

# Hydrogen Separation

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Office of Science & Technology  
Fuels and Process Chemistry Division**

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This presentation does not include any proprietary or confidential information

**Project ID# PDP25**

# Overview

## Timeline

- Start Date: 10/01/04
- End Date: 9/30/05
- % Complete: 67

## Budget

- Total Project Funding (FE)
  - DOE Share = \$960
  - Contractor = \$0
- FY04 Funding = \$0
- FY05 Funding = \$960k

## Barriers

(from FE's H<sub>2</sub> from Coal RD&D Plan)

- WGS Reaction—Barrier E--  
Operating Limits
- H<sub>2</sub> Separation—Barriers H, I, J--  
Thermal Cycling, Impurity  
Intolerance, & Undesired Atomic  
Rearrangement

## Partners

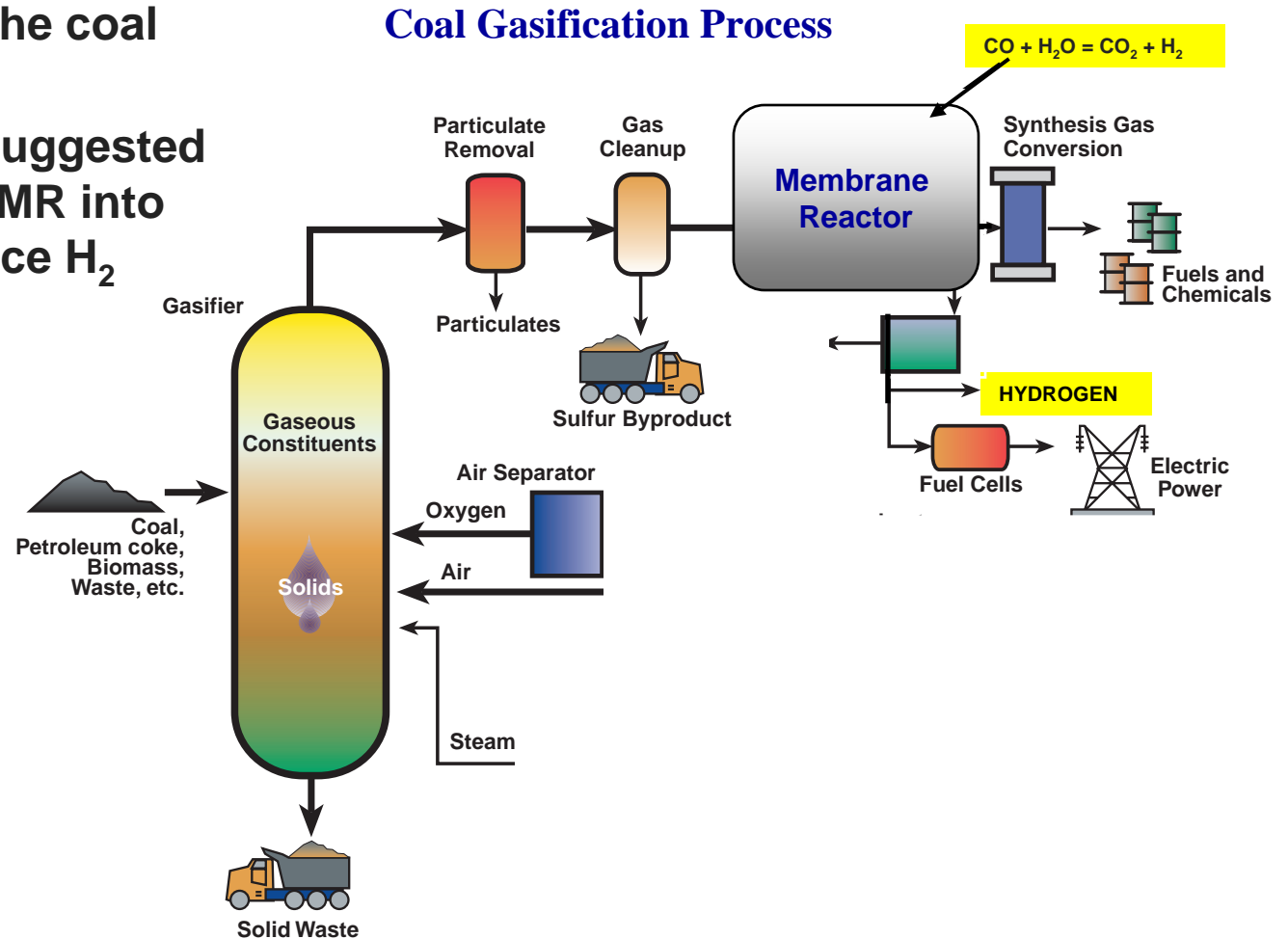
- U. Balachandran, ANL
- R. Buxbaum, REB Research
- F. Lau, GTI
- R. Judkins/B. Bischoff, ORNL
- T. Armstrong, ORNL



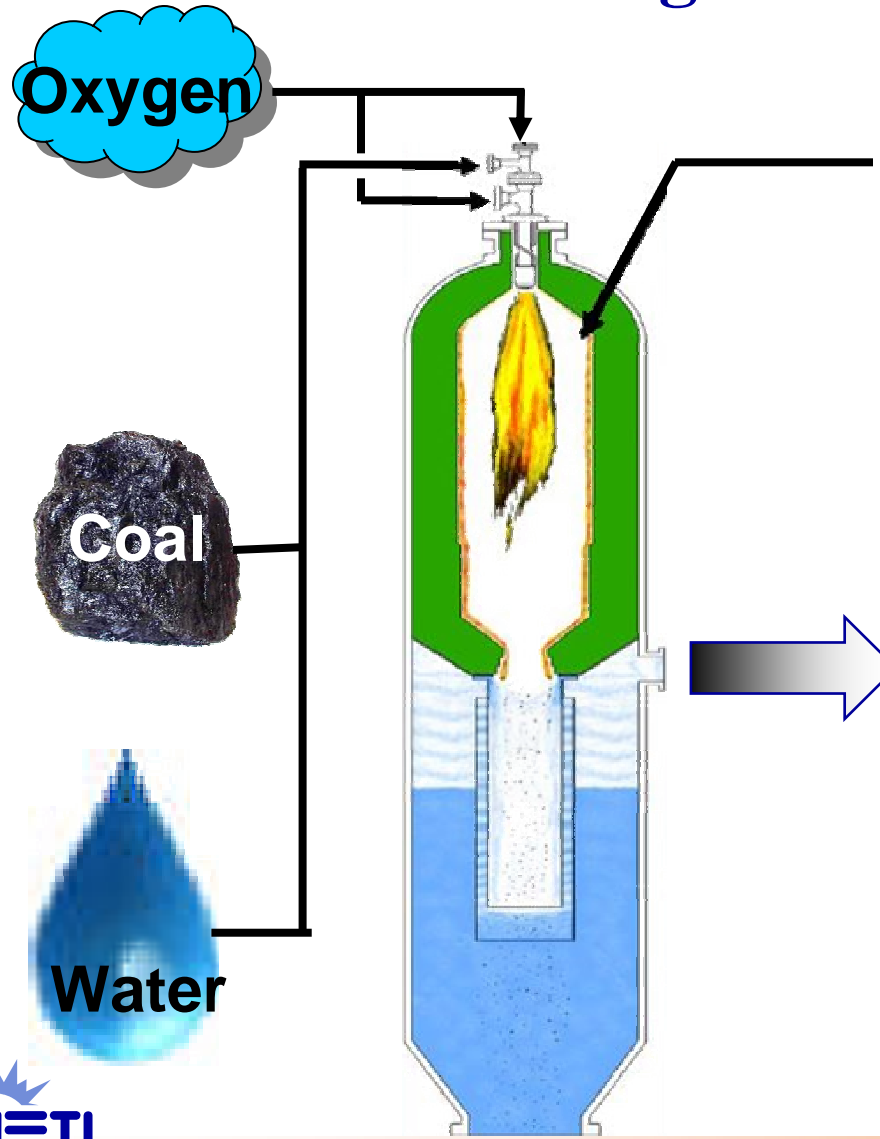
# Background

- Overall goal of project:  
Integrate a MR into the coal gasification process
- NETL studies have suggested that incorporating a MR into the gasifier can reduce H<sub>2</sub> cost by up to 30%

("H<sub>2</sub> from Coal", D. Gray, Mitretek, 07/02)



## Background (Cont.)



### Extreme Conditions:

- 1,000 psig or more
- ~1400°C
- Corrosive slag and H<sub>2</sub>S gas

### Typical composition of O<sub>2</sub> blown coal gasifiers

	Texaco	Shell	Dow
H <sub>2</sub> vol %	35.1	30.1	41.4
CO vol %	51.8	66.2	38.5
CO <sub>2</sub> vol %	10.6	2.5	18.5
CH <sub>4</sub> vol %	0.1	2.5	0.1

H<sub>2</sub>S 0.2 – 1%

COS 0 - 0.1%

N<sub>2</sub> 0.5 – 4%

Ar 0.2 – 1%

NH<sub>3</sub>, HCN, HCl 0 - 0.3%

Ash/Slag/PM



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## Objectives

- **Task 1. WGS Membrane Reactors -- demonstrate that a Pd-Cu membrane reactor (MR) can enhance CO conversion of the fWGSR and recover H<sub>2</sub> in the presence of sulfur.**
- **Task 2. Pd-Cu Membranes -- a) determine degree of S resistance of Pd-Cu membranes, b) investigate the mechanism of any Pd-Cu S resistance, and c) determine the effects of other gas impurities (e.g., Cl, NH<sub>3</sub>, COS) on permeability.**
- **Task 3. Novel H<sub>2</sub> Production and Separation-- conduct exploratory research in new areas related to hydrogen.**



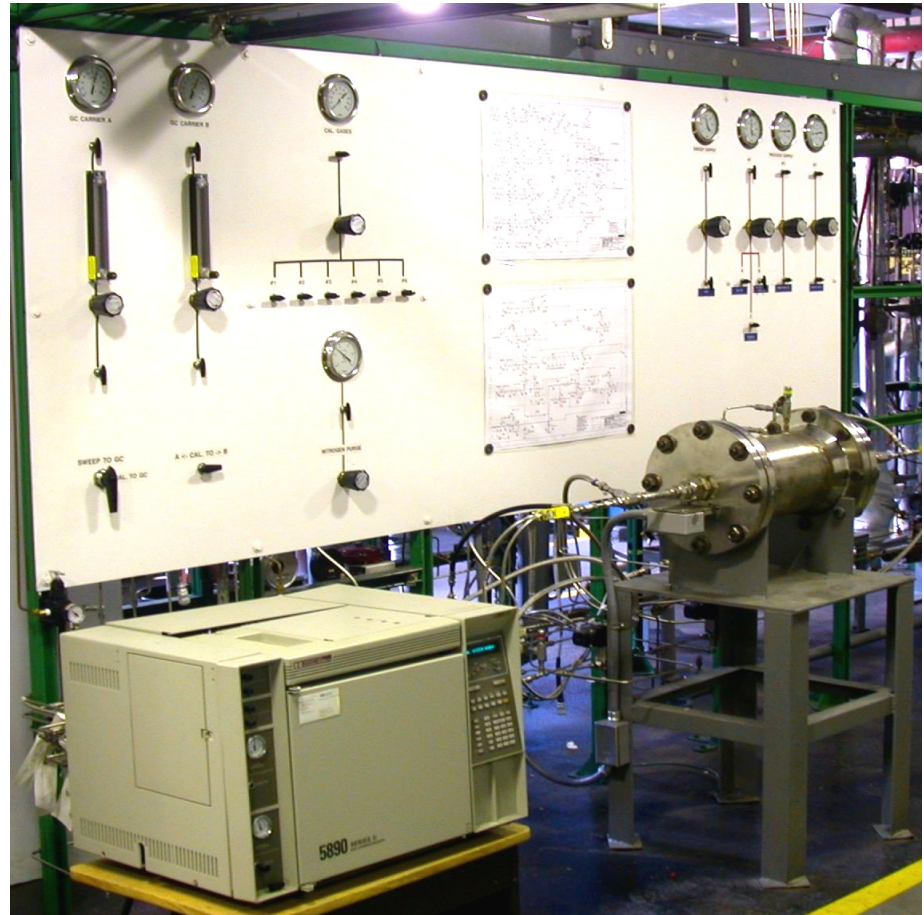
## Approach

- **Task 1. WGS Membrane Reactors** -- a) determine the optimum MR configuration and sweep rate for steady-state testing, b) evaluate performance of Pd & Pd-Cu MRs over a range of conditions, c) examine effect of H<sub>2</sub>S on MR performance
- **Task 2. Pd-Cu Membranes** -- a) determine effect of Cu content on S resistance, b) evaluate effect of S concen. and exposure on Pd-Cu permeability, and c) initiate study of non-S impurities on Pd-Cu permeability.
- **Task 3. Novel H<sub>2</sub> Production and Separation** -- a) CO<sub>2</sub> permeable membranes for separating CO<sub>2</sub> and H<sub>2</sub>, b) ternary membrane materials that are contaminant resistant, and c) performance testing of novel membranes from external membrane developers.

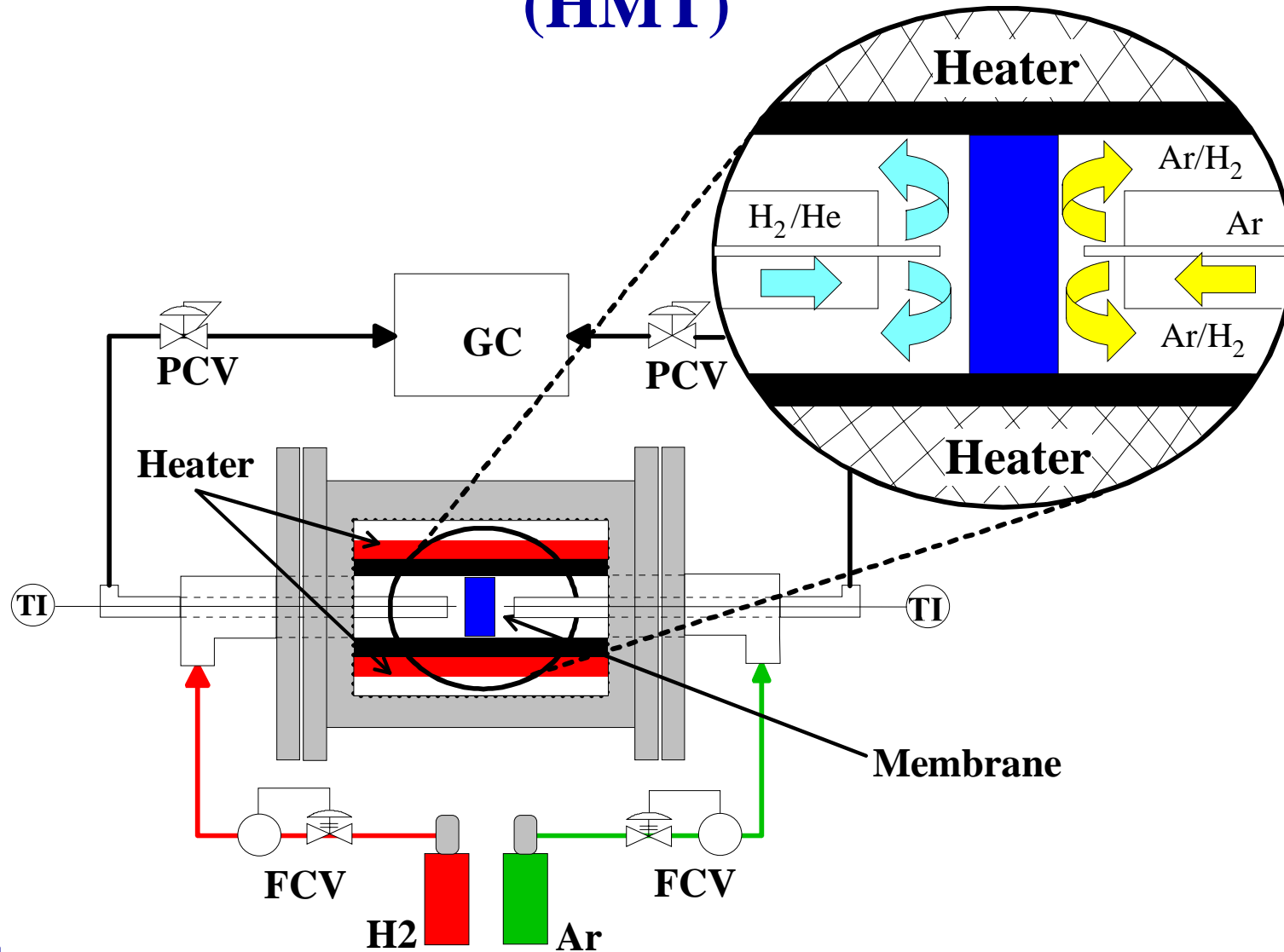


# NETL Hydrogen Separation Facilities

- 3 H<sub>2</sub> Membrane Test Units
- Temperatures to 900°C
- Pressures to 400 psi
- Disk & tubular membranes
- 1/4" to 1/2" membranes
- Membrane separation & reactor configurations
- “Clean” and “sulfur-laden” gas feedstocks
- Online analysis of products by GC
- 2 Membrane Screening Systems for unsteady state or exposure tests



# NETL Hydrogen Membrane Testing Unit (HMT)





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# Technical Accomplishments

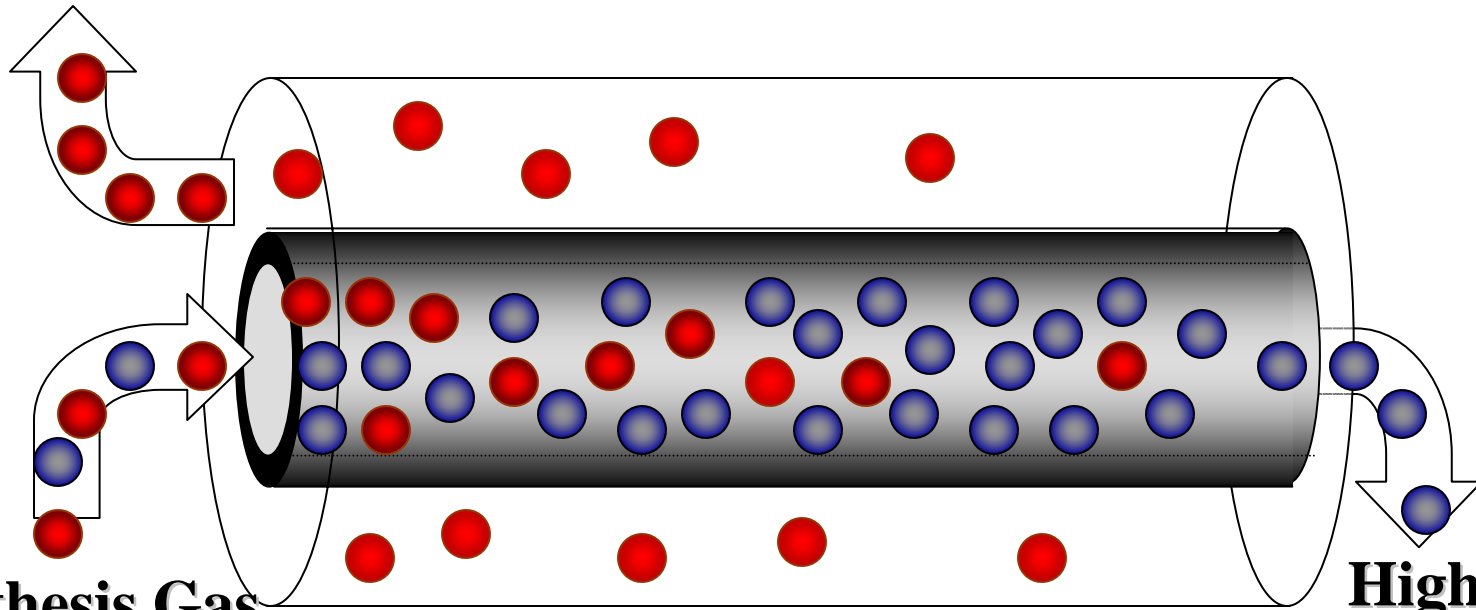
## Task 1—WGS Membrane Reactors

- **Effect of H<sub>2</sub>O on Pd-Cu Permeability:**
  - Water (steam) was shown to have a negligible effect on H<sub>2</sub> permeance through the Pd(80)-Cu(20) membrane.
  - The membrane surfaces were pitted after exposure to H<sub>2</sub>O.
- **Effect of CO on Pd-Cu Permeability:**
  - CO was observed to slightly reduce H<sub>2</sub> permeance at **T < 350** and **T > 765°C**
  - CO, or the byproducts produced from CO, was shown to have little or no effect on H<sub>2</sub> permeance of Pd(80)-Cu(20) at 475°C.
  - However, at **T ~ 635°C** significant permeance reduction is observed. This is probably due to the deposition of carbon, the formation of which is strong at this temperature.
  - Pitting was also observed after exposure to CO.



# WGS Membrane Reactor Concept

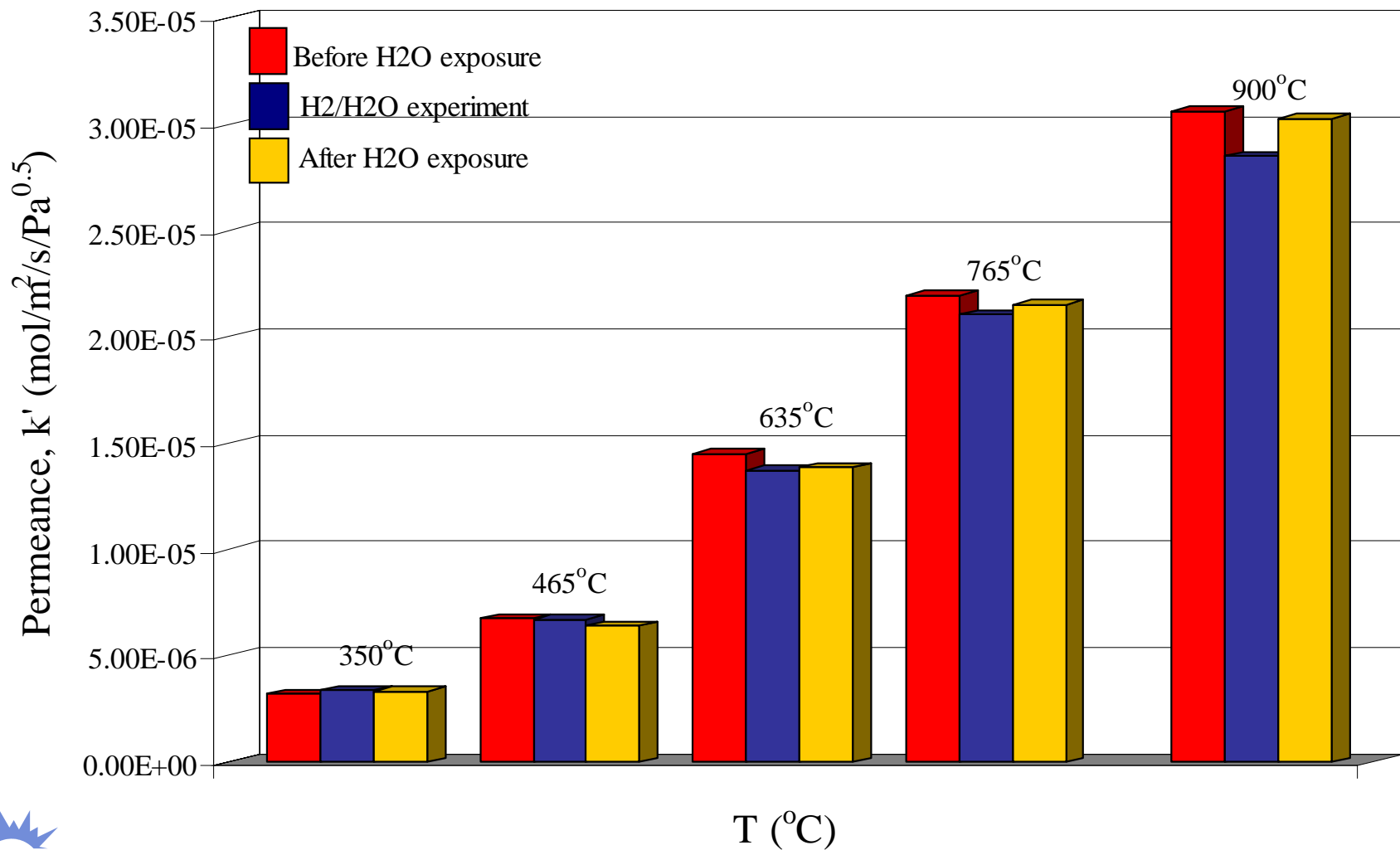
**Pure  
Hydrogen**



**Synthesis Gas**  
( $H_2$ ,  $CO_2$ ,  $CO$ ,  
 $H_2O$ , Impurities)

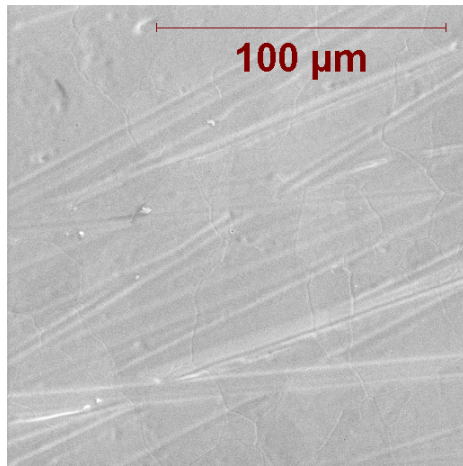
**High  
Pressure  $CO_2$**

# Effect of H<sub>2</sub>O on Permeability of Pd(80)-Cu(20)

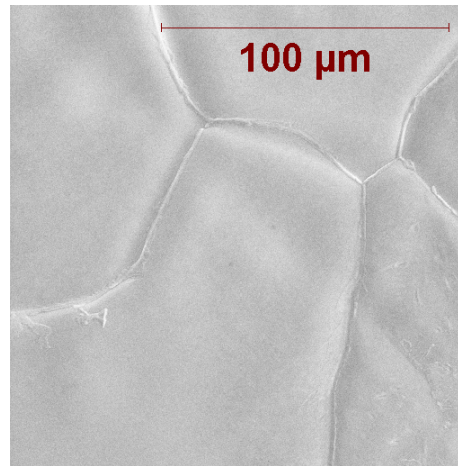


# Effect of H<sub>2</sub>O on Surface Morphology of 1mm Pd(80)-Cu(20)

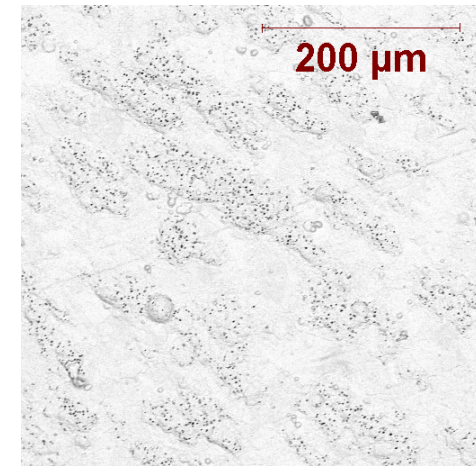
## SEM/EDS Analysis



Fresh sheet



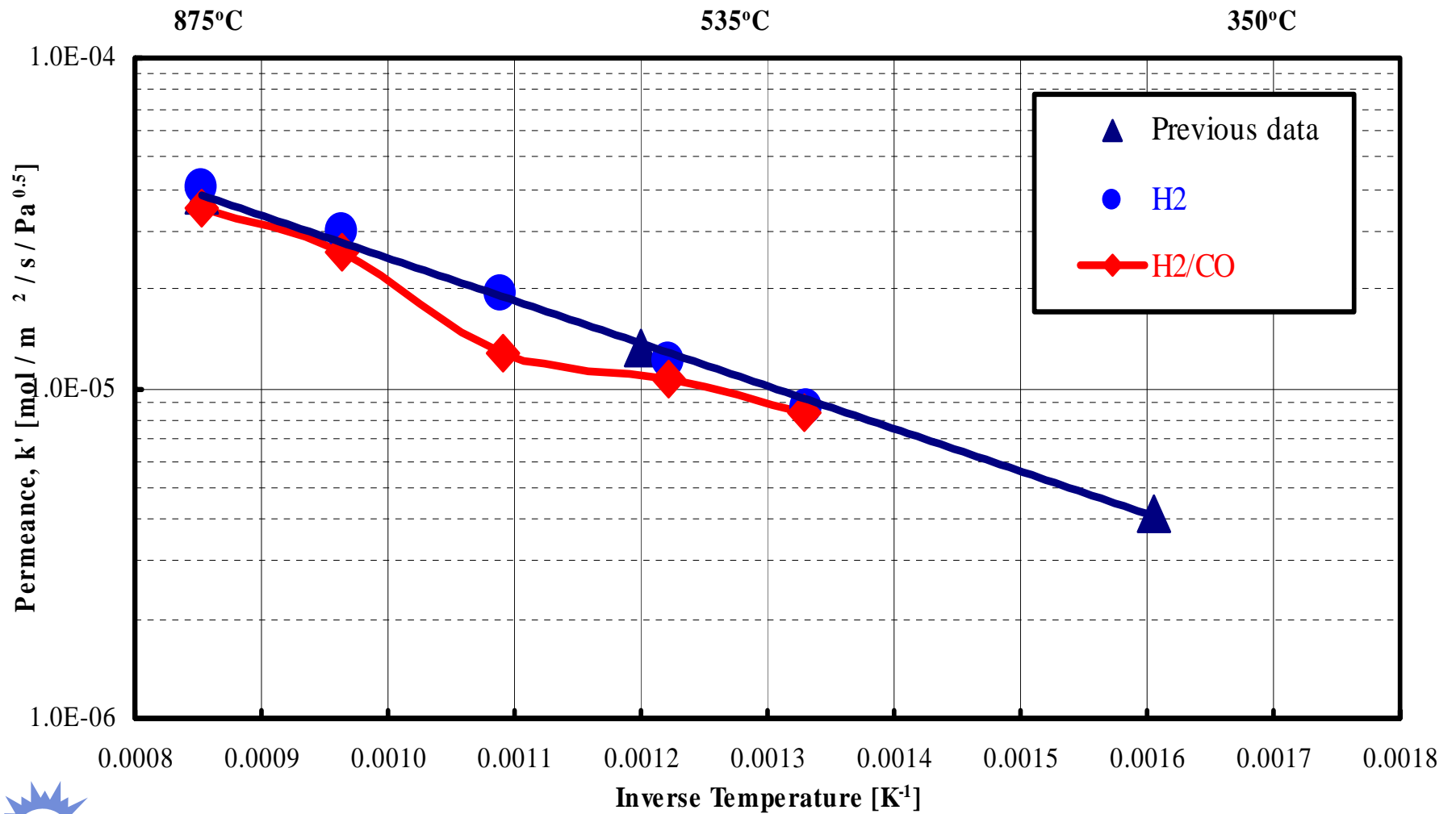
After H<sub>2</sub> exposure



After H<sub>2</sub>O exposure  
(50:50 H<sub>2</sub>:H<sub>2</sub>O at  
350 – 900°C and 75–400 psig)

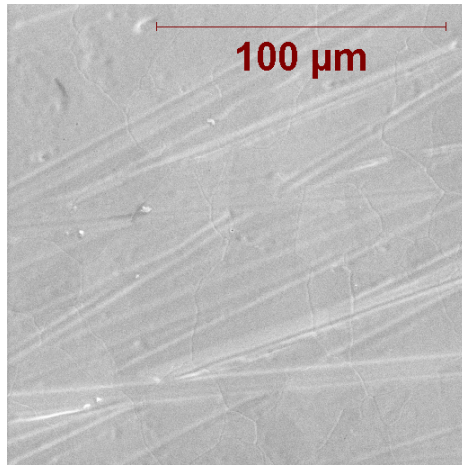
- \* Roughening/pitting of the Pd-Cu surface is observed after exposure to steam
- \* Research on “pitting” depth versus exposure time underway

# Effect of CO on Pd(80)-Cu(20)

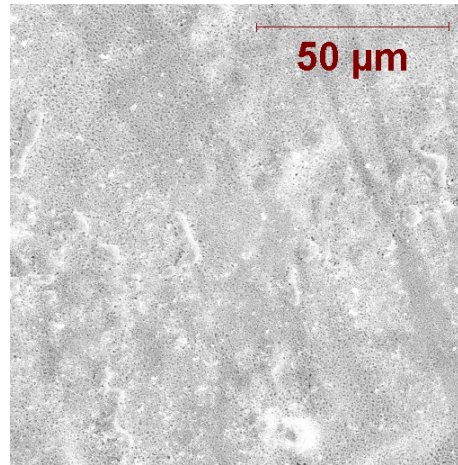


# Effect of CO on Surface Morphology of 1mm Pd(80)-Cu(20)

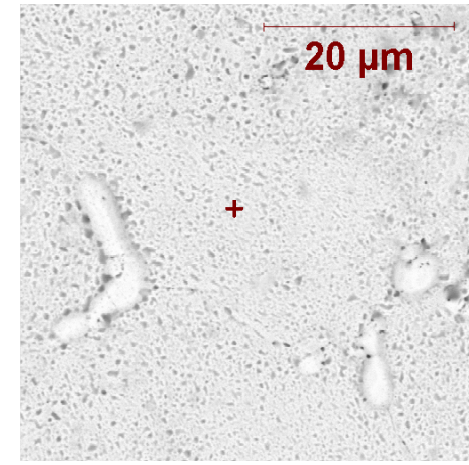
## SEM/EDS Analysis



SEM micrograph of fresh sheet



SEM micrograph of membrane surface after CO exposure (H<sub>2</sub>/CO at 75 psig and 465, 635, 765 and 900°C)



- \* Roughening/pitting of the Pd-Cu surface is observed after exposure to CO
- \* Research on “pitting” depth verses exposure time underway

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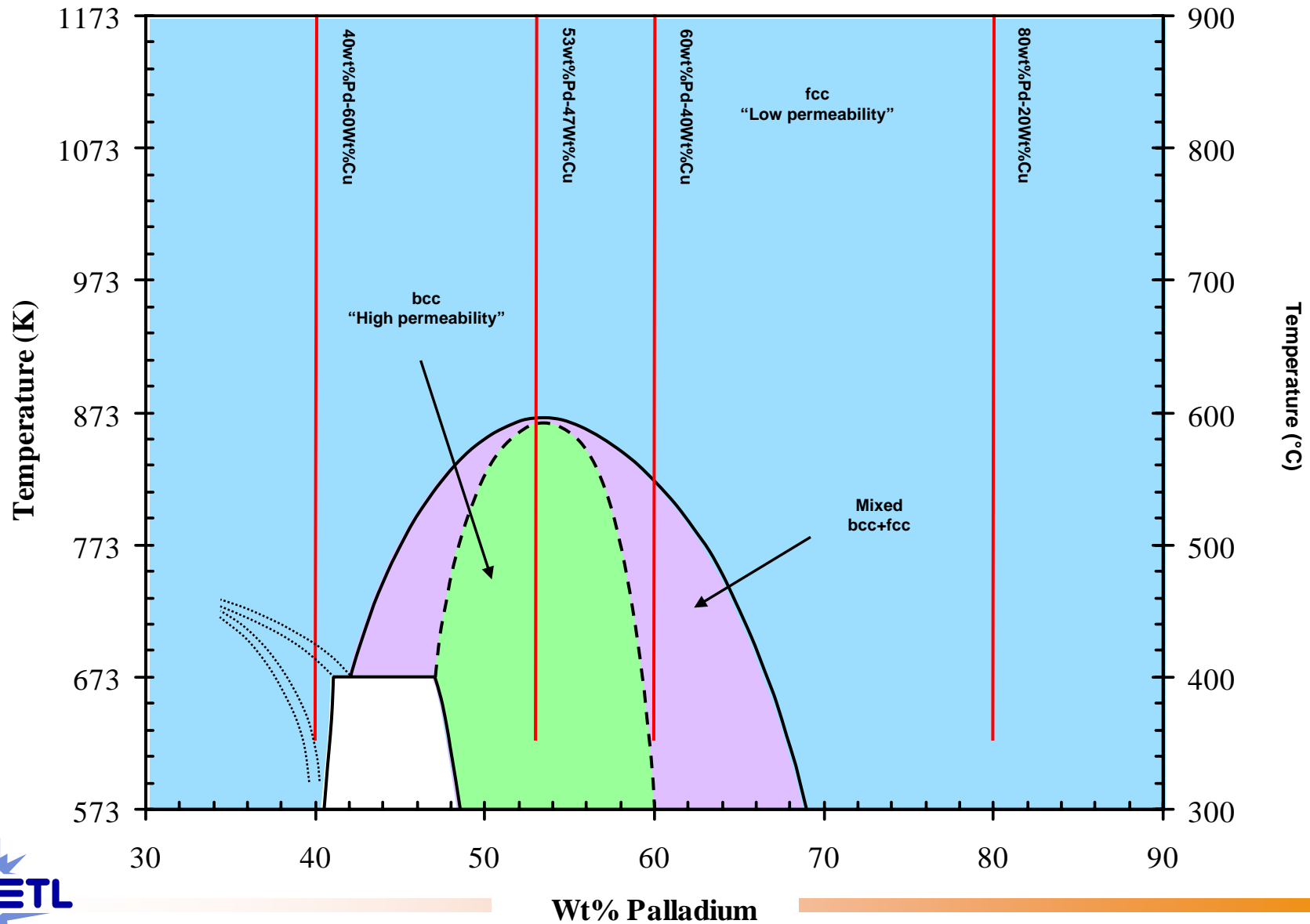
# Technical Accomplishments

## Task 2—Pd-Cu Membranes

- **Effect of H<sub>2</sub>S on Pd-Cu Permeability:**
  - The fcc phase of Pd-Cu alloys was shown to be resistant to H<sub>2</sub>S with respect to permeance.
  - Information on effect of S on surface morphology is still being gathered

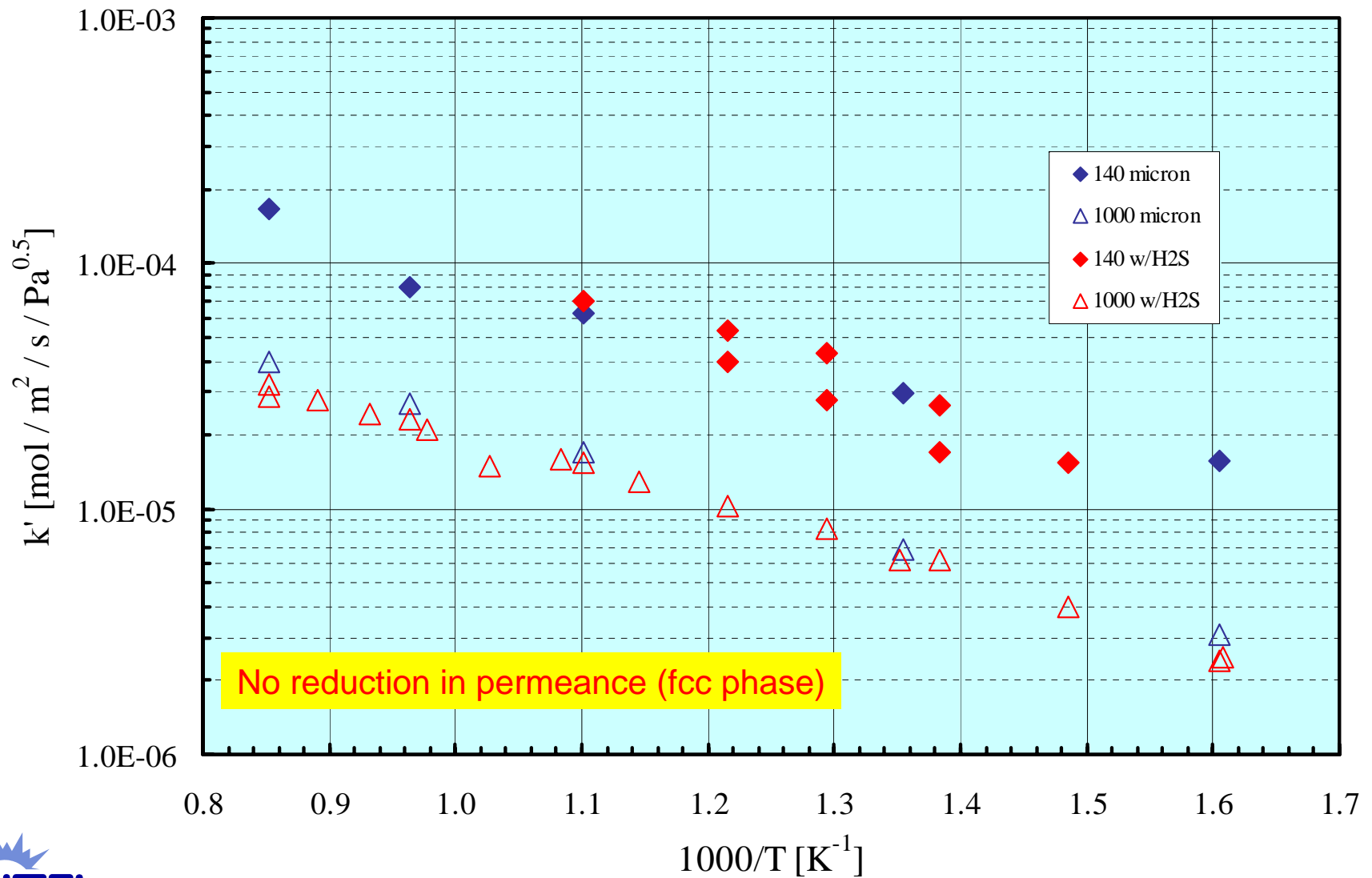


# Pd-Cu Alloy Phase Diagram

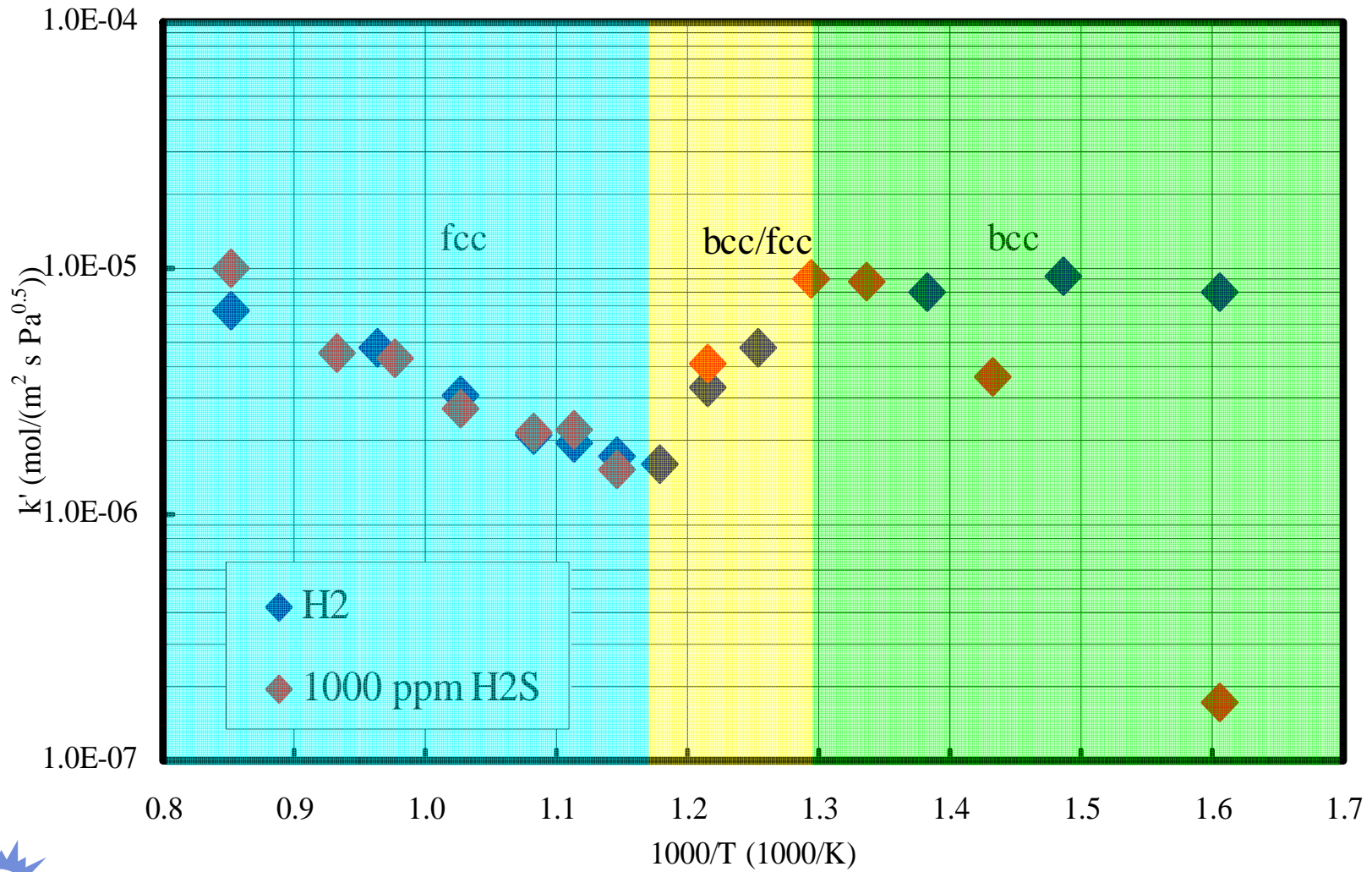




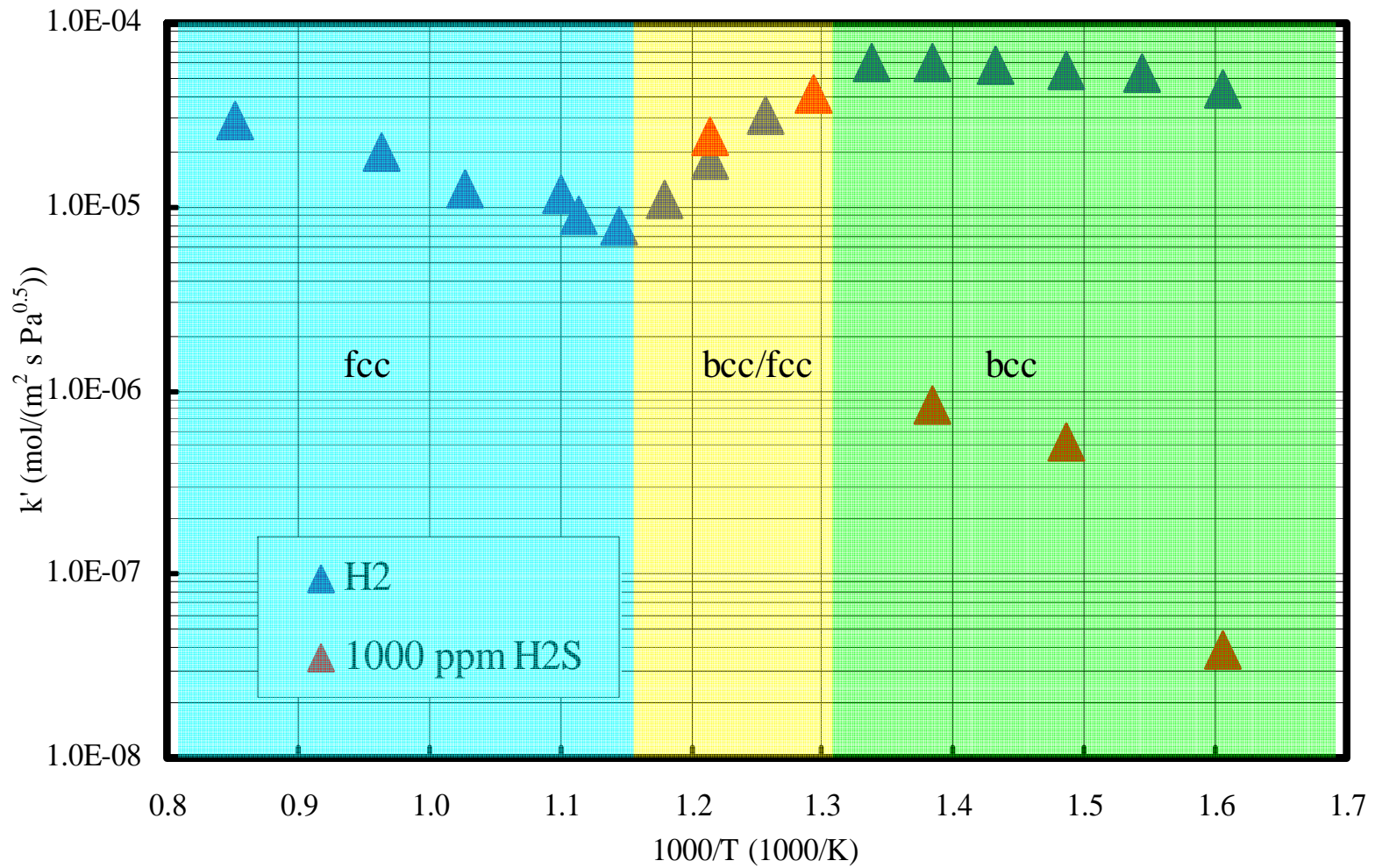
# Pd(80)-Cu(20)



# Pd(60)-Cu(40), 1000 $\mu$ m



# Pd(60)-Cu(40), 100 $\mu$ m



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# **Technical Accomplishments**

## **Task 3—Novel H<sub>2</sub> Production and Separation**

- **Preliminary permeability tests were completed with a Pd-based ternary alloy. Flux results compared to Pd, but no data on S resistance yet.**
- **Initiated experiments in a laboratory sulfur exposure chamber--Pd-Cu alloys (100 to 0% Pd) at 350, 450, 765°C for 1 h to 7 d under H<sub>2</sub> and 1000 ppm H<sub>2</sub>S. SEM-EDS and XRD to observe the effect of sulfur exposure on the alloy.**
- **Completed or planning membrane performance tests in collaboration with ANL, ORNL, Eltron, and Synkera.**



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# Responses to Reviewers' Comments Last Year

- This project was not reviewed last year



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## Future Work

- Determine temperature and time dependence of membrane pitting in the presence of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}$ .
- Conduct testing on the influence of other contaminants, such as  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{HCl}$  on Pd-Cu alloy membranes.
- Conduct WGS membrane reactor tests in fabricated Pd(80)-Cu(20) helical coils
- Conduct WGS MR experiments in the presence of  $\text{H}_2\text{S}$
- Determine the mechanism of sulfur poisoning and resistance of Pd-Cu alloys



# 2004-05 Publications and Presentations

- ✓ K. Rothenberger et al., "Permeability of WPI's Pd-Coated Stainless Steel Membrane", Journal of Membrane Science, V244, pp55-68,07/04.
- ✓ F. Bustamante et al., "Kinetics of the Uncatalyzed Reverse WGS Reaction at Elevated Temperature and Pressure", AIChE Journal, Vol. 50, No. 4, 04/04.
- ✓ B. Howard et al., "H<sub>2</sub> Permeability of Supported Pd-Cu Alloy Membranes Over a Wide Range of Temperature and Pressure," Journal of Membrane Science, V241/2, pp207-218, 04/04.
- ✓ B. Morreale et al., "Effects of Sulfur on H<sub>2</sub> Permeability of Pd-Cu at Unsteady State," Journal of Membrane Science, V241/2, pp219-224, 04/04.
- M. Ciocco et al., "Sulfur Resistance of Pd-Cu Membranes," International Technical Conference on Coal Utilization and Fuel Systems, Clearwater FL, 04/04.
- F. Bustamante et al., "Conducting the Hi-T, Hi-P WGS in a Pd Membrane Reactor," Int'l Technical Conference on Coal Utilization and Fuel Systems, Clearwater FL, 04/04.
- R. Enick et al., "Conducting the Homogeneous WGS in a Pd-Cu Alloy Membrane Reactor at High T & P," National Hydrogen Association Conference, Los Angeles CA, 04/04.
- R. Killmeyer et al., "WGS Membrane Reactor Studies," poster in proceedings--EERE Annual Review, Philadelphia PA, 05/04.
- ✓ F. Bustamante et al., "Kinetics of the Hi-T Forward WGS Reaction in an Empty Quartz Reactor and Quartz Reactors Packed with Inconel, Pd or Pd-Cu," in press, AIChE Journal, 04/05.
- ❖ B. Howard, B. Morreale– submitted Record of Invention for discovery of correlation between S tolerance and crystalline structure of Pd-Cu, 04/04
- K. Rothenberger et al., "High Pressure Permeance of Porous Stainless Steel Coated with a Thin Pd Film via Electroless Plating", Journal of Membrane Science, Vol. 244, pp. 55-68, 11/04.
- O. Iyoha et al., "Conducting the Hi-T, Hi-P WGS Reaction in Pd and Pd-based Reactors," presentation only--AIChE Meeting, Austin TX, 11/04.
- K. Rothenberger et al., "Exper. & Comp. Chemistry Approaches to Develop Advanced H<sub>2</sub> Separation Membranes," presentation only--Pittsburgh-Cleveland Catalysis Soc., Pittsburgh PA, 12/04.
- P. Kamakoti et al., "1st Principles Predictions of H<sub>2</sub> Flux Thru Sulfur-Tolerant Dense Binary Alloy Membranes," Science, Vol. 307, January 28, 2005.
- K. Rothenberger et al., "An Analytical Scheme for Evaluation of H<sub>2</sub> Permeability in Metals at High T&P," poster only--PITTCO 2005, Orlando FL, 02/05.
- K. Rothenberger et al., "Summary of Pd-Cu Testing in the Presence of H<sub>2</sub>S," National Hydrogen Association Conference, Arlington VA, 03/05

Indicates refereed journal paper



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# Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is:**
  - A continuous leak of hydrogen from one of our test units
- **Our approach to deal with this hazard is:**
  - All H<sub>2</sub>-related reactors are contained in purge vessels through which an inert gas (N<sub>2</sub>) is continually streaming and venting.
  - Gas alarm systems are in place in areas where gases such as H<sub>2</sub>, H<sub>2</sub>S, CO, CO<sub>2</sub>, etc. are in use.

