Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

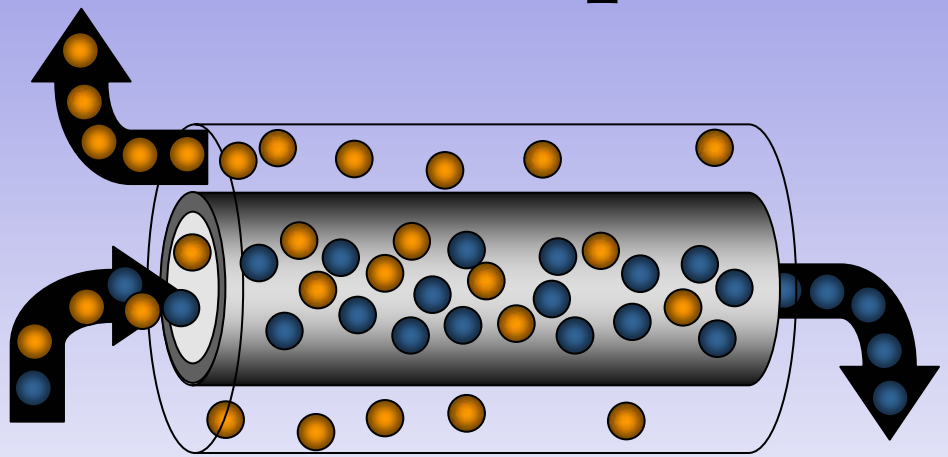
Capture - Membranes

Novel Polymeric-Metallic Composite Membranes for CO_2 Separations at Elevated Temperatures

Kathryn A. Berchtold

May 2-5, 2005, Hilton Alexandria Mark Center, Alexandria Virginia

Novel Polymeric-Metallic Composite Membranes for CO_2 Separations at Elevated Temperatures



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Fourth Annual Conference on
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Alexandria, VA
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Separation and Capture – National Needs/Membrane Opportunities

- High Temperature Membranes are in Great Demand…
  - Membrane reactors, Synthesis gas separations (Power systems, IGCC, Gas-To-Liquids, Hydrogen production, Carbon sequestration), Fuel Cells (Reforming – Centralized, Distributed)
    - The proceedings of the National Hydrogen Energy Roadmap Workshop identify improved separation and purification methods and materials as one of the most critical crosscutting technologies required to achieve the vision of a hydrogen economy.
  - Alternative technologies (PSA, TSA, amine scrubbing, cryogenic separation) have drawbacks
    - Energy intensive
    - Produce CO_2 at atmospheric pressure
    - Low temperature processes
    - Can be high maintenance and cost compared to membrane technology
- But are in Short Supply – Materials
  - Existing membrane materials have limiting temperatures, selectivity, productivity, chemical resistance, material properties

Stated DOE Need for Membranes *

- Production and Delivery: Conduct research on lowering cost of distributed H_2 production from natural gas including membranes
- Advanced shift and separations technologies including membranes for producing H_2 from coal
- RD&D to integrate carbon capture and sequestration technologies into fossil based production systems
- FutureGen: Emission free, coal fired electricity and H_2 production

* Hydrogen Posture Plan DOE February 2004

Collaborators

- Los Alamos National Laboratory
  - Jennifer Young
- Pall Corporation
  - Scott Hopkins, Jim Acquaviva, Frank Onorato, Bill Palmer, Sean Meenan
- University of Colorado
  - Alan Greenberg, Vivek Khare
- Idaho National Laboratory
  - Eric Peterson, John Klaehn

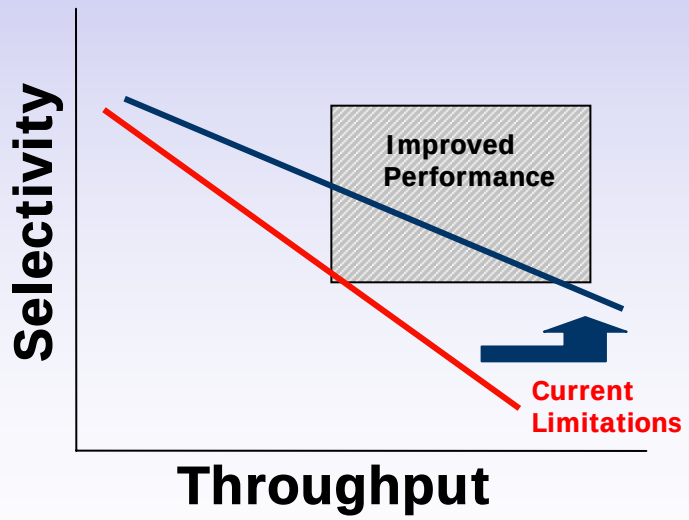
Objective

Produce a high temperature membrane and module capable of operation at temperatures significantly higher than 150 °C and industrially relevant conditions.

- Temperature Stability
- Chemical Stability
- Industrially Attractive Separation Characteristics

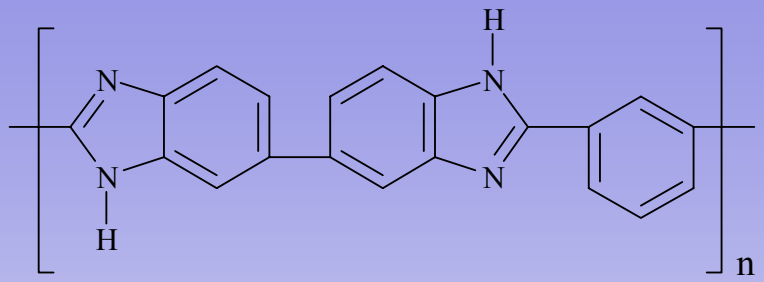
High T_g Polymeric Membranes

- Commercially available polymer membranes are limited to 150 °C operating temperature
  - Economic advantages of membrane separations are strongly tied to process/separation temperature
- Tradeoff between selectivity and productivity has proven difficult to overcome
- Chemical & mechanical stability and durability are often elusive

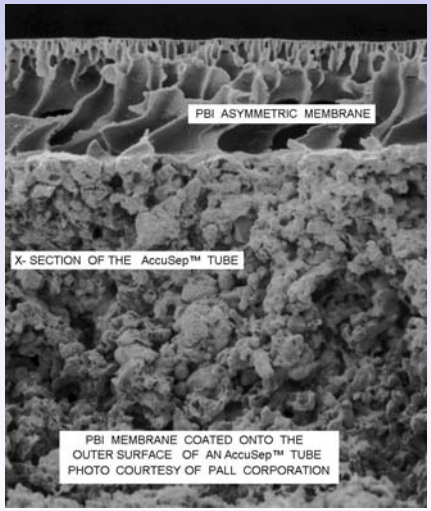


Approach

- Begin with High T_g polymer (polybenzimidazole (PBI))
  - Thermally stable (T_g ~ 450°C)
  - Chemically resistant
  - Processable



- Modify via functionalization, blending, crosslinking, 2nd phase additions and combinations thereof
  - Modify membrane selectivity, productivity, processability, chemical resistivity, etc.
- Use specially designed porous metal substrates to provide mechanical support for the polymer film



- Develop tools for predicting long-term membrane performance and insights regarding optimization

Scale-Up and Optimization

Scale-up and optimization are ongoing

Uncoated

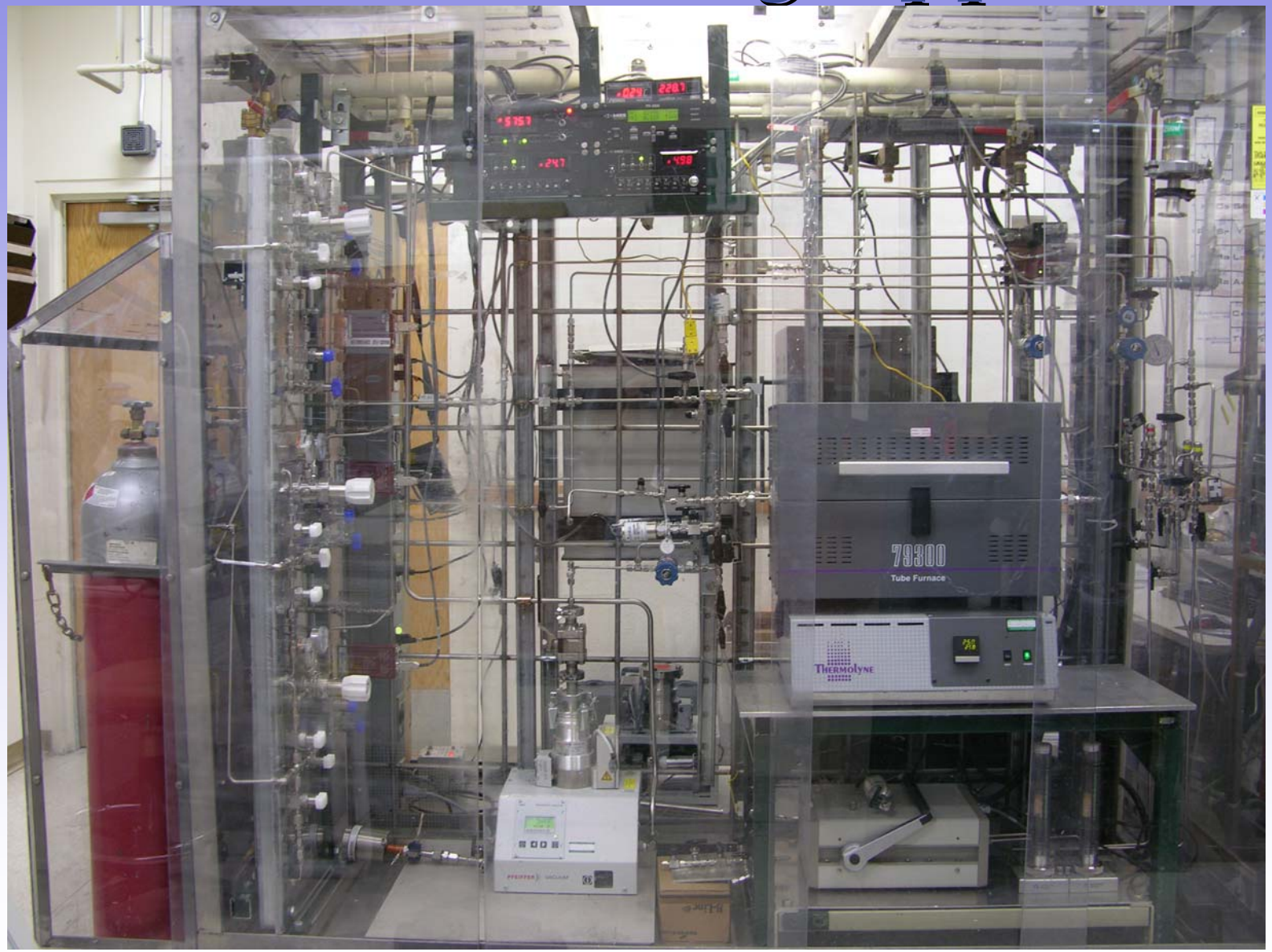
Coated

- Scale-up
  - Membrane area scale-up has been significant ($0.5\ cm^2 \rightarrow 67\ cm^2$)
  - Scalability of permselectivity characteristics demonstrated
- Minimization of Defect Free Film Apparent Thickness
  - Membrane thickness continues to be optimized ($100+\ \mu m \rightarrow < 7\ \mu m \rightarrow < 2\ \mu m$)
  - A > 40 % reduction in apparent thickness has been realized over the first single tube module tested
  - A > five-fold permeance increase was realized during single tube module testing as a result of thickness optimization efforts

LANL Testing Capabilities

- Gas Separations of Industrially Relevant Feedstocks at Industrially Relevant Temperatures
  - Membrane Testing Capabilities Over a Broad Temperature Range (ambient – 1000 °C)
  - Single Gas Testing (pressure rise and pressure decay)
  - Multi/Mixed Gas (flow through system)
  - Experimental testing on various size thin film disk and tubular membrane modules
  - Testing of Industrially Relevant Feed Streams (Inert, Flammable and Toxic gas capability – e.g., H_2, CO_2, CH_4, N_2, CO and H_2S)
  - Fixturing for broad range of membrane materials (e.g., polymers, metals, ceramics) over a wide temperature range

Permeation Testing Apparatus



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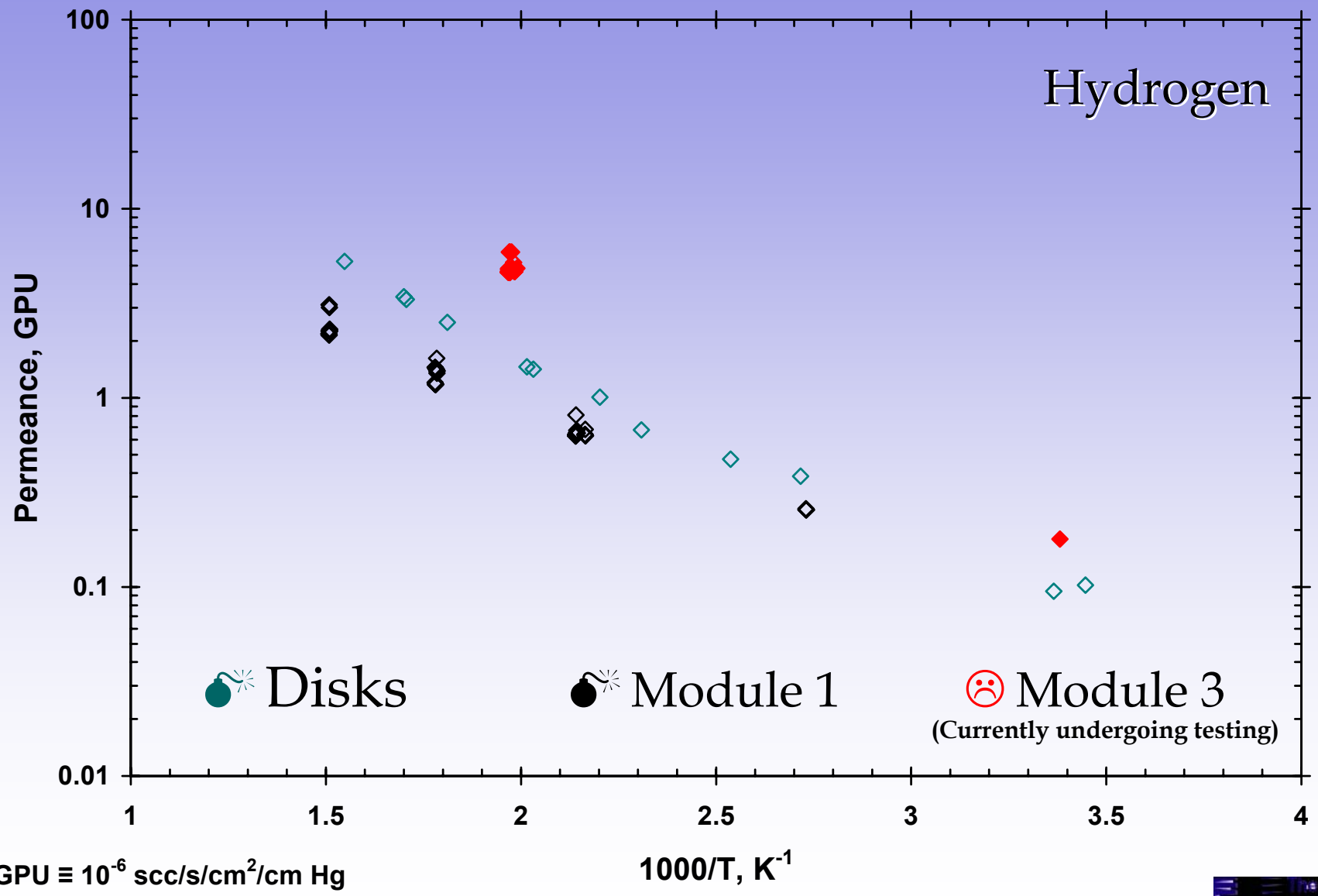
Membrane Fabrication Optimization



GPU ≡ 10^{-6} scc/s/cm^2/cm Hg

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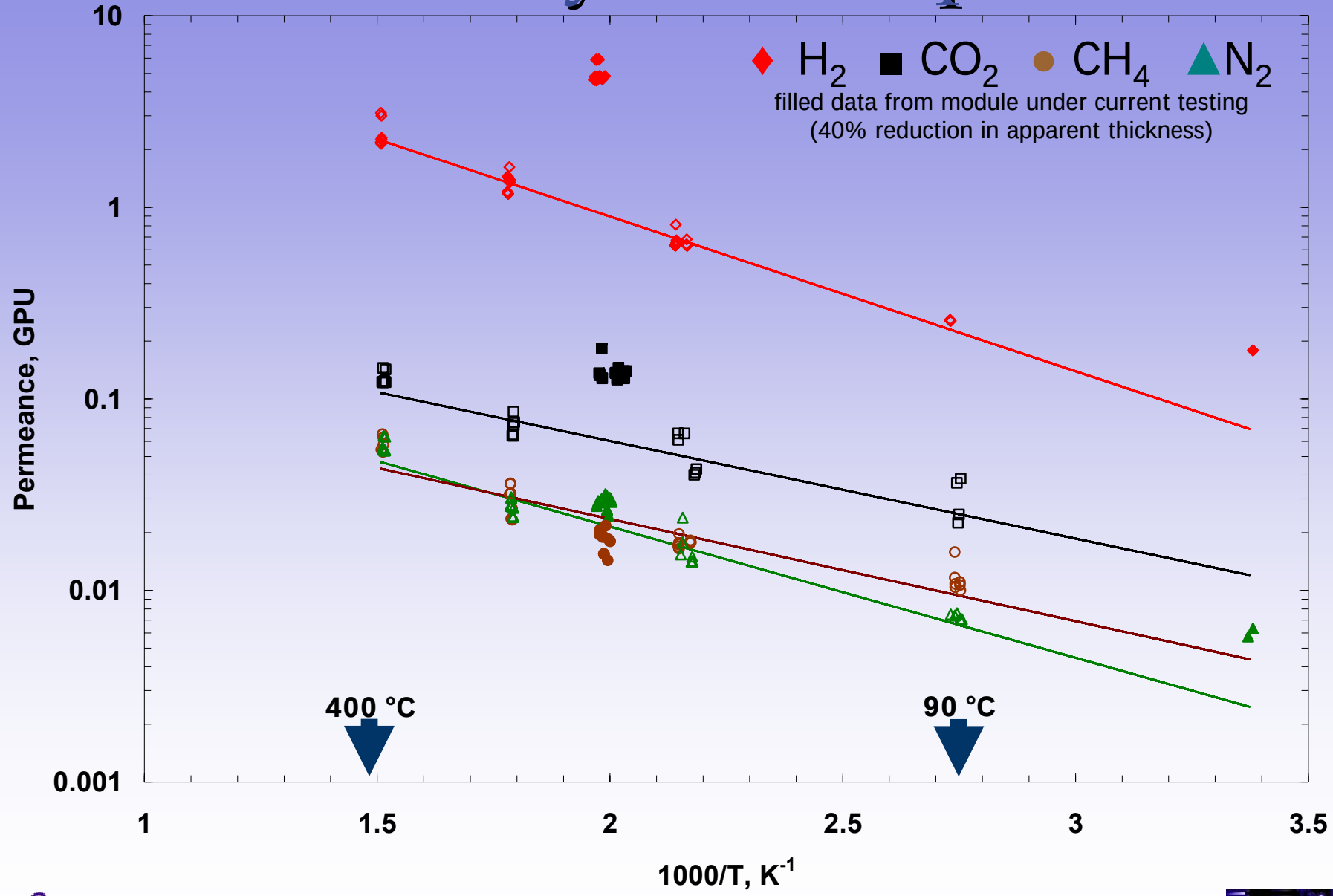
Permeability vs. Temperature

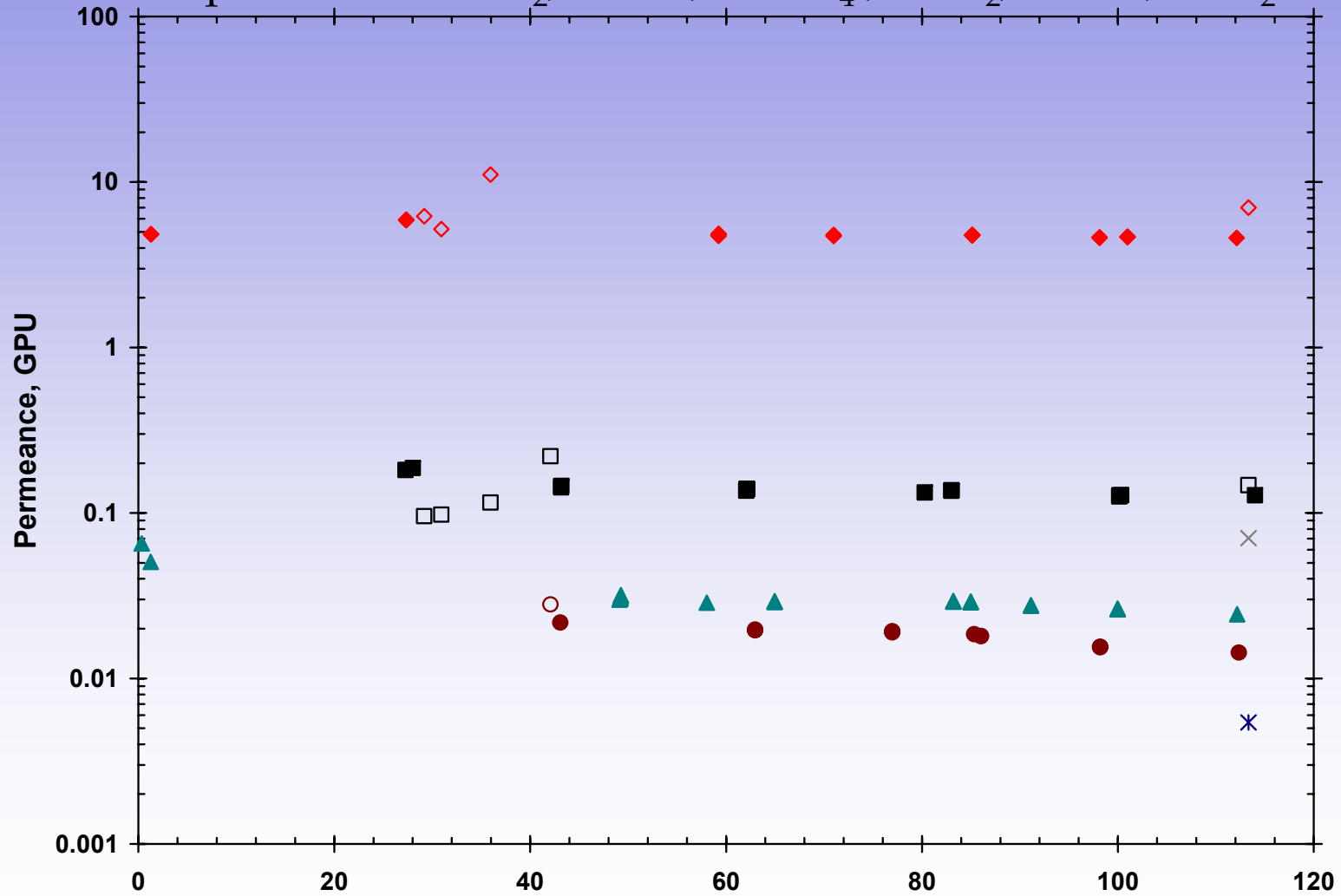


GPU - 10^{-6} scc/s/cm^2/cm Hg

Durability

Single Gas Experiments: H_2, CO_2, CH_4, N_2

Mixed Gas Experiments: H_2, CO, CH_4, N_2, 5 CO, 6 H_2S



GPU ≡ 10^{-6} scc/s/cm^2/cm Hg

Module Time @ 250 °C, days

120 days = 2880 hrs

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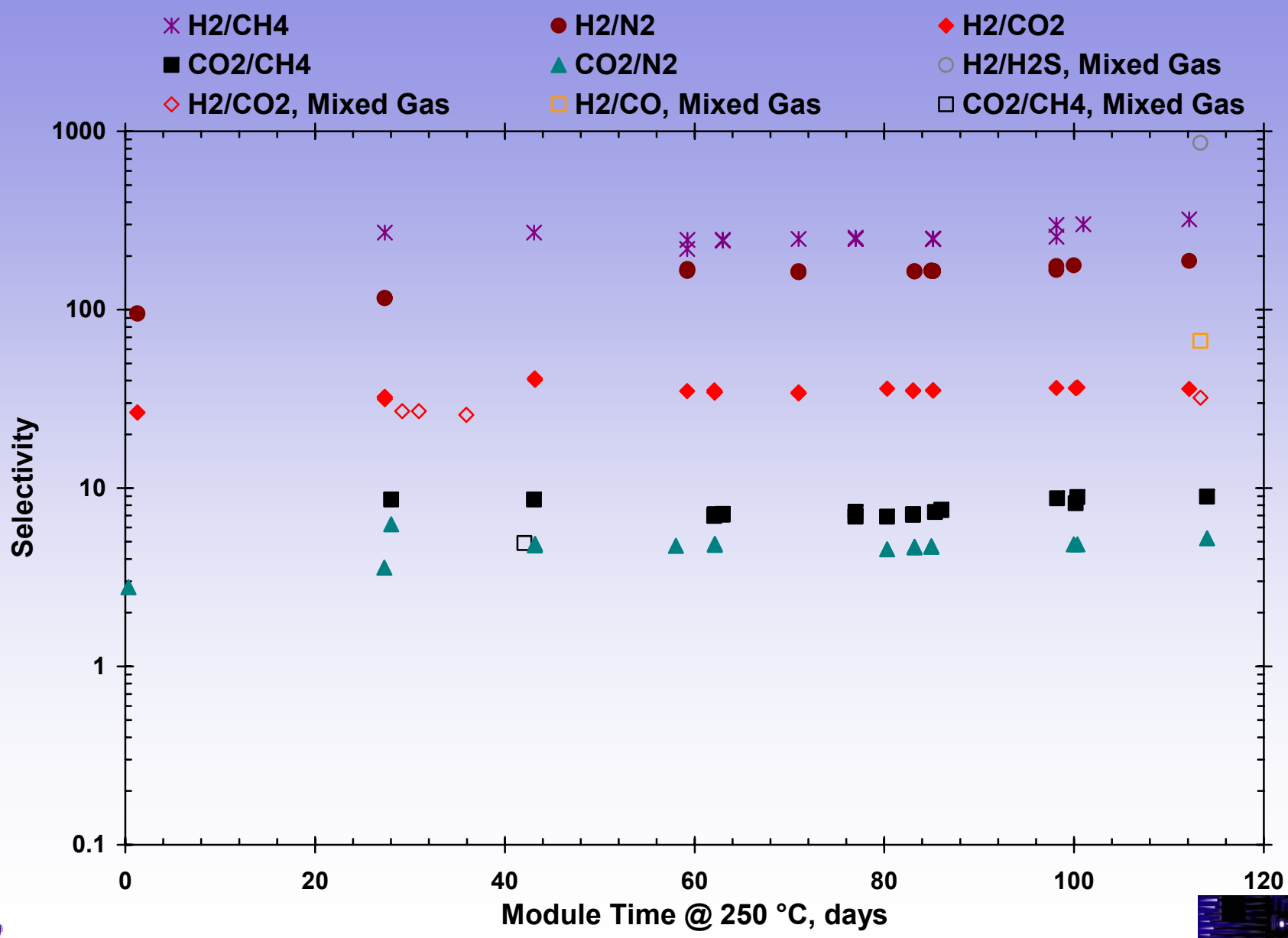
Selectivity



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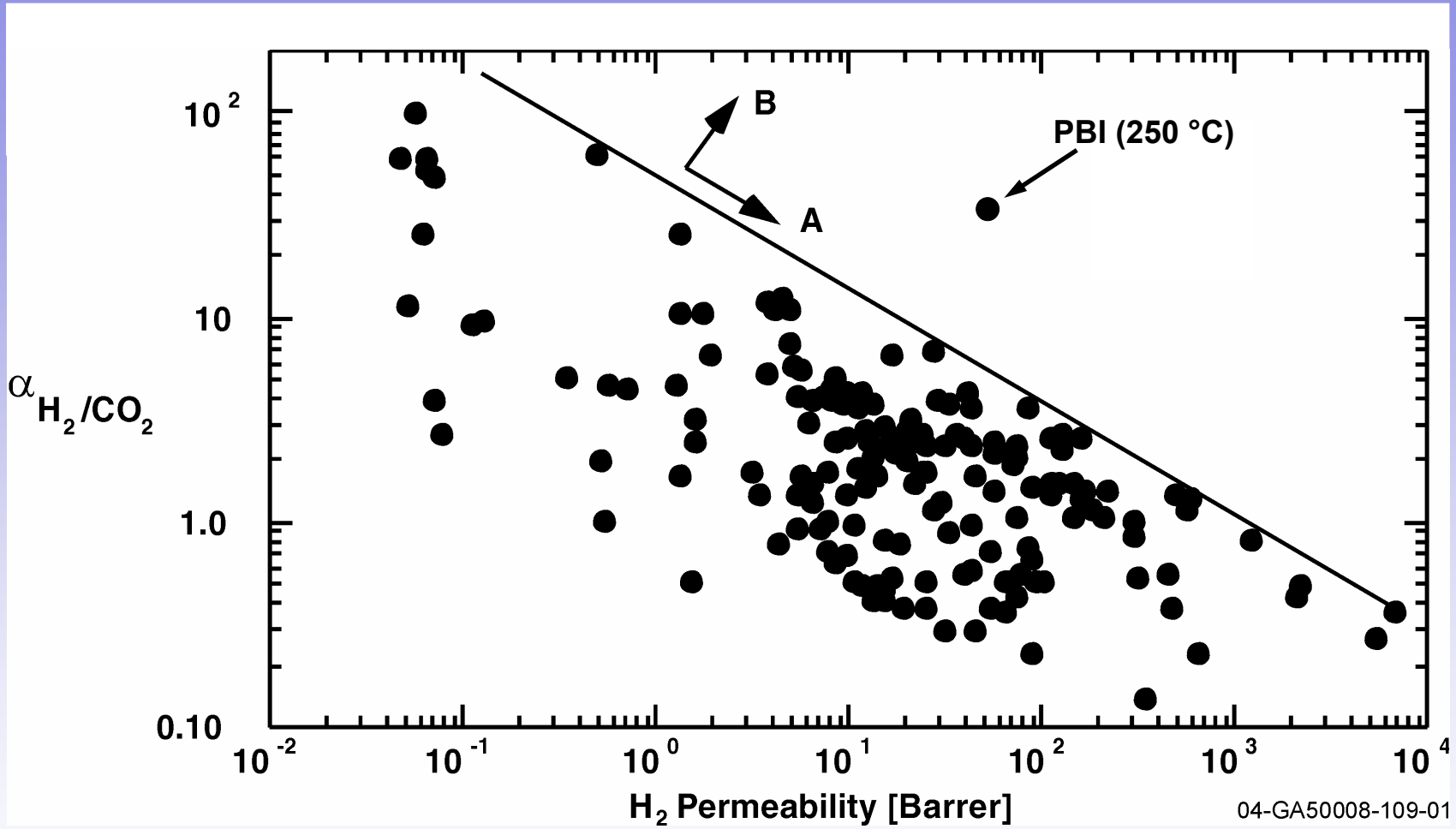
Selectivity vs. Permeability: H_2/CO_2



We have demonstrated improved selectivity over the state-of-the-art while operating at industrially attractive conditions

1 barrer = 10^{-10} cm^3-cm/s-cm^2-cmHg

From J. Membr. Sci. 62, L.M. Robeson, Correlation of Separation Factor Versus Permeability for Polymeric Membranes, 1991.

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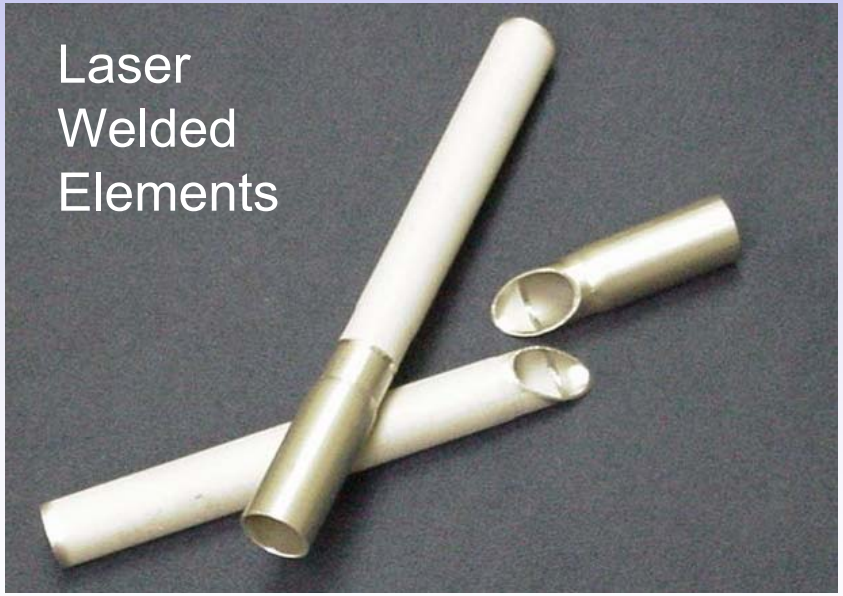
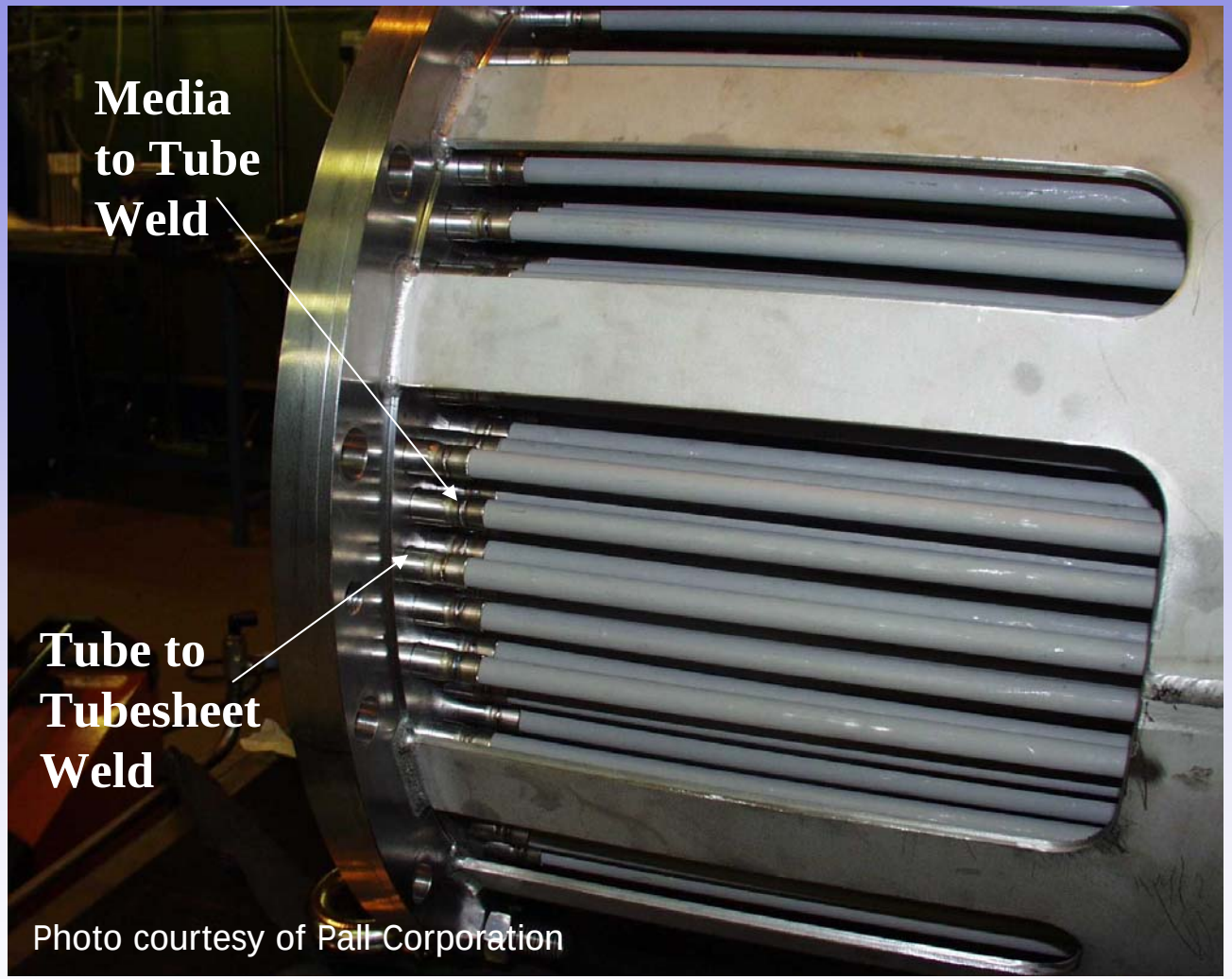
Next Generation Module

AccuSep® Elements and Modules



Multi Tube Filtration Module

Industrial Scale Module Design



AccuSep Tubes Welded into module for Industrial Liquid Separation Application

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Significant Accomplishments

- Successful fabrication of PBI polymer-metal composite membranes
- Highest demonstrated operating temperature (400 °C) of polymer-based membrane with permeabilities and selectivities of interest
- Successfully coating tubular metal supports for implementation in a module
- Modification of PBI to obtain polymers that are readily soluble in common solvents and to manipulate material properties
- First-ever simultaneous gas permeation – creep measurement at elevated temperature
- This work has led to several patent applications and has demonstrated promise for future commercialization as evinced by Pall Corporation's continued and ever increasing participation.

The Future

- Cost vs. Performance benefit of the membrane
  - Increase in selectivity and / or permeability due to polymer modification still a work in progress
  - Minimum film thickness not yet achieved
  - Full scale manufacturing process for thin films not yet established

- Process Design for Industrial CO_2 Separation
  - Variation in membrane properties over time to be determined
  - Optimized process design / performance to be determined based on "final" membrane properties
  - Incorporation into pilot unit for "in plant" testing

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(Project FE-01-0003)

Collaborators

Pall Corporation

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