The Hydrogen Permeability of Palladium-Copper Alloy Composite Membranes Over a Wide Range of Temperatures and Pressures

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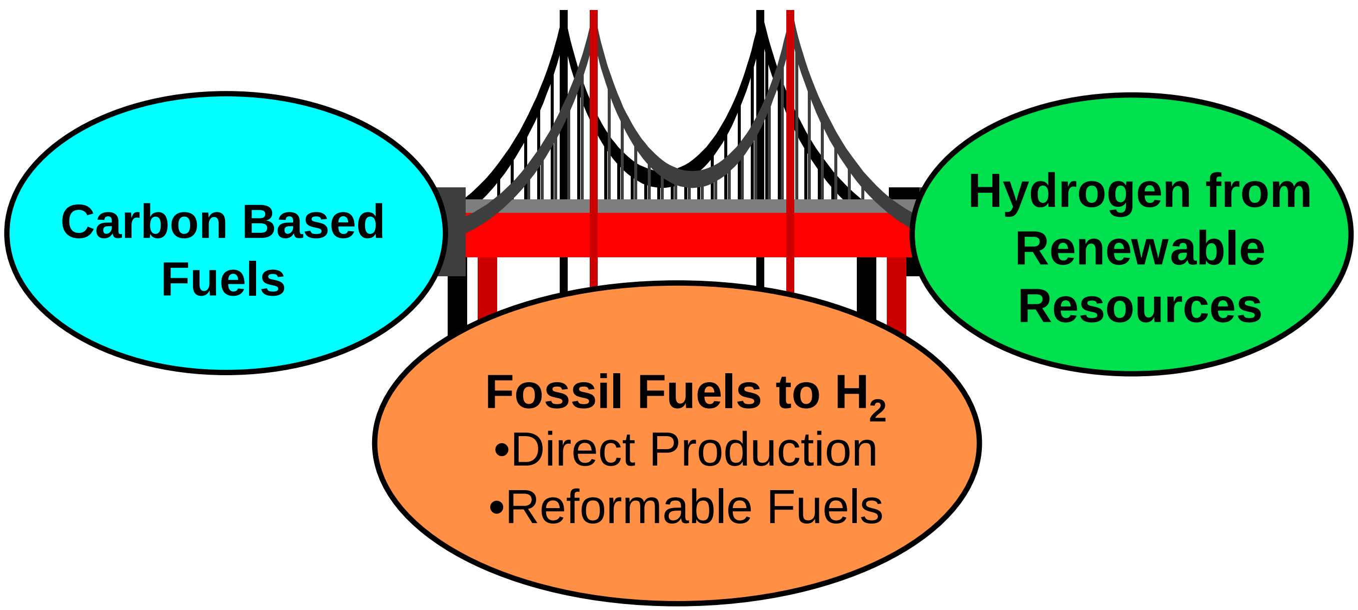
NETL's Hydrogen Separation Team

Vision

Fossil fuels are viewed as the transition feedstocks for the production of hydrogen in the "Hydrogen Economy".

Mission

Investigate technologies to produce and separate hydrogen for downstream uses, both in advanced energy plant applications and in off-site applications.



Pd is Not Appropriate for Post-Gasifier Membrane Reactor Conditions

Severe conditions are associated with coal gasification membrane reactors

- **Temperature range: 448-1173 K (175-900ºC)**
- **Pressure range: 1-7 MPa (145-1000 psi)**
- **Composition of Gasifier Effluent**
  - H_2, CO_2, CO, H_2O
    - H_2S (2000-10000 ppm): **known to poison Pd**
    - NH_3 + HCN (0-3000 ppm)
    - COS (0-1000 ppm)
    - CH_4 (0-50000 ppm)

Pd-Cu Alloys Have Been Proposed as Sulfur Resistant Hydrogen Membrane Materials

- **Certain Pd-Cu alloys have high permeability**
- **Certain Pd-Cu alloys may exhibit H_2S resistance**
- **Published literature focuses on the 60wt%Pd-40wt%Cu alloy at 623 K (350ºC), low H_2 partial pressure (0.1 MPa)**

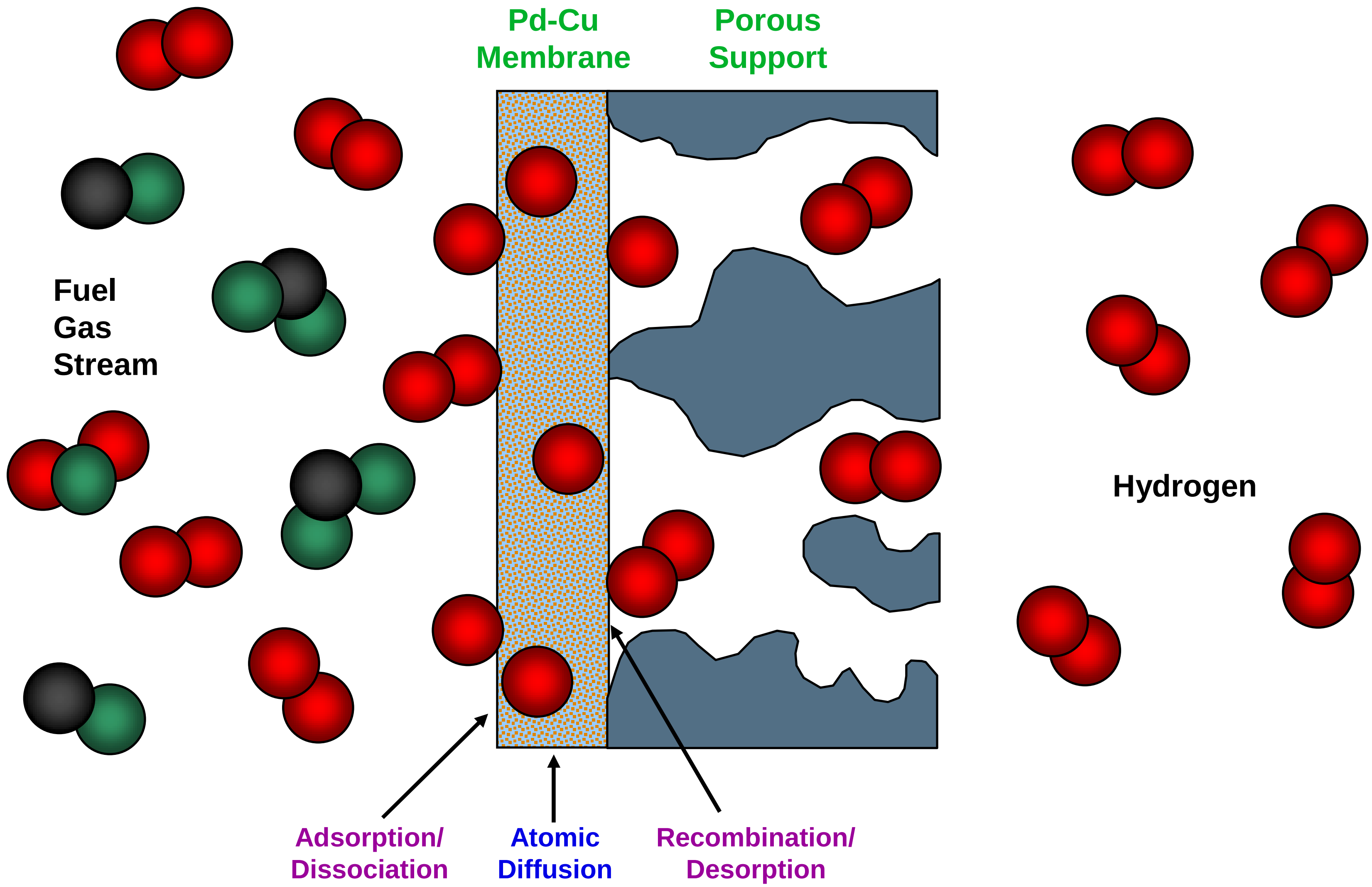
Project Objective

Evaluate the permeability of Pd-Cu alloys over a wide range of conditions encompassing those characteristic of gasification.

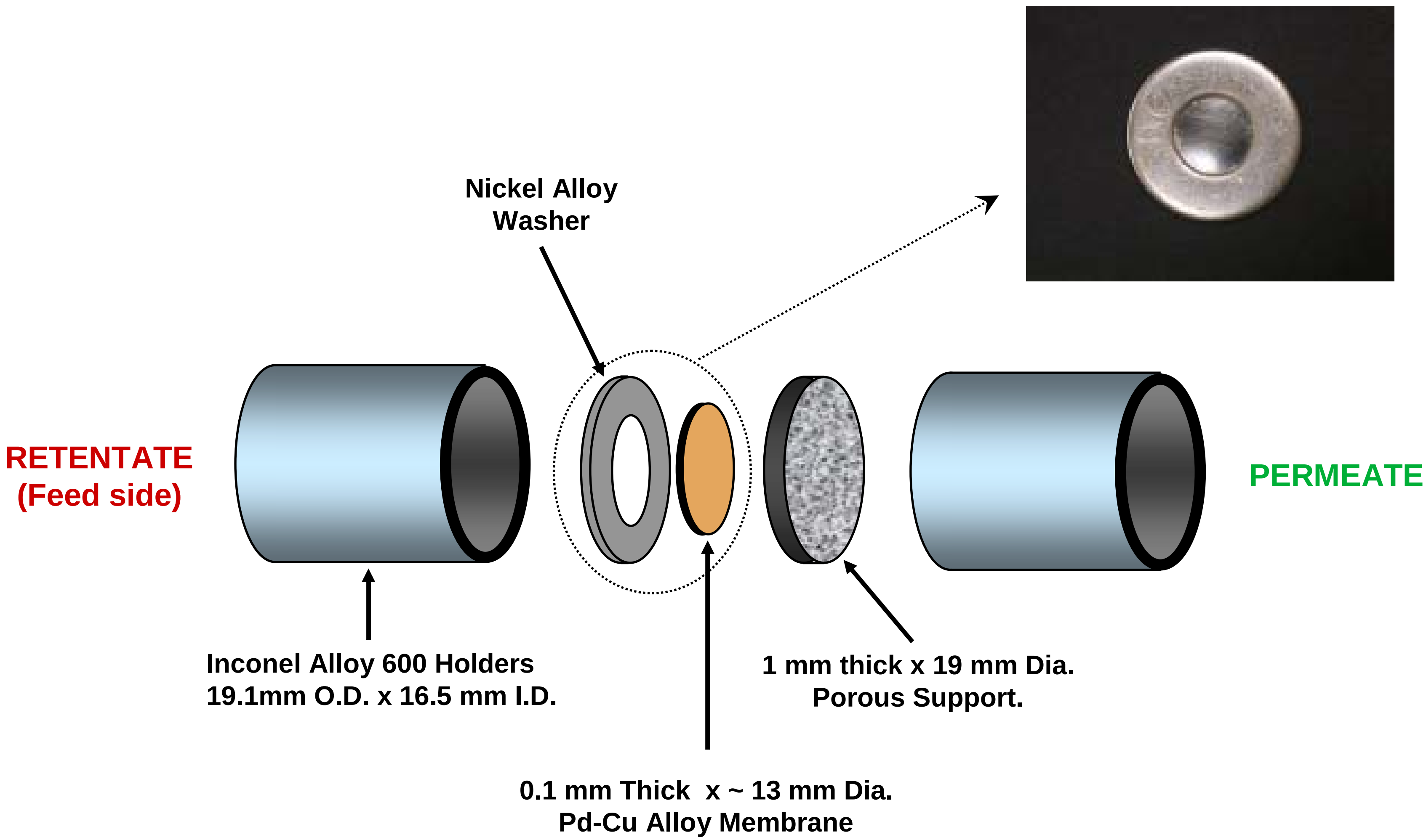
- Temperature range: 623-1173 K   (350 - 900ºC)
- P_{H2} range: 0.1-2.6 MPa   (14 - 380 psi)
- Composition (80-20, 60-40, 53-47, 40-60 wt% Pd-Cu)
- Crystal structure (bcc, fcc, mixed bcc-fcc)

Goal: To Provide a performance baseline for Pd-Cu alloys for ongoing poisoning resistance studies.

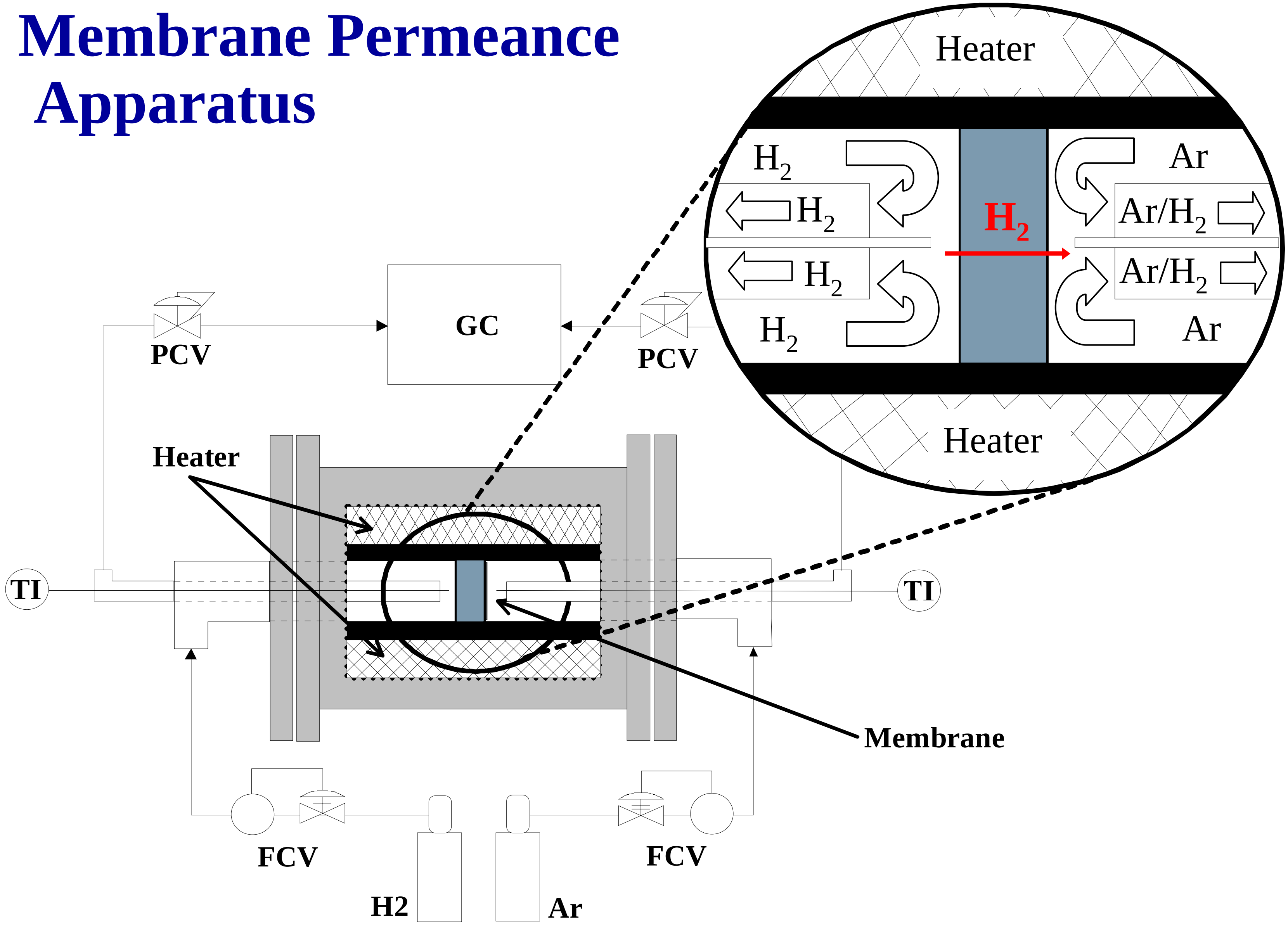
Composite Membrane Mechanism



Membrane Holder



Membrane Permeance Apparatus

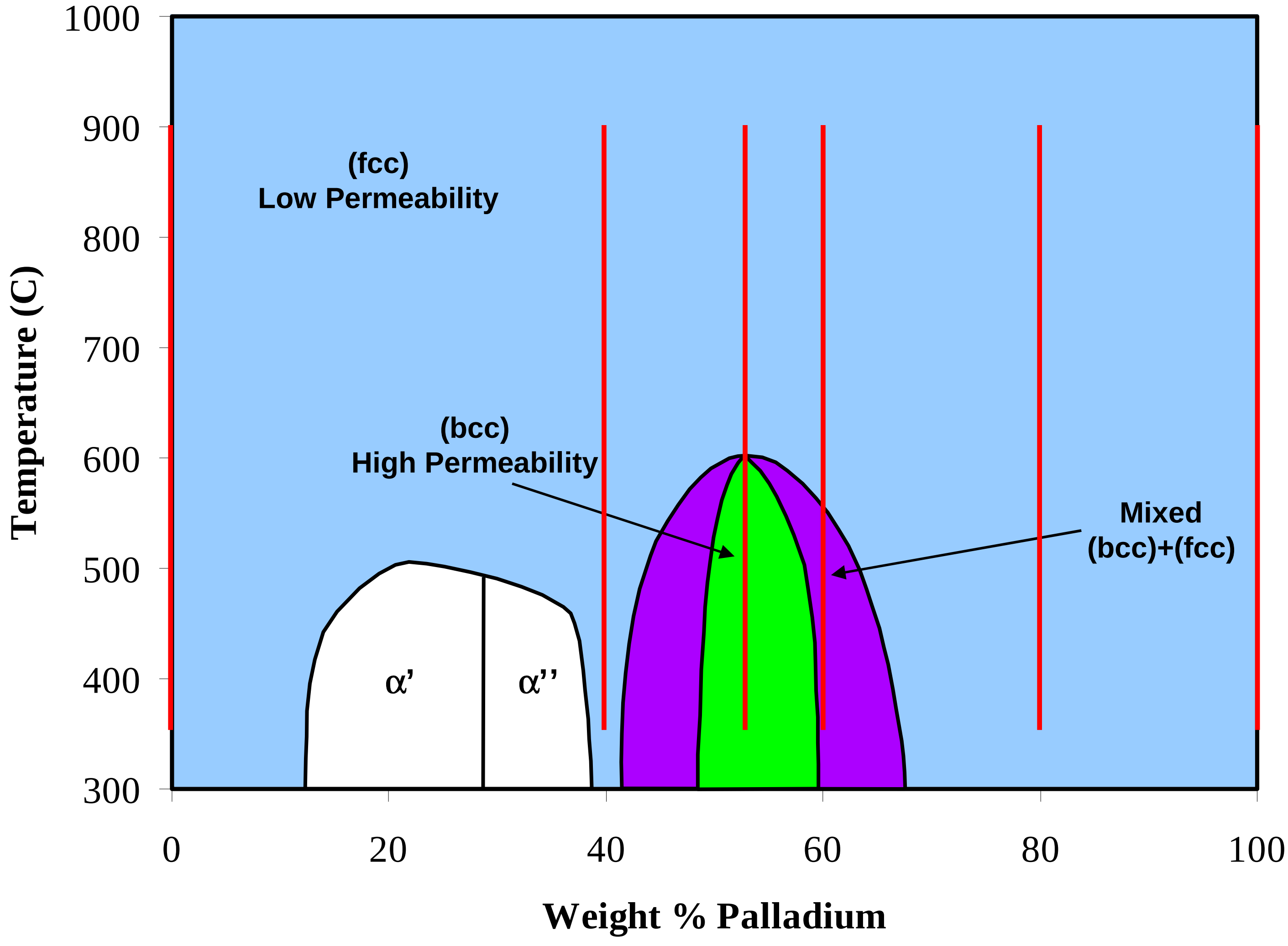


NETL Hydrogen Separation Facilities

- **3 H_2 Membrane Test Units**
- **Constructed FY99 to FY02**
- **Temperatures to 900°C**
- **Pressures to 1000 psi**
- **Disk & tubular membranes**
- **Feed gas flexibility**
- **Membrane separation & reactor configurations**
- **"Clean" and "sulfur-laden" gas feedstocks**
- **Online analysis of products by GC**

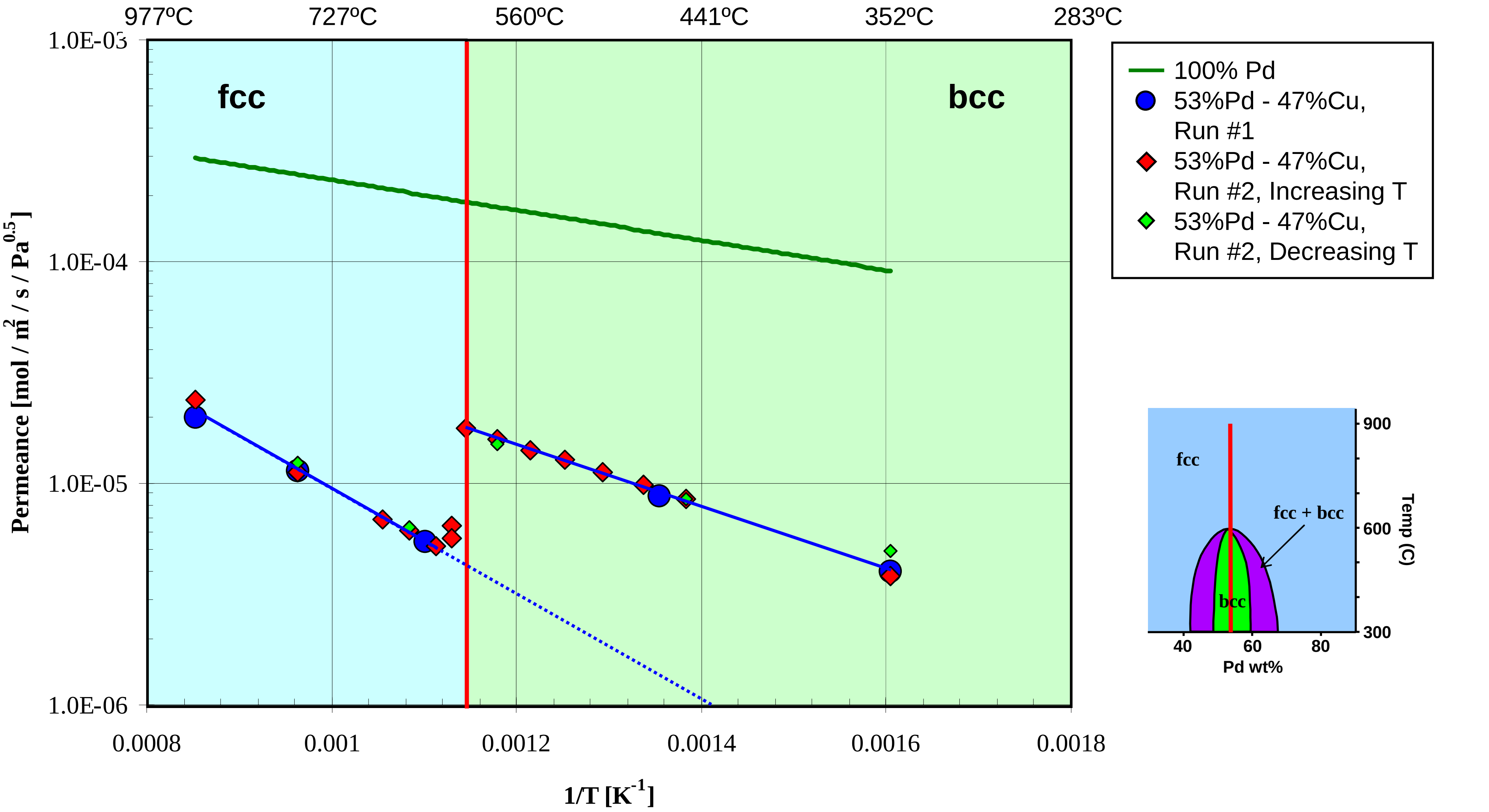
Pd-Cu Phase Diagram*

Red vertical lines represent compositions tested at NETL.

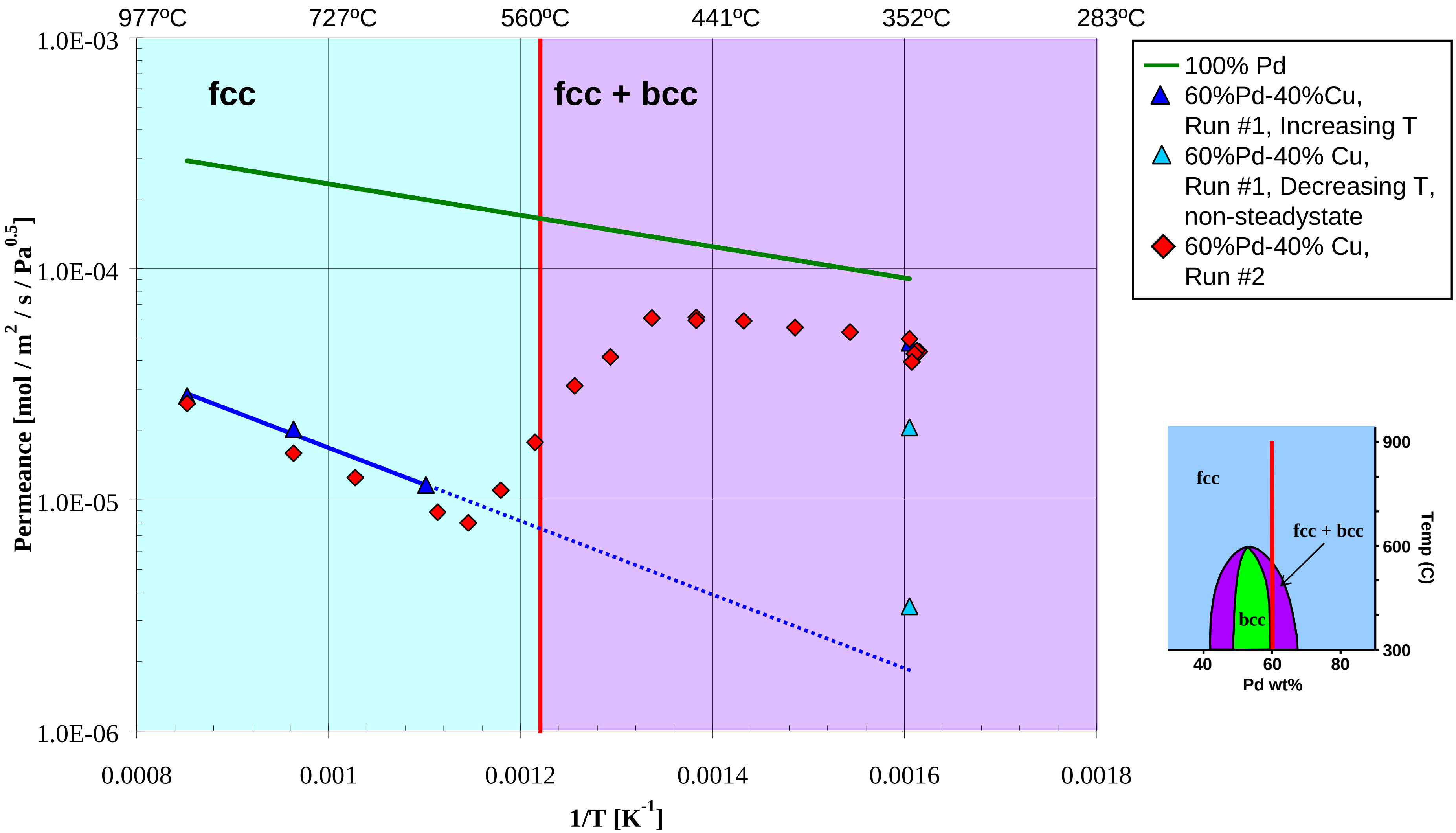


*Derived from: M. Henson, *Constitution of Binary Alloys*, (McGraw-Hill 1958), pp. 612-613.

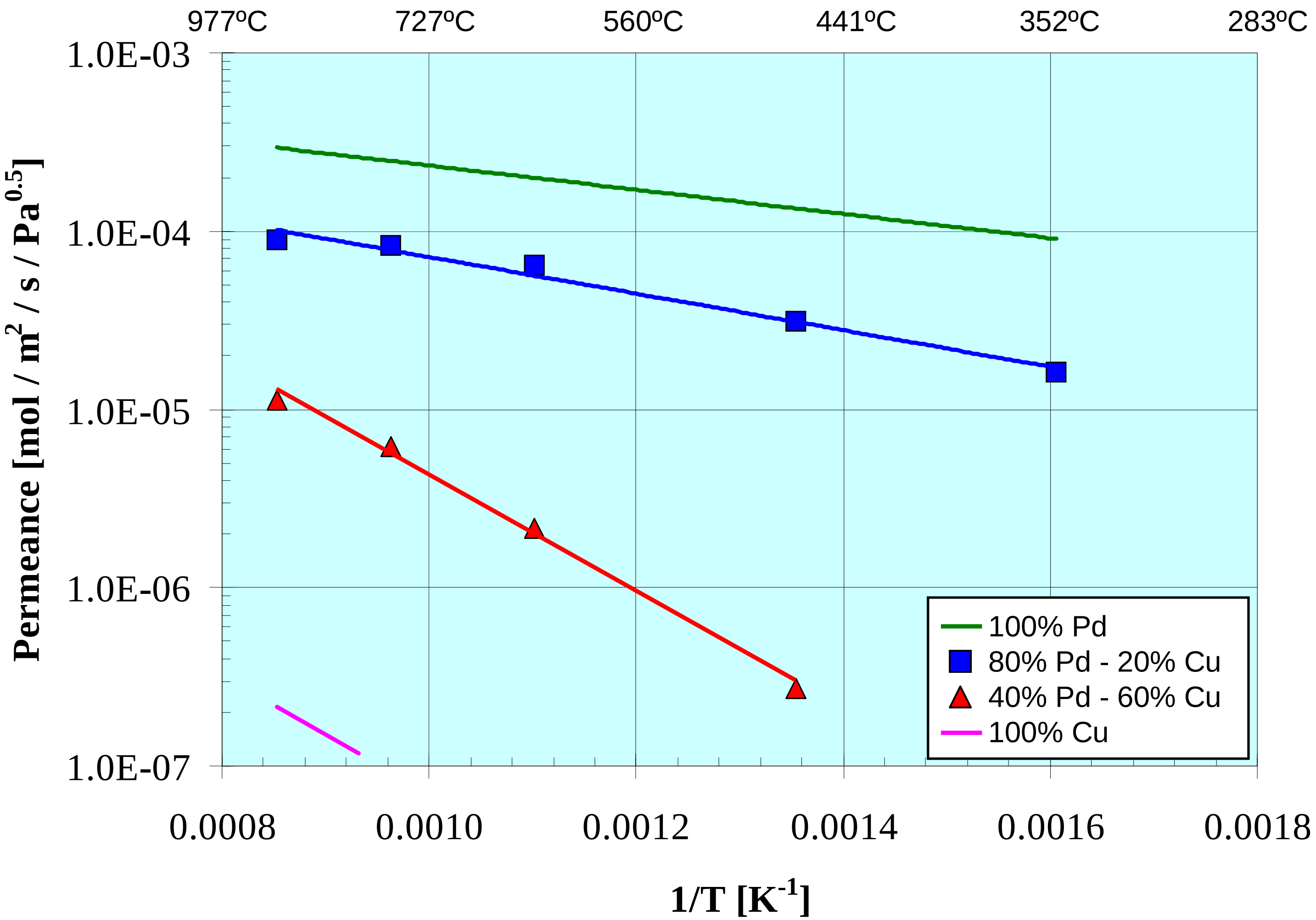
53%Pd-47%Cu Alloy Permeance Through Phase Transition

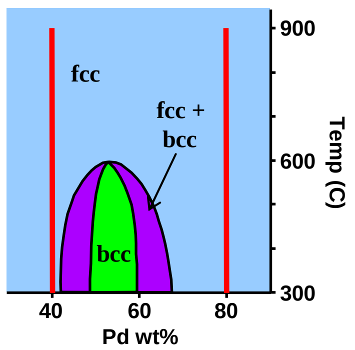


60%Pd-40%Cu Alloy Permeance Through Phase Transition

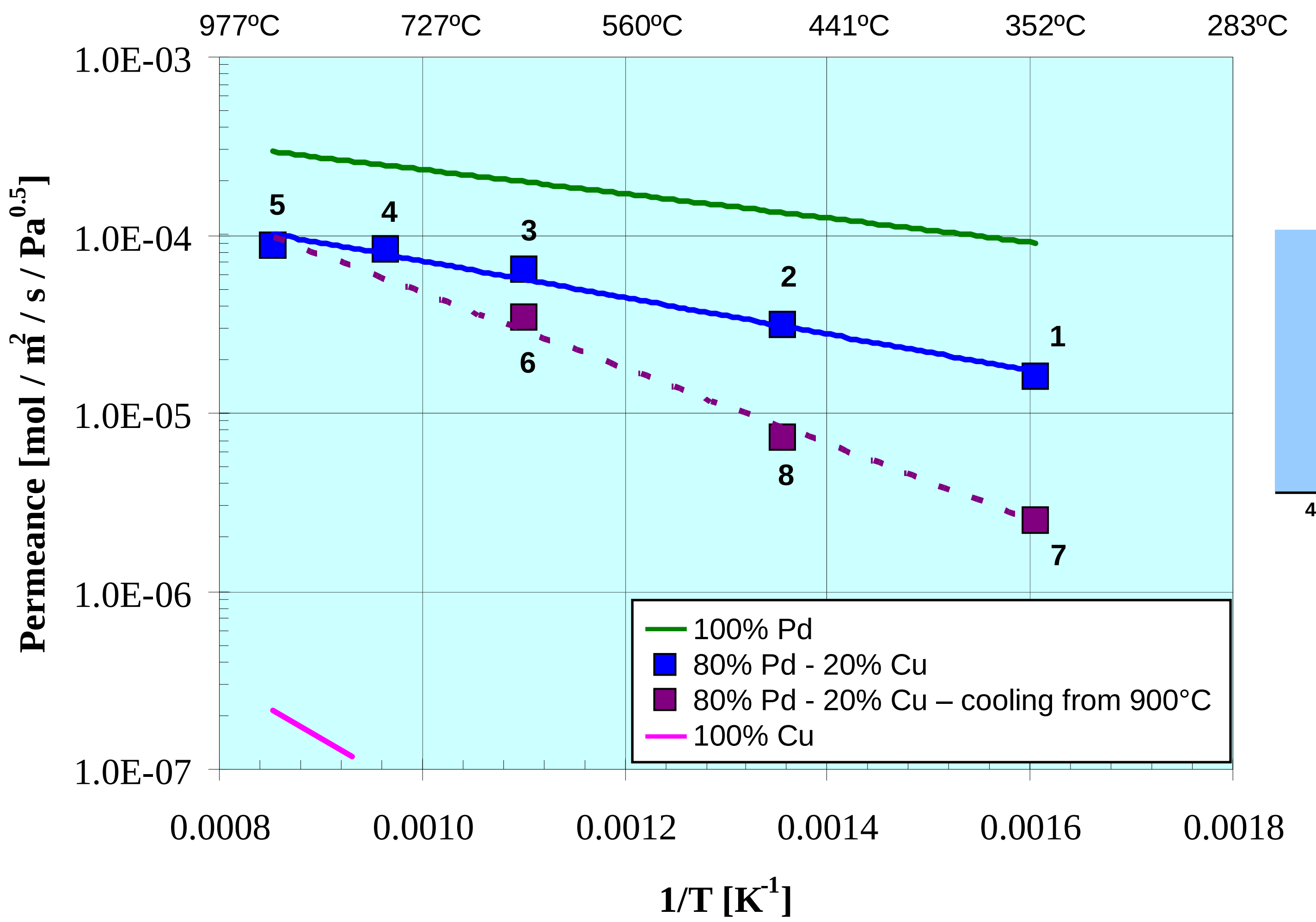


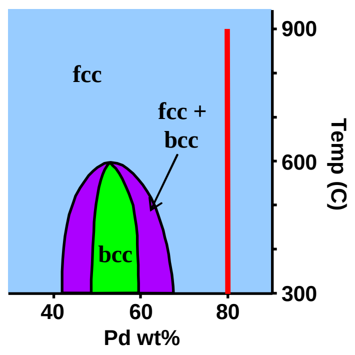
80%Pd-20%Cu and 40%Pd-60%Cu Alloy H_2 Permeance



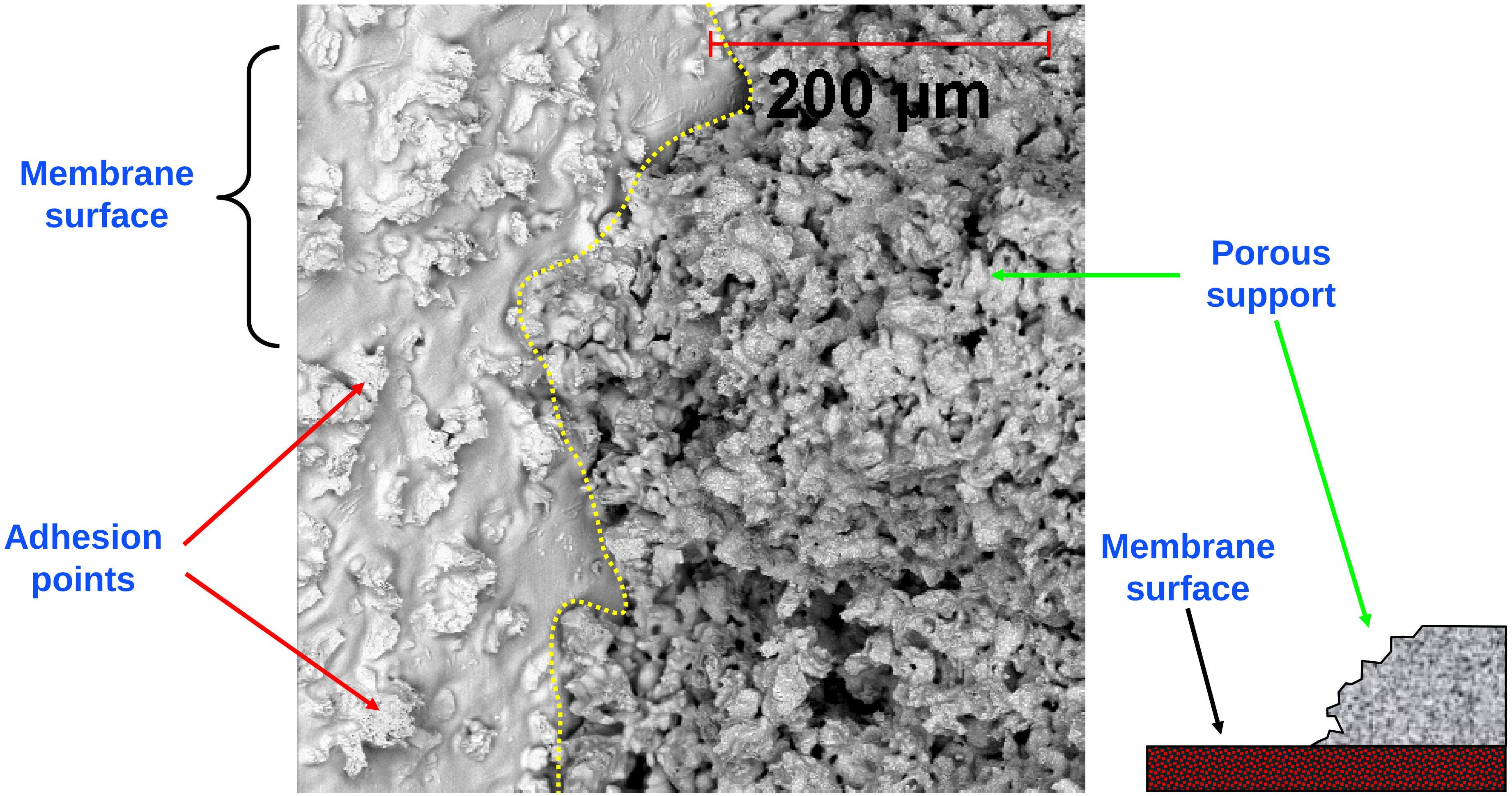


80%Pd-20%Cu Alloy H_2 Permeance Showing Decrease Caused by Intermetallic Diffusion



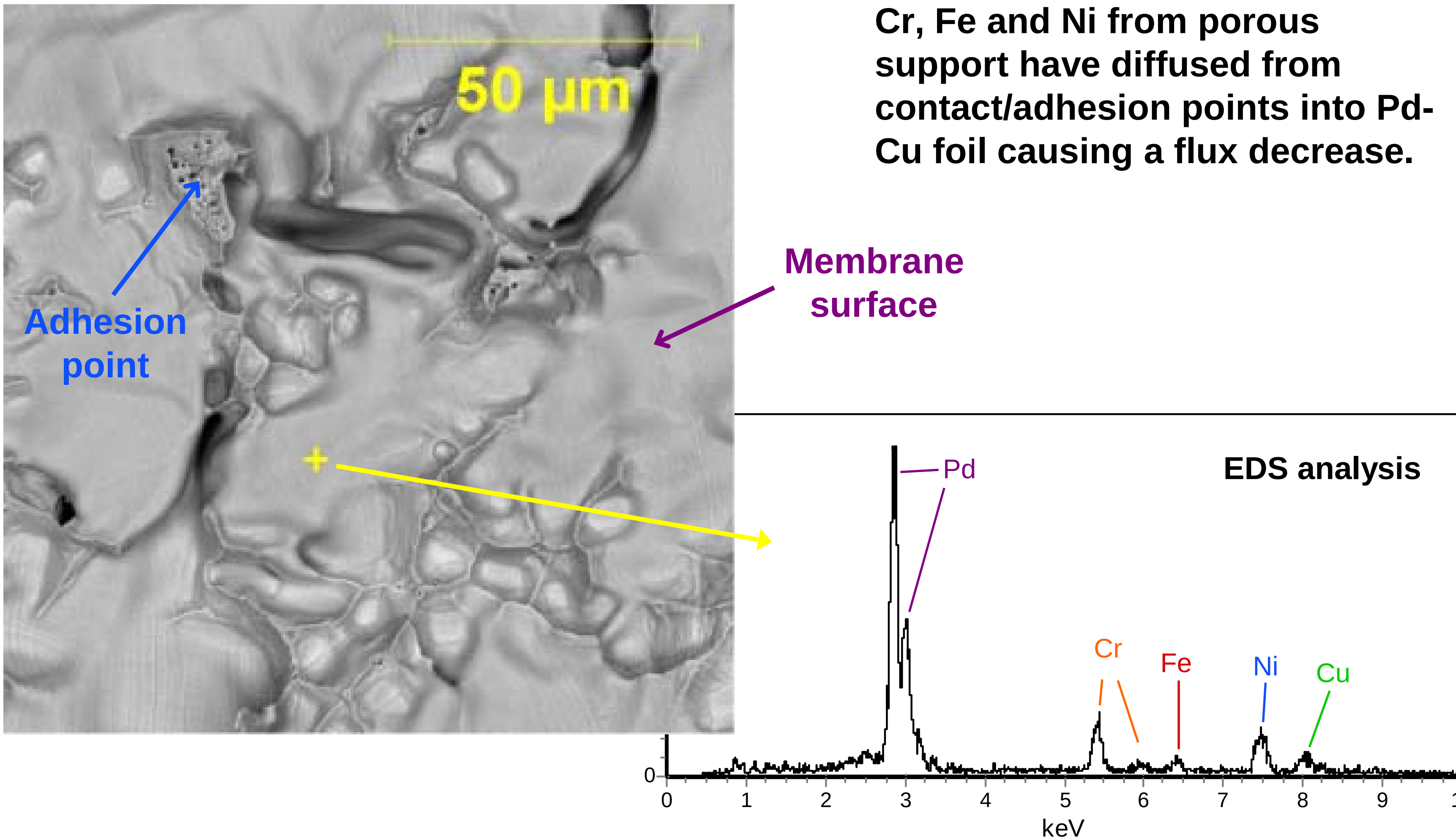


Interface Between Membrane and Support



Intermetallic Diffusion Between Membrane and Support

Cr, Fe and Ni from porous support have diffused from contact/adhesion points into Pd-Cu foil causing a flux decrease.



Conclusions

- The Pd-Cu alloys exhibited predictable permeance.
- 53Pd-47Cu and 60Pd-40Cu alloys exhibited a distinct drop in permeance at the T associated with the bcc to fcc transition.
- 80Pd-20Cu and 40Pd-60Cu alloys remained in the fcc region and exhibited no discontinuities in permeance over the 350 to 900ºC range.
- 60Pd-40Cu alloy yielded the highest permeance but only at 350ºC (bcc).
- fcc permeance increases with %Pd.
- A passivation layer is necessary for composite membrane applications at high temperatures.

Future Work

- Evaluate permeance in the presence of H_2S.
- Investigate membrane recovery after H_2S exposure.
- Evaluate permeance in the presence of major WGS gas components: H_2O, CO, CO_2 and other gas impurities, such as NH_3.
- Evaluate thinner foil Pd-Cu membranes supported on porous substrates.
- Consider other alloys.