Sulfur Thermochemical Processes with Inorganic Membranes to Produce Hydrogen

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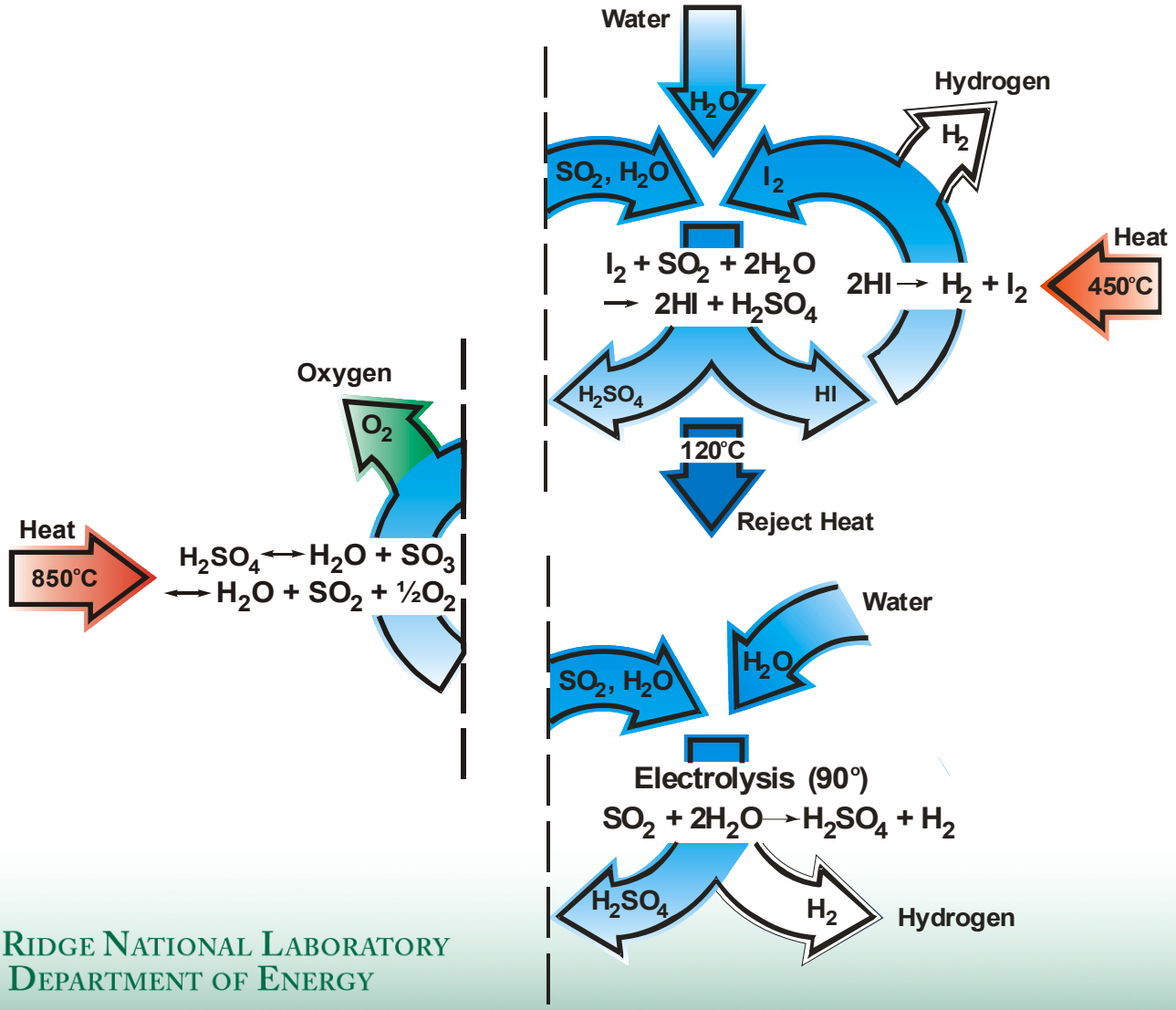
Challenges in Hydrogen Production

- Major efforts are under way to produce hydrogen using nuclear reactors with thermochemical cycles
  - Water + Heat $\Rightarrow$ Hydrogen + Oxygen
  - Sulfur-based thermochemical cycles are the leading options
- Sulfur cycles require very high temperatures (850ºC)
  - Massive R&D effort is required to reach these temperatures
    - At the limits of reactor technology
    - At the limits of practical materials
  - Large incentives exist to reduce temperatures
- A method to lower peak temperatures by 100 to 200ºC is being developed using inorganic membranes

Sulfur Family of Thermochemical Cycles

High-Temperature Reaction

Low-Temperature Reactions



Sulfur Iodine

Hybrid Sulfur

(Westinghouse, GA-22, and Ispra Mark II)

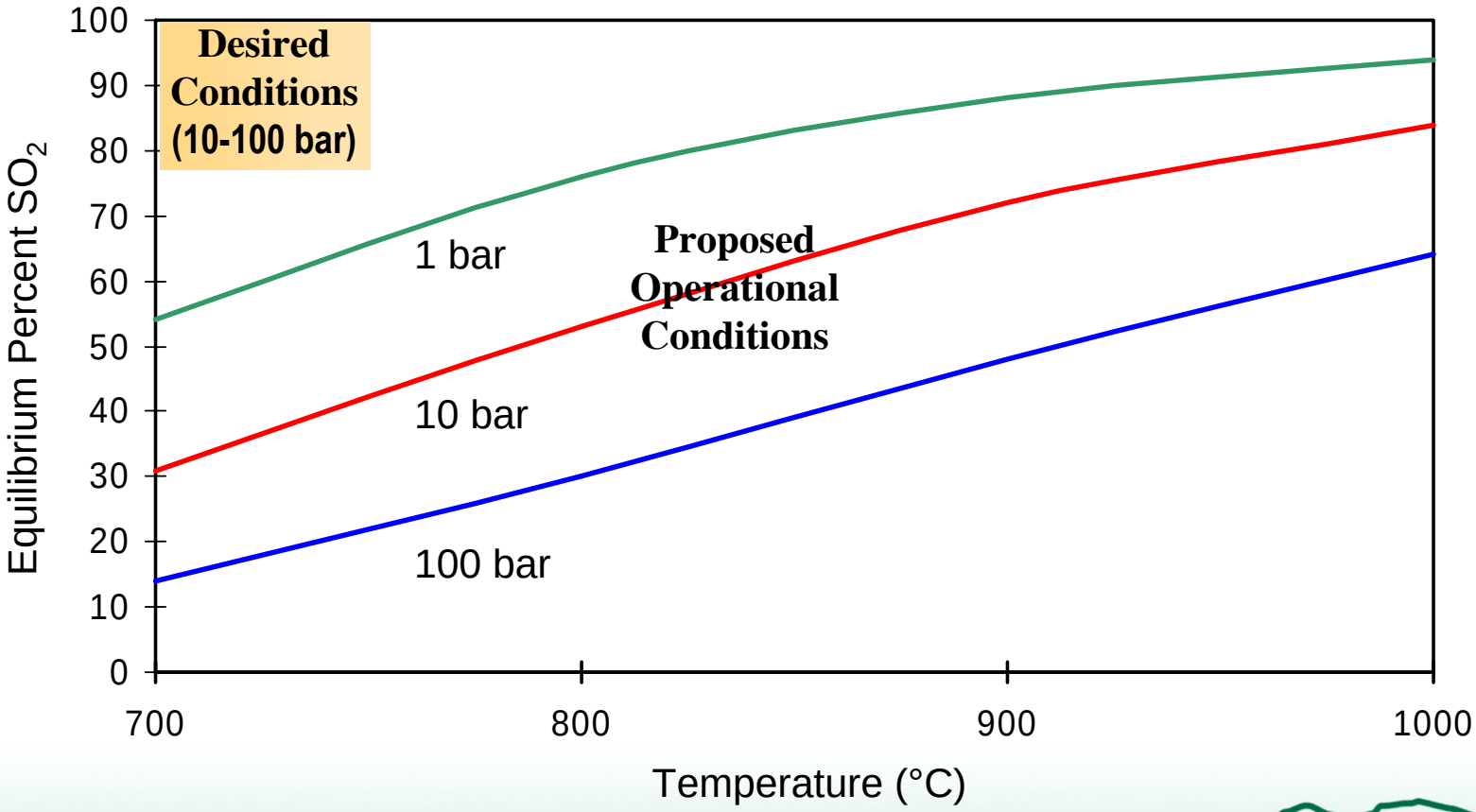
The High-Temperature Step in Sulfur Cycles Is The Thermal Decomposition of Sulfuric Acid

$$H_2SO_4 \Leftrightarrow SO_3 + H_2O \Leftrightarrow SO_2 + H_2O + 1/2O_2$$

- The second decomposition reaction (far right) requires high-temperatures (850ºC)
- Lower-temperature operation (e.g., 700ºC) results in limited dissociation of SO_3 and low process efficiency via the following sequence of events:
  - Unreacted H_2SO_4 and reaction products are cooled
  - Components are separated
  - Unreacted H_2SO_4 is reheated
  - High internal recycle with high costs and lower efficiency results

Concentration of SO_2 Versus Temperature

$(H_2SO_4 \Leftrightarrow SO_3 + H_2O \Leftrightarrow SO_2 + H_2O + 1/2O_2)$



One Solution for Complete H_2SO_4 Dissociation

- Push the equilibrium high-temperature reaction to completion by removing the reaction products:

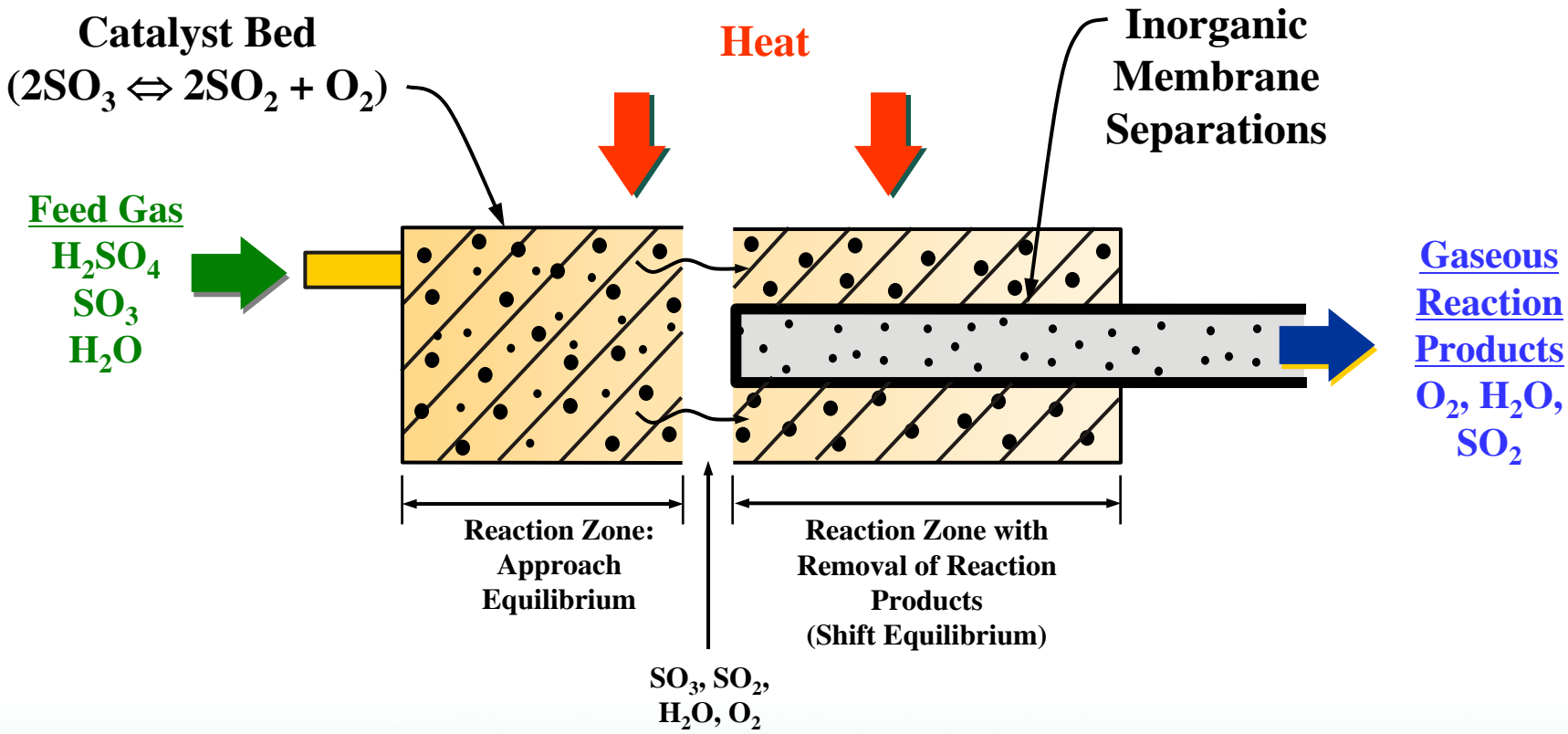
$$H_2SO_4 \Leftrightarrow SO_3 + H_2O \Leftrightarrow SO_2 + H_2O + 1/2O_2$$

- Membrane separation of O_2, H_2O, and SO_2 from SO_3 drives reaction to the right, thus allowing high conversion at lower reaction temperatures

Potential exists to reduce peak temperature to between 650 and 750°C

Sulfur Oxide Decomposition System Design

(SO_2, O_2, and H_2O Separation Allows the Reaction to Be Driven to Completion)



Membrane Theory

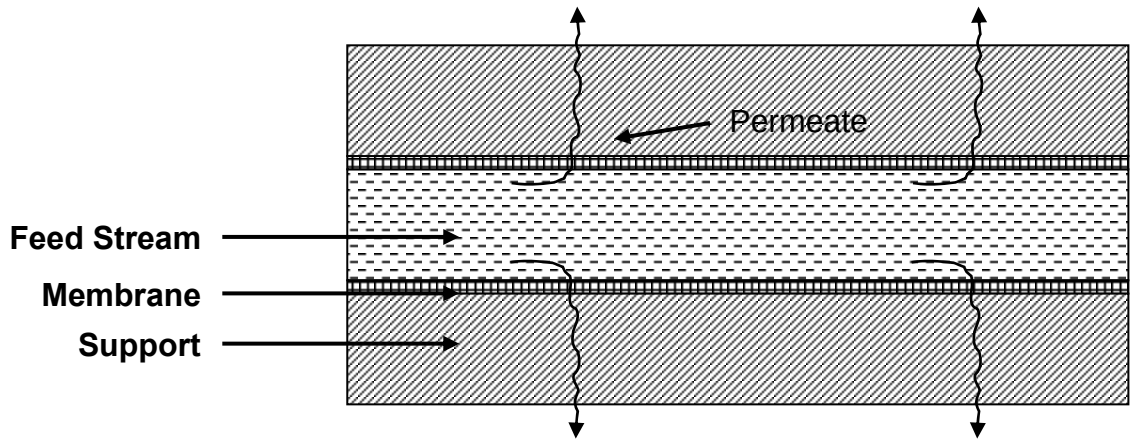
Technologies Developed at

Oak Ridge National Laboratory

The Separation Mechanism Depends upon the Pore Size, Molecular Species, and Other Factors

- **Membrane Transport Mechanisms for Larger Pores**

  - Viscous Flow
  - Surface Diffusion
  - Knudsen Diffusion
  - Capillary Condensation

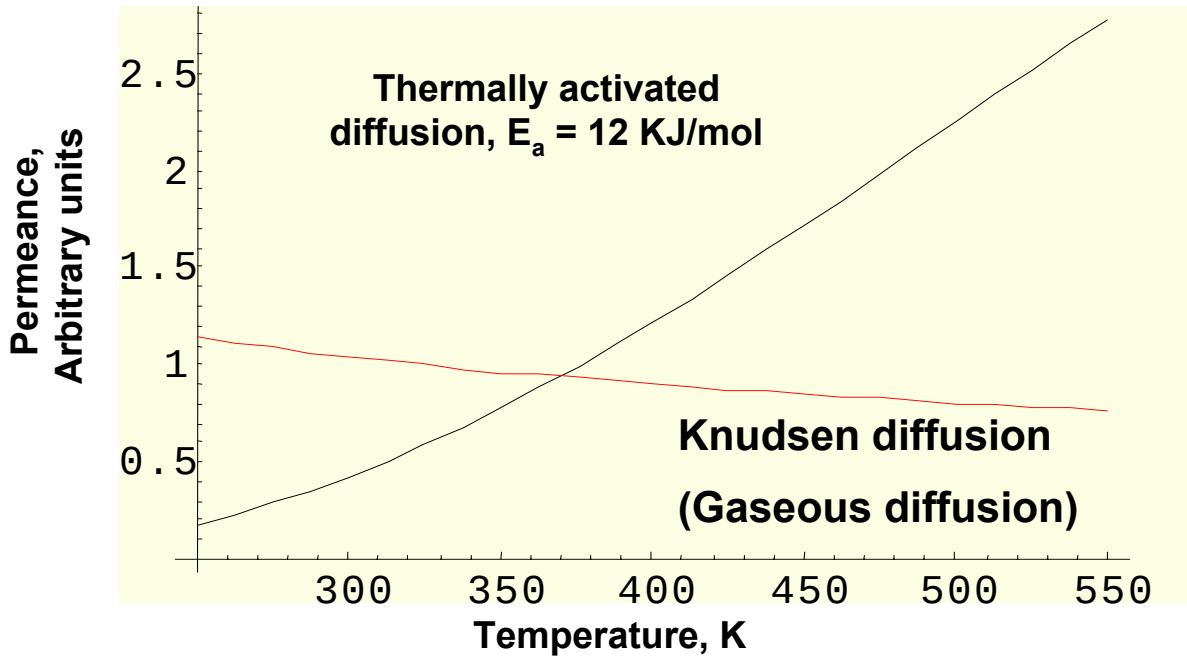


- **Membrane Transport Mechanisms for Smaller Pores (≤1 nm)**

  - Molecular sieve
  - Thermally activated diffusion
    (Transport in this regime is not fully understood)

For High-Temperature Separations, Membrane Separation via Thermally Activated Diffusion Is Desired Because Performance Improves with Temperature

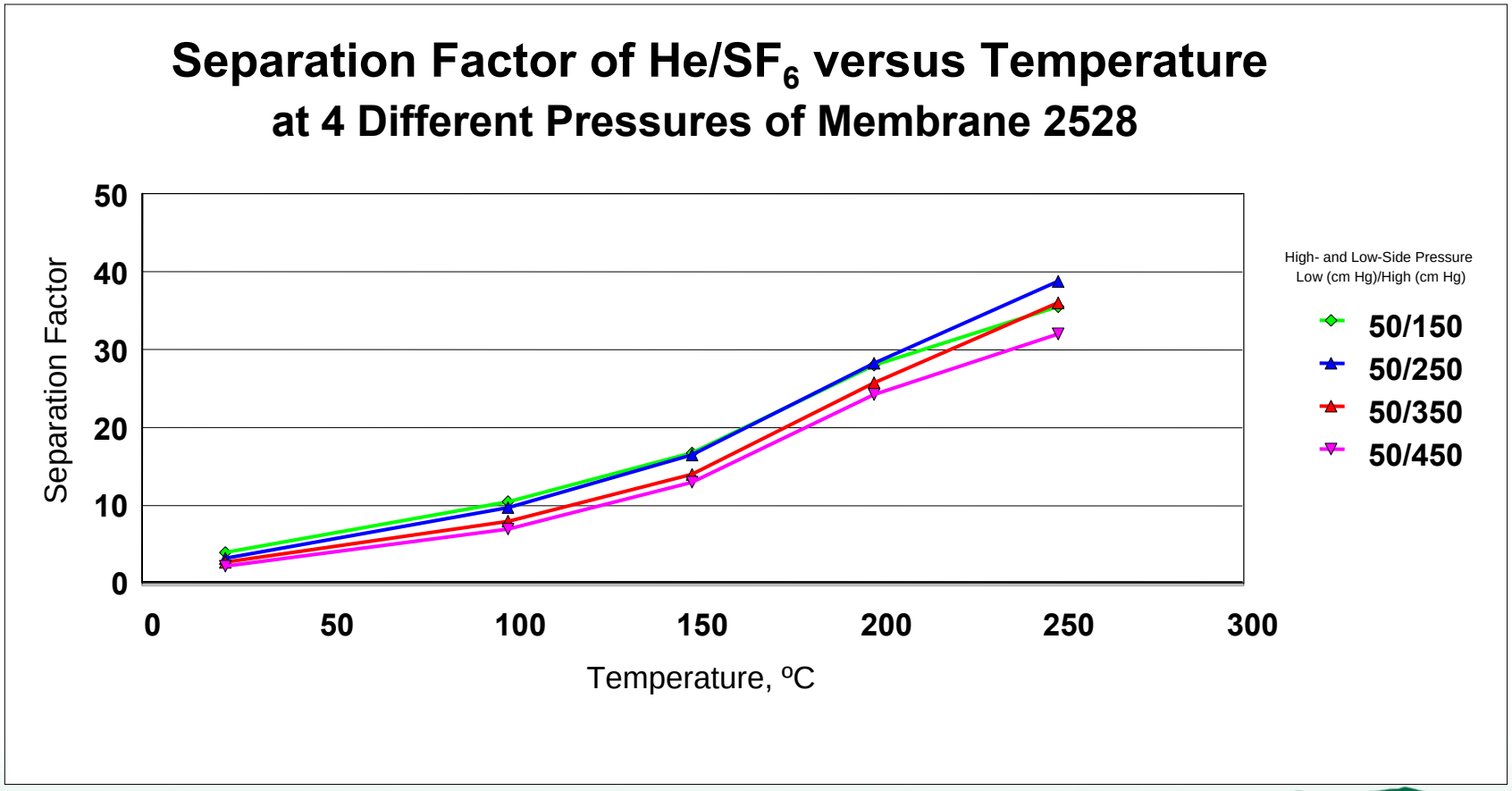
$$Q \sim \exp\left(\frac{-E_{ef}}{RT}\right)$$



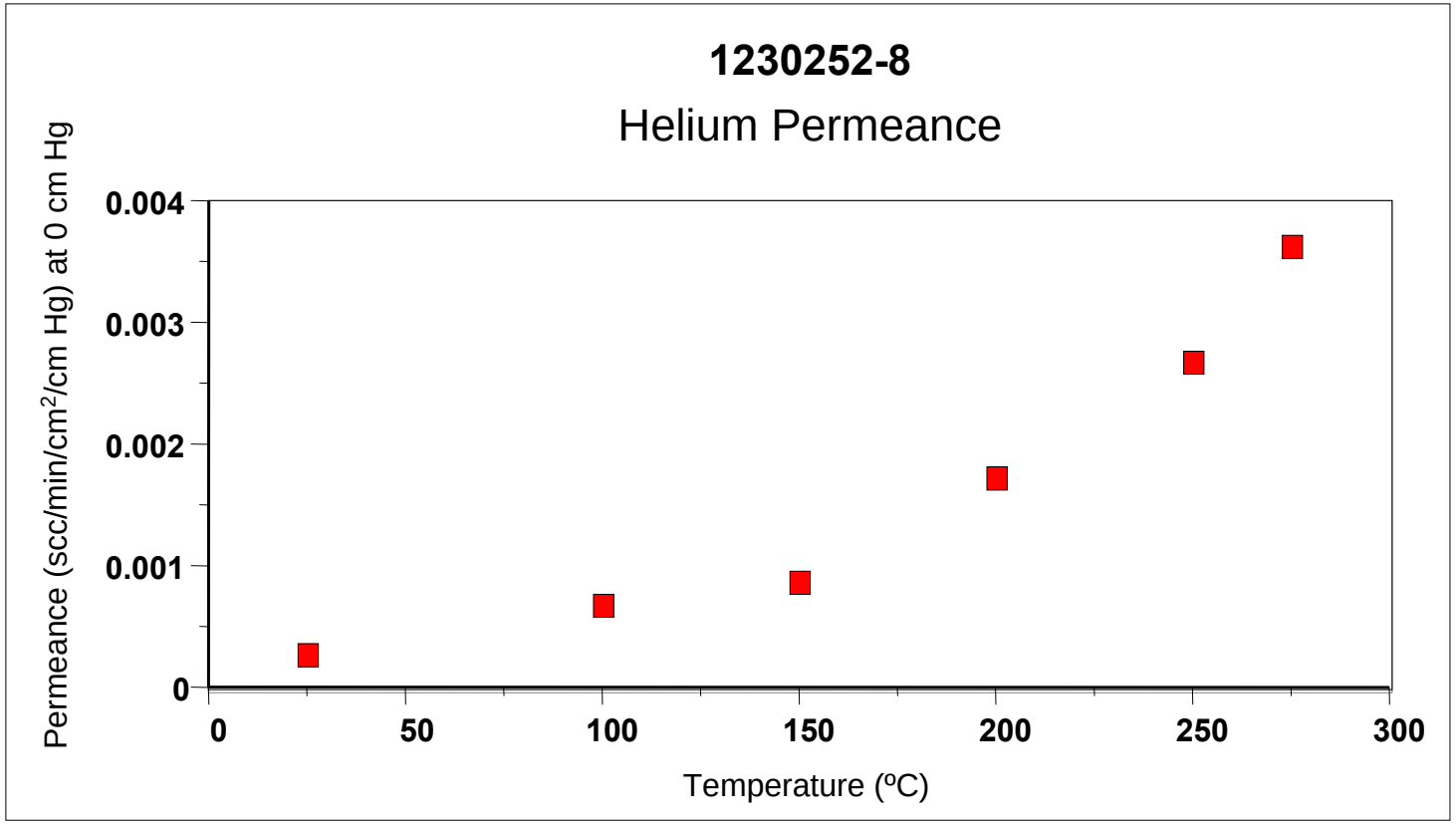
- Desired mechanism defines required pore size
- For thermally activated diffusion, small pore size (≤1 nm) is required
- These behaviors are not fully understood on a physical basis

Thermally-Activated-Diffusion Separation Factors Increase with Temperature

Separation Factor: [Y/(1−Y)] [(1−X)/X]



Permeance Increases with Temperature
(Gas Flow Through Membrane per Unit Area)



Inorganic Membrane Technology

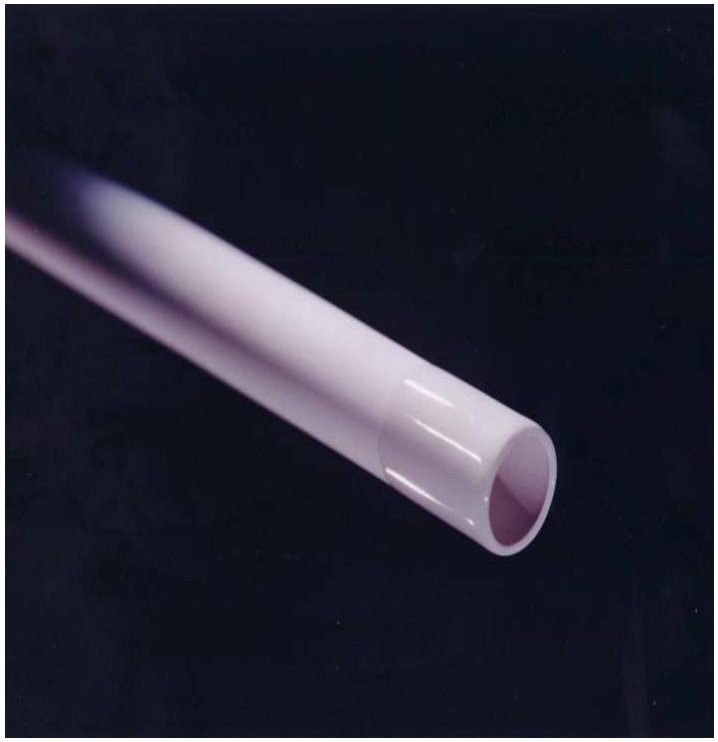
Multiple Inorganic Membranes Have Been Developed for Commercial Production at ORNL

- 316L stainless steel filters
- Nickel-on-nickel HEPA-like filters (400−900 nm)
- Titania-on-alumina ultrafilter (60 nm)
- Inconel 600 filters (6300 nm)
- 310 stainless steel filters (6400 nm)
- 304L stainless steel filters (6500 nm)
- Hastelloy X filters (7100 nm)
- Nickel depth filter (500−5000 nm)
- Zirconia-on-stainless steel ultrafilter (40−70 nm; 40−150 nm)
- Zirconia-on-Hastelloy ultrafilter (40−70 nm)
- Any 300 series stainless steel, Monel, Inconel, and Hastelloy filters (500−15000 nm)
- Titania filter (500−9000 nm)
- Others pending

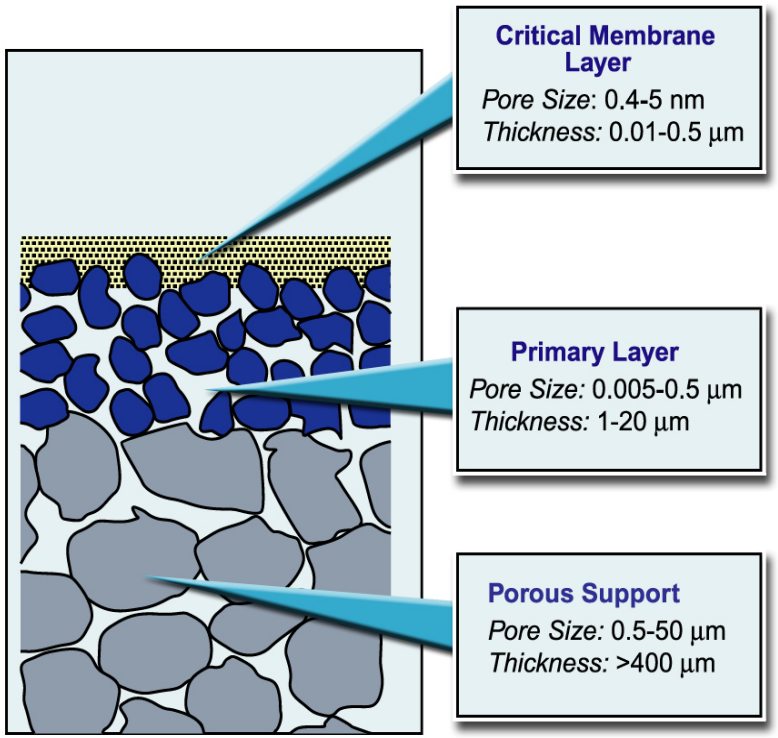
Photograph of an industrial system based on Pall's AccuSep™ inorganic membranes

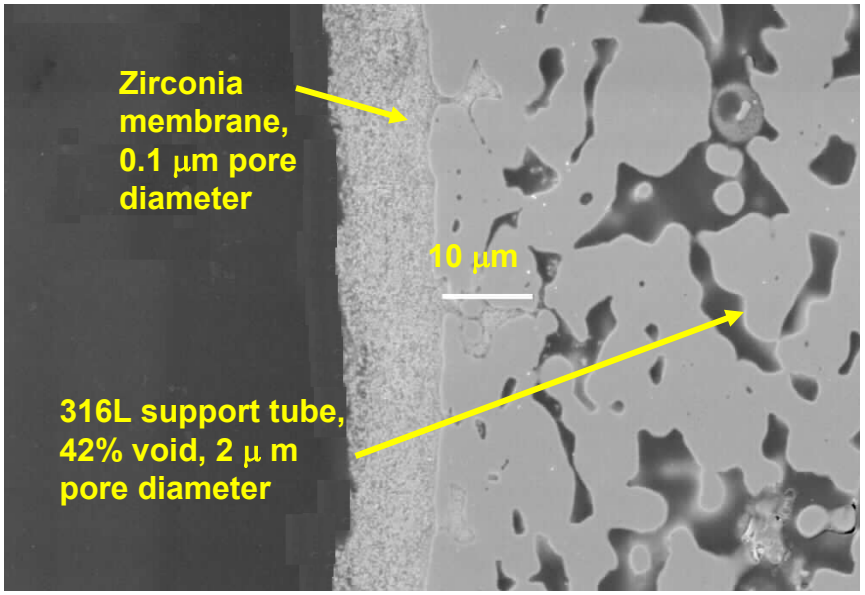
Inorganic Membrane Fabrication Processes Are Versatile (ORNL Technology)

- Choice of pore diameters from 0.5 to 20,000 nm
- Support structure and layer made of variety of metals and ceramics
- Mechanical, thermal, and chemical stability
- Membrane layer thickness of 2 µm or less yielding a high permeance at low pressure drop
- Proven scalability



Thin Critical Membrane Layer Allows High Permeance of Fluids Through Small Pore Membranes



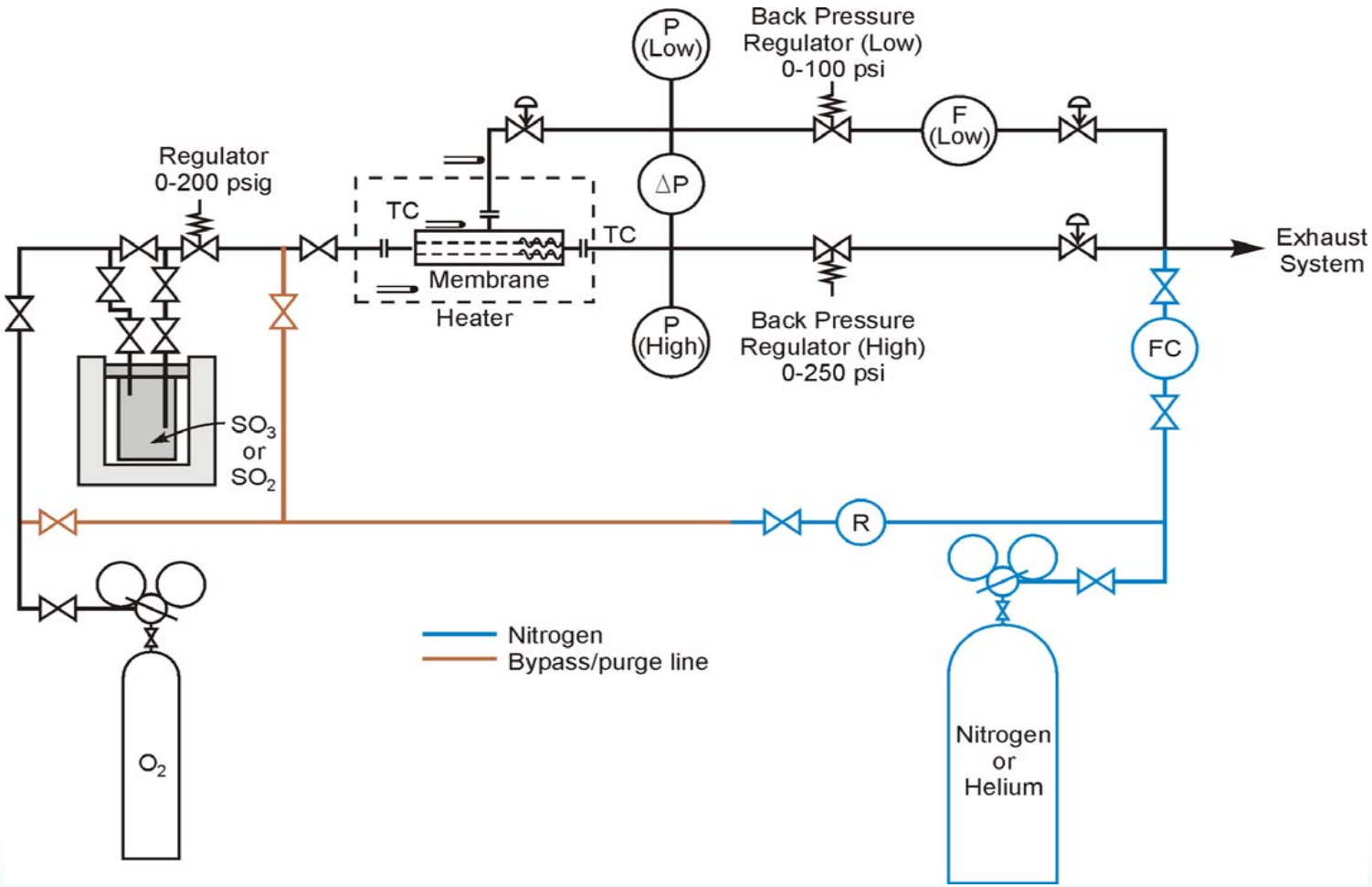


Development of Sulfur Species Separation Membrane

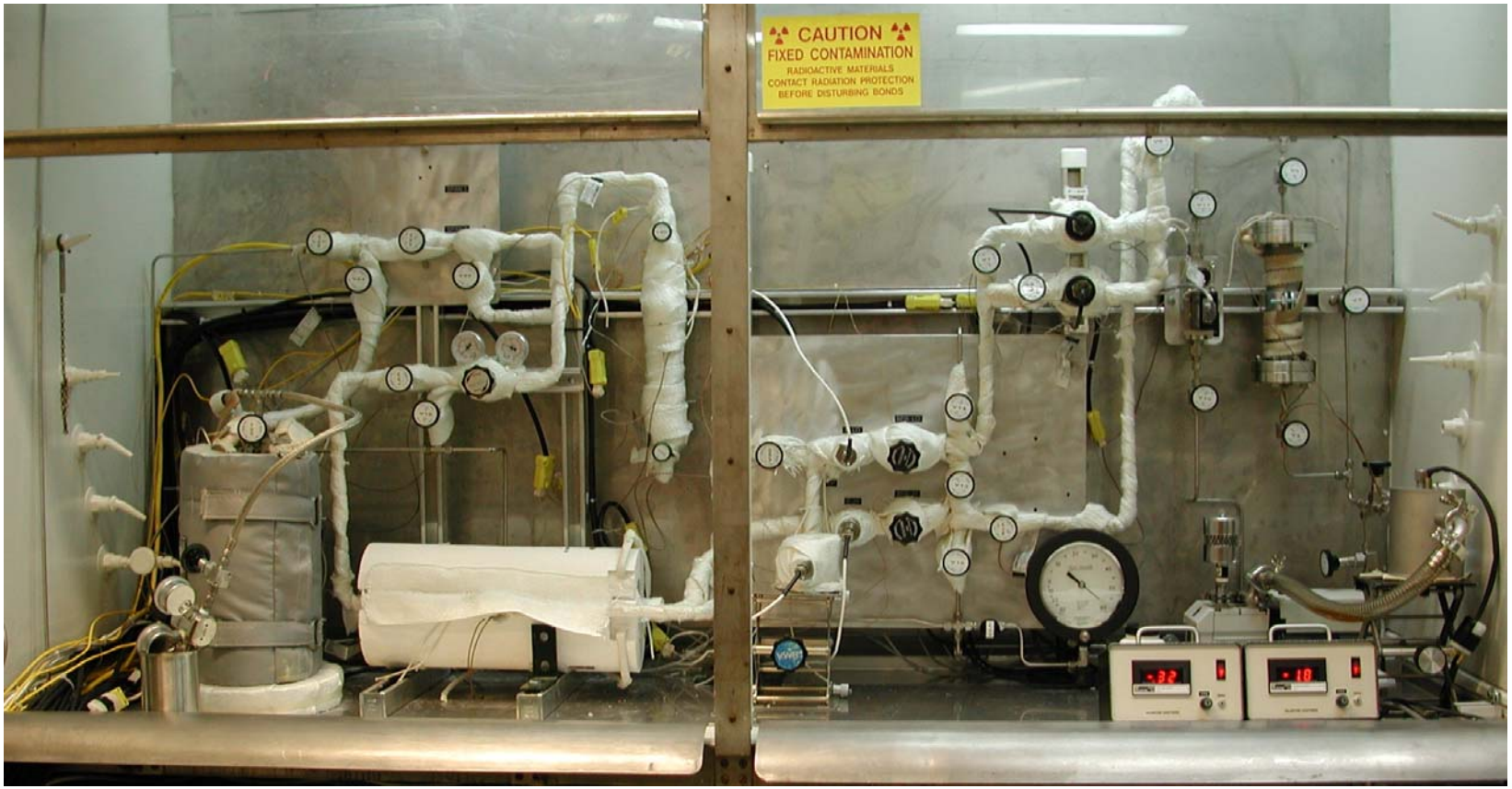
Technical Approach

- Current technology does not allow design of inorganic membranes from first principles
- Based on previous experience, a membrane is chosen
  - ORNL has a large inventory of membranes with different properties
- Separation tests are conducted to determine separations efficiency for key components: SO_3, SO_2, H_2O, and O_2
- Experimental results and theory are used to chose the next membrane for testing
- The cycle of selecting membranes, testing, and analysis is repeated several times
- After desired membrane properties have been defined, new membranes are fabricated with the desired properties
- New, custom-designed membranes are tested with complex gas mixtures

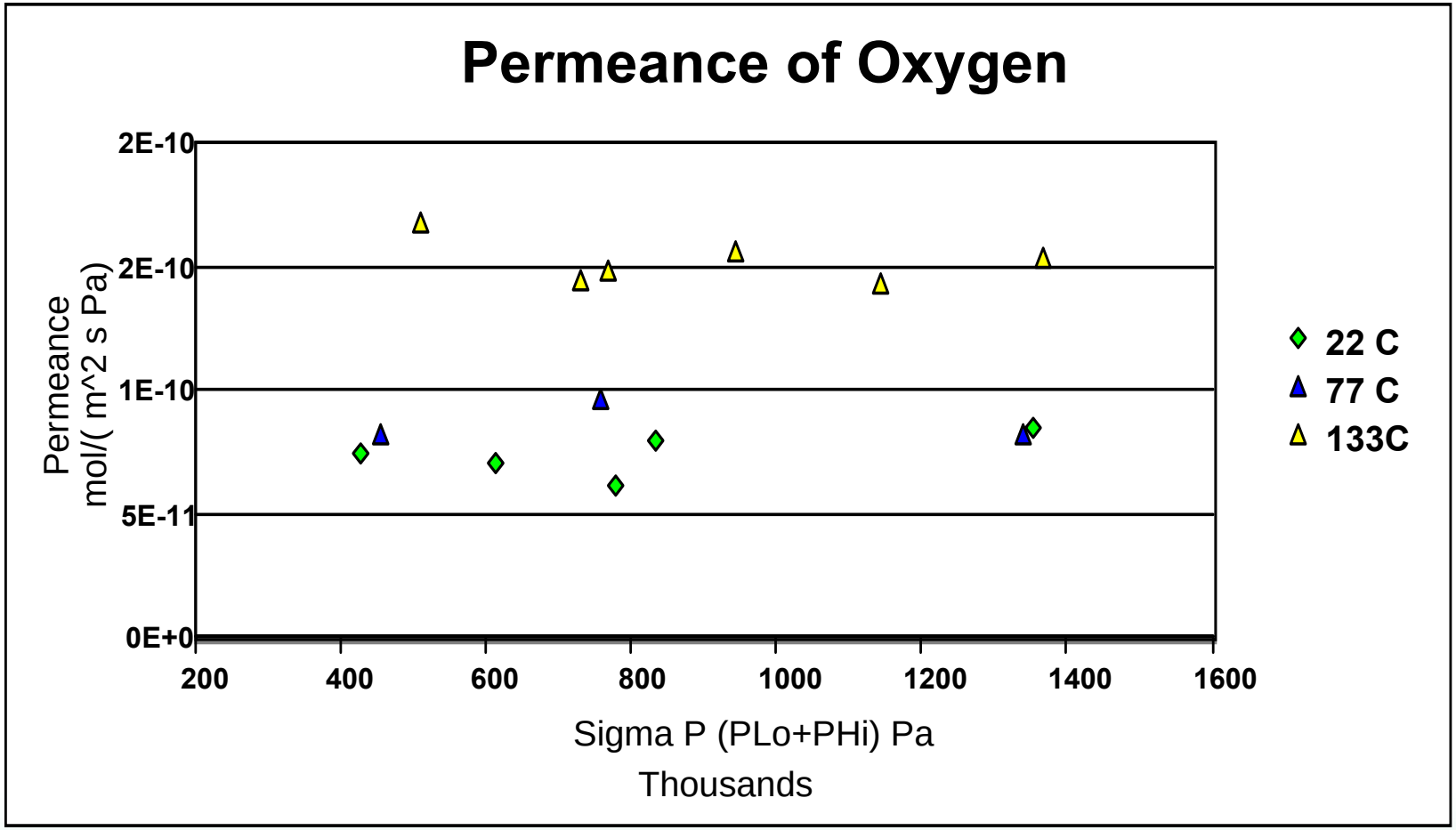
Experimental Test Facility



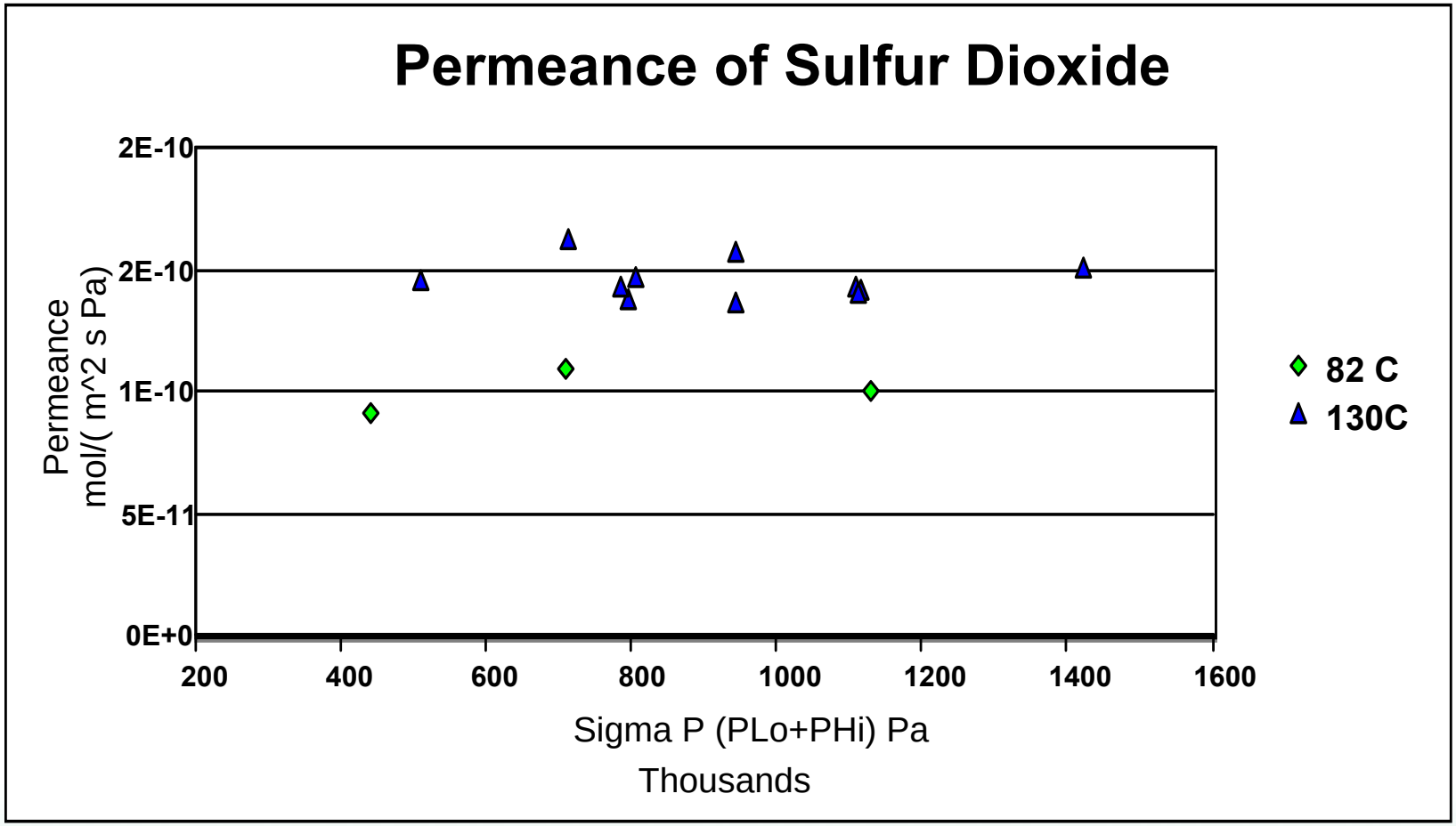
Operational Membrane Test System



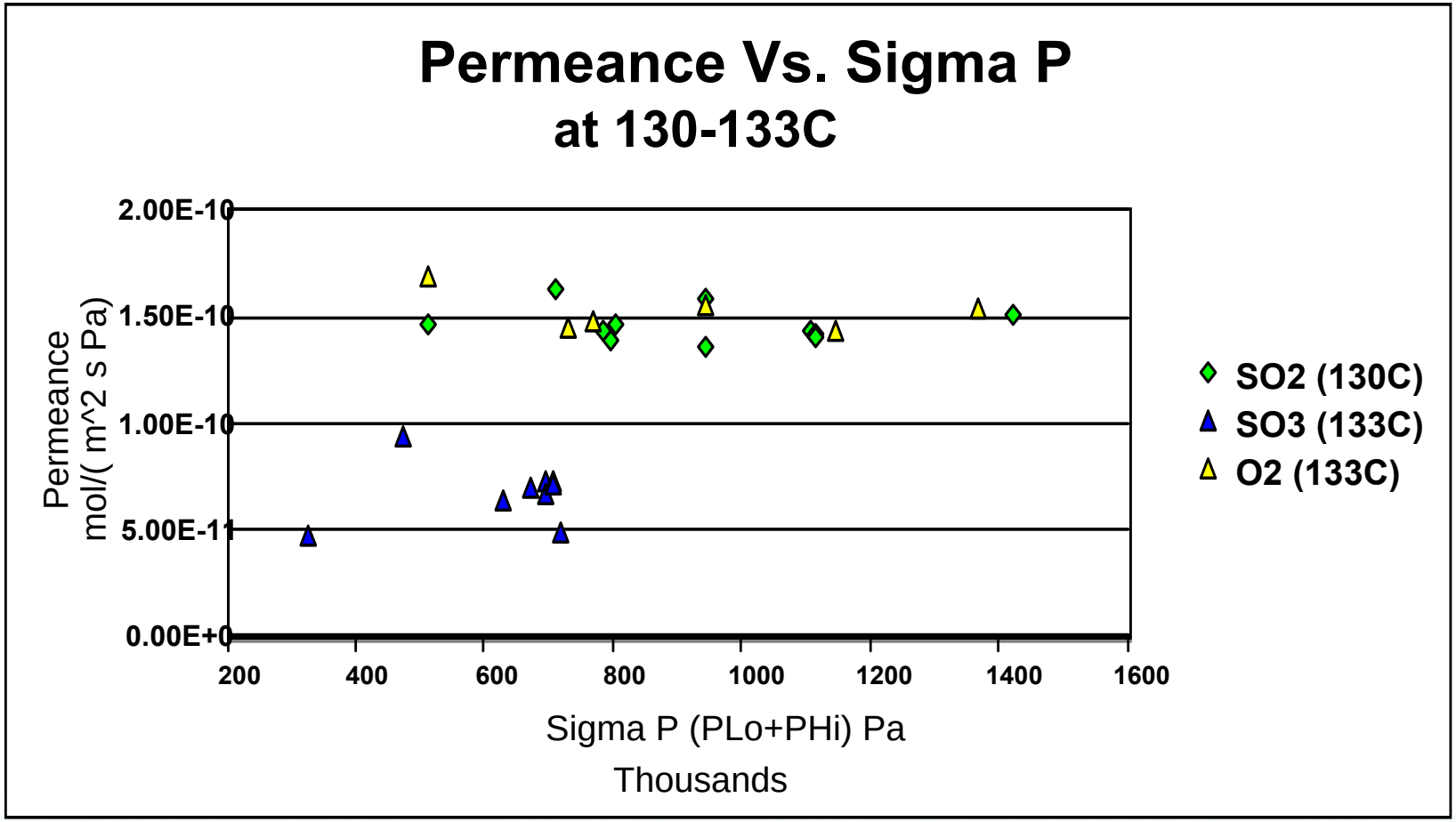
1st Generation Membrane Tests: Oxygen Data Shows Flow Through Membrane Increases with Temperature: Indicative of Desirable Thermally-Activated Diffusion



1st Generation Membrane Tests: SO_2 Data Shows Flow Through Membrane Increases with Temperature Indicative of Desirable Thermally-Activated Diffusion



1st Generation Membrane Tests: SO_2 /SO_3 and O_2/SO_3 Separation Factors Exceed 2 in Low-Temperature Tests

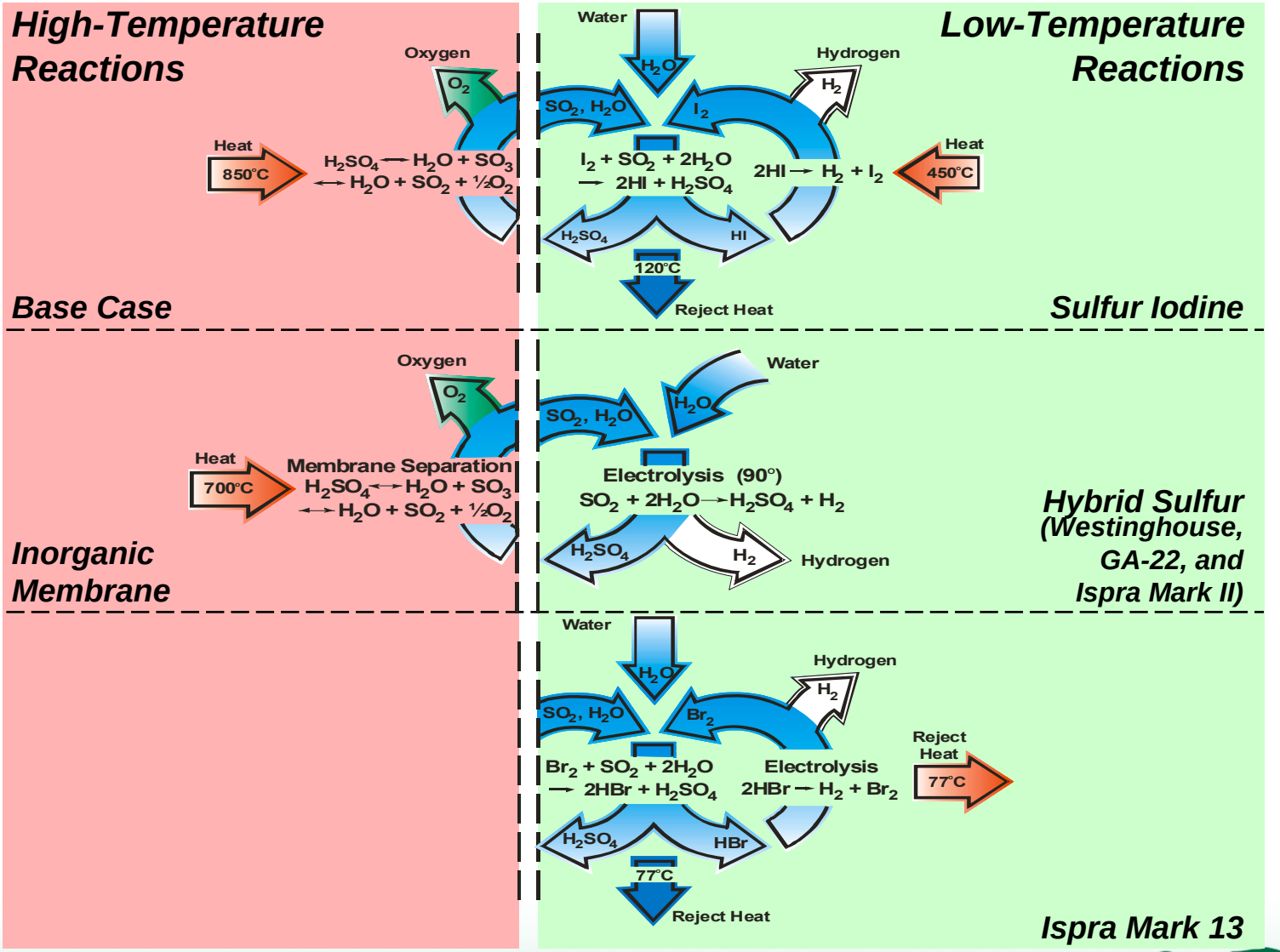


Conclusions and Path Forward

- Inorganic membranes are compatible with process chemicals
- Initial experiments show nanopore diffusion with permeance increasing with temperature—the desired behavior for a sulfur thermochemical membrane
- Initial experiments with first-generation membranes show low-temperature separation of O_2 and SO_2 from SO_3
  - Separation factor for O_2/SO_3: 2.3
  - Separation factor for SO_2/SO_3: 2.2
- Preliminary work is highly encouraging and suggests that a practical separations membrane can be developed
- Based on first experiments, a second membrane has been chosen and higher temperature experiments with the second membrane are underway

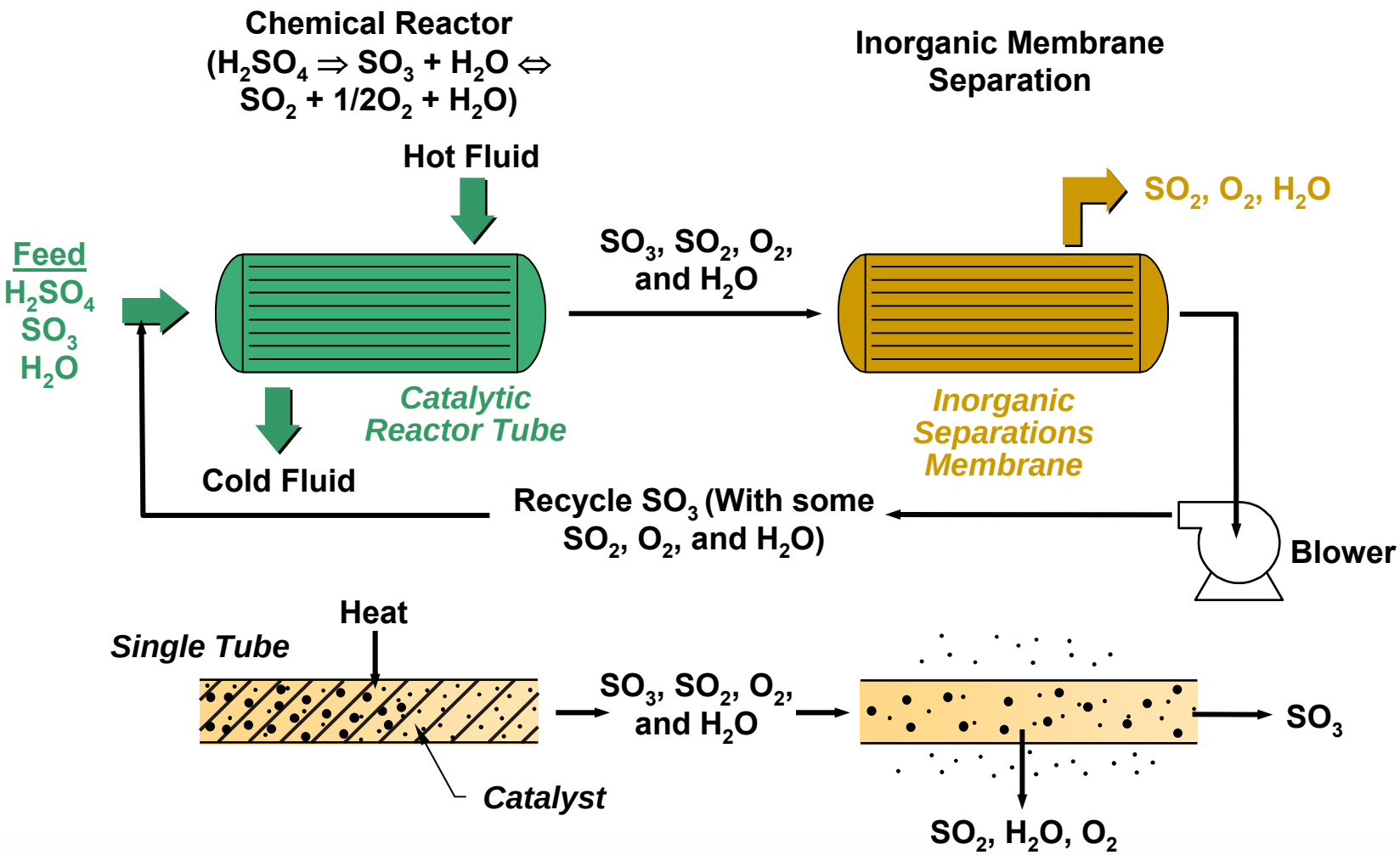
Backup

Sulfur Family of Thermochemical Cycles



Alternative Sulfur Oxide Decomposition System Design

(SO_2, O_2, and H_2O Separation Allows the Reaction to Be Driven to Completion)

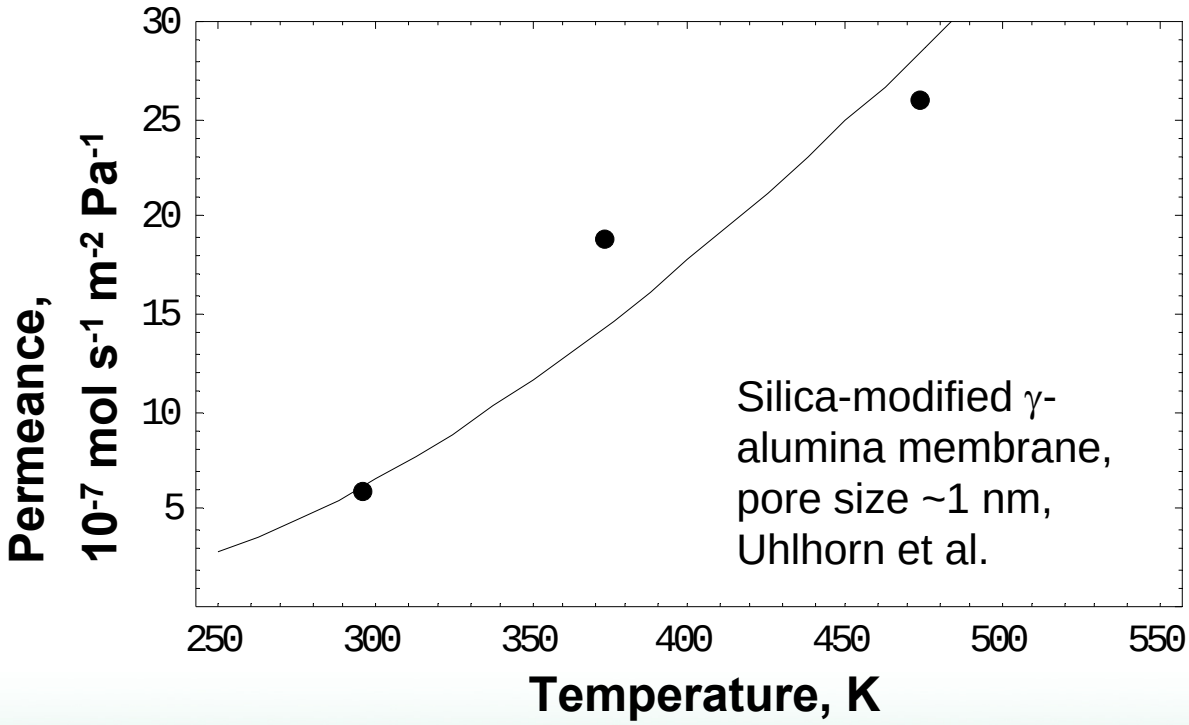


Permeance and Separation Factor Are Critical Membrane Attributes

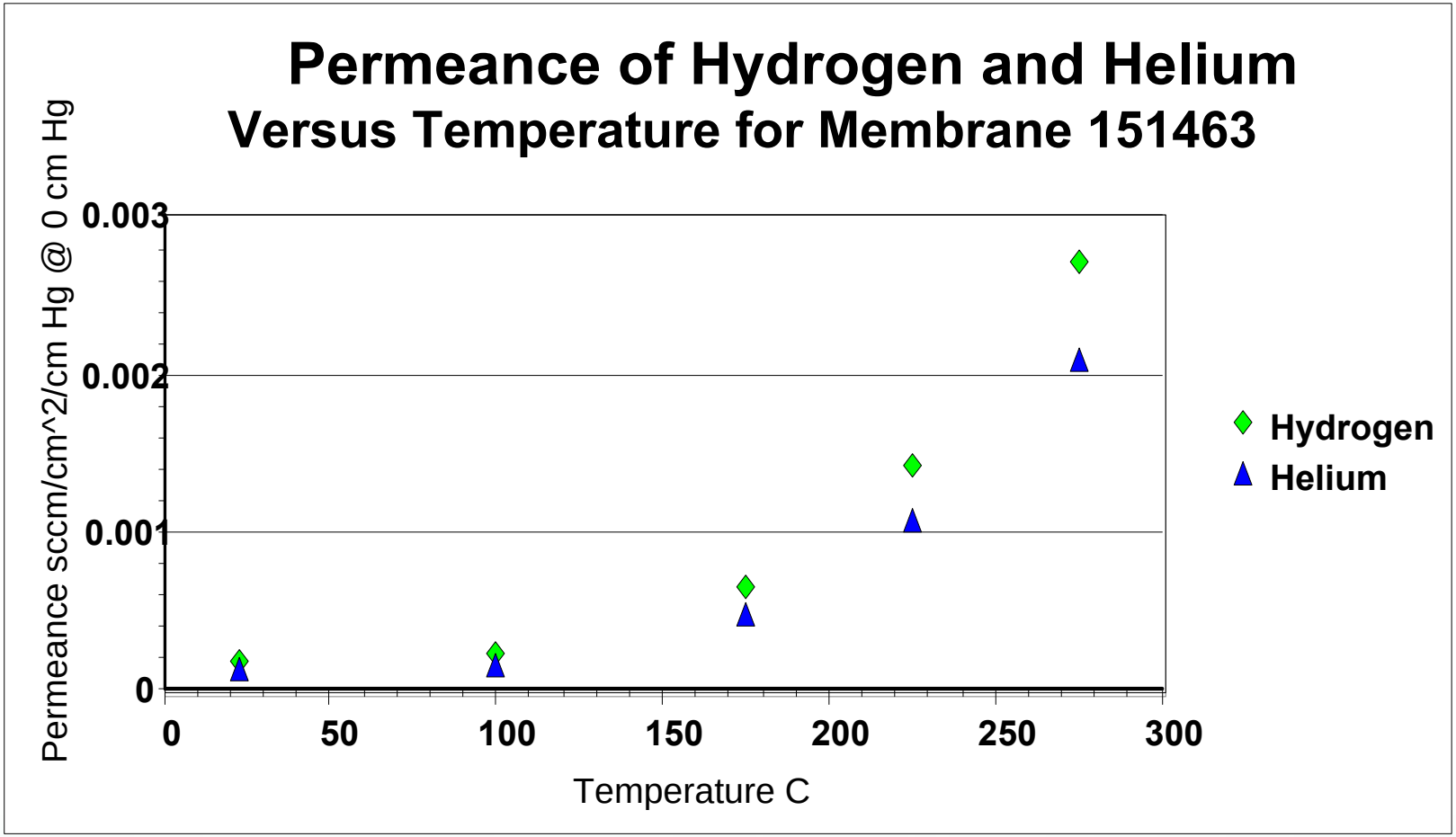
- Permeance is the volumetric flow per unit of time per unit of membrane surface area per unit of pressure difference between the feed stream and product stream
- Permeability is the product of permeance times membrane thickness
- Separation factor is the ratio of flow rate of gases in a binary gas mixture and is indicative of the separation effectiveness of a membrane
- Larger values of permeance and separation factors are desirable

For Membranes with Pore Size ≤1 nm

- **Positive temperature dependence discovered**
- **Opposite to classical mechanisms**
- **Example: Permeance observed for H_2**



Helium and Hydrogen Permeances Increase by an Order of Magnitude with Increasing Temperature



Membrane Design and Fabrication

Molecular Diameters

Water: 0.2641 nm

Oxygen: 0.3467 nm

SO_2 : 0.4112 nm

SO_3 (a larger planar molecule)

First-Generation Membrane – Experimental Characterizations

	He Perm	SF6 Perm	Ideal Separation	Hard Sphere Model Diameter
Tube	250°C	250°C	Factor	nm
HT5021b	3.22E-03	2.39E-05	134.9	0.624
HT5022a	5.71E-03	1.32E-04	43.4	0.682
HT25210a	4.62E-03	1.17E-04	39.4	0.736
HT108b	6.51E-04	5.01E-05	13.0	0.895
HT54220a	2.88E-03	3.80E-04	7.6	0.895