

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

Presented by

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Eltron Research & Development Inc.

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Project PD-39

Overview

Timeline

- Phase I Start 1 Oct 2005
- Phase II Start 1 Apr 2009
- Phase II End 30 Jun 2013

Budget (\$000)

- Phase I Funding \$ 5,415
 - ✓ DOE share: \$ 4,330
 - ✓ Contractor share: \$ 1,085
- Funding for FY08 \$ 2,000
- Phase II Funding \$40,000
 - ✓ DOE Share \$31,000
 - ✓ Contractor share \$ 9,000

Barriers Addressed

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

Technical Targets

- Low-cost system to produce H₂ from coal-derived synthesis gas and enable cost effective capture of CO₂ for sequestration
- Obtain engineering scale-up data in 220 lb H₂ /day unit
- Design, build and operate 4 ton/day unit
- Tolerant to syn gas contaminants

Partners (prior to October 1, 2007)

- NORAM Engineering
- CoorsTek
- Praxair

DOE Project Manager – Arun Bose

DOE Contract DE-FC26-05NT42469

Program Objectives

- Develop H₂/CO₂ Separation System, which
 - ✓ Retains CO₂ at coal gasifier pressures
 - ✓ Operates near water-gas shift conditions
 - ✓ Tolerates reasonably achievable levels of coal-derived impurities
 - ✓ Delivers pure H₂ for use in fuel cells, gas turbines, and hydrocarbon processing
 - ✓ Is cost effective compared to alternative technologies for carbon capture

Milestones

➤ FY07

- ✓ **1Q** – Establish optimum operating conditions for metal membranes to achieve DOE 2010 flux, selectivity, and cost targets and select candidate membranes for scale-up and tests in the sub-scale engineering prototype.
- ✓ **2Q** - Complete fabrication of new alloy materials and select metal materials for further scale-up and tests in the sub-scale engineering prototype.
- ✓ **3Q** - Complete the design and cost estimate of the Impurity Management System upstream of the hydrogen membrane separation module unit to achieve the designed membrane operating life and engineering performance.
- ✓ Select candidate catalyst composition and deposition technique to be scaled up for tests in the sub-scale engineering prototype.
- ✓ **4Q** - Complete the economic analysis of hydrogen separation membrane modules and balance of plant.
- ✓ Deliver capital and operating cost estimates for large-scale membrane structures and identify a cost-effective means to manufacture large-scale membranes required for the SEP.

➤ FY08

- ✓ **1Q** – Complete commissioning activities on high pressure lifetime skid units
- ✓ **2Q** – Begin operations of high pressure lifetime skid units
- ✓ **3Q** – Select feed catalyst composition for impurity testing
- ✓ **4Q** – Update process flow sheets and demonstrate improved economics utilizing HTM in IGCC plants

Stage Gate Prior to Phase 2

- Clearly establish the economic advantages of our system applied to an IGCC flow sheet;
- Understand the manufacturability and costs for a scaled-up membrane system;
- Demonstrate the performance of the membranes in long term use - with and without sulfur impurities; and,
- Develop a design basis for the PDU.

Plan and Approach

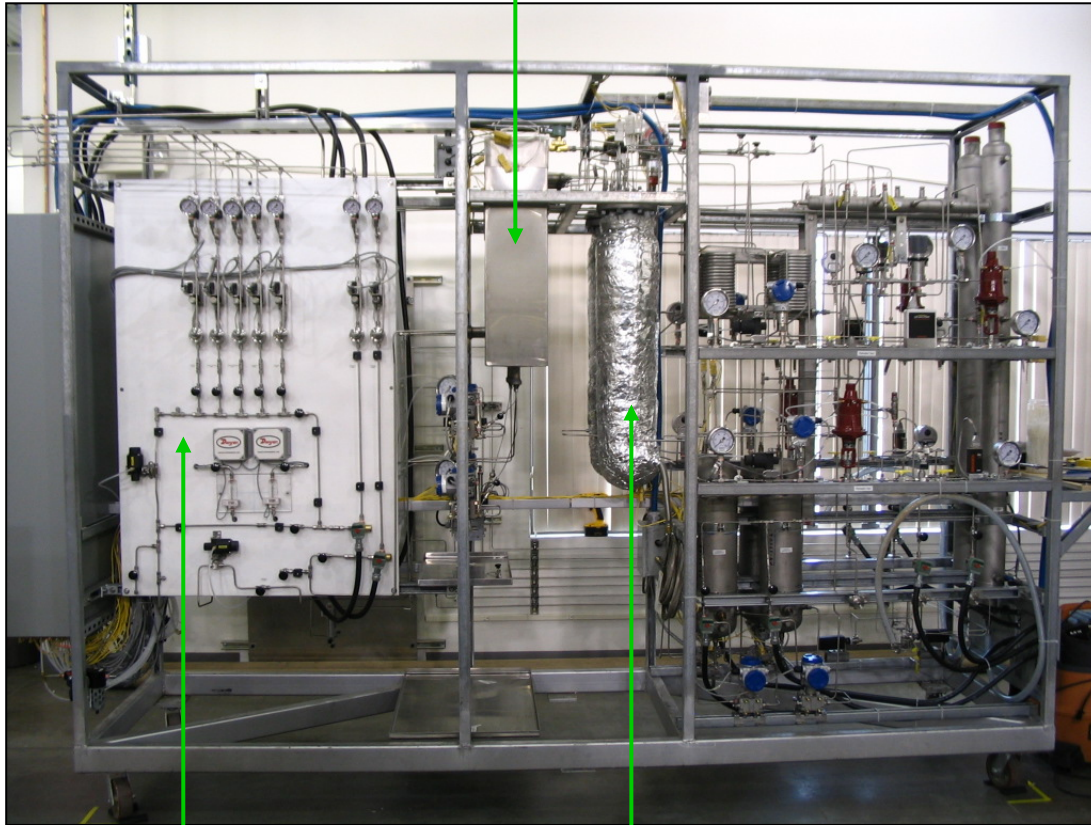
- Materials Development
 - ✓ Examine membrane and catalyst compositions
 - ✓ Develop preparation techniques
 - ✓ Develop improved analytical characterization
- Performance Screening
 - ✓ Evaluate flux, life, impurities effects using WGS composition
 - ✓ Establish range of operating conditions
- Mechanical Design
 - ✓ Assess strength of materials, embrittlement, welding techniques, et al
 - ✓ Address manufacturing costs and maintenance issues
- Process Design and Economics
 - ✓ Integrate into IGCC flow sheets – with and without co-production of H₂ & power
 - ✓ Determine methods for impurity management
 - ✓ Develop models for membrane performance and design
 - ✓ Compare process economics versus other technologies
- Scale-up steps
 - ✓ 1.5 lbs/day H₂ production – lab scale using simulated gas compositions
 - ✓ 220 lbs/day H₂ production – using coal-based SG slipstream
 - ✓ 4 tons/day H₂ production – complete engineering data package
 - ✓ Commercial module expected to be ~ 35 TPD H₂ Production (4-8 required for 275 MW FutureGen plant)

Accomplishments Summary

- Designed, constructed and began operations on high pressure lifetime skids
- Improved characterization of membranes leading to better understanding of preparation and performance
- Developed alloys for membranes and catalysts leading to improved performance and manufacturability
- Demonstrated more stable membrane performance at lower temperature
- Developed modeling tools to characterize and design membranes/systems
- Improved membrane-based IGCC flow sheets showing:
 - ✓ Carbon capture over 95%
 - ✓ HHV efficiency ~6% better than conventional technology
 - ✓ Cost of electricity ~10% better than conventional technology

Lifetime High Pressure Reactors

Steam Generation / Pre-Heat



Flow Control

Membrane Modules



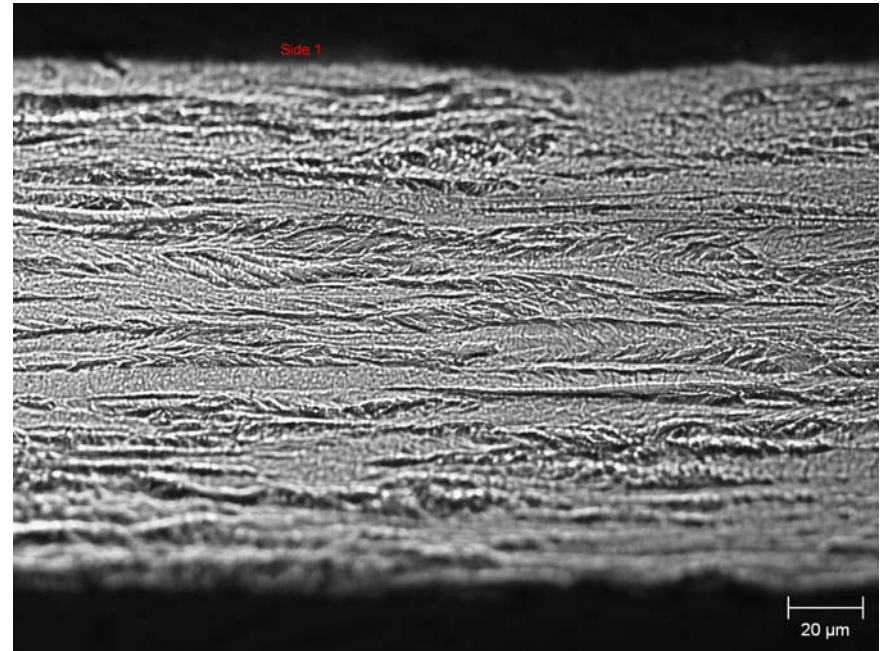
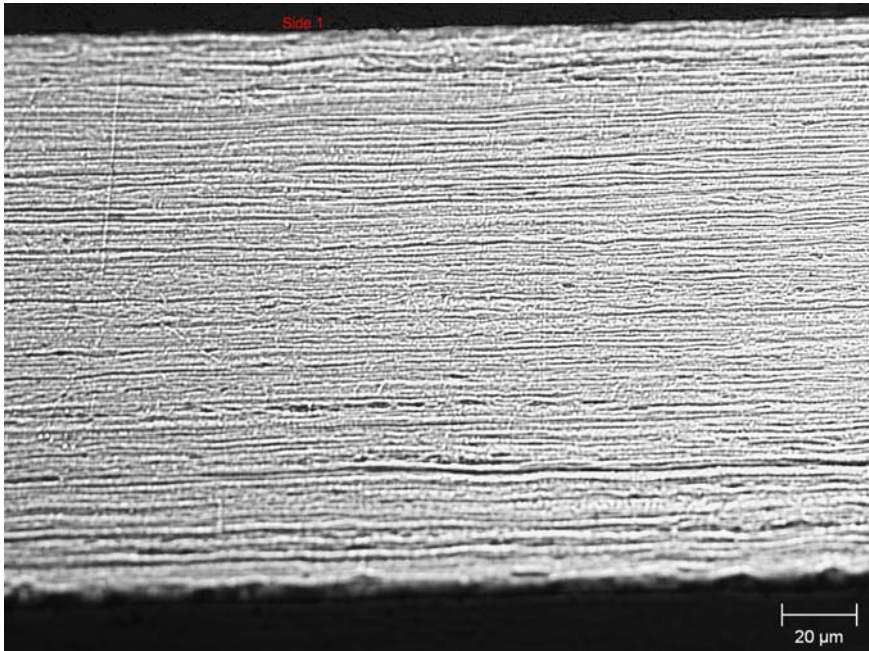
HTM System Capabilities

- Ambient Reactors (2)
 - ✓ Used for materials/parameter screening
 - ✓ Flow rates <500 ml/min
- Lab Reactors (2)
 - ✓ High pressure screening; not WGS-capable
 - ✓ Flow rates 3-5 L/min
- High Pressure Lifetime Test Units (2)
 - ✓ Full WGS capability
 - ✓ Fully automated for unattended operation
 - ✓ Flow Rates 1-2 L/min
- Scale-up Unit (1-4 reactors)
 - ✓ Full WGS capability
 - ✓ Flow rates >30 L/min

Membrane Characterization

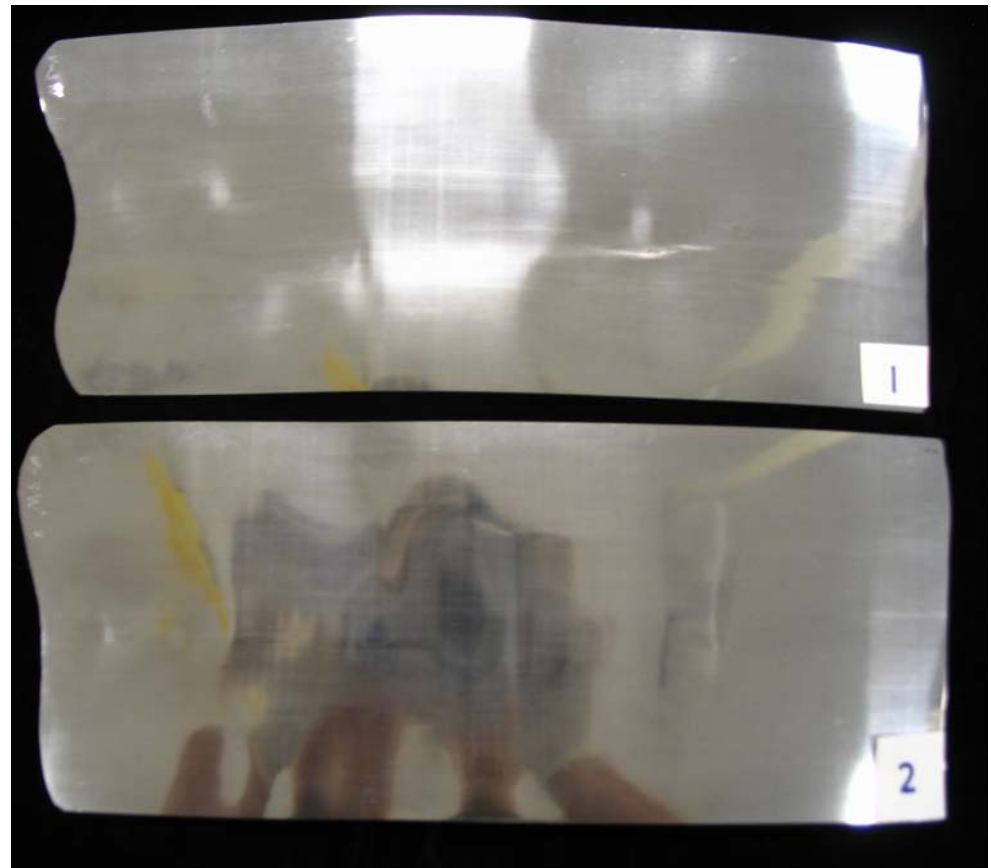
Analytical Technique	Membrane Feature Characterized
X-ray Diffraction	<ul style="list-style-type: none">• Phase(s)• Crystallite size• Orientation
XPS / Auger Depth Profiling	<ul style="list-style-type: none">• Element Analysis• Contaminants
SEM <ul style="list-style-type: none">• High Resolution• EDX	<ul style="list-style-type: none">• Morphology• Contaminants• Grain Structure
TEM	<ul style="list-style-type: none">• Catalyst Thickness• Element Analysis• Catalyst / Membrane Interface

Membrane Microstructure Cold-rolled vs. Deep Drawn



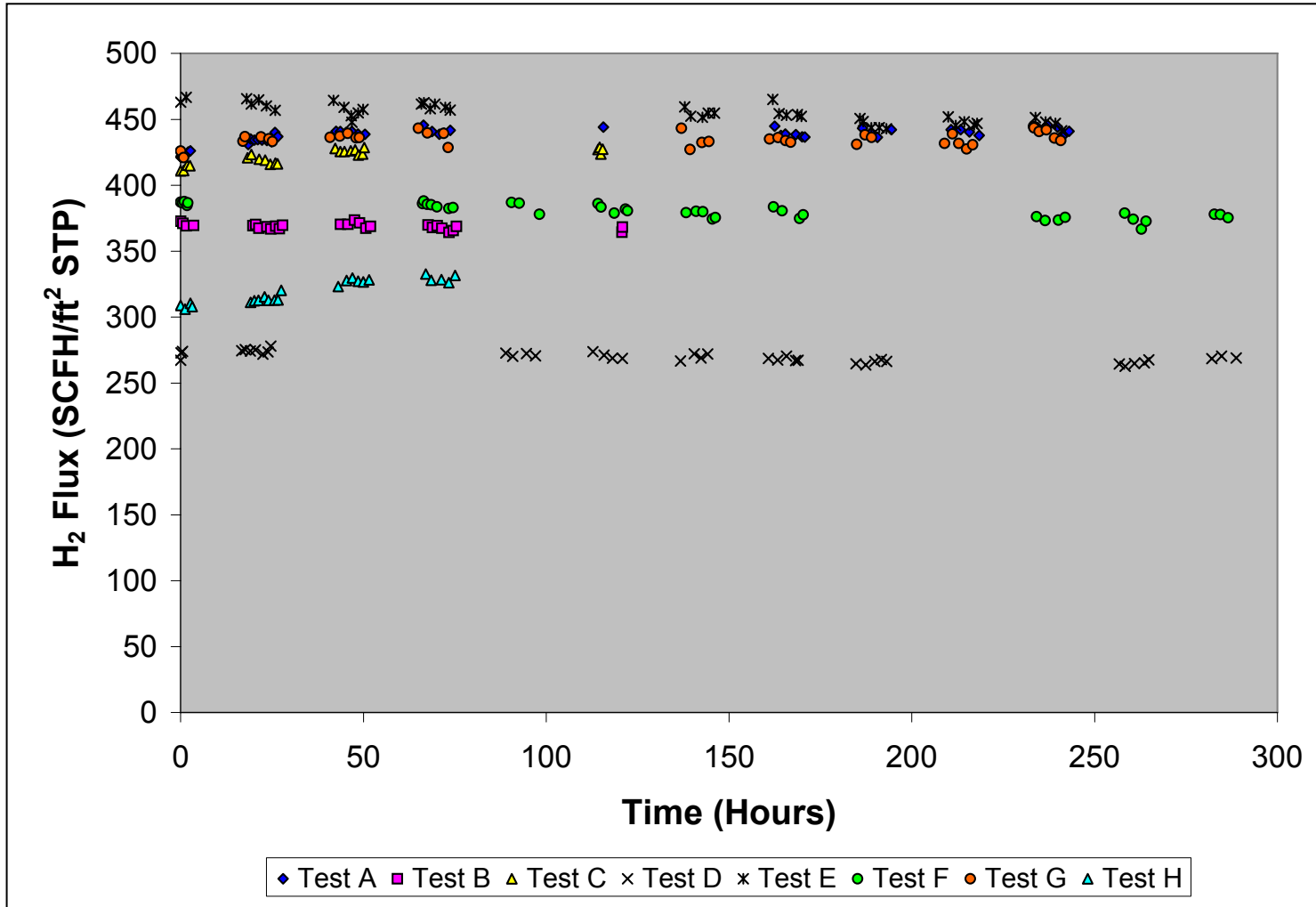
Alloy Sheets Prepared by Commercial Manufacturer

- 5" x 10"
- 225 μm thick
- Prepared by commercial method – low C,O,N impurities
- 4 alloys tested
- 6 additional alloys ordered



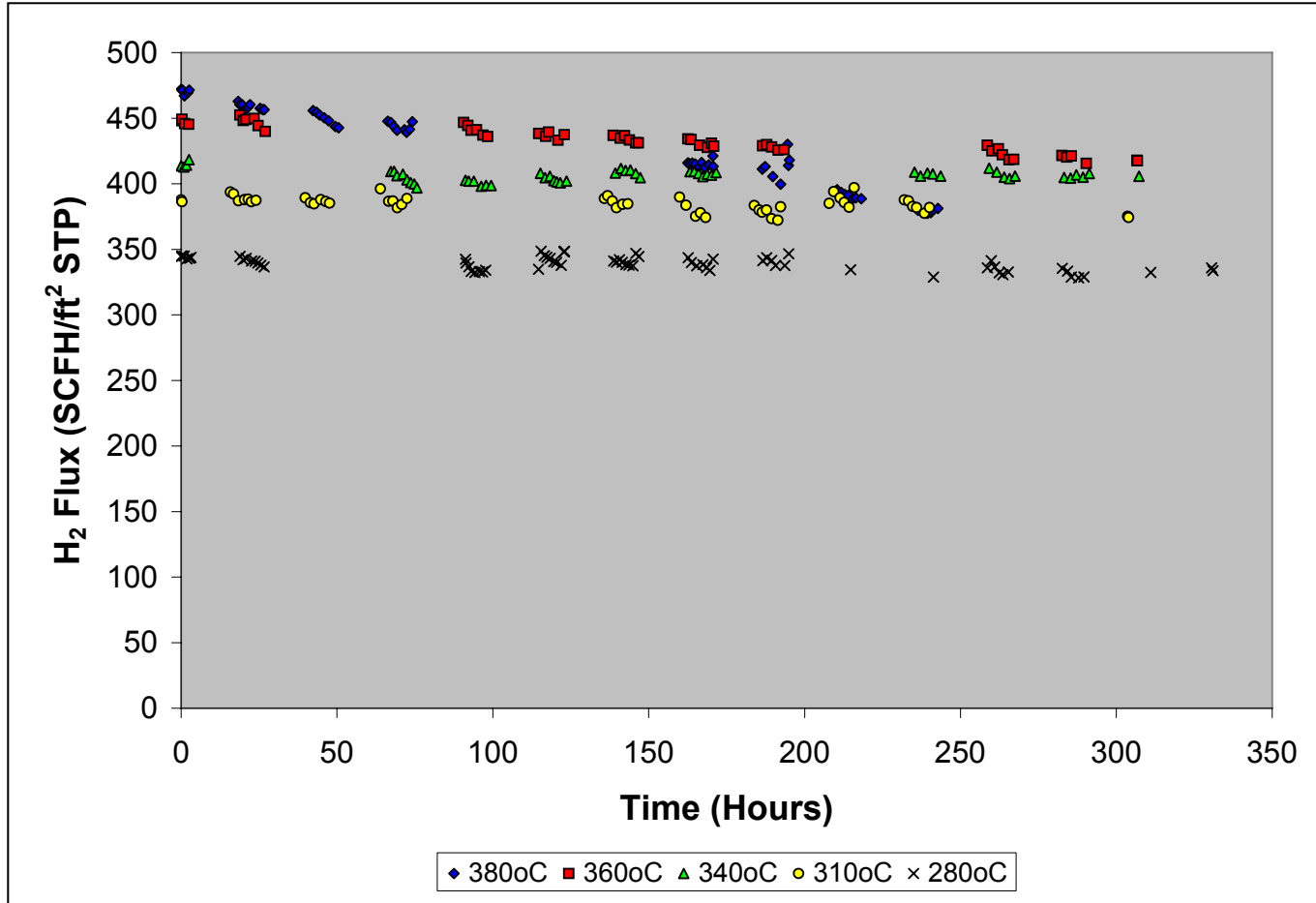
Membrane Alloy & Catalyst Alloy Permeation Data

➤ 340°C



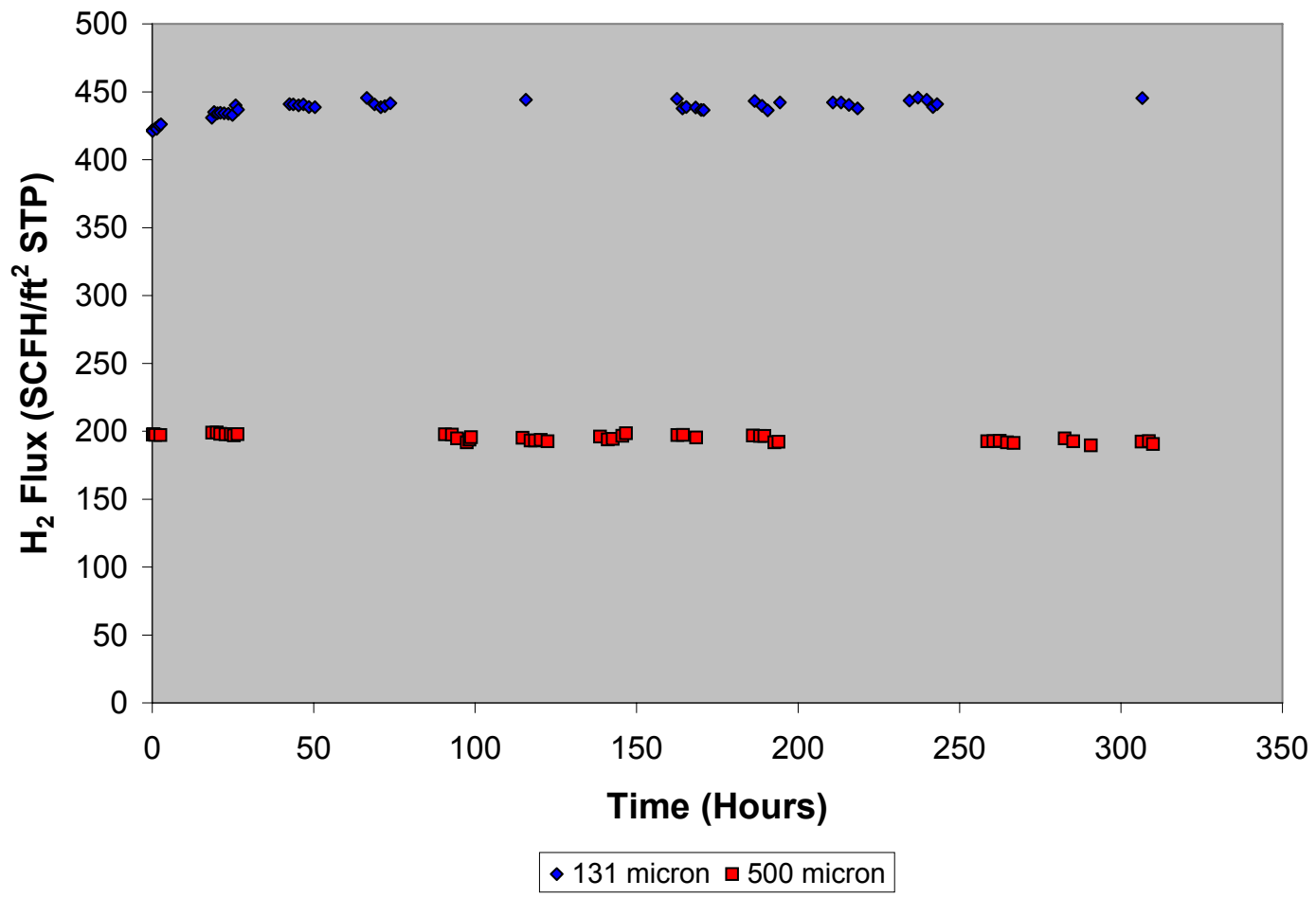
Effect of Temperature on Membrane Stability

- 150 μm
- Feed
 - ✓ 40% H_2
 - ✓ 60% He
 - ✓ 450 psig
- Sweep
 - ✓ Ar
 - ✓ 50 psig



Membrane Thickness

➤ 340°C



Model Development

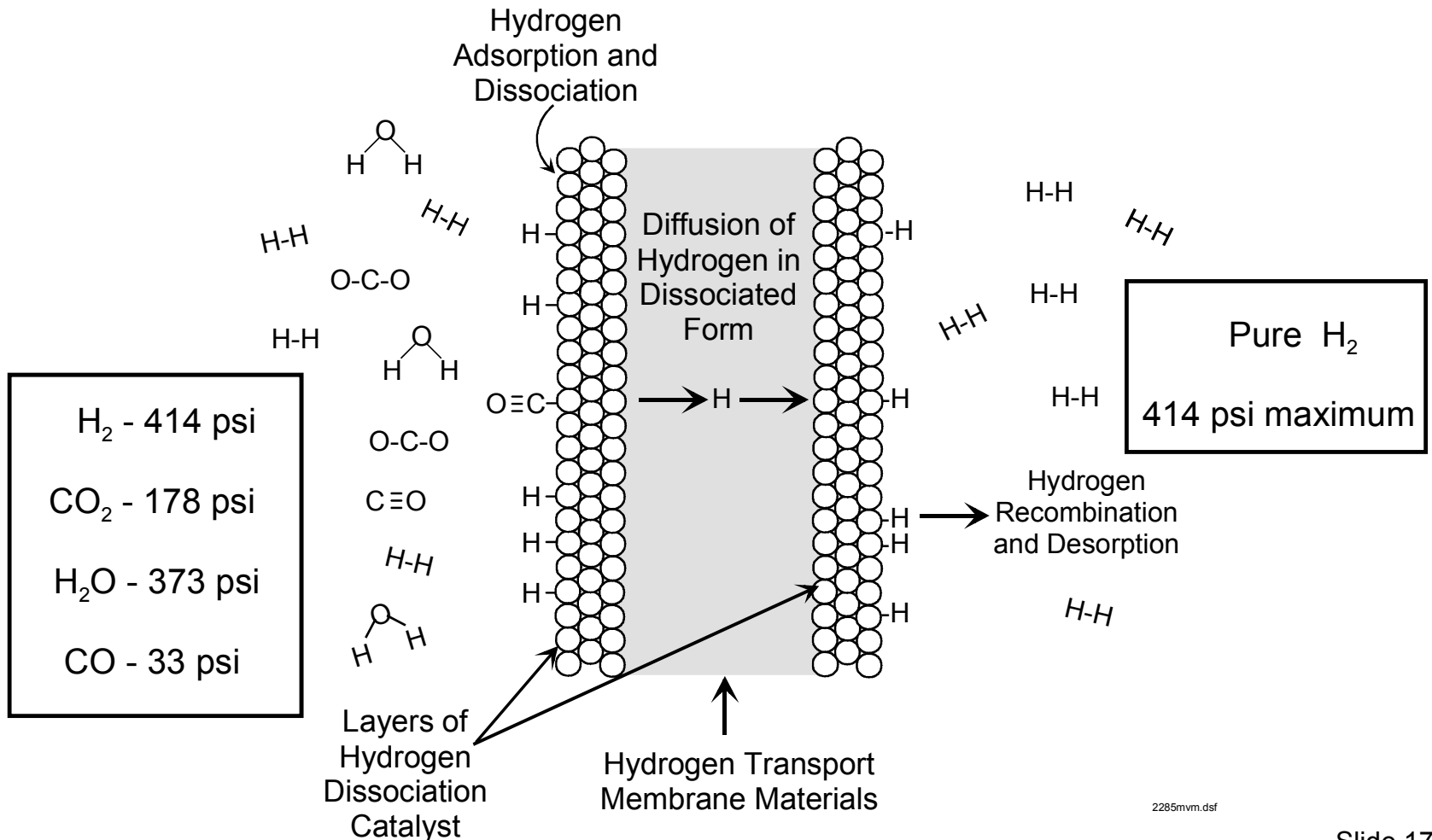
- Transport resistance model
- Process model
- Integration into IGCC flow sheet
- Process Economics

Goal is to improve carbon capture, decrease cost of electricity, improve thermal efficiency, and ensure membrane performance and lifetime.

Membrane Fundamentals

Retentate
(Water-Gas Shift Mixture)

Permeate
(Pure Hydrogen)



Hydrogen Transport Resistance Model

- Mass transport from feed gas to feed side catalyst surface
- Dissociation of hydrogen on feed side catalyst surface
- Hydrogen transport through feed side catalyst layer
- Resistance at feed side catalyst-membrane interface
- Hydrogen transport through membrane
- Resistance at permeate side catalyst-membrane interface
- Hydrogen transport through permeate side catalyst
- Recombination/desorption of hydrogen on permeate side
- Mass transport of hydrogen into permeate stream

Experiments being performed to furnish data to validate model for improving membrane design and performance

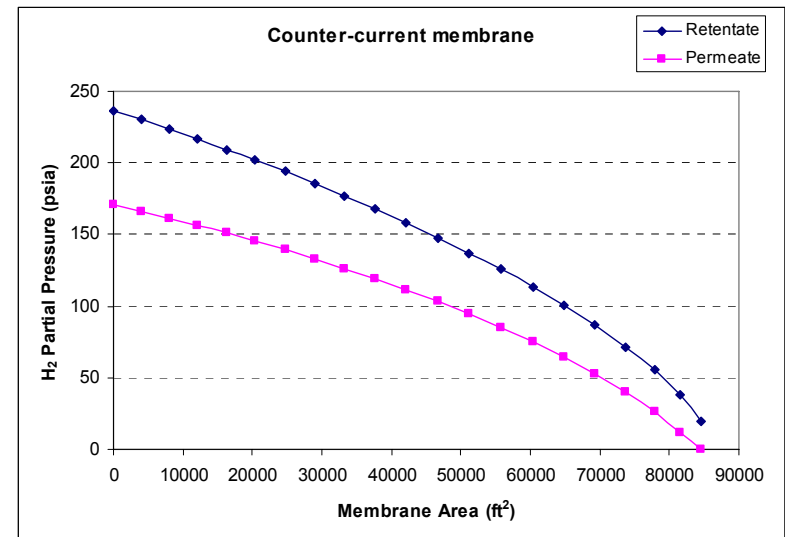
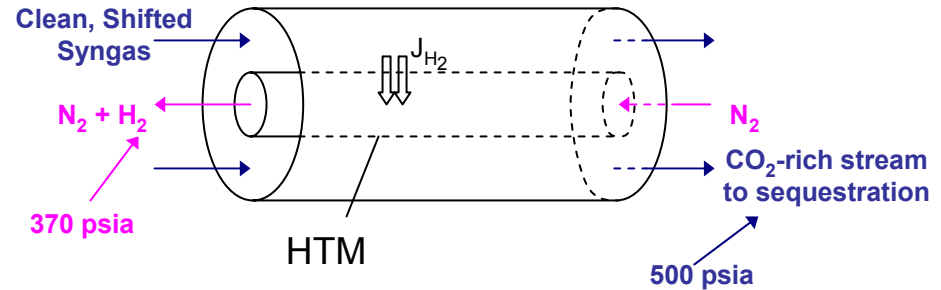
HTM Model

- Modeled as a subflowsheet of unit operations in Hysys

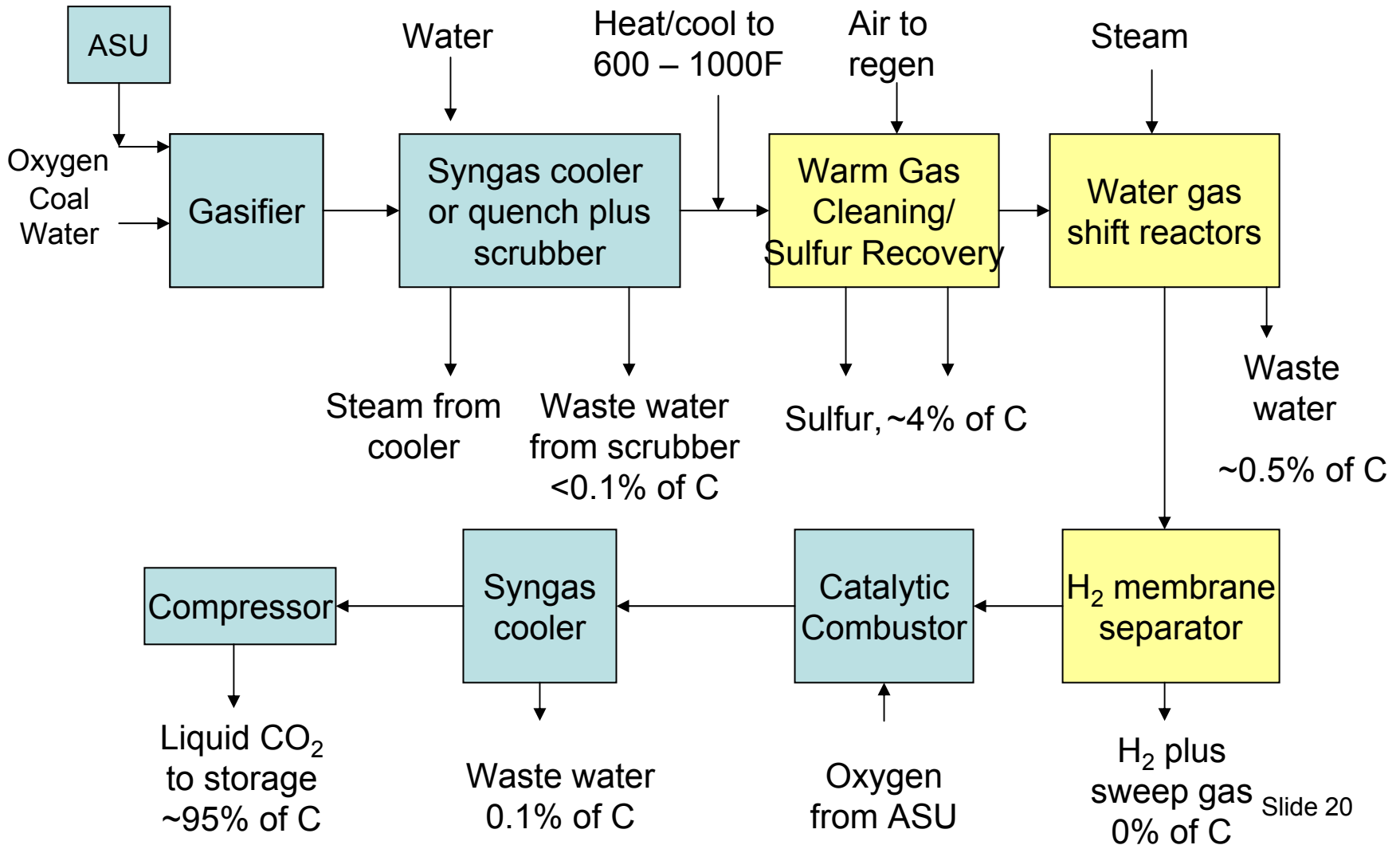
$$Flow_{H_2} = J_{H_2} A_{HTM}$$

$$J_{H_2} = \frac{P_0}{l} \exp\left(\frac{-E_A}{RT}\right) \left(P_{H_2,Ret}^{1/2} - P_{H_2,Perm}^{1/2}\right)$$

- Model parameters derived from Eltron membrane data



Pre-combustion CO₂ capture with membrane technology and warm gas cleaning



Economic Results Summary

CO ₂ Capture Method	None ¹	Pre-combustion Selexol	Eltron WGCU & Membrane	Δ Selexol vs. Eltron WGCU & Membrane
Coal Feed (tpd)	5,876	3,258	3,526	268
Net Power (MW)	640	239	318	79
HHV Efficiency	38.2%	27.4%	33.6%	6.2%
% CO ₂ Captured	0%	91.3%	95.3%	4.0%
Cost of Electricity (\$/MWh)	78.0	115.5	106	77.3 ²
Plant Cost (\$/kW)	1,813	2,434	2,292	1,863 ²

¹ NETL Report, “Cost and Performance Baseline for Fossil Energy Plants,” May 2007

² Cost applicable only to the incremental net power produced

Future Work

- Develop design basis for scale-up to 220 lb/day Process Development Unit (PDU)
 - ✓ Discussions initiated with host facilities
- Continue to work with commercial suppliers on manufacturing of full-size alloy membranes
 - ❖ Catalyst deposition
 - ❖ Testing/Evaluation
- Life testing
- Understand impacts of contaminants
 - ✓ Experimentally
 - ✓ Process design
- Improve techno-economic models
 - ✓ Process optimization
 - ✓ Guide research/scale-up studies

Summary

- Eltron is currently bringing together all aspects of membrane technology
 - ✓ Ability to test long term under expected operating conditions
 - ✓ Substrate alloys / manufacturing
 - ✓ Catalyst alloys / deposition
 - ✓ Tubular membrane geometry
 - ✓ Demonstration of economic performance
- Results obtained to date show that this system is on track to meet DOE targets for 2010/2015

Progress Towards DOE FutureGen Targets

<i>Performance Criteria</i>	<i>2007</i>	<i>2010 Target</i>	<i>2015 Target</i>	<i>Current Eltron Membrane</i>
Flux, SCFH/ ft ²	320	200	300	450
Operating Temperature, °C	380-440	300-600	250-500	250-440
Sulfur Tolerance (ppmv)	20 (prelim.)	2	20	20 (prelim.)
System Cost (\$/ft ²)	<200	500	<250	<200
ΔP Operating Capability (psi)	1,000	400	800-1000	1,000
Carbon monoxide tolerance	Yes	Yes	Yes	Yes
Hydrogen Purity (%)	>99.99	99.5	99.99	>99.99
Stability/Durability (years)	0.9	3	>5	0.9
Permeate Pressure (psi)	270	N/A	N/A	400