

# Scale-up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

Presented by

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# Overview

## Timeline

- Project start date: 1 Oct 2005
- Project end date: 30 Sep 2010
- 5% percent complete

## Budget (\$000)

- Total project funding: \$15,300
  - ✓ DOE share: \$12,240
  - ✓ Contractor share: \$ 3,060
- Funding received in FY05:\$ 0
- Funding for FY06: \$ 966

## Barriers Addressed

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

## Technical Targets

- Low-cost H<sub>2</sub> production system to produce CO<sub>2</sub> and H<sub>2</sub> from coal-derived synthesis gas
- Demonstrate in 220 lb H<sub>2</sub> /day unit
- Design for 4 ton/day unit
- Tolerant to syn gas contaminants

## Partners

- NORAM Engineering
- CoorsTek
- Praxair

**DOE Contract DE-FC26-05NT42469**

# Objectives

- Continue Vision 21 project for high-throughput, low-cost H<sub>2</sub> separation system: scale-up and improve tolerance to contaminants (S, Hg, etc.)
- Determine optimum mechanical configuration (tube vs. plate; metal vs. cermet) based on manufacturability, cost & performance of membrane and system
- Scale up membrane & system from 0.45 lb/day of H<sub>2</sub> using lab gases to 220 lb/day in coal-derived syn gas
- Integrate membrane design into a 4 ton/day H<sub>2</sub> production unit
- Determine optimum process design & cost and compare vs. other systems

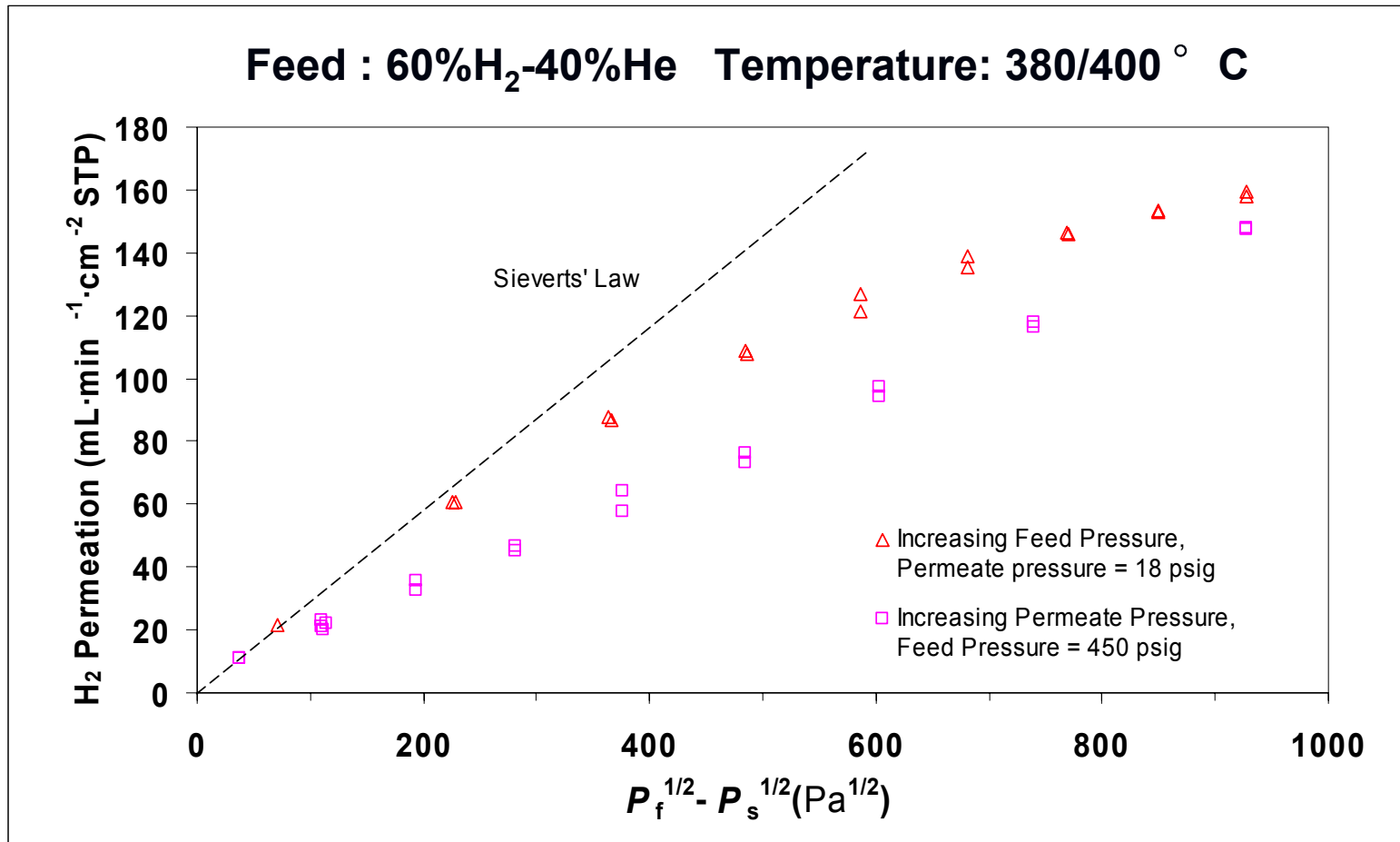
# Advances in Past Year

- Process Design and Cost Estimating
- 1,000 psi  $\Delta P$  across membrane
- Elimination of sweep gas
- Outlet Pressure up to 270 psi
- Initial testing of Sulfur tolerance to 200 ppm
- Excellent results of integrating Water-Gas Shift into membrane reactor (separately funded SBIR project)

# Current Performance Results

- 99.999%+ H<sub>2</sub> selectivity consistently
- Demonstrated 1,000 psi  $\Delta P$
- Demonstrated 270 psi permeate pressure (limited by experimental setup)
- 11 months continuous operation in a simulated synthesis gas stream containing H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O (steam)
- Eltron H<sub>2</sub> flux = 423 ml/min-cm<sup>2</sup> (Pd = 15, Pd-Cu alloy = 8)
- Flux rates validated by DOE NETL

# Recent Flux Data

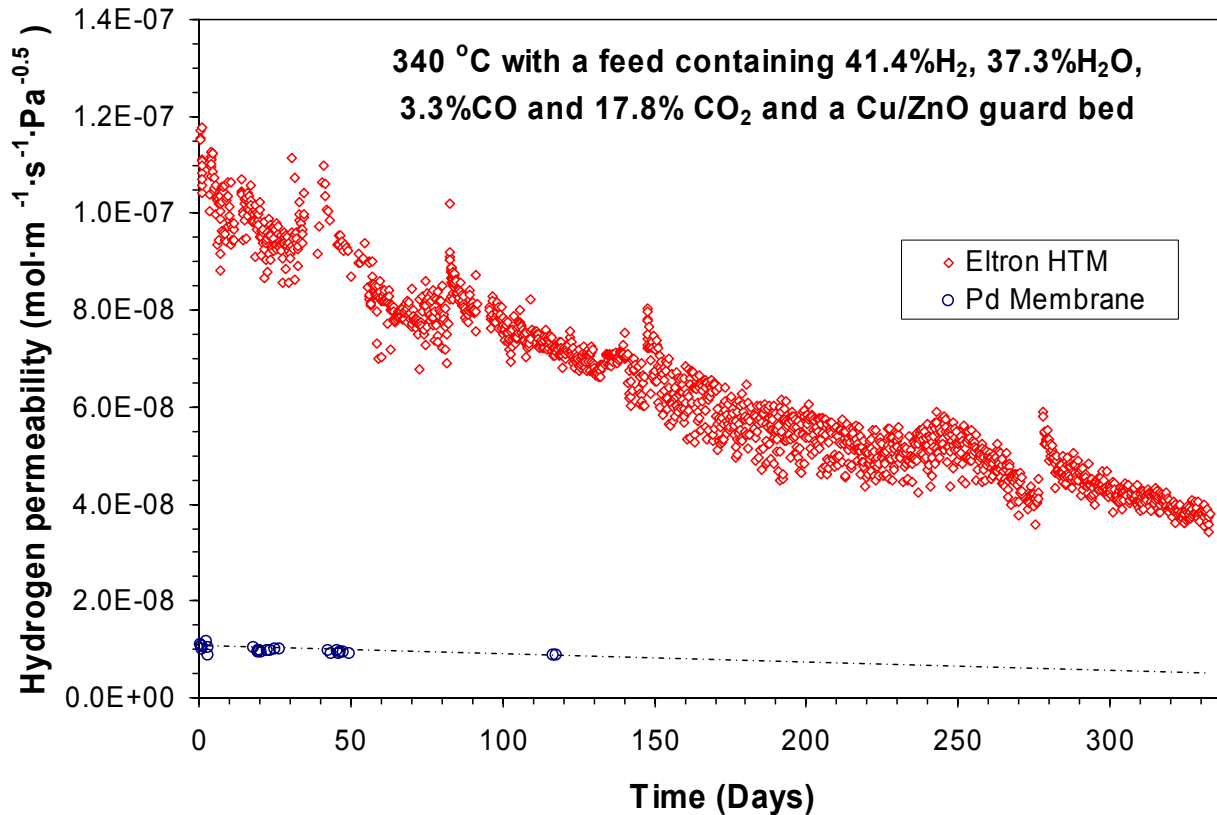


**Outlet pressure ranged from 0 – 275 psig**

**Sieverts' Law deviation – gas phase diffusion limited (reactor configuration)**

**not membrane limited**

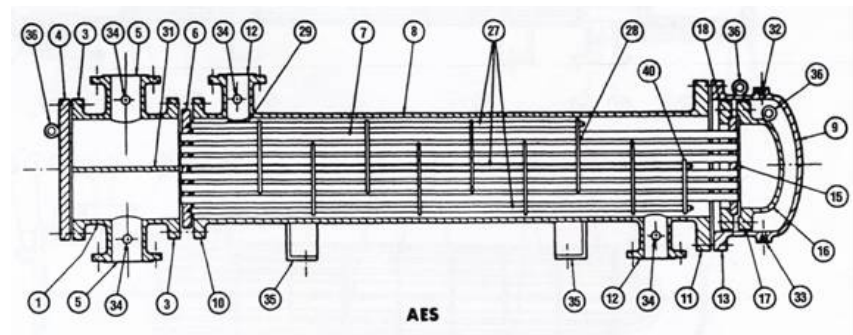
# Membrane Long-Term Stability under WGS Conditions



- One of few known membrane studies that was conducted for 11 months under a simulated WGS conditions.
- Still about five times better than Pd membrane after one year operation.

# Vision 21 Process Modeling Results (NORAM)

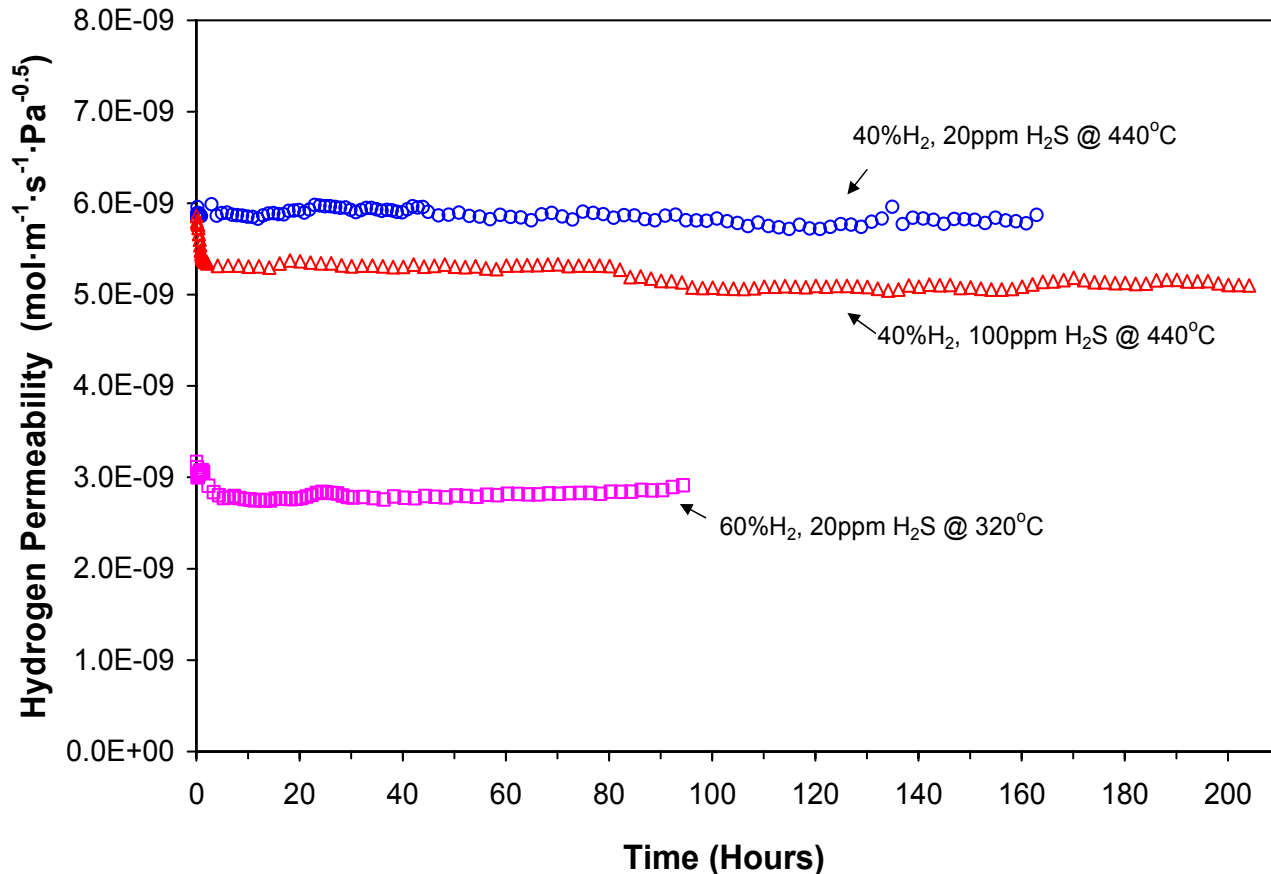
- 35 TPD H<sub>2</sub> Separator Unit
  - ✓ Tubular Heat Exchanger Type Geometry
  - ✓ \$21K Capital / TPD H<sub>2</sub>
- x8 = 265 TPD H<sub>2</sub> FutureGen
- Total Incremental System Cost ~ \$23 M
  - ✓ Includes membrane cost, separator assembly / installation, gas cleaning, H<sub>2</sub> cooling
- For Comparison
  - ✓ PSA ~ \$41M



Source: ASME VIII, Div. 1, Section UHX



# Sulfur Tolerance of an Alloy Catalyst



- Several alloy catalysts display a good stability with a 40% H<sub>2</sub> stream containing 20 ppmv of H<sub>2</sub>S.
- Emerging warm-gas cleaning technology can clean sulfur impurity below 2 ppmv.

# Progress Towards DOE FutureGen Targets

<i>Performance Criteria</i>	<i>2005 Target</i>	<i>2010 Target</i>	<i>2015 Target</i>	<i>Current Eltron Membrane</i>
Flux (sccm/cm <sup>2</sup> /100 psi ΔP)	50	100	150	<b>160</b>
Operating Temperature (°C)	400-700	300-600	250-500	300-400
S Tolerance (ppmv)	N/A	2	20	<b>20 (early)</b>
System Cost (\$/ft <sup>2</sup> )	1000	500	<250	<b>&lt;200</b>
ΔP Operating Capability (psi)	100	400	800-1000	<b>1,000</b>
Carbon Monoxide Tolerance	Yes	Yes	Yes	<b>Yes</b>
Hydrogen Purity (%)	95	99.5	99.99	<b>&gt;99.999</b>
Stability/Durability (years)	1	3	>5	0.9
Permeate Pressure (psi)	N/A	N/A	N/A	<b>270</b>

# Simplified Project Schedule

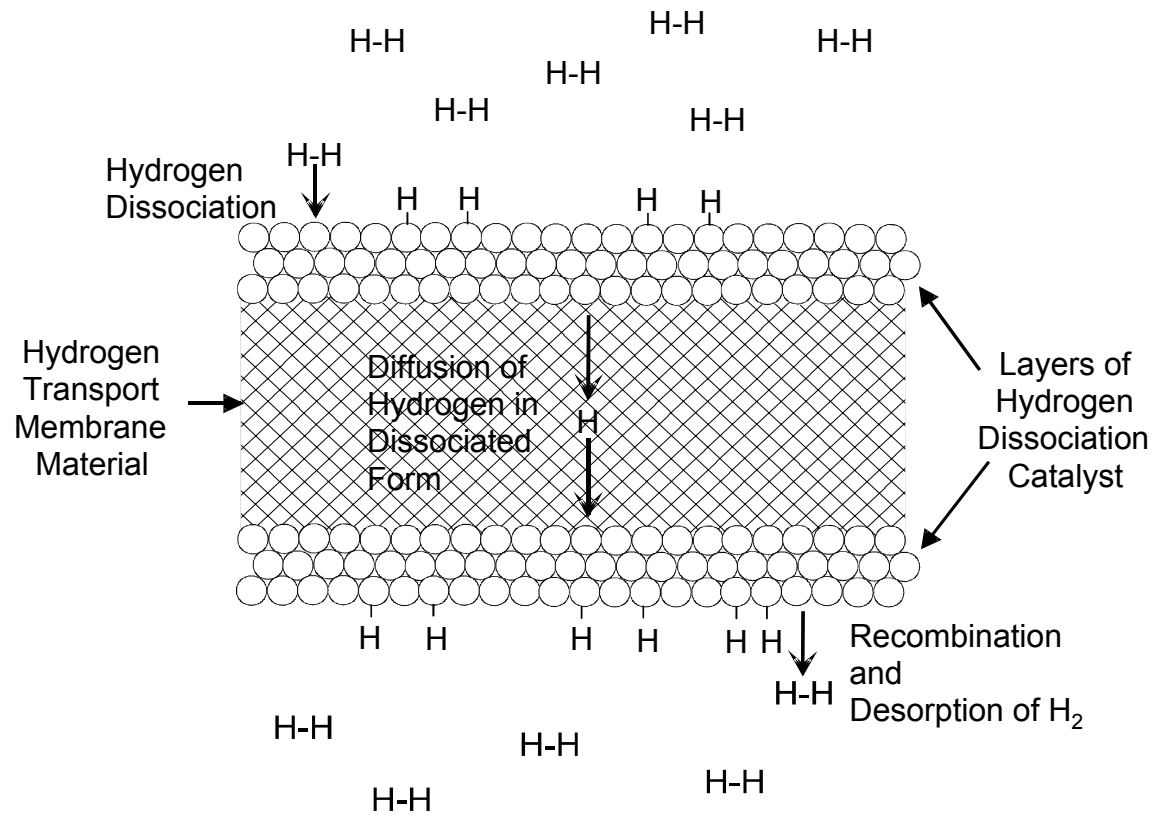
**Scale Up Hydrogen Transport Membranes for IGCC and FutureGen Coal to Hydrogen Production Plants**

	FY2006				FY2007				FY2008				FY2009				FY2010			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Design/Build 1.3 lb/day H2 Sep Unit	█	█	█	█	█	█	█													
Improved Membrane Components	█	█	█	█	█	█	█													
Develop Methods of Low-Cost Membrane Manufacturing			█	█	█	█	█	█	█	█	█	█	█	█	█	█	█			
Process Economic Analysis	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█
Develop & Test & Optimize Impurity Management System	█	█	█	█	█	█	█	█	█	█	█									
Design / Build / Test 5.5 lb/day PDU							█	█	█	█	█									
Design / Build / Test 220 lb/day Subscale Engineering Prototype											█	█	█	█	█	█	█			
Design 4 tpd Field Demonstration Unit																		█	█	

DOE Contract #DE-FC26-05NT42469



# Hydrogen Transport Across Eltron's Membrane



# Sputtering System for Membrane Catalyst Deposition



# Material Focus – FY06

- Top/Bottom Catalyst Layer
  - ✓ Increased sulfur tolerance (alloys) [top layer]
  - ✓ Optimal application to bulk membrane (CVD, Electroplating, Electroless, Sputtering)
  - ✓ Tubular vs. Plate
- Bulk Membrane
  - ✓ Diffusional barriers with top/bottom layers
  - ✓ Cost reduction (cermets) [with CoorsTek]

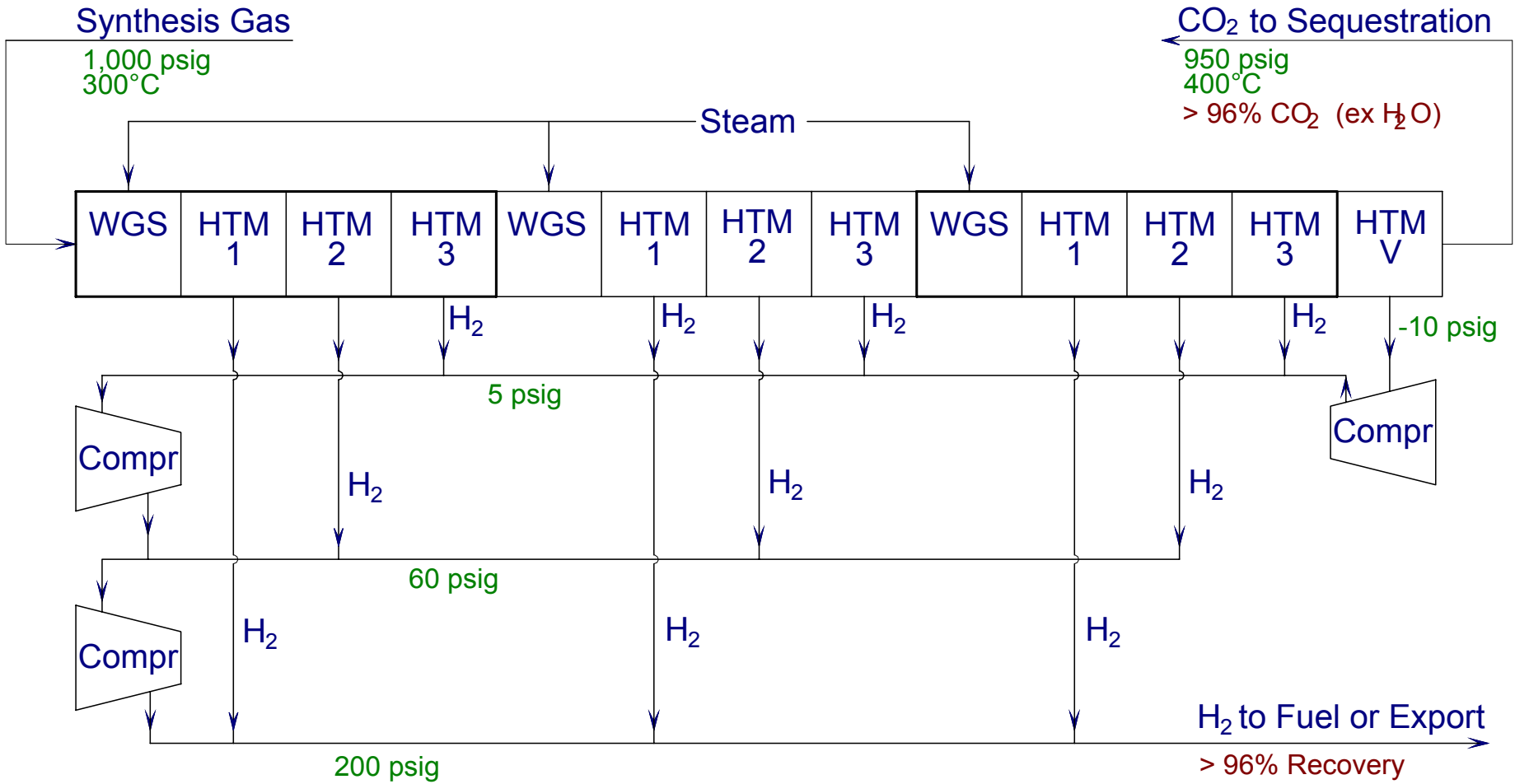
# Process Design Focus – FY06

- Eltron System
  - ✓ Staged WGS/HTM optimum balance
    - ❖ Number of stages
    - ❖ Permeate pressure per stage
    - ❖ Membrane size (hence throughput) per stage
    - ❖ Heat management issues (if any)
  - ✓ Operability
    - ❖ Start-up, shutdown, run-times
  - ✓ Refined Capital & Operating Cost Estimation
- Comparison to Other H<sub>2</sub> &/or CO<sub>2</sub> Systems
  - ✓ Pressure Swing Absorption
  - ✓ Post-combustion amine scrubbing

**Note – Above with NORAM & Praxair**

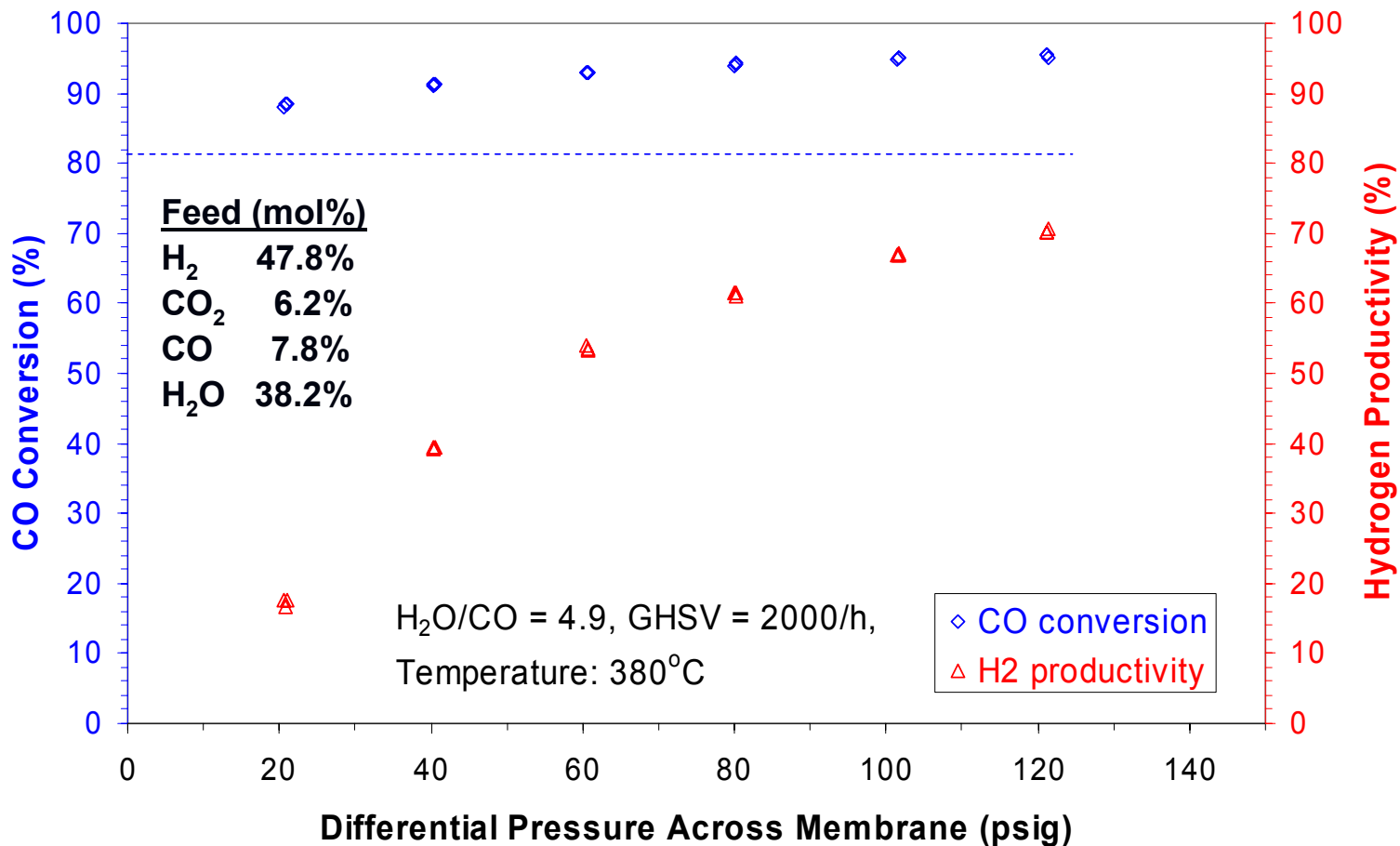


# Simplified Flowsheet Staged WGS / HTM System Maximum H<sub>2</sub> and CO<sub>2</sub> Production



# Integrated WGS / HTM Conversion “Beyond Equilibrium”

F81-34AB



# Challenge for Funding

- Contract between Eltron & DOE is for first 2 years only. Last 3 years will be committed after a replacement subcontractor has been identified.
- Eltron is in discussions for participation with 25+ companies including coal and energy producers, technology providers, E&C's, gasifier providers, turbine manufacturers and materials suppliers.
- Eltron will likely propose to accelerate the program to skip the 5.5 lb/day unit and add a functioning 4 ton/day unit (instead of the current paper design) when the new partner(s) is finalized.

# Summary

- Eltron's membrane continues to show stable, high fluxes using relatively low-cost materials.
- Contaminant handling, durability, and fabrication are materials focus areas.
- The project has moved well beyond materials R&D into engineering and cost analysis.
- Improvements have been made in materials and process design which are leading to additional cost reductions and performance enhancements.
- The project is on schedule and budget.

# Back-Up Slides

➤ See following slides

# Response to 2005 Reviewer Comments

- **Lack of focus on durability testing prior to scale up**
  - ✓ Some sulfur testing has been done with encouraging results
  - ✓ Lifetime demonstrated at 11 months to-date
  - ✓ Lifetime testing with contaminants is part of the program
  
- **100% selectivity and recovery will not be achieved**
  - ✓ >99.999% selectivity is routinely achieved
  - ✓ Recovery will be based on economics which are favored by simplicity and cost of membrane system
  
- **No economic analysis performed**
  - ✓ Economics were run after last year's presentation that show almost a 50% improvement versus PSA
  - ✓ The CCP Team calculated that Eltron's membrane had the potential for 60% cost reduction vs post-combustion amine scrubbing and 40% better than PSA. This was before permeate pressure staging was possible due to discovery of method for higher than atmospheric permeate pressure which reduces costs by another 20%.

# Recent Publications and Presentations

- **Hydrogen Separation Membranes, A Key to Carbon Sequestration** - Energy Frontiers International (EFI) Conference; "Emerging Energy Technologies: State of the Art - Challenges Ahead", Orlando, FL, Feb 2006 [Paul Grimmer]
- **Membranes for the Purification of Hydrogen Produced from Coal-Derived Water-Gas Shift Mixtures** - 22nd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, Sept 2005 [Michael V. Mundschau, Xiaobing Xie, Carl R. Evenson IV, Anthony F. Sammells]
- **Dense Membranes for Methane Conversion to Hydrogen with Carbon Dioxide Sequestration** - 7th International Conference on Catalysis in Membrane Reactors, Cetraro - CS, Italy, Sept. 2005 [A. F. Sammells, M. V. Mundschau, X. Xie, C. R. Evenson]
- **Membrane Technologies for Oxygen Production and Hydrogen Separation** - International Congress on Membranes and Membrane Processes (ICOM 2005), Seoul, Korea, Aug. 2005 [Arun C. Bose, Phillip A. Armstrong, A. F. Sammells, S. Elangovan]
- **Performance of Palladium Catalysts on Hydrogen Transport Membranes Exposed to Water-Gas Shift Reactants at High Pressure** - North American Catalysis Society, 19th North American Meeting, Philadelphia, PA, May 2005 [M.V. Mundschau, X. Xie, A.F. Sammells]
- **Advances in Hydrogen Separation Membrane Technology for the Separation of CO<sub>2</sub> 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]
- **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]
- **Dense Membranes for Separation of H<sub>2</sub> from CO<sub>2</sub> 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]
- **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]
- **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]
- **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]