Hydrogen Separation

Richard Killmeyer, Bret Howard, Kurt Rothenberger, Michael Ciocco, Bryan Morreale, Robert Enick, Osemwengie Iyoha

National Energy Technology Laboratory (NETL)
Office of Science & Technology
Fuels and Process Chemistry Division

May 25, 2005

Project ID# PDP25

Overview

Timeline

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

Barriers

(from FE's H_2 from Coal RD&D Plan)

- WGS Reaction—Barrier E--Operating Limits
- H_2 Separation—Barriers H, I, J--Thermal Cycling, Impurity Intolerance, & Undesired Atomic Rearrangement

Budget

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

Partners

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

Background

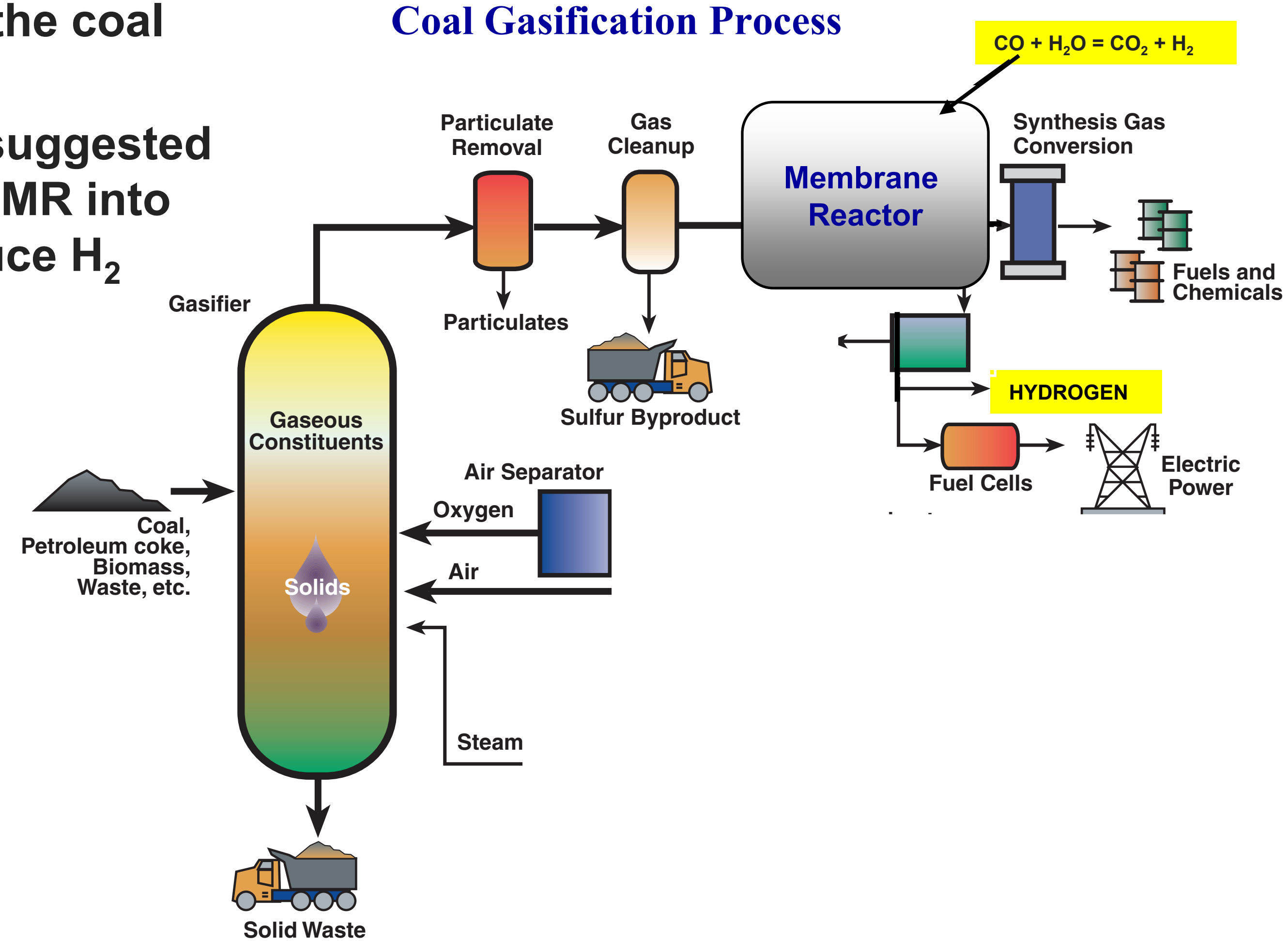
- Overall goal of project:

  Integrate a MR into the coal gasification process

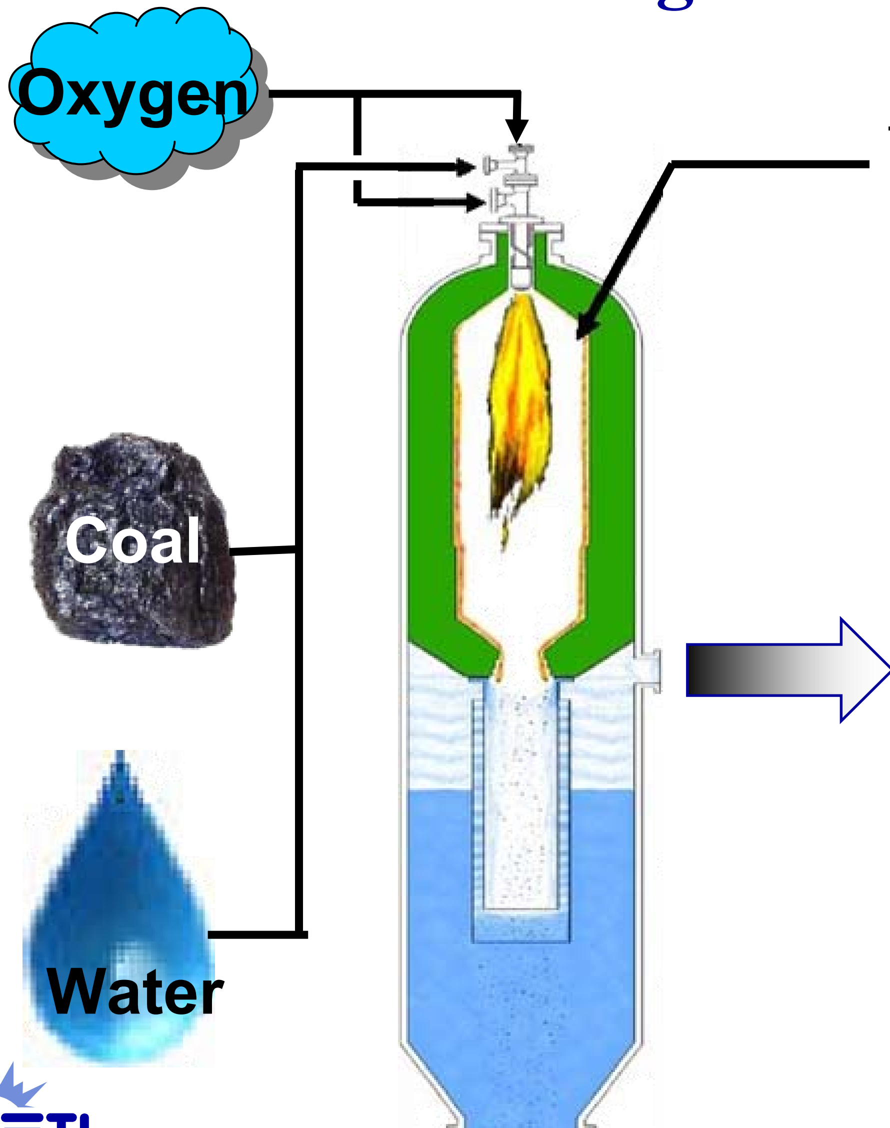
- NETL studies have suggested that incorporating a MR into the gasifier can reduce H_2 cost by up to 30%

  ("H_2 from Coal", D. Gray, Mitretek, 07/02)

Coal Gasification Process



Background (Cont.)



Extreme Conditions:

- 1,000 psig or more
- ~1400^{o}C
- Corrosive slag and H_2S gas

Typical composition of O_2 blown coal gasifiers

	Texaco	Shell	Dow
H_2 vol %	35.1	30.1	41.4
CO vol %	51.8	66.2	38.5
CO_2 vol %	10.6	2.5	18.5
CH_4 vol %	0.1	2.5	0.1

H_2S	0.2 – 1%
COS	0 - 0.1%
N_2	0.5 – 4%
Ar	0.2 – 1%
NH_3,HCN, HCl	0 - 0.3%

Ash/Slag/PM

T. Golden et al., Ind. Eng. Chem. Res. 1991, 40, 502-507

Objectives

- Task 1. WGS Membrane Reactors -- demonstrate that a Pd-Cu membrane reactor (MR) can enhance CO conversion of the fWGSR and recover H_2 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_3, COS) on permeability.
- Task 3. Novel H_2 Production and Separation-- conduct exploratory research in new areas related to hydrogen.

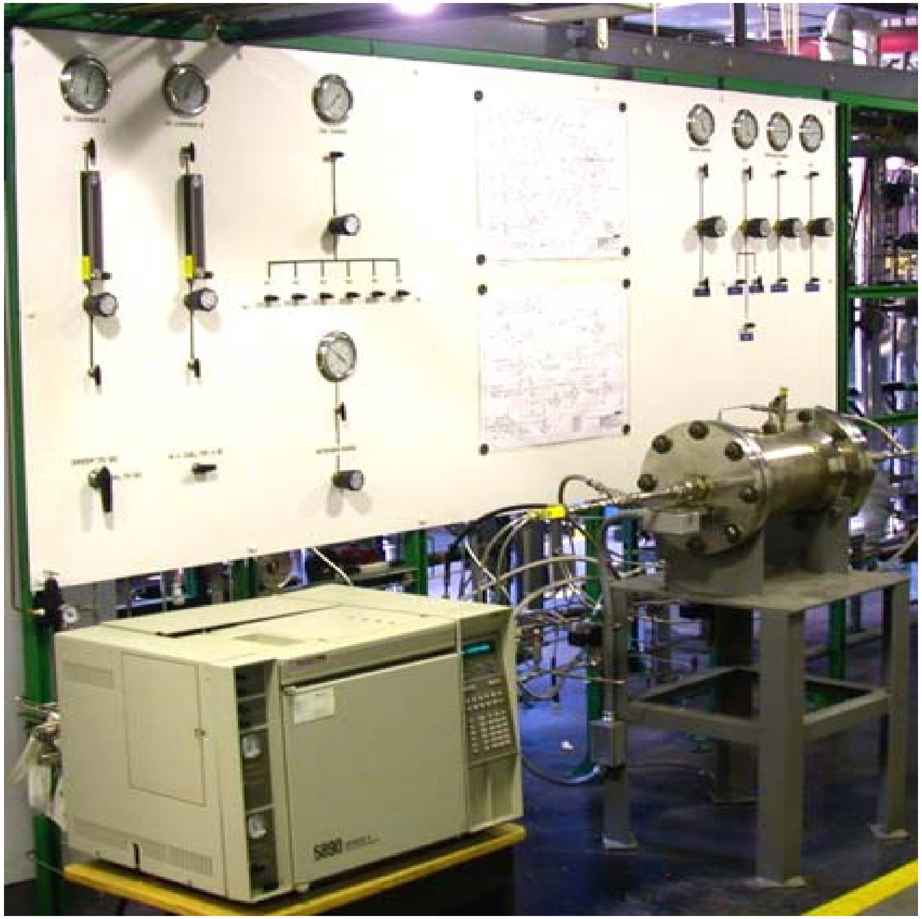
Approach

- *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_2S 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_2 Production and Separation* -- a) CO_2 permeable membranes for separating CO_2 and H_2, b) ternary membrane materials that are contaminant resistant, and c) performance testing of novel membranes from external membrane developers.

NETL

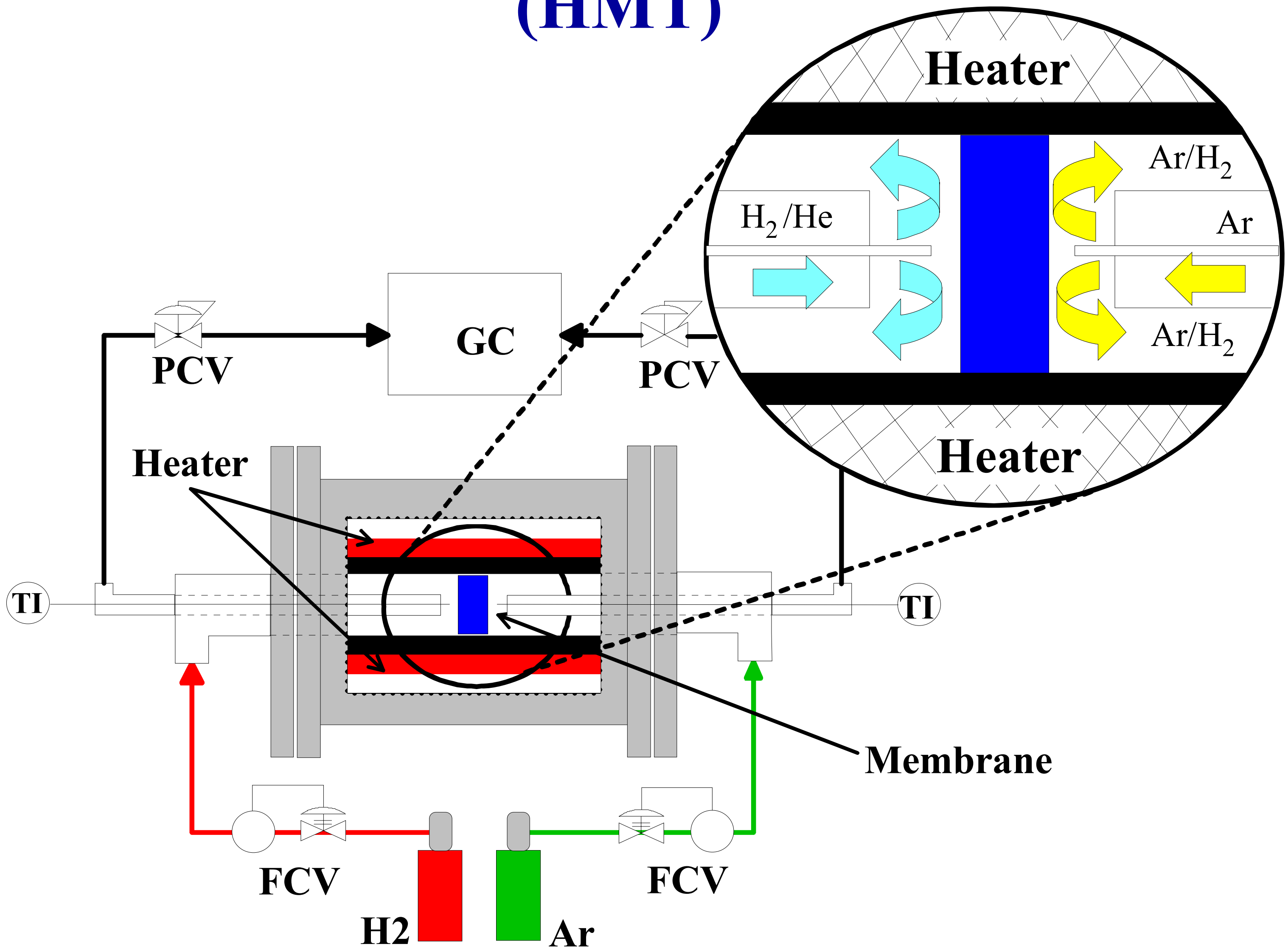
NETL Hydrogen Separation Facilities

- 3 H_2 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

NETL Hydrogen Membrane Testing Unit (HMT)

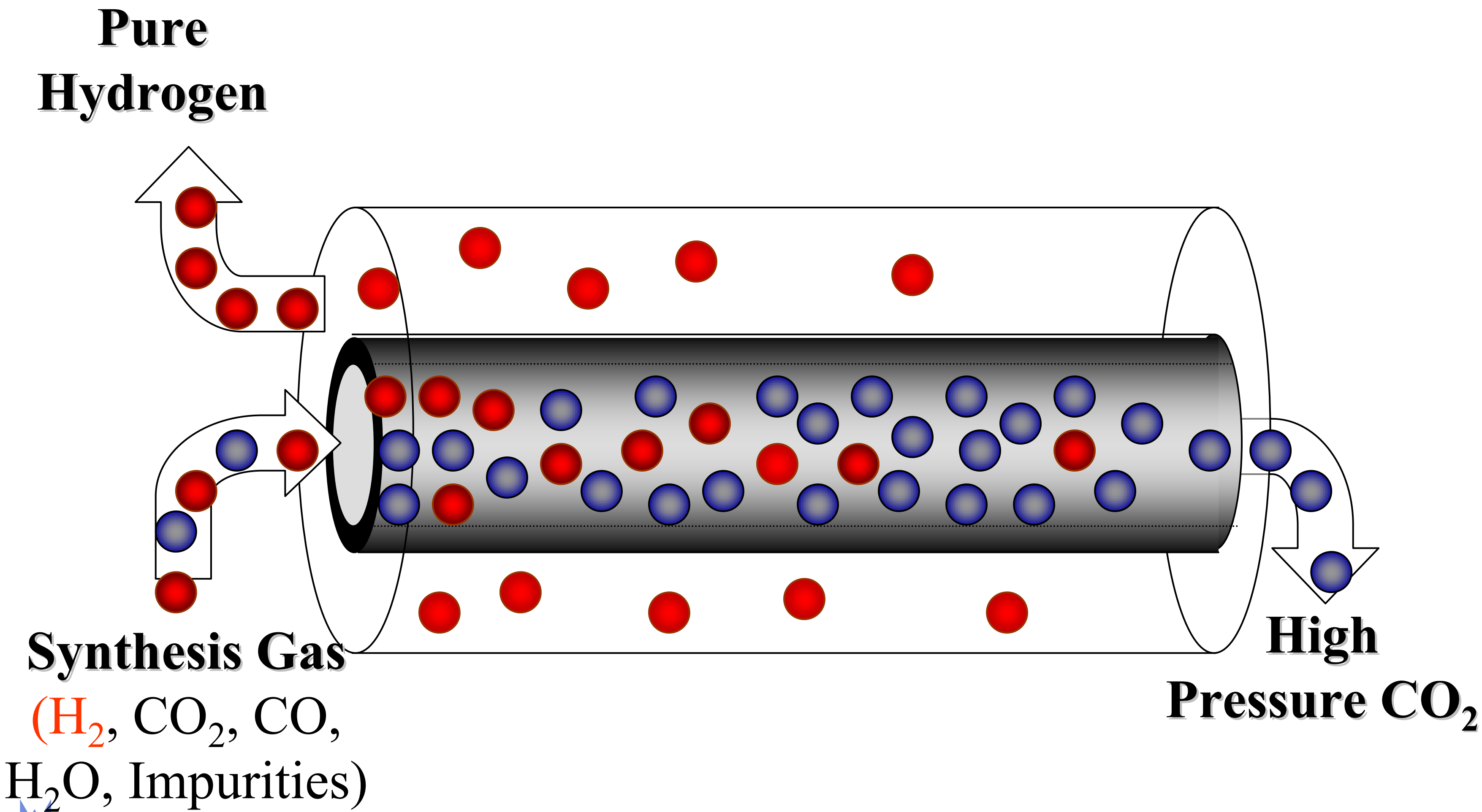


Technical Accomplishments
Task 1—WGS Membrane Reactors

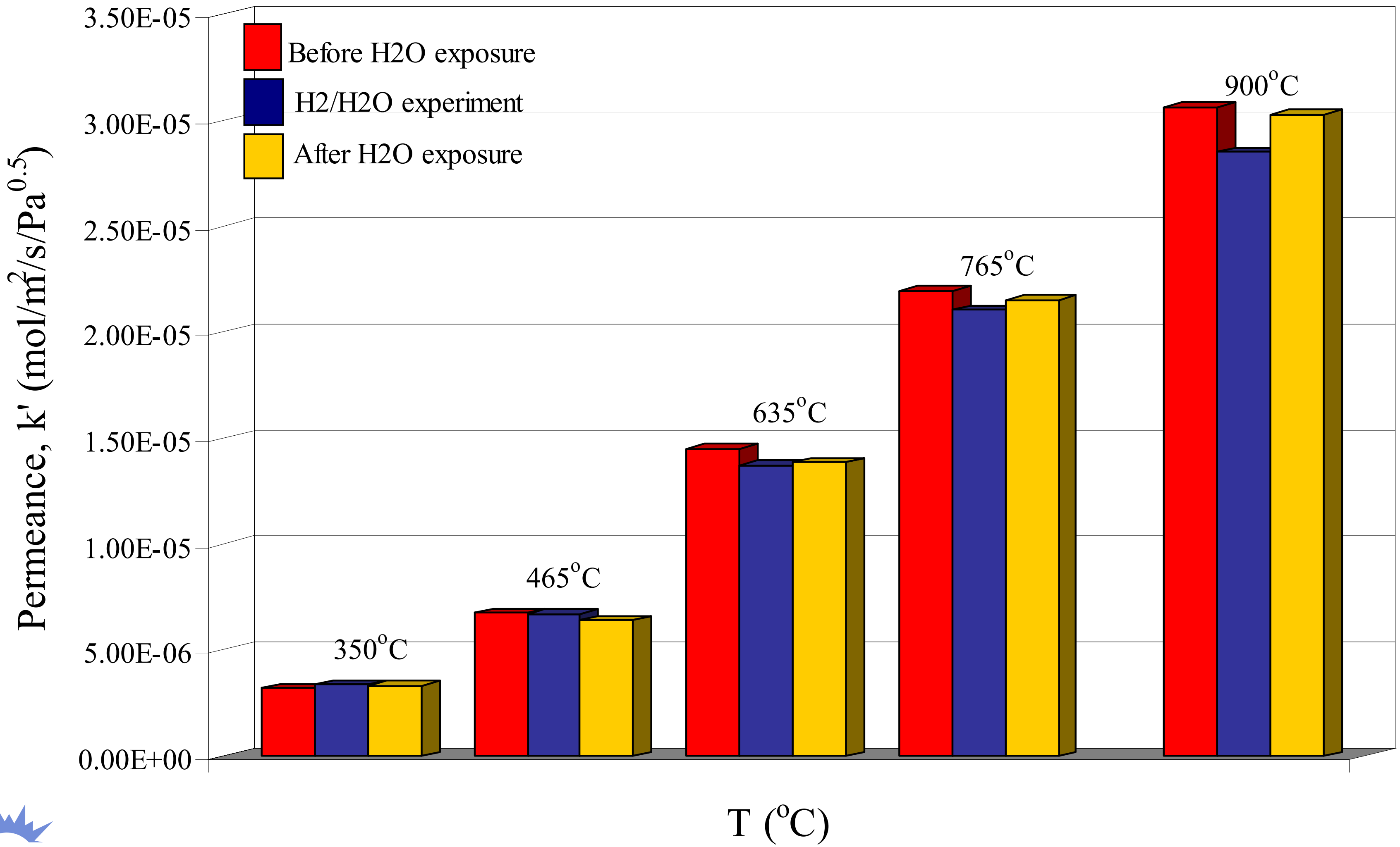
- **Effect of H_2O on Pd-Cu Permeability:**
  - Water (steam) was shown to have a negligible effect on H_2 permeance through the Pd(80)-Cu(20) membrane.
  - The membrane surfaces were pitted after exposure to H_2O.
- **Effect of CO on Pd-Cu Permeability:**
  - CO was observed to slightly reduce H_2 permeance at T**<350** and T**>765°C**
  - CO, or the byproducts produced from CO, was shown to have little or no effect on H_2 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.

NETL

WGS Membrane Reactor Concept

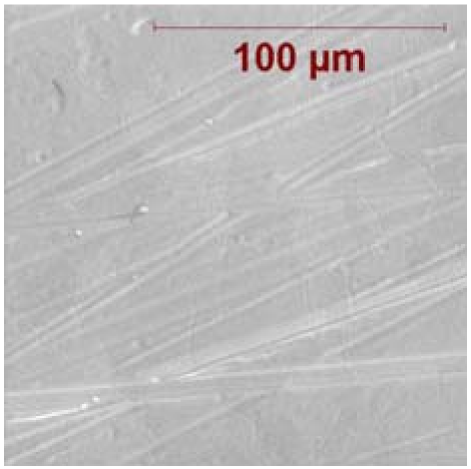


Effect of H_2O on Permeability of Pd(80)-Cu(20)

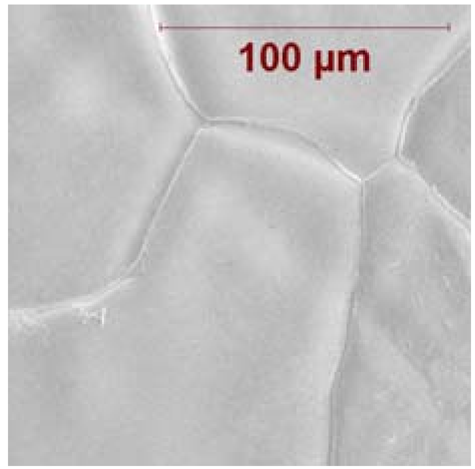


Effect of H_2O on Surface Morphology of 1mm Pd(80)-Cu(20)

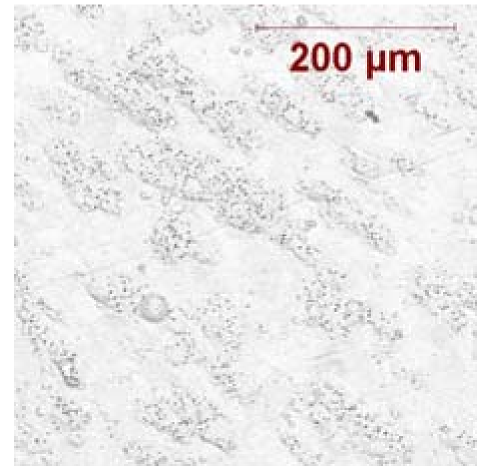
SEM/EDS Analysis



Fresh sheet



After H_2 exposure

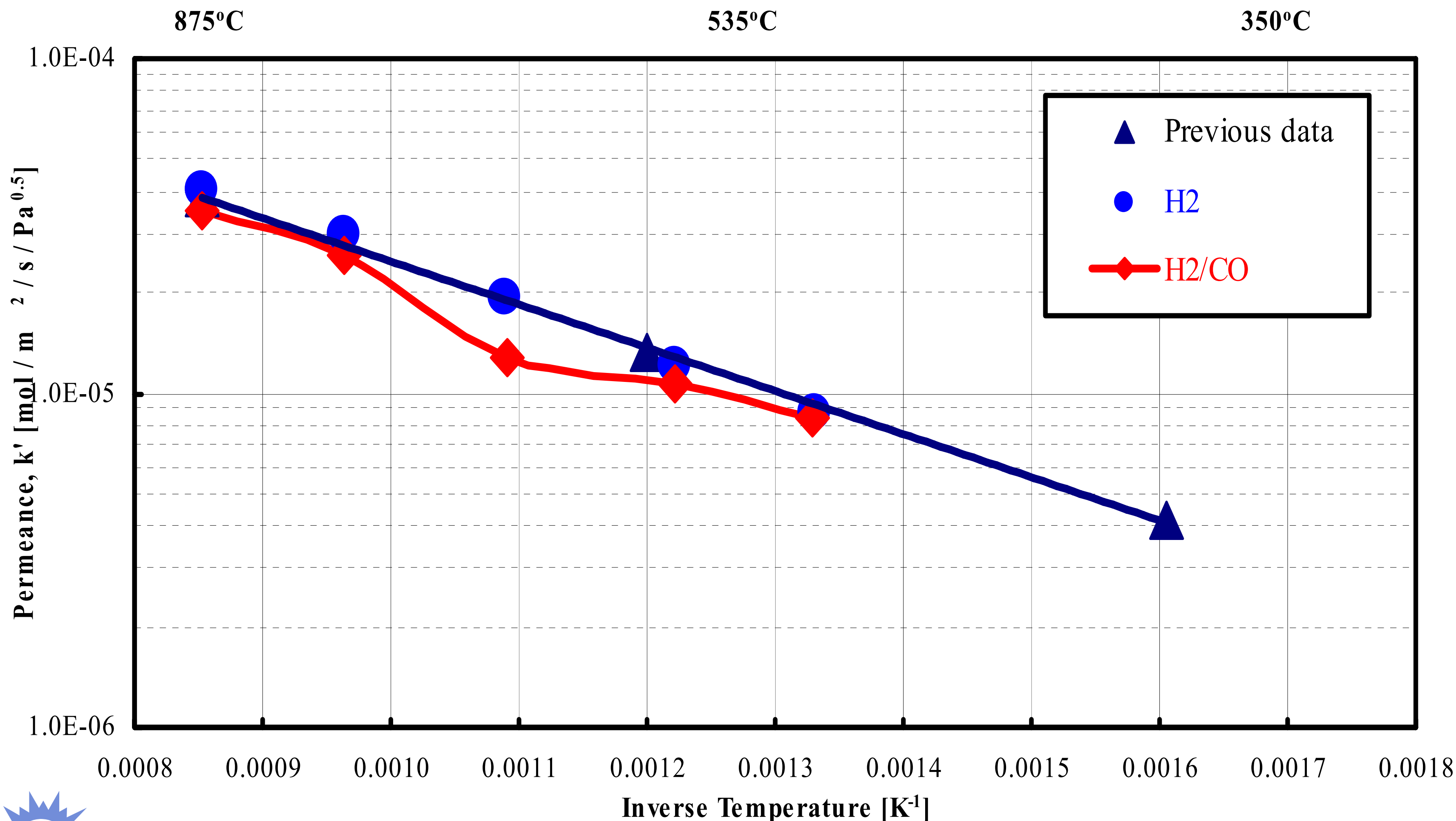


After H_2O exposure
(50:50 H_2:H_2O at
350 – 900°C and 75–400 psig)

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

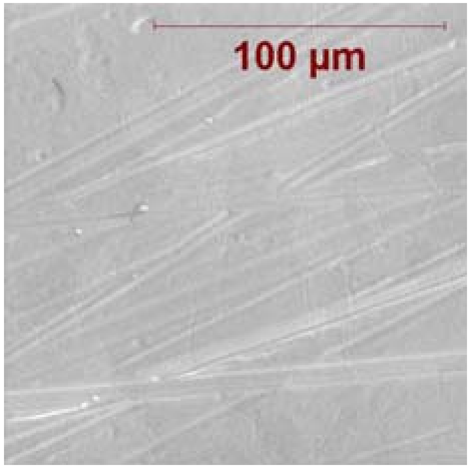
NETL

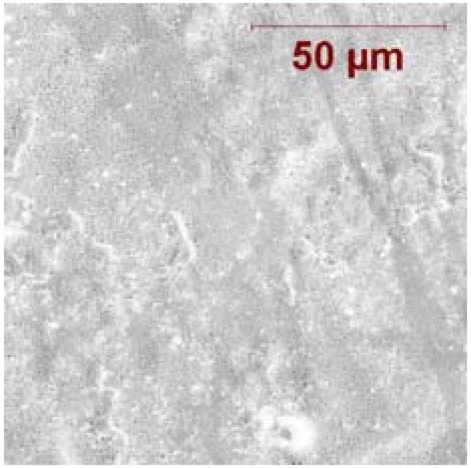
Effect of CO on Pd(80)-Cu(20)

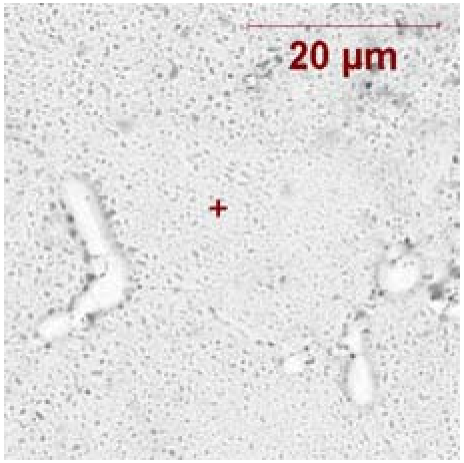


Effect of CO on Surface Morphology of 1mm Pd(80)-Cu(20)

SEM/EDS Analysis







SEM micrograph of fresh sheet

SEM micrograph of membrane surface after CO exposure (H_2/CO at 75 psig and 465, 635, 765 and 900°C)

*** Roughening/pitting of the Pd-Cu surface is observed after exposure to CO**

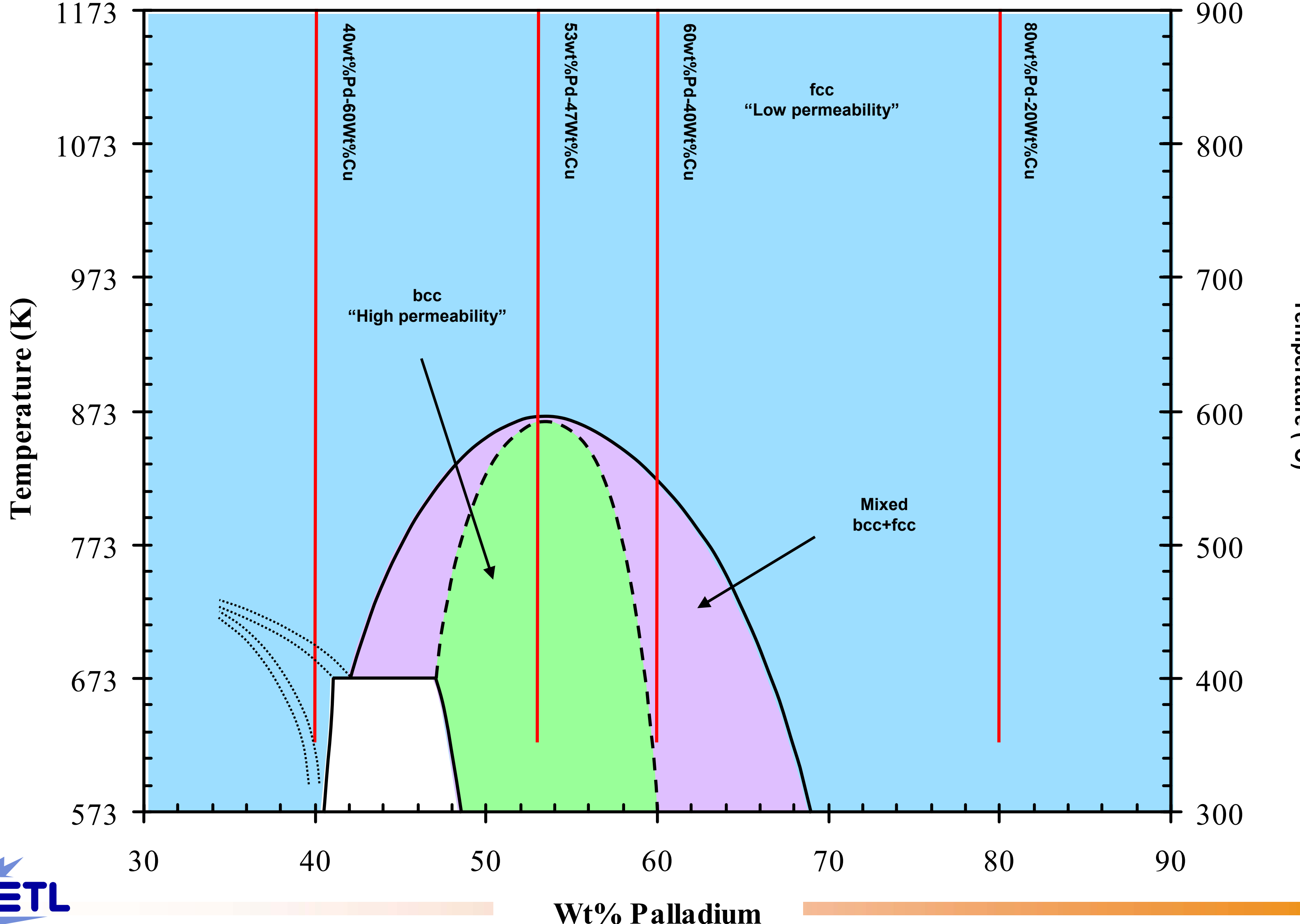
*** Research on "pitting" depth verses exposure time underway**

NETL

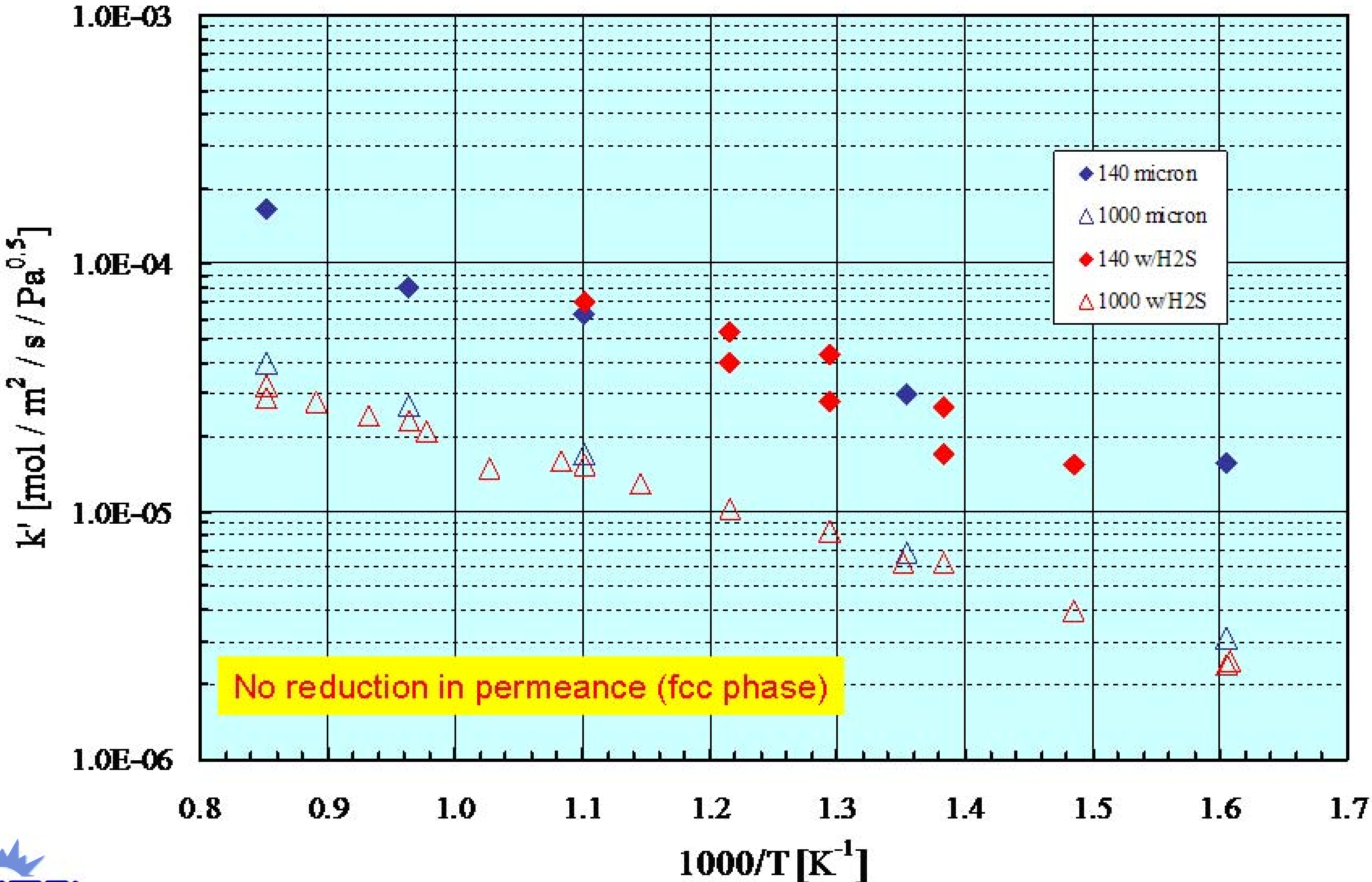
Technical Accomplishments
Task 2—Pd-Cu Membranes

- **Effect of H_2S on Pd-Cu Permeability:**
  - The fcc phase of Pd-Cu alloys was shown to be resistant to H_2S with respect to permeance.
  - Information on effect of S on surface morphology is still being gathered

Pd-Cu Alloy Phase Diagram

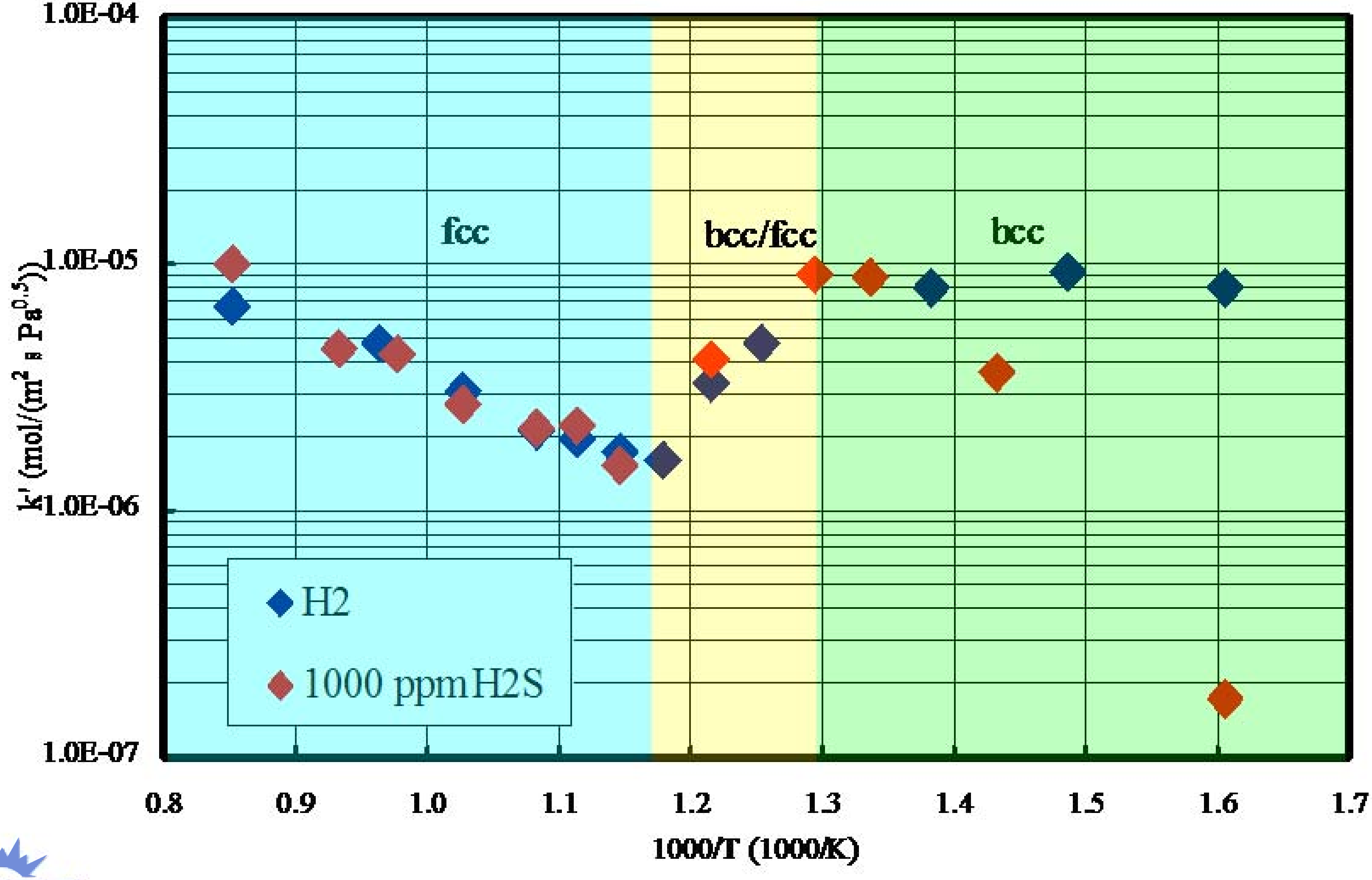


Pd(80)-Cu(20)

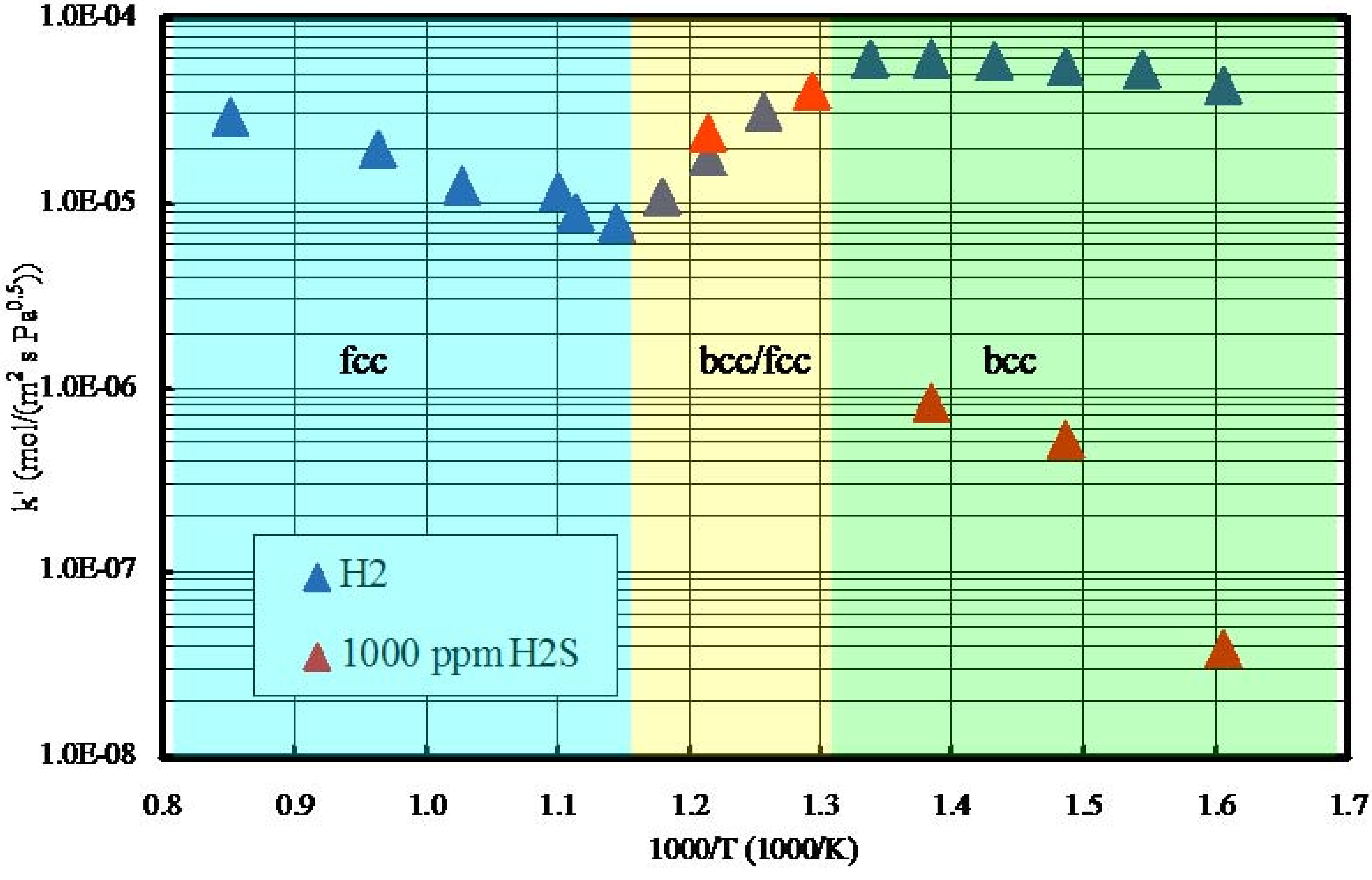


NETL

Pd(60)-Cu(40), 1000μm



Pd(60)-Cu(40), 100µm



Technical Accomplishments
Task 3—Novel H_2 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^{o}C for 1 h to 7 d under H_2 and 1000 ppm H_2S. 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.

Responses to Reviewers' Comments Last Year

- This project was not reviewed last year

Future Work

- Determine temperature and time dependence of membrane pitting in the presence of H_2S, H_2O, and CO.
- Conduct testing on the influence of other contaminants, such as CO_2, NH_3, and 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 H_2S
- Determine the mechanism of sulfur poisoning and resistance of Pd-Cu alloys

NETL

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., “H2 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 H2 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 WGSR 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 WGSR 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 H2 Separation Membranes,” presentation only--Pittsburgh-Cleveland Catalysis Soc., Pittsburgh PA, 12/04.
- P. Kamakoti et al., “1st Principles Predictions of H2 Flux Thru Sulfur-Tolerant Dense Binary Alloy Membranes,” Science, Vol. 307, January 28, 2005.
- K. Rothenberger et al., “An Analytical Scheme for Evaluation of H2 Permeability in Metals at High T&P,” poster only--PITTCON 2005, Orlando FL, 02/05.
- K. Rothenberger et al., “Summary of Pd-Cu Testing in the Presence of H2S,” National Hydrogen Association Conference, Arlington VA, 03/05

✓ **Indicates refereed journal paper**

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_2-related reactors are contained in purge vessels through which an inert gas (N_2) is continually streaming and venting.
  - Gas alarm systems are in place in areas where gases such as H_2, H_2S, CO, CO_2, etc. are in use.