# Water-Gas Shift Membrane Reactor Studies

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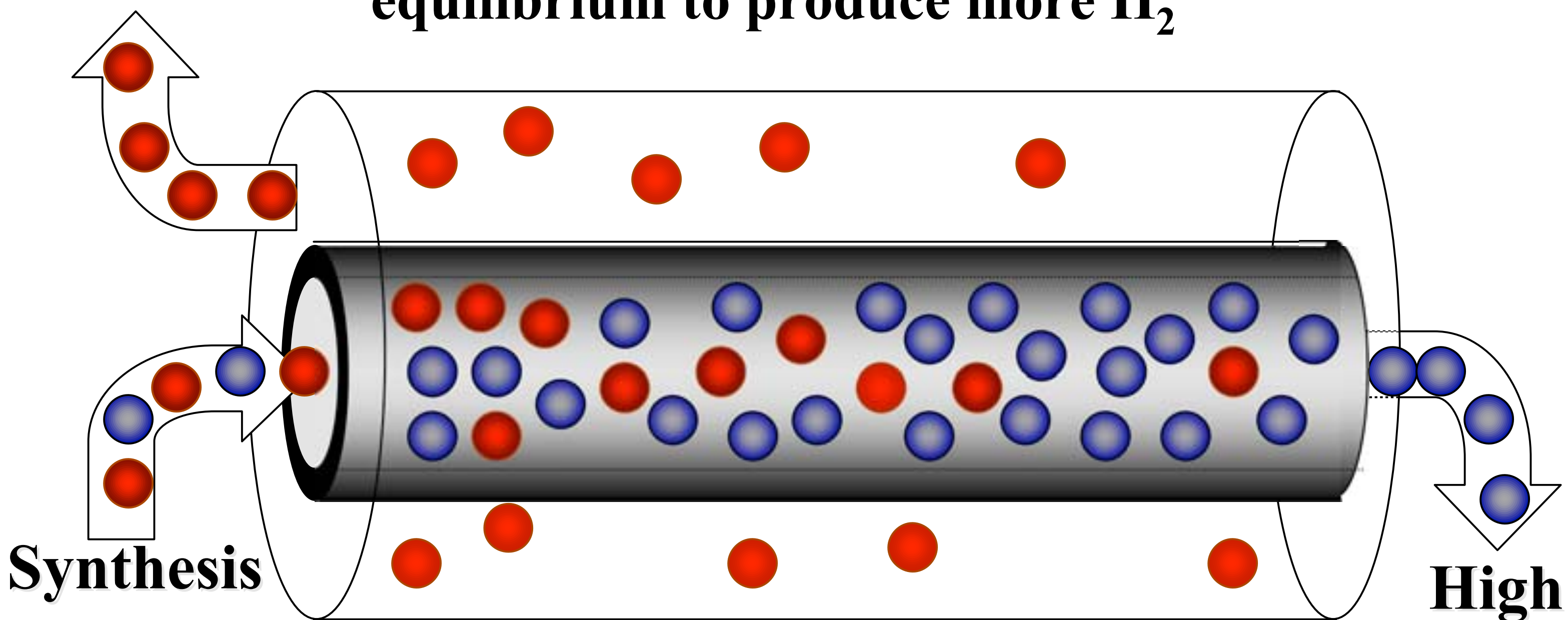
# $H_2$ Membrane Reactor Concept

*WGS Reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$

*High-T for favorable kinetics

*Membrane removes $H_2$ to "shift" unfavorable equilibrium to produce more $H_2$



# Project Rationale

- **Designing WGS membrane reactors requires the consideration of reaction kinetics and mass transport phenomena**
  - Forward and Reverse Water-Gas Shift Kinetics
  - Catalytic Effect of Reactor Materials, Membrane Materials
  - Need for Heterogeneous Catalysis?
  - Hydrogen Flux and Selectivity Through Membrane
  - Durability of Membrane in Extreme Environments
- **Lab-scale approach**
  - Address scientific issues using mainly thick (i.e. 10's of microns), easy-to-manufacture membranes of precise composition
  - Incorporate the optimal alloy composition into membrane reactors of various geometries that have high flux with a highly permeable support

# Objectives

- **Evaluate water-gas shift (WGS) reaction kinetics and membrane flux using industrial gas mixtures and conditions**

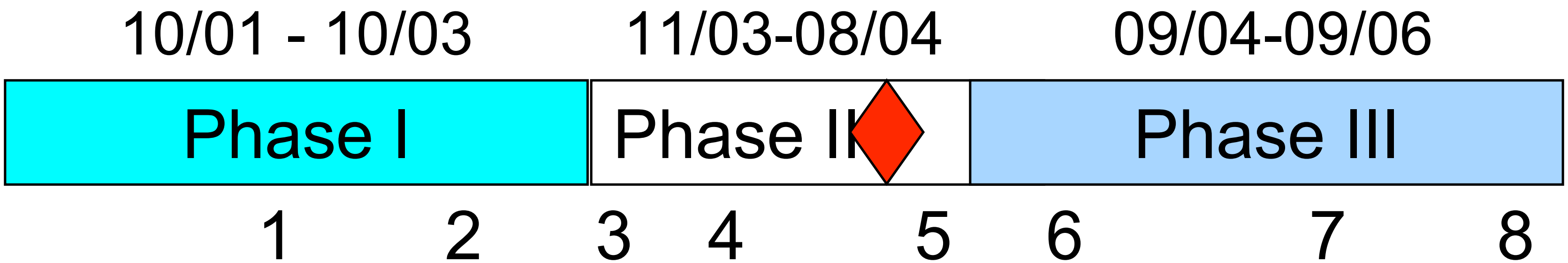
- **Test the feasibility of enhancing the WGS at high temperature without added catalyst particles by using a membrane reactor**

- **Determine the catalytic effect of metal shell materials (e.g. Inconel) and membrane surfaces (e.g. Pd) on the WGS reaction**

# Budget

- Funding determined yearly thru submission of Annual Operating Plan proposals to EERE
- FY04 Funding = $200k
- EERE funding is 50% contribution to overall project; the other 50% is from FE

# Project Timeline




- **Phase I – Hi-T, Hi-P WGS Reaction Kinetics**
  1. Complete reverse WGS reaction kinetics study
  2. Complete forward WGS reaction kinetics study
  3. Determine catalytic effects of membrane/reactor materials
- **Phase II – Membrane Reactor Development**
  4. Fabricate different Pd membrane reactor prototypes
  5. Determine feasibility of Pd membrane reactor prototypes
- **Phase III – WGS Membrane Reactor Testing**
  6. Complete baseline testing of Pd-Cu membrane reactor
  7. Complete validation testing of optimized WGS MR system
  8. Operate WGS MR in presence of contaminants (e.g. $H_2S$)

# Technical Barriers and Targets

- **Barrier A: Fuel Processor Capital Costs—specifically single-step shift w/integrated membrane technology**
  - Related 2005 Targets: Purification at a Cost of $0.11/kg $H_2$ and $H_2$ Efficiency of 82%
- **Barrier AB: $H_2$ Separation & Purification—specifically membrane separation with the shift reaction in one unit operation**
  - Related 2005 Targets: Flux Rate of 100 scfh/ft$^2$, Cost of $100-150/ft$^2$, Durability of 50,000 hours, Operating Temperature of 300-600°C, and Parasitic Power of 3.0 kWh/1000 scfh

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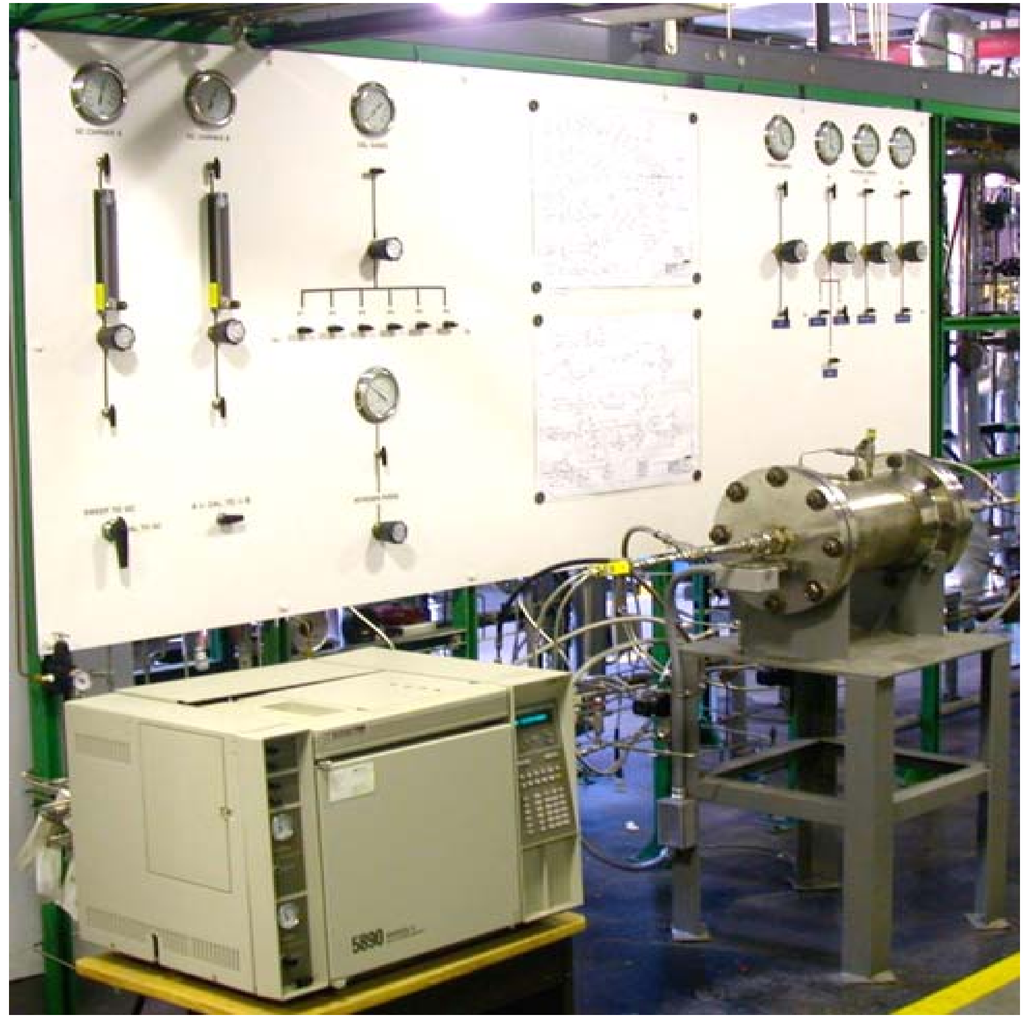
# NETL Hydrogen Separation Facilities

- 3 $H_2$ Membrane Test Units
- Constructed FY99 to FY02
- Temperatures to 900°C
- Pressures to 400 psi
- Disk & tubular membranes
- 1/4” to 1/2” membranes
- Feed gas flexibility
- Membrane separation & reactor configurations
- “Clean” and “sulfur-laden” gas feedstocks
- Online analysis of products by GC

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# Project Safety

- Safety vulnerability is addressed thru NETL's Safety Analysis & Review System (SARS). This process identifies, analyzes, minimizes all ES&H hazards. It ensures that all projects have a SARS Permit before operations begin.
- Management of changes is also addressed for any project or facility modifications thru the NETL SARS process.
- All $H_2$-related reactors are contained in purge vessels thru which an inert gas ($N_2$) is continually streaming.
- Gas alarm systems are in place in areas where gases such as $H_2$, $H_2S$, $CO$, $CO_2$, etc. are in use.

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# FY04 Approach

- Conduct baseline testing of the fWGS reaction at high pressure with no catalyst in the 300-900°C range in the prototype Pd & PdCu membrane reactors.

- Re-design the PdCu membrane reactor to maximize membrane area and minimize thickness in order to enhance conversions of CO and $H_2O$ to $H_2$ and $CO_2$.

- Determine $H_2$ permeance of PdCu in the presence of major gasifier components, such as CO, $H_2O$, $CO_2$.

# FY04 Accomplishments

- **Completed forward WGS kinetics study**
  - Gas phase kinetics
  - Correlation developed for high T, high P fWGS reaction
- **Determined catalytic effect of membrane and reactor shell materials**
  - Inconel – example of reactor shell material
  - Pd and Pd/Cu – examples of membrane materials
- **Evaluated effect of CO and H2O on $H_2$ permeability**
- **Fabricated 3 types of Pd MR for trials**
  - Pd flat disk in Inconel: assessment of effect of side reactions
  - Thin Pd tubes: effect of temperature, pressure, reactant ratio
- **Incorporated WGS kinetics results into MR model**

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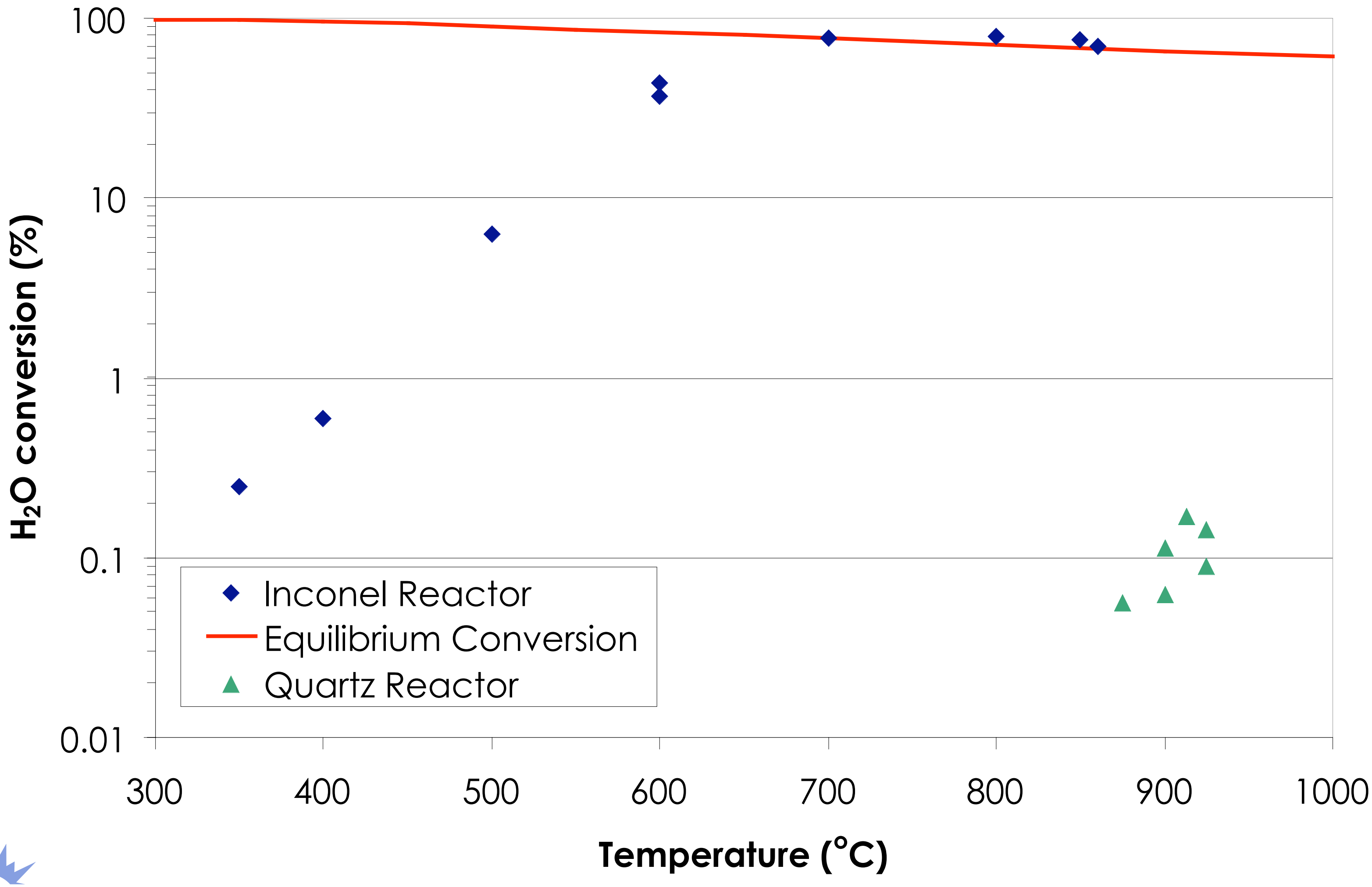
# Forward WGS Kinetics

- *Inconel walls catalyze the reaction*
- *Gas-phase reaction appears to be slow*

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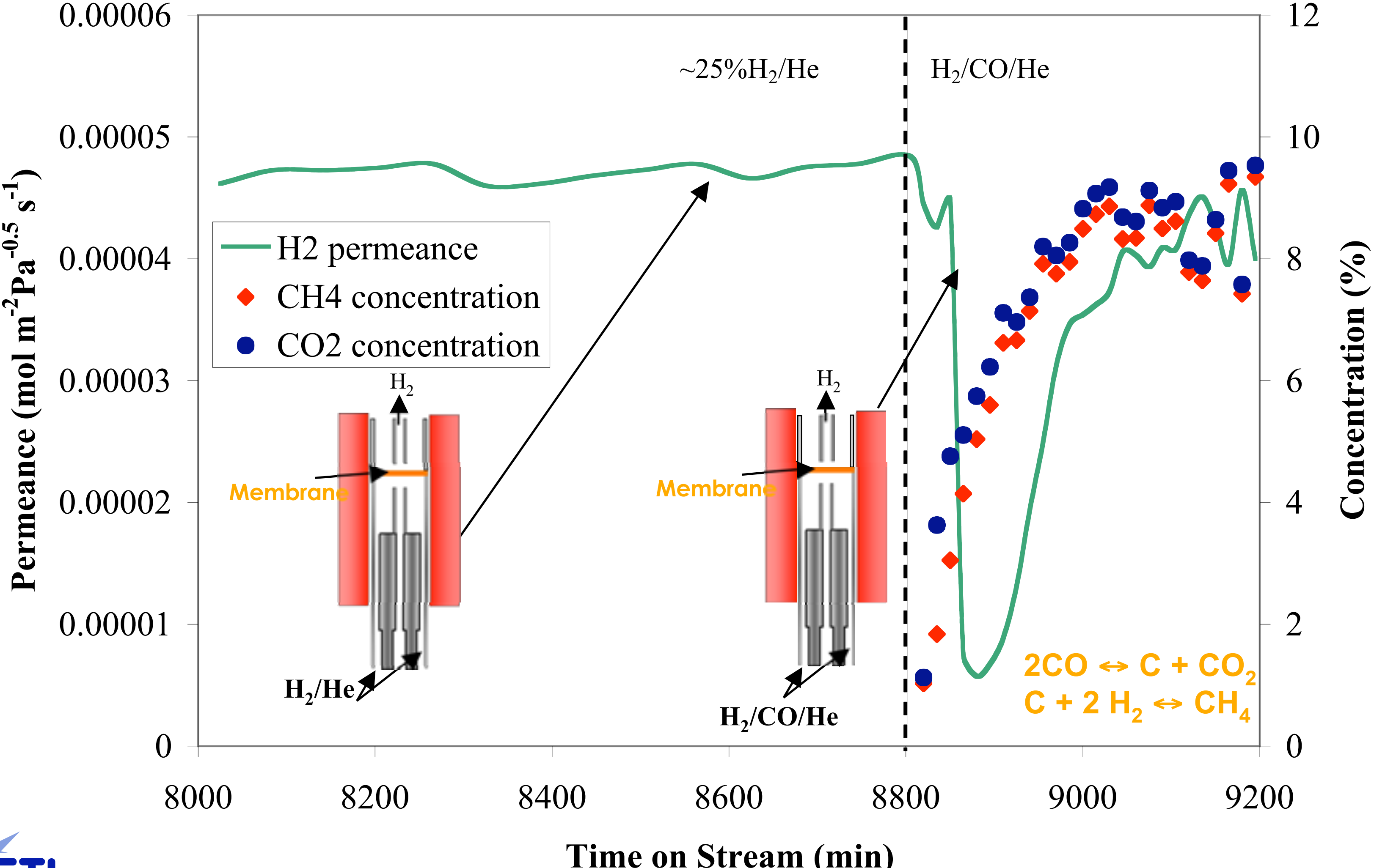
$(x_{CO})_0 = 0.72$, $(x_{H2O})_0 = 0.28$, $(x_{CO2})_0 = (x_{H2})_0$, $\tau \sim 0.5 - 1$ s

# CO not a Poison for Pd Membranes at Hi-T

- *Physical, transient drop due to C deposition–permeability restored*
- *$H_2O$ doesn't exert any effect on $H_2$ permeation (not shown)*




T = 900°C, Pretentate= 220 psig, Ppermeate= 5 psig, $H_2$/CO/He (~33% ea)

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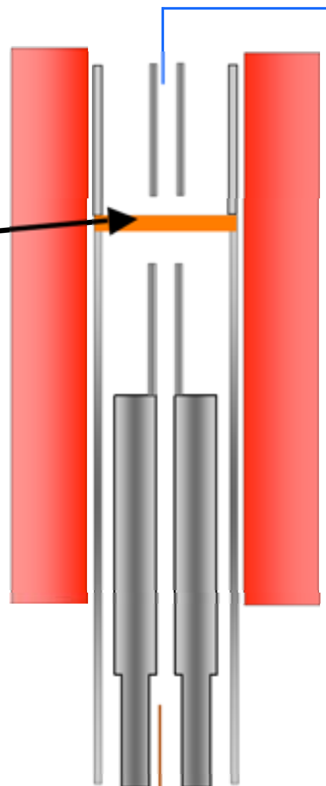
# Inconel Enhances Kinetics & Pd Removes $H_2$

*_Good synergy between Inconel & Pd*

*_Side reactions on Inconel are significant*

$H_2$ removed by membrane* _ 24.2%

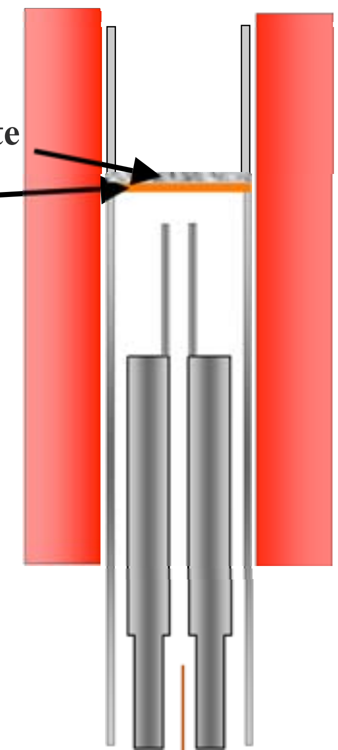
Pd Membrane



Blank Reactor

Non-porous substrate

Thin Pd film



Conversions if only WGS in quartz reactor

CO _ 14.2 %
H2O _ 79.7 %

$CO_2/H_2 = 5.84$

Conversions:
CO _ 77.72 %
$H_2O$ _ 66.25 %

$CO_2/H_2 = 4.10$

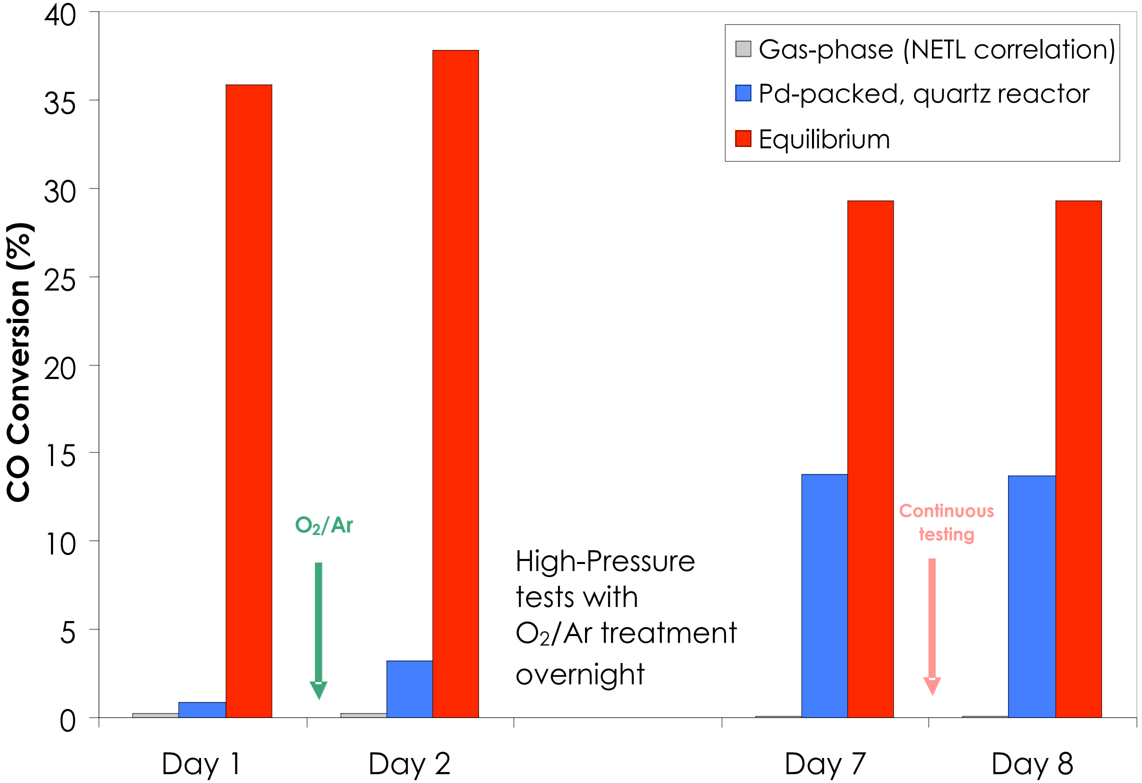
Conversions:
CO _ 77.16 %
$H_2O$ _ 55.78 %

$$^{*}\left(\frac{F_{H_2,permeate}}{F_{H_2,permeate}+F_{H_2,retentate}} * 100\right)$$

$T = 900°C$, $P = 16$ bar, $\tau = 2.5$ s, $y_{CO,0} = 0.85$, $y_{H2O,0} = 0.15$

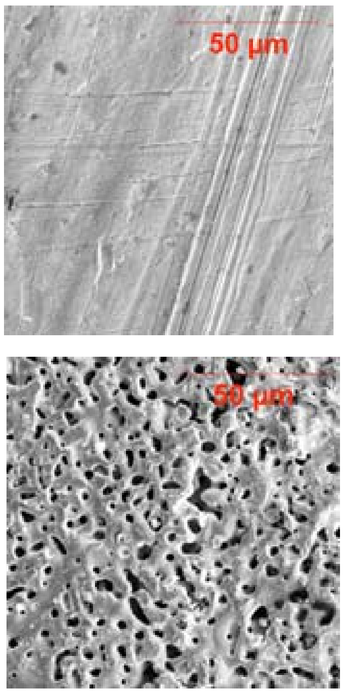
# Pd or PdCu membrane surfaces enhance the WGS

- *Exposure of the Pd to $O_2$ to remove C roughens the membrane*
- *This increases surface area and enhances conversion activity,*
- *Need to operate at conditions where C deposits do not form*




**$T = 900^oC$, $P = 1$ bar, $\tau = 0.7$ s, $y_{CO,0} = 0.70$, $y_{H2O,0} = 0.30$**

**SEM images of fresh (top) & oxidized (bottom) Pd packing shows increase in roughness; PdCu displays a similar behavior**

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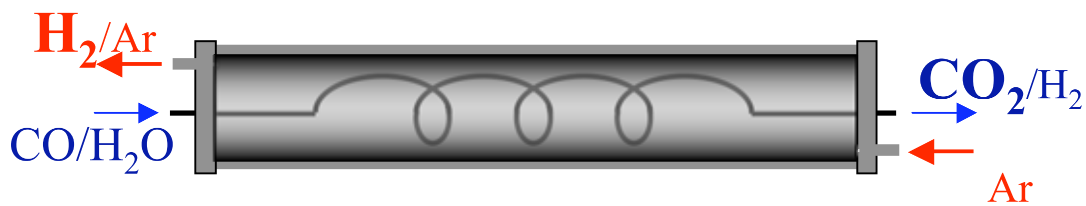
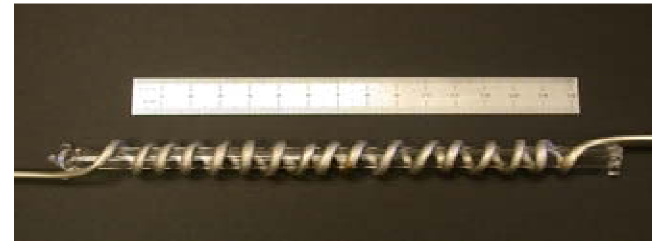
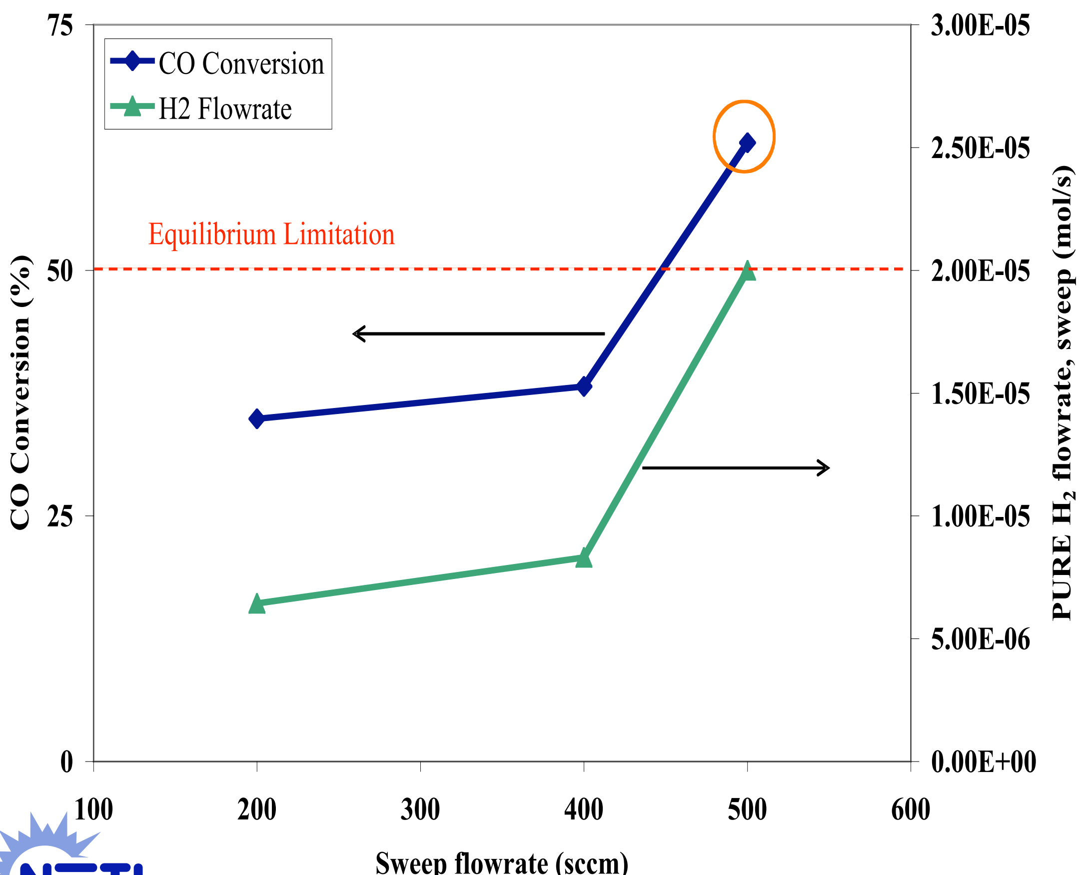
# WGS Membrane Reactor Prototype






1) Helix design used to optimize surface-to-volume ratio
2) Graph shows CO conversions above equilibrium
3) In summary, WGS w/ membrane reactor yields more H2 than conventional WGSR at hi-temperature

# Interactions, Collaborations, Papers

- Synetix (Johnson-Matthey) in the UK: Dr. Jim Abbott – informal exchange of WGS information
- Princeton Environmental Institute: Dr. Tom Kreutz – membrane reactor systems analyses
- Collaborations with ultra-thin Pd/Cu membrane developers: Dr. Doug Way (Pd/Cu/porous ceramic), Dr. Robert Buxbaum (Pd/Cu/dense metals), and Dr. Ed Ma (Pd/Cu/porous SS)

- F. Bustamante et al., "Hi-T, Hi-P WGS Reaction in a Membrane Reactor," AIChE Mtg., San Francisco, 11/03
- R. Enick et al., "Towards the Development of Robust Water-Gas Shift Reactors," ACS Mtg., New York, 8/03
- F. Bustamante et al., "Hi-T Kinetics of the Homogeneous rWGS Reaction," AIChE Journal, 05/04
- M. Ciocco et al., "Conducting the Hi-T&P WGSR in a Pd Membrane Reactor," Coal Util. Conf., Clearwater FL, 04/04

# Responses to Reviewers' Comments Last Year

- Summary Comment — "emphasize feasibility of hi-temp WGS under realistic operating conditions"
- Response — project focus has shifted from kinetics studies to actual WGS membrane reactor testing using syngas components, reactor materials, high T&P, novel reactor designs

- No weaknesses specified in reviewers comments

# Future Plans

- **FY04**
  - Conduct baseline testing of Pd membrane reactor (MR) to determine feasibility of prototype design
  - Fabricate Pd-Cu MR based on results of Pd testing and begin baseline testing
- **FY05**
  - Complete baseline testing of Pd-Cu MR
  - Determine effect of syngas components and impurities (S, Cl, NH3, etc.) on WGS MR
  - Complete initial validation tests under gasification conditions