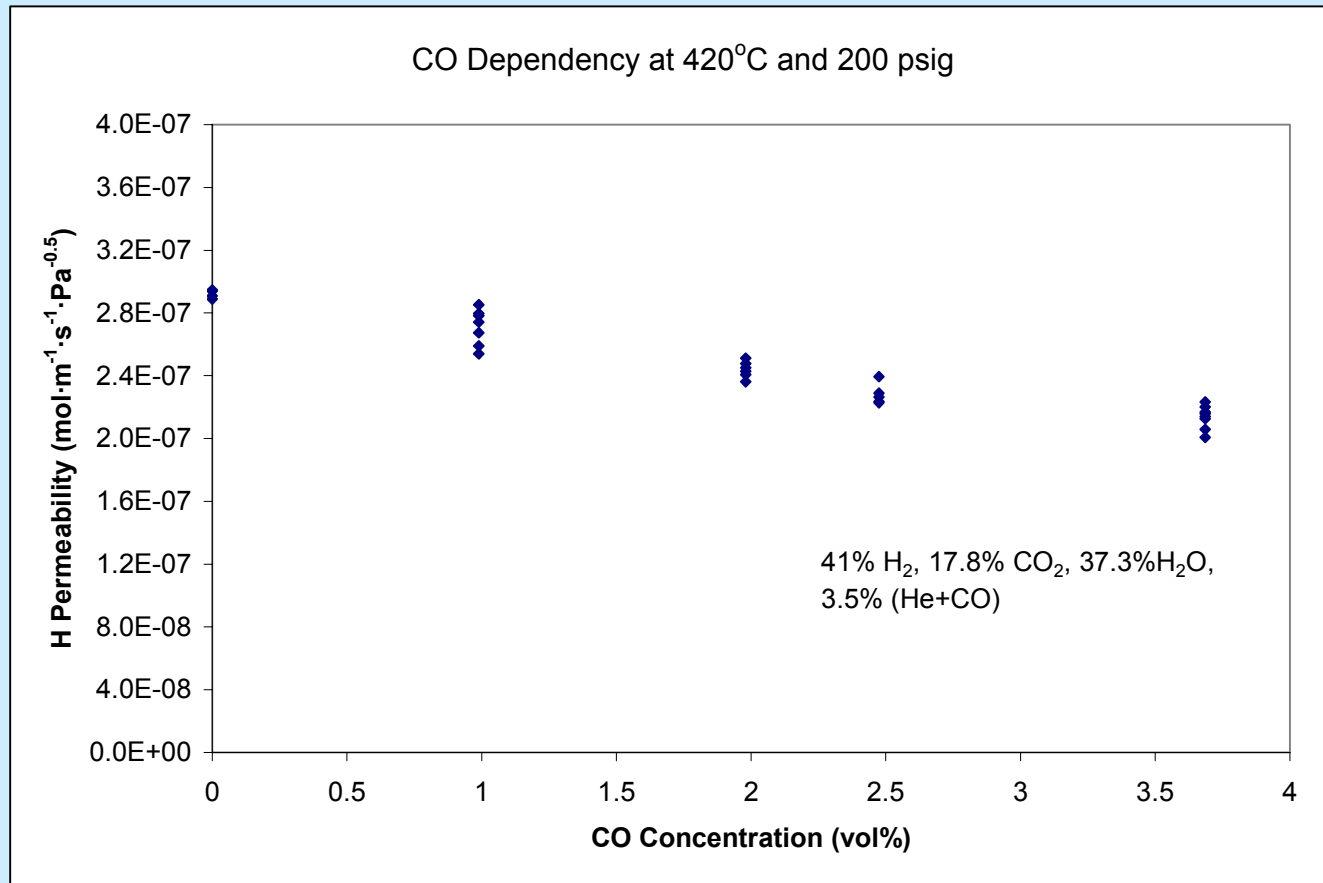
Long-term test @ 340 °C with a feed containing 41.4% H_2 , 37.3% H_2O , 3.3% CO and 17.8% CO_2 and a Cu/ZnO guard bed



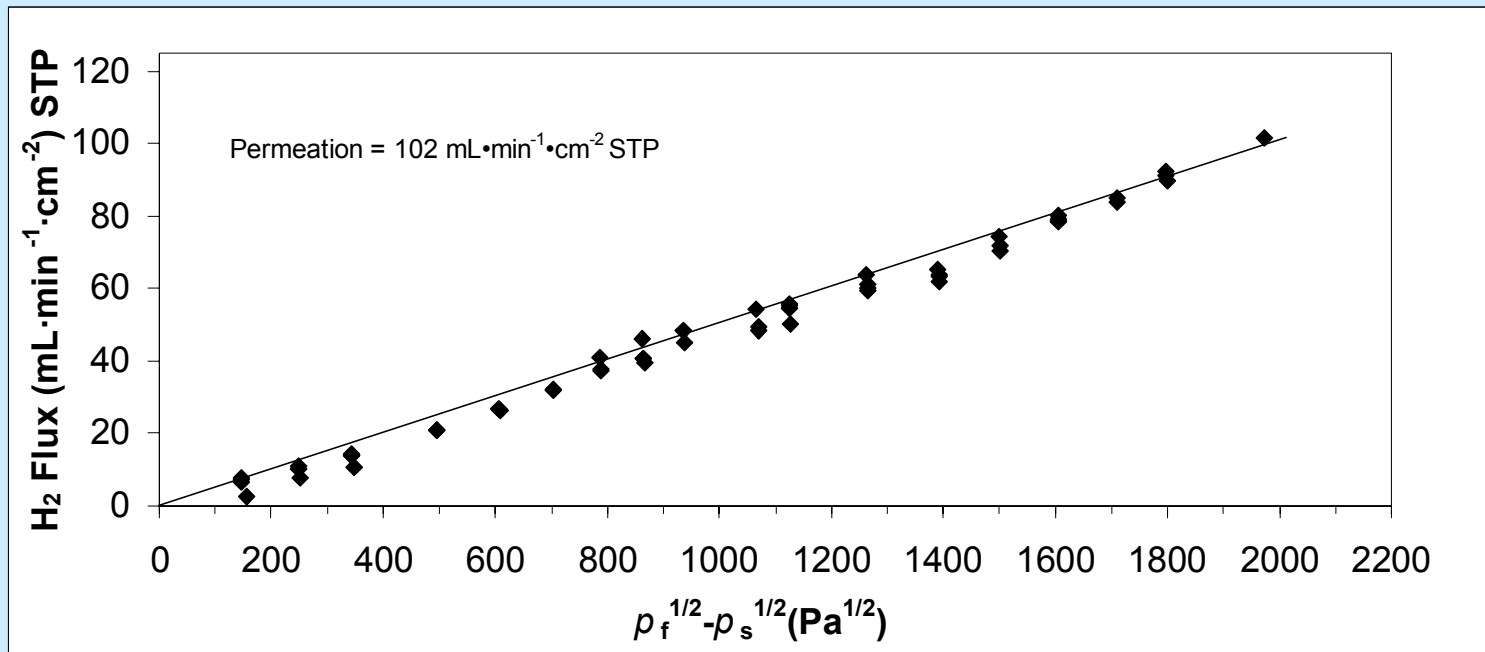
Membrane Performance upon Going from Ideal to Syngas Conditions



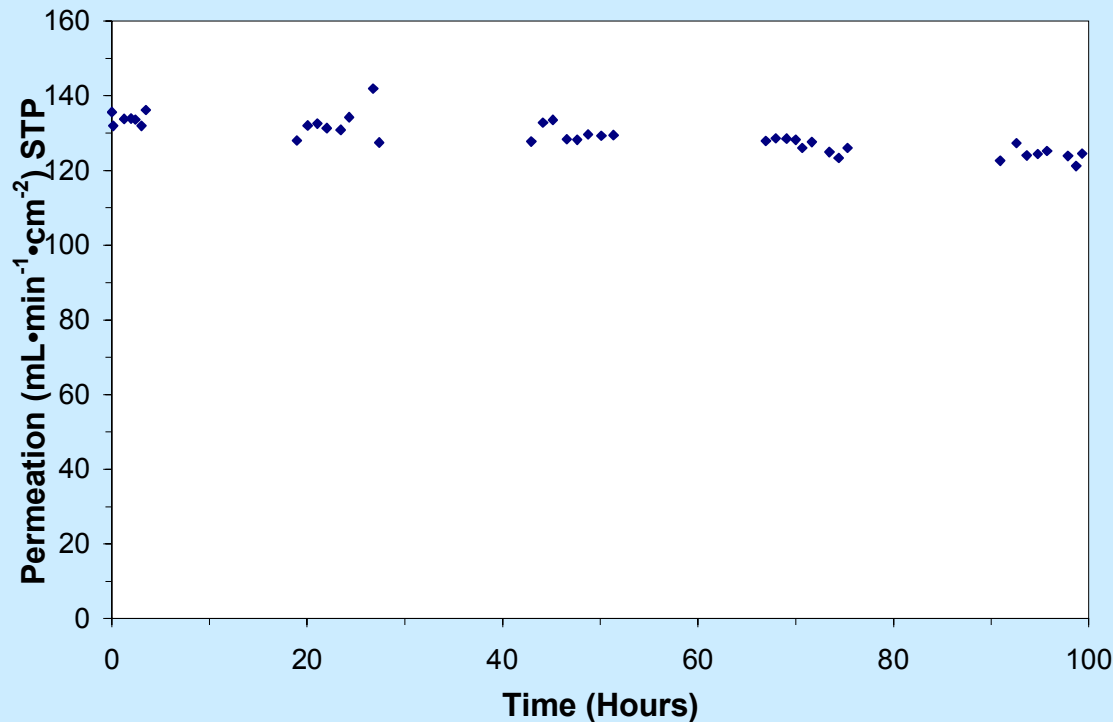
Dependency of Membrane Performance on Carbon Monoxide Fraction



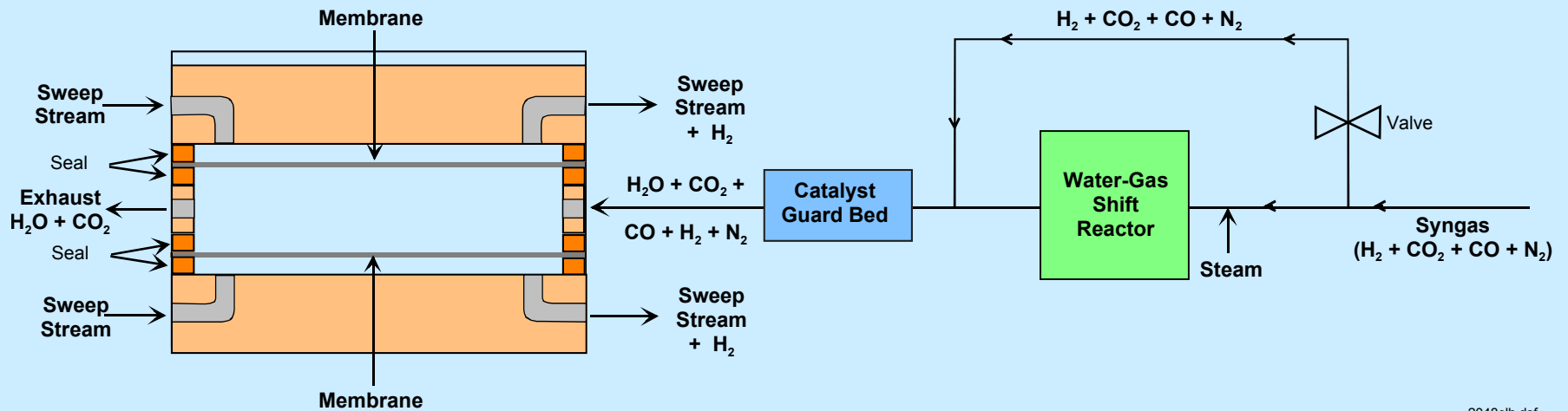
Performance of a 250-Micron Hydrogen Transport Membrane up to 1000 psi Pressure Differential at 420°C



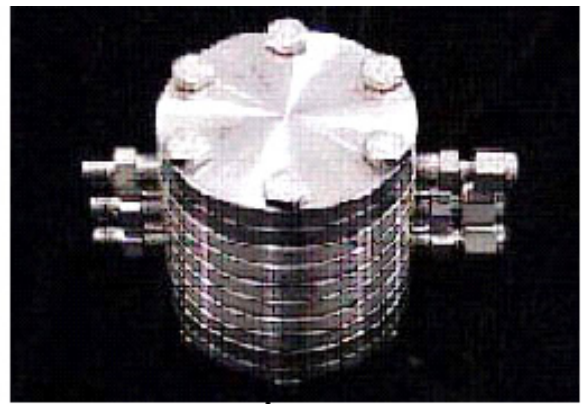
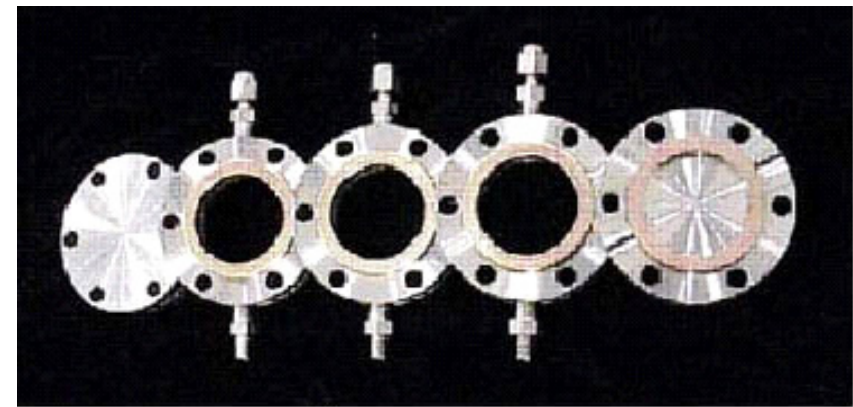
Membrane Performance under Pressure (300 psig); 40% Hydrogen; No Sweep Gas. Hydrogen Pressure on Permeate Side 15 psia.



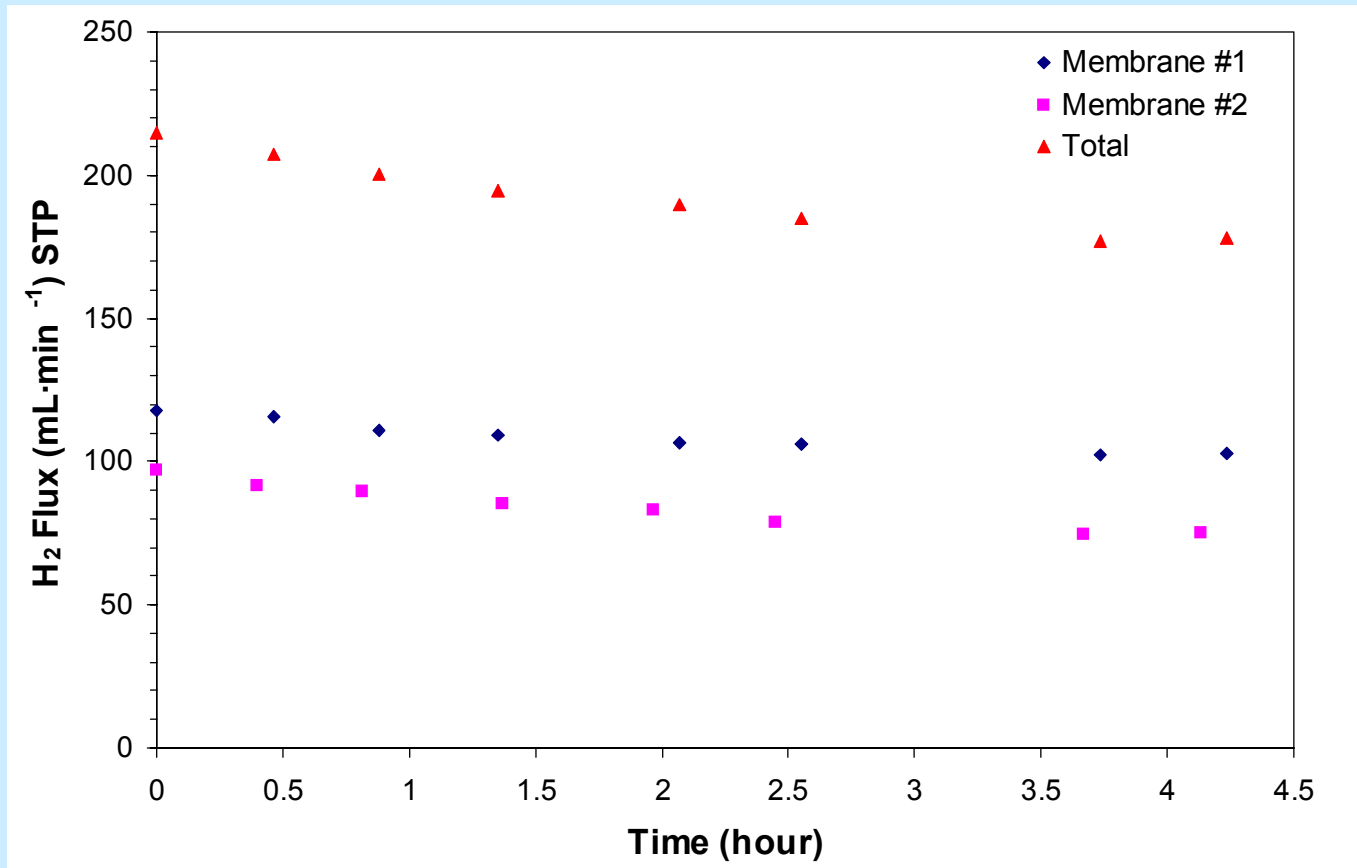
Cross-Sectional Schematic of Stacked Hydrogen Separation Membrane Unit



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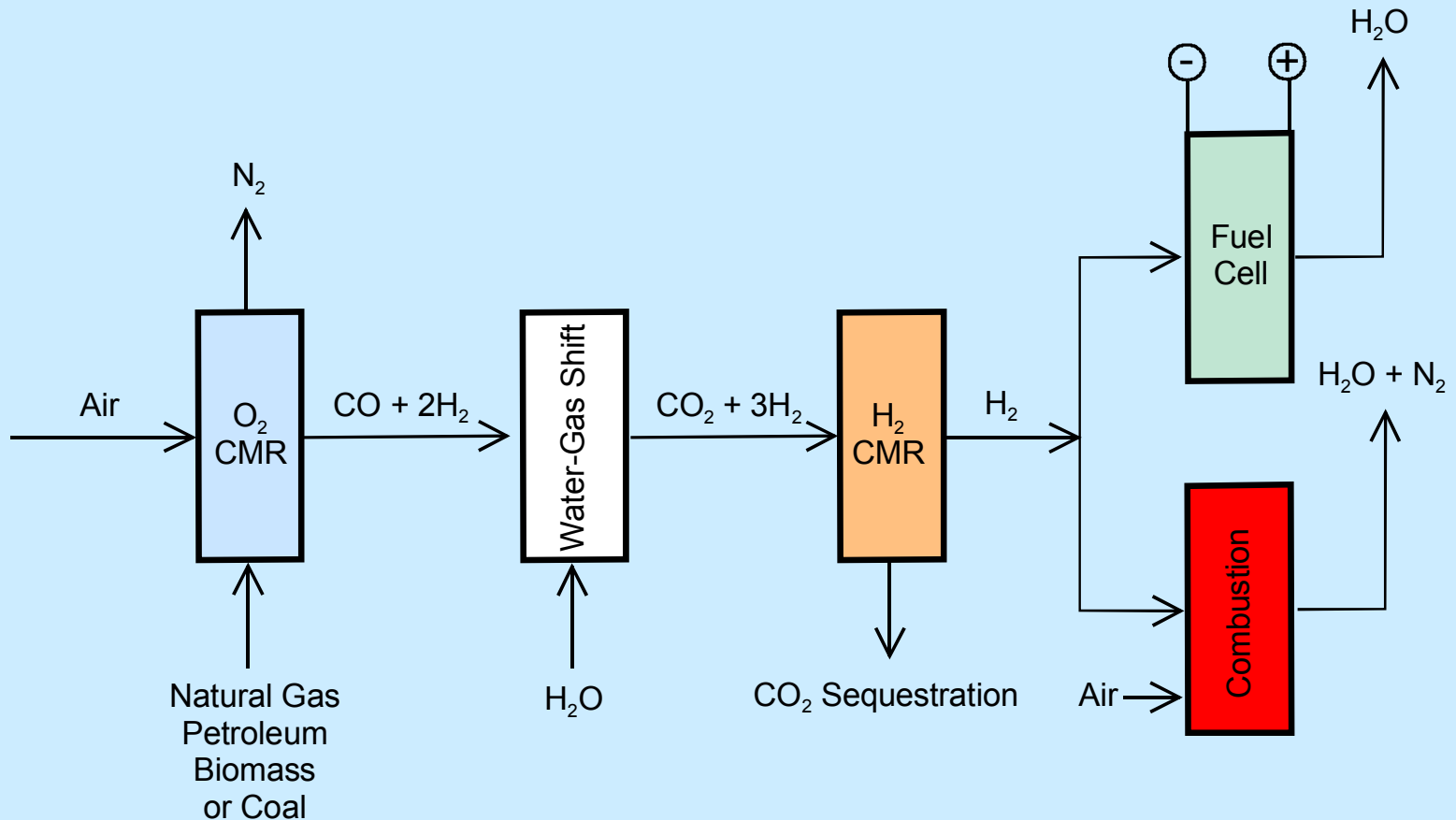
Performance of Two Membrane Stack at Ambient Pressure



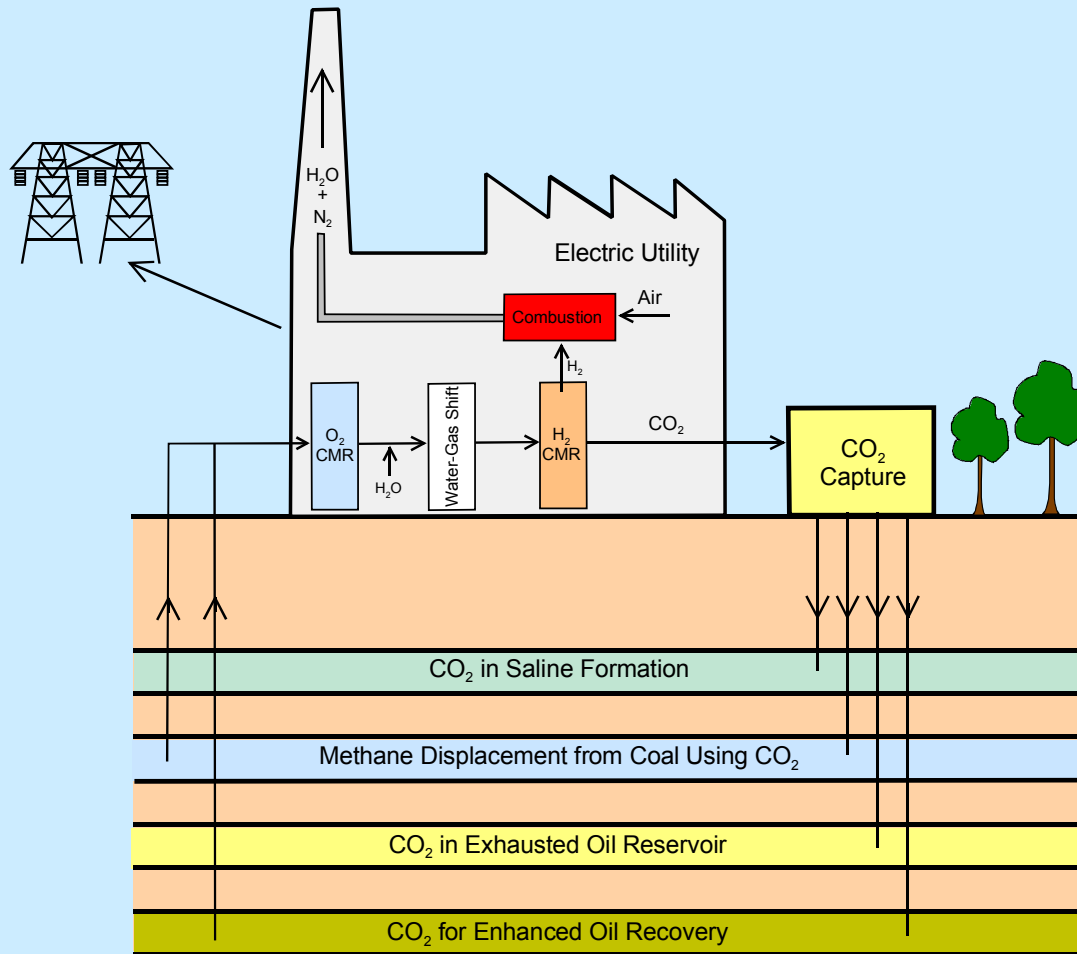
Relative Costs of H₂ Production Using Membrane Technologies

- 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

- DOE Vision 21 Contract
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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 H₂ from CO₂ 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 CO₂ 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