A Lower-Temperature Iodine-Westinghouse-Ispra Sulfur Process for Thermochemical Production of Hydrogen

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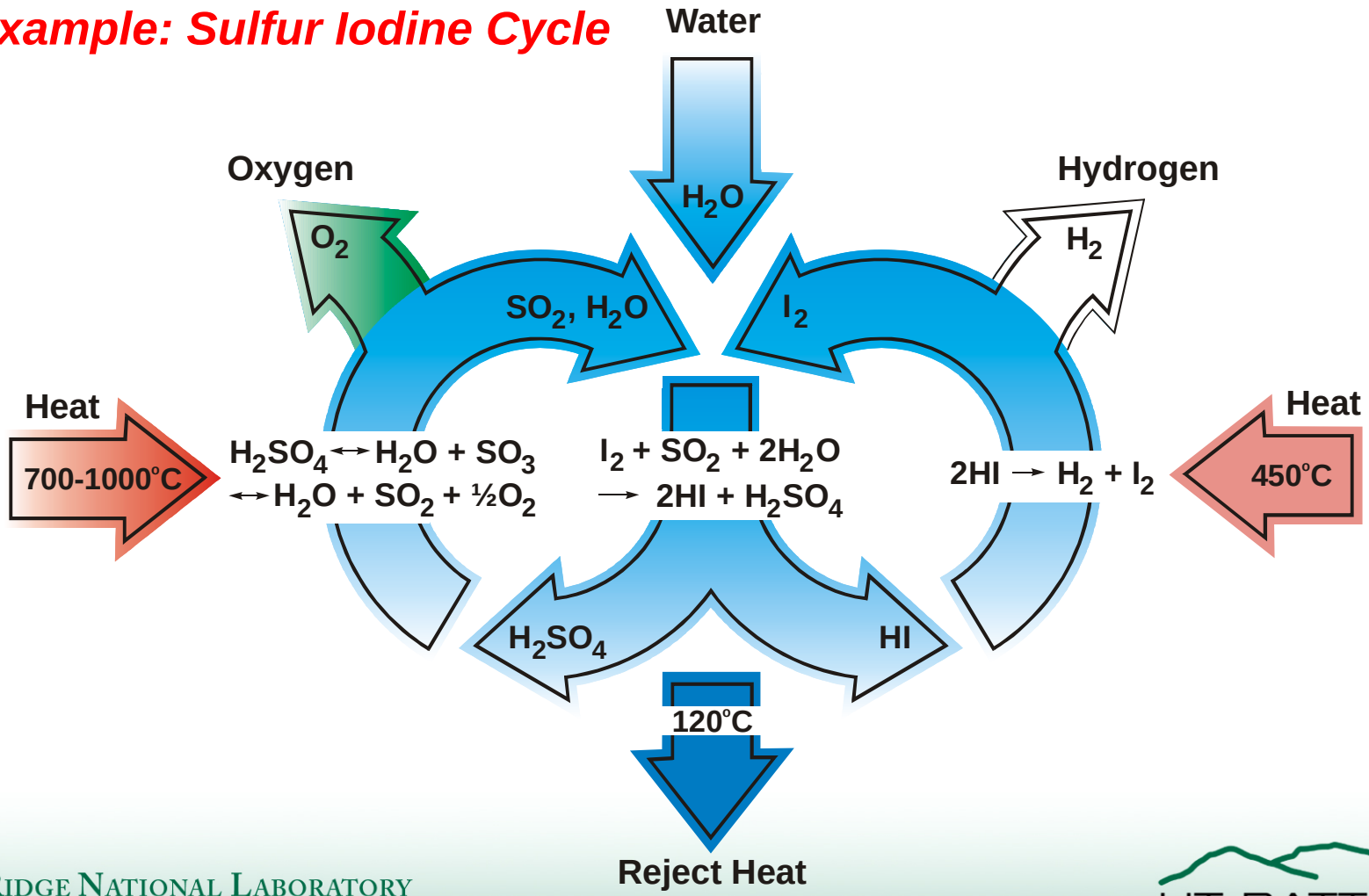
Challenges In Hydrogen Production

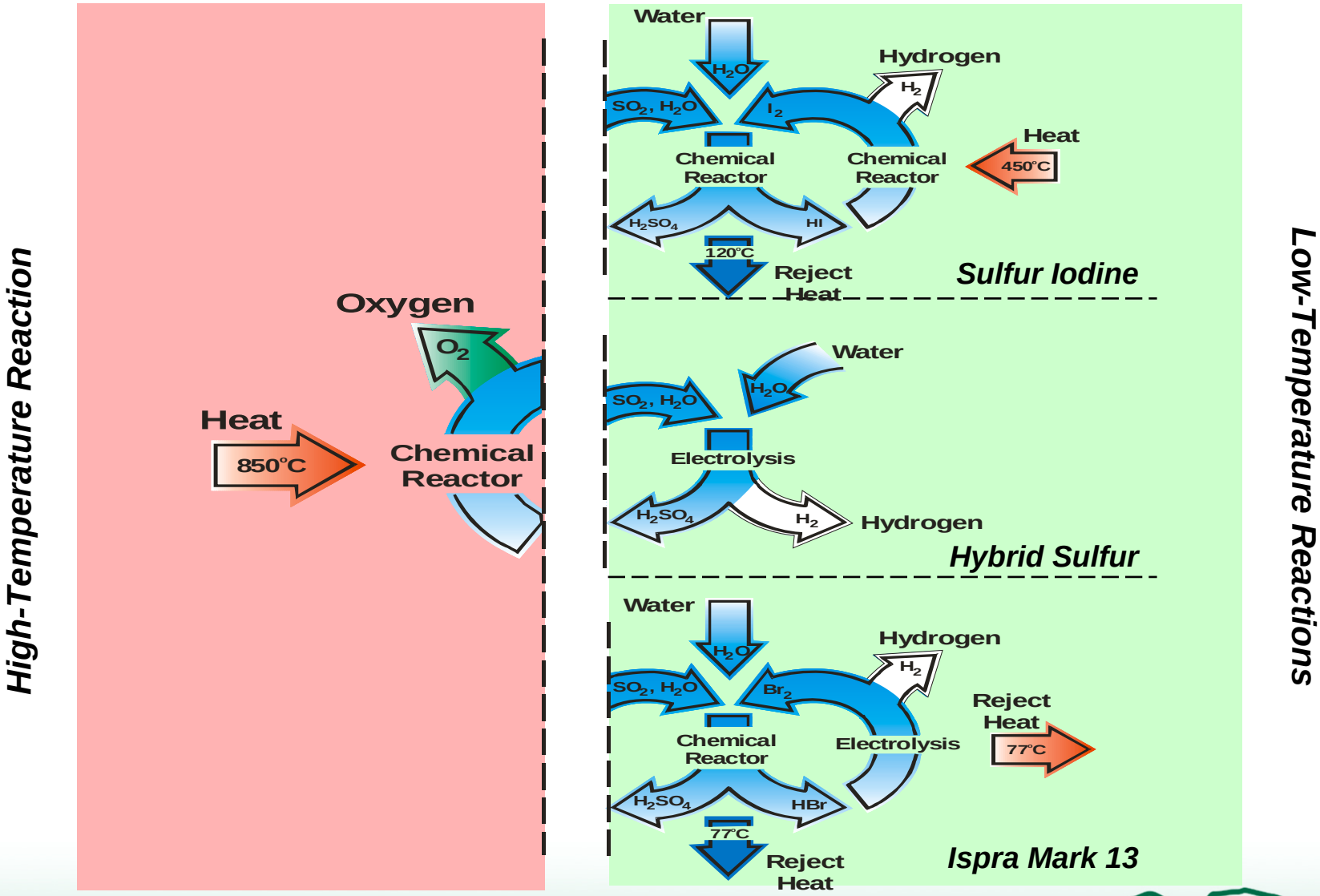
- Major efforts are underway to produce hydrogen using nuclear reactors with thermochemical cycles
  - Water + Heat $\Rightarrow$ Hydrogen + Oxygen
  - Sulfur-based thermochemical cycles are the leading options
- Sulfur cycles require very high temperatures (850ºC)
  - Massive R&D effort is required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

Thermochemical Cycles Convert Heat And Water Into Hydrogen and Oxygen

Example: Sulfur Iodine Cycle



Sulfur Family of Thermochemical Cycles



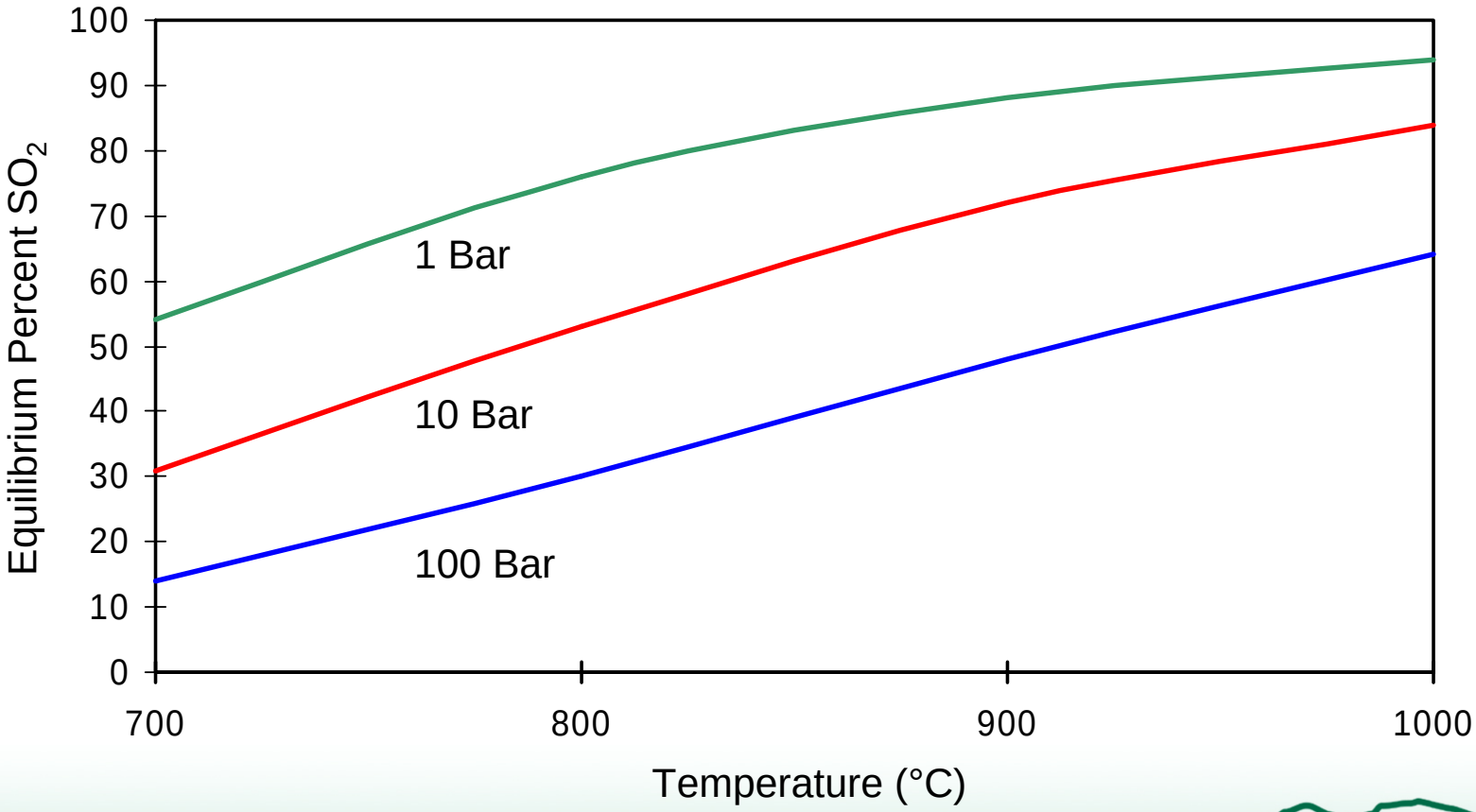
The High-Temperature Step In Sulfur Cycles Is The Thermal Decomposition of Sulfuric Acid

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

- 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

Concentration of SO_2 Versus Temperature

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



One Solution For Complete H_2SO_4 Dissociation

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

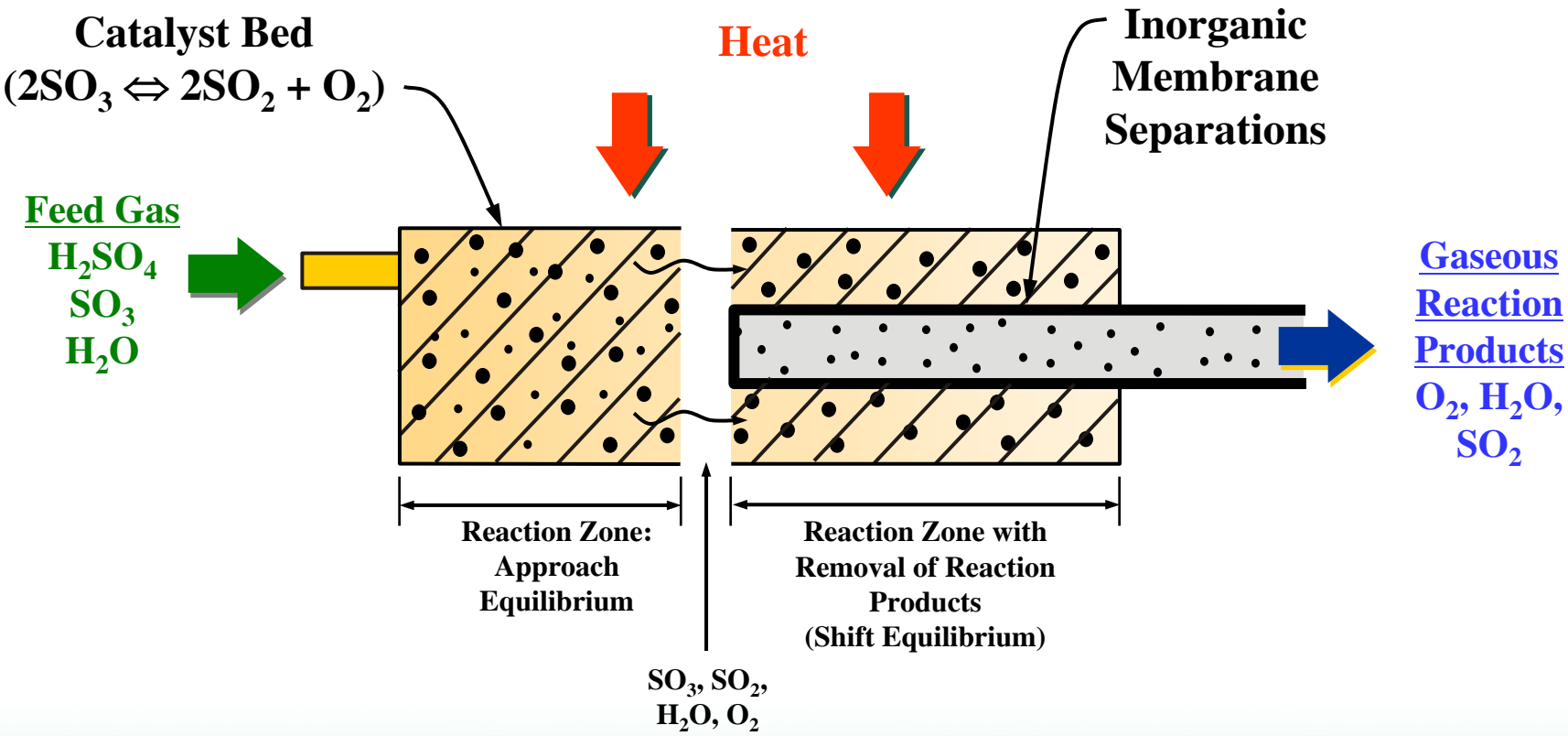
$$H_2SO_4 \Leftrightarrow SO_3 + H_2O \Leftrightarrow SO_2 + H_2O + 1/2\ O_2$$

- 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 to reduce peak temperature to between 650 and 750°C

Sulfur Oxide Decomposition System Design

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



Inorganic Membrane Technology

Technologies Developed At

Oak Ridge National Laboratory

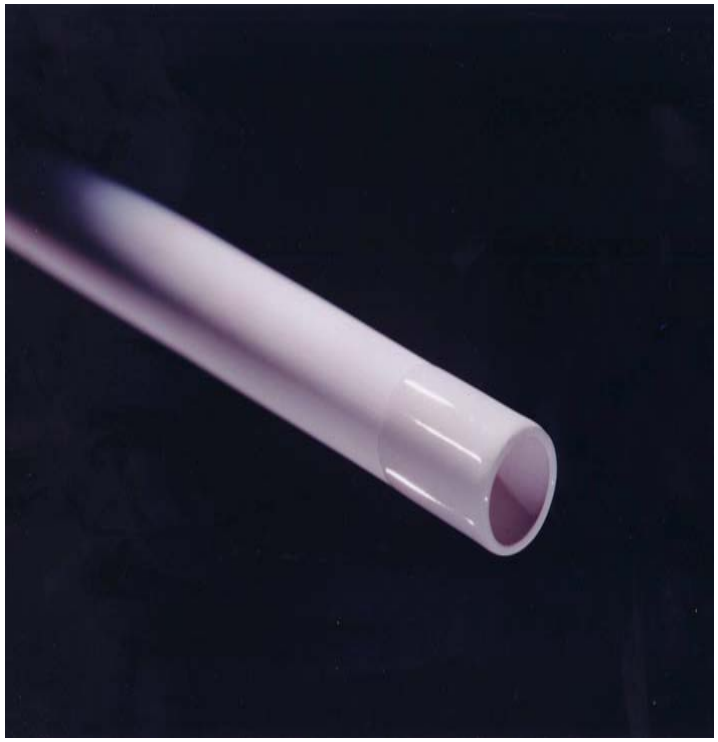
Inorganic Membranes Have Been Developed for Commercial Production

- 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

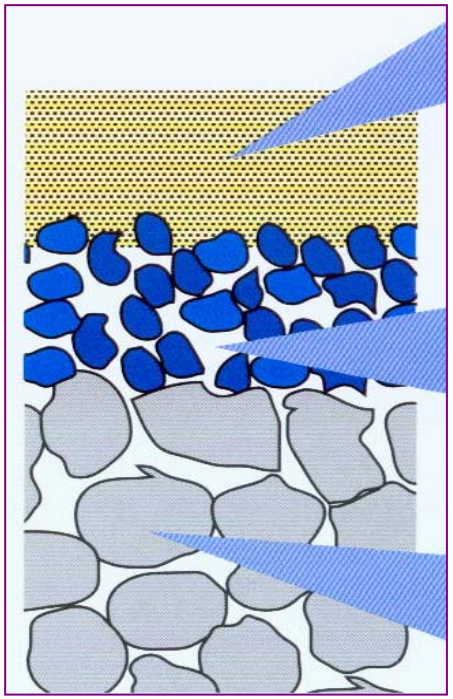
Photograph of an industrial system based on Pall's AccuSep™ inorganic membranes

Inorganic Membrane Fabrication Processes Are Versatile
(ORNL Technology)

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



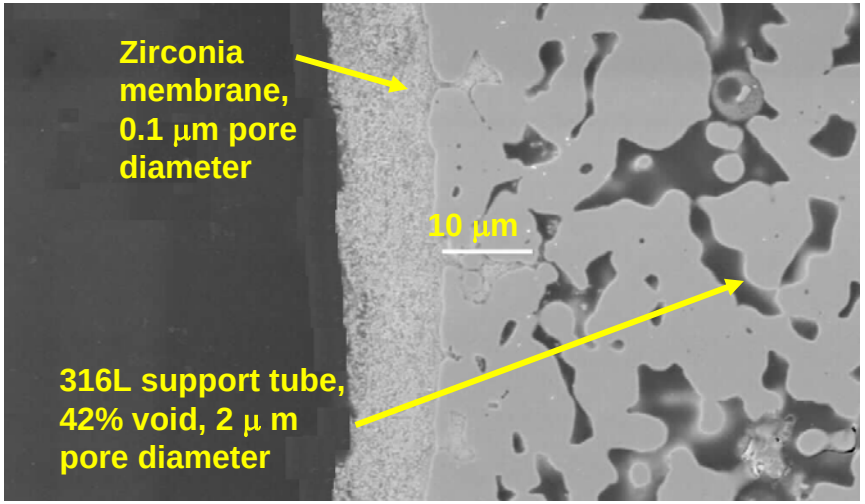
Separation Occurs at the Critical Separation Layer



Critical membrane Layer
Pore Size: 0.4-5nm
Thickness: 0.01-0.5 µm

Primary Layer
Pore Size: 0.005-0.5 µm
Thickness: 1-20 µm

Porous Support
Pore Size: 0.5-50 µm
Thickness: >400 µm



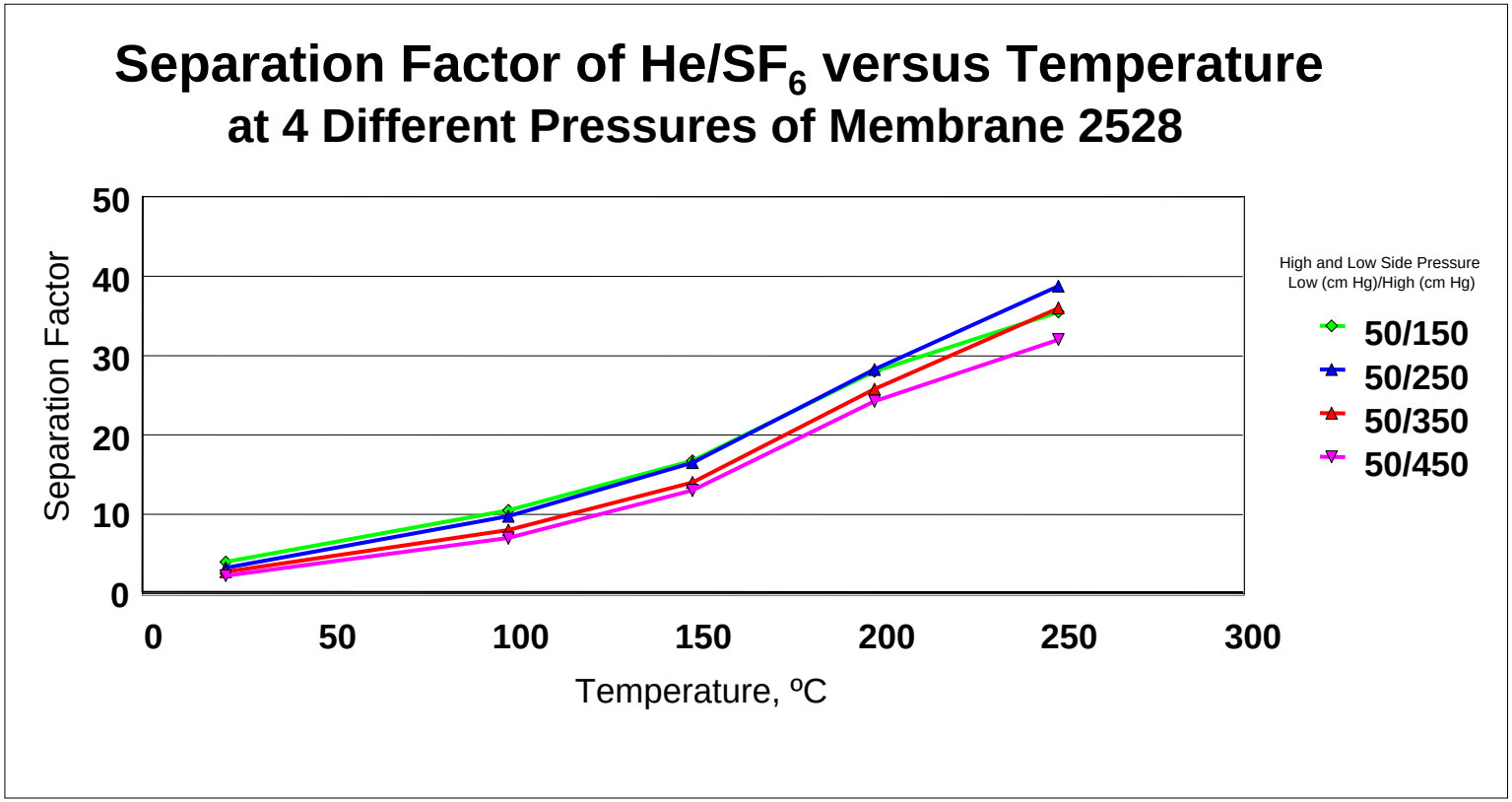
Separation of Sulfur Species

Status of High-Temperature Inorganic Membrane Separation Technology

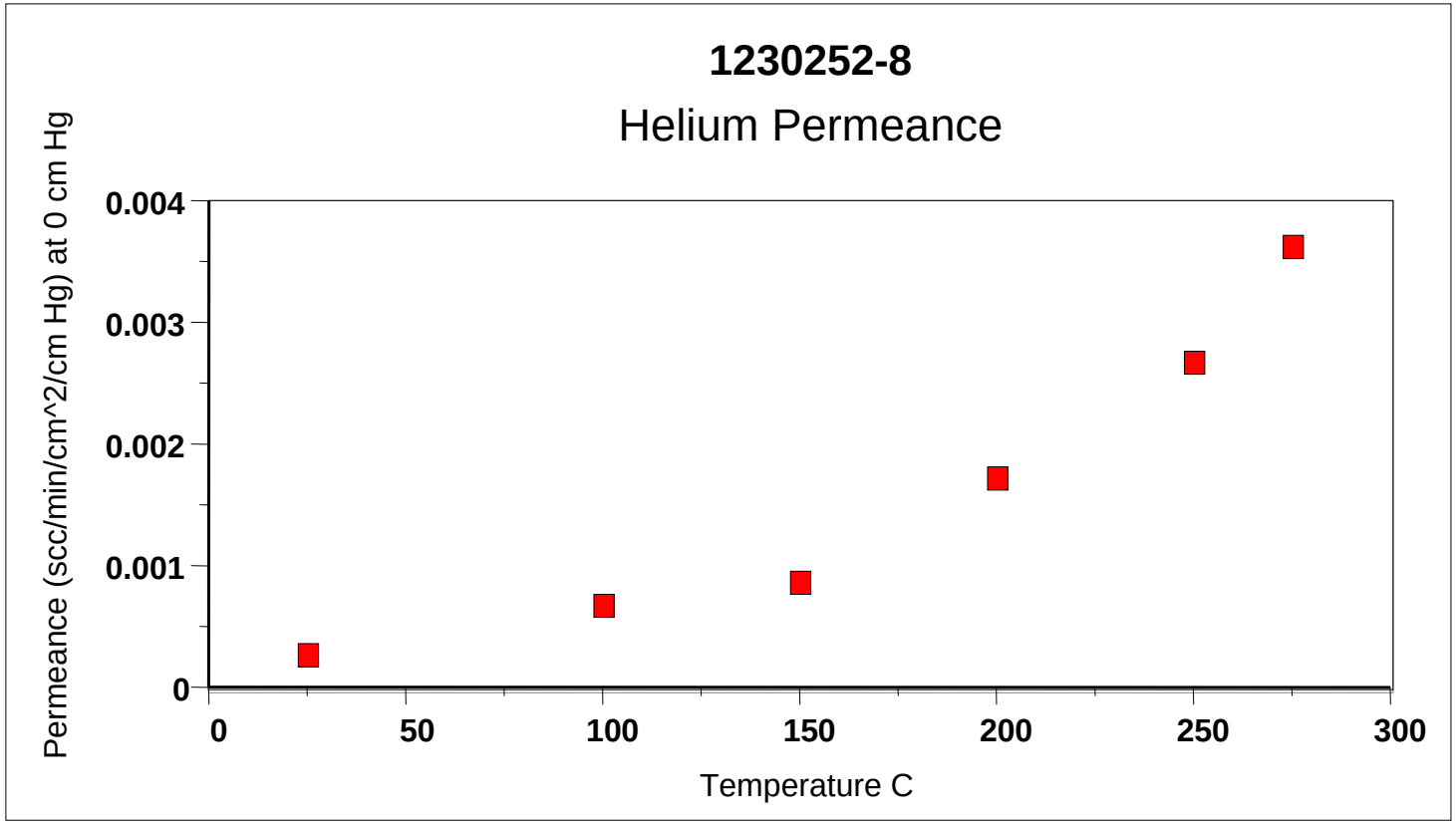
- Fabrication technology can make high-temperature membranes
- Experimental data and theory indicate performance of membranes improves with temperature
  - Require nanopore membranes
  - Performance based on thermally activated diffusion
  - Experiments with He/SF_6 and other systems
- No data on sulfur species separations
  - Test loop under construction

Separation Factors Are Dependent on Temperature

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

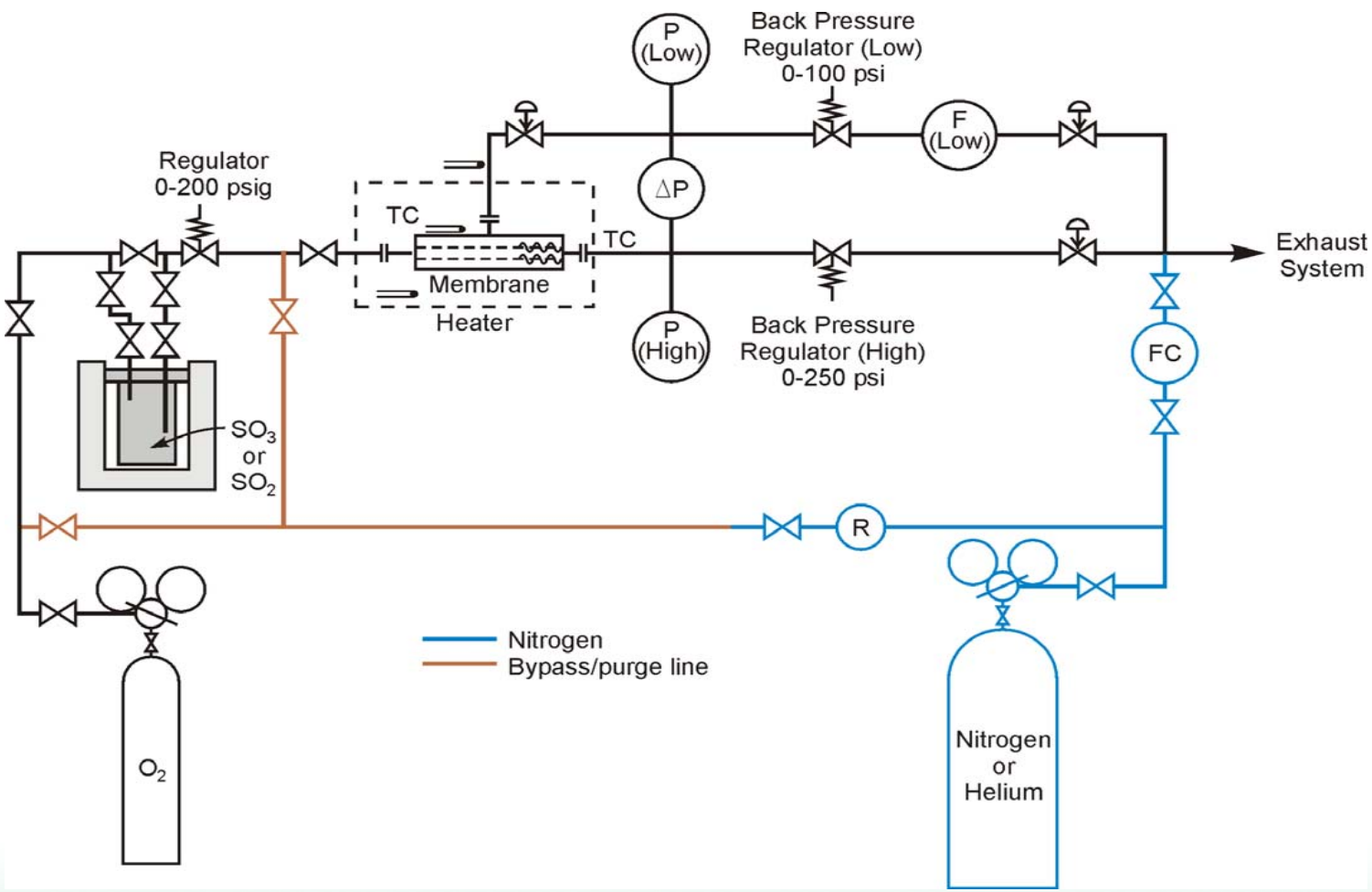


Permeance Increases With Temperature
(Gas Flow Through Membrane Per Unit Area)

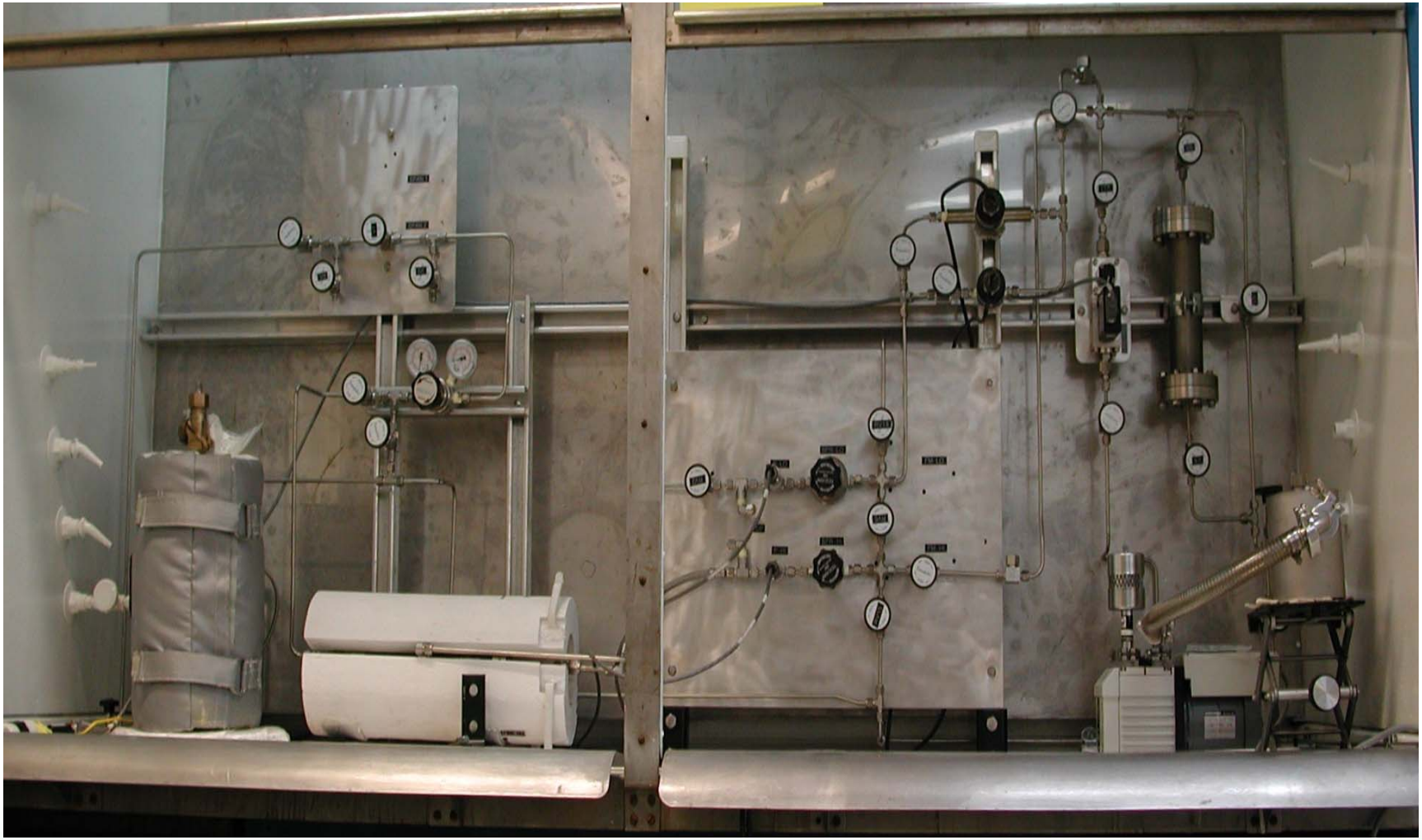


Path Forward To Sulfur Species Inorganic Membrane Separation

Experimental Test Facility



Experimental Apparatus (Under Construction)

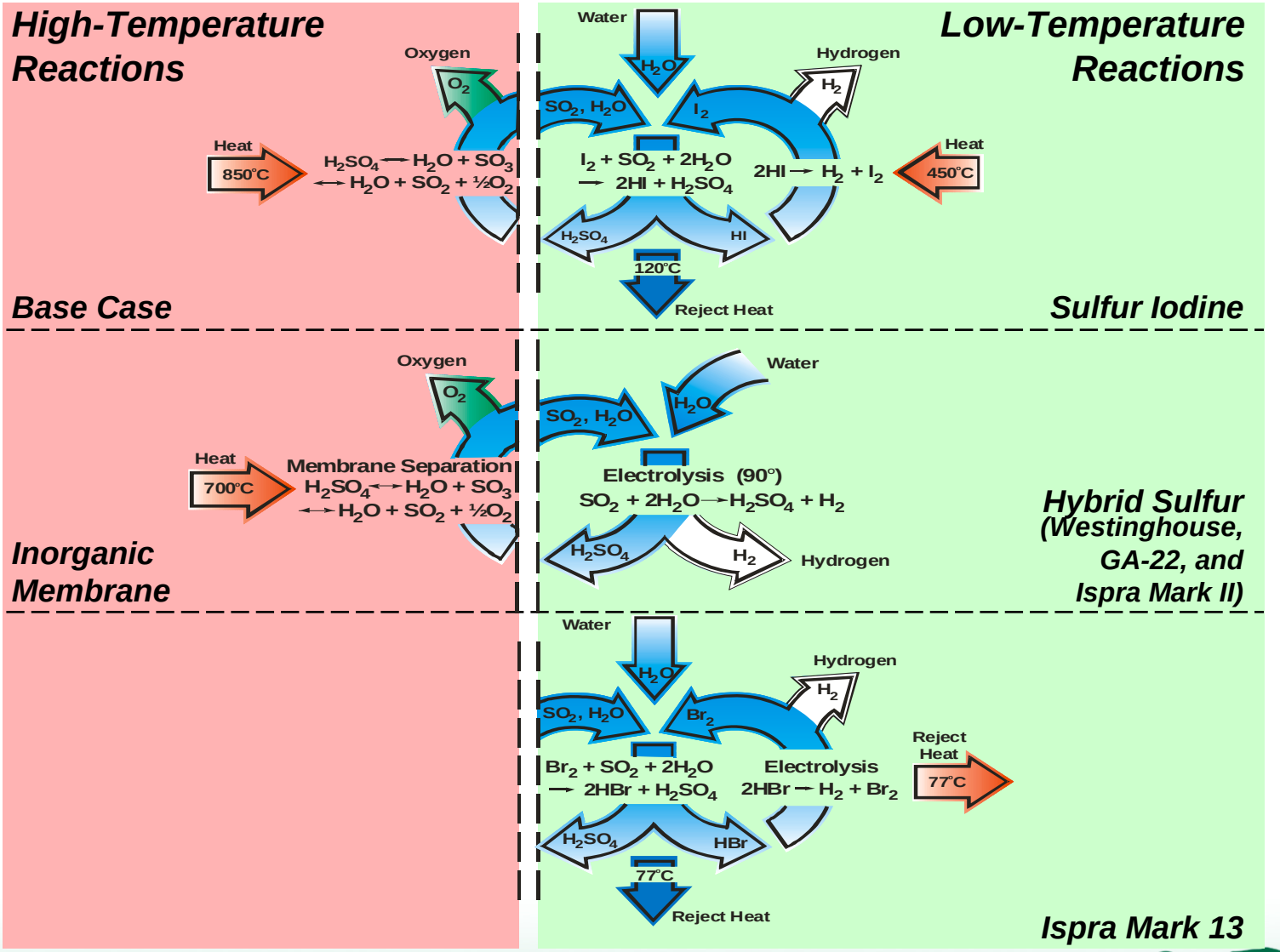


Conclusions

- Inorganic high-temperature membranes may reduce peak temperatures of sulfur thermochemical cycles
- There is large-scale industrial experience in fabricating inorganic membranes
- Earlier experiments with other gas separations shows that membrane performance improves with temperature
- Theory indicates the potential for high-performance membranes for sulfur-species separations
- Test facilities now operational
- First experimental results by the end of 2003

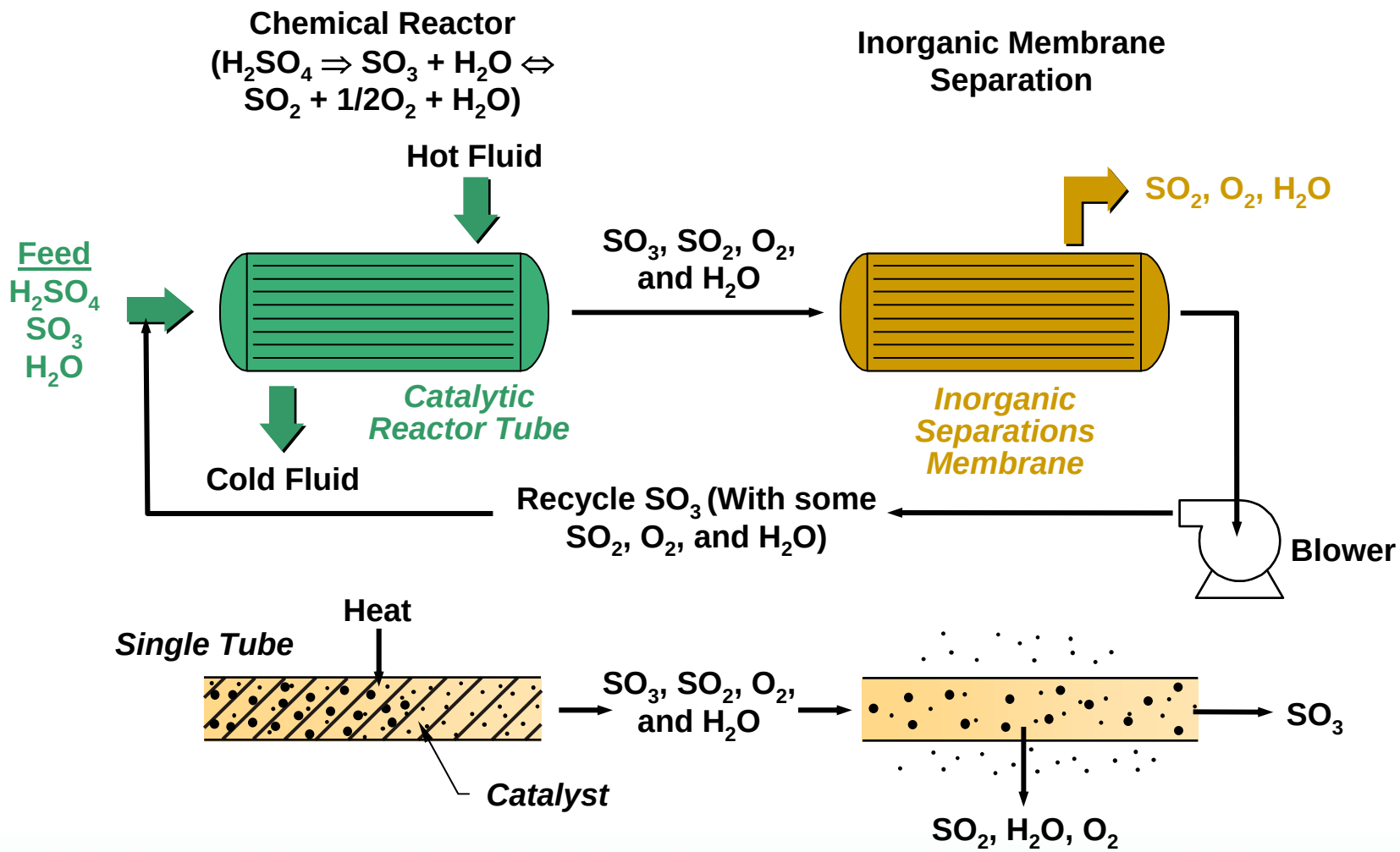
Backup

Sulfur Family of Thermochemical Cycles



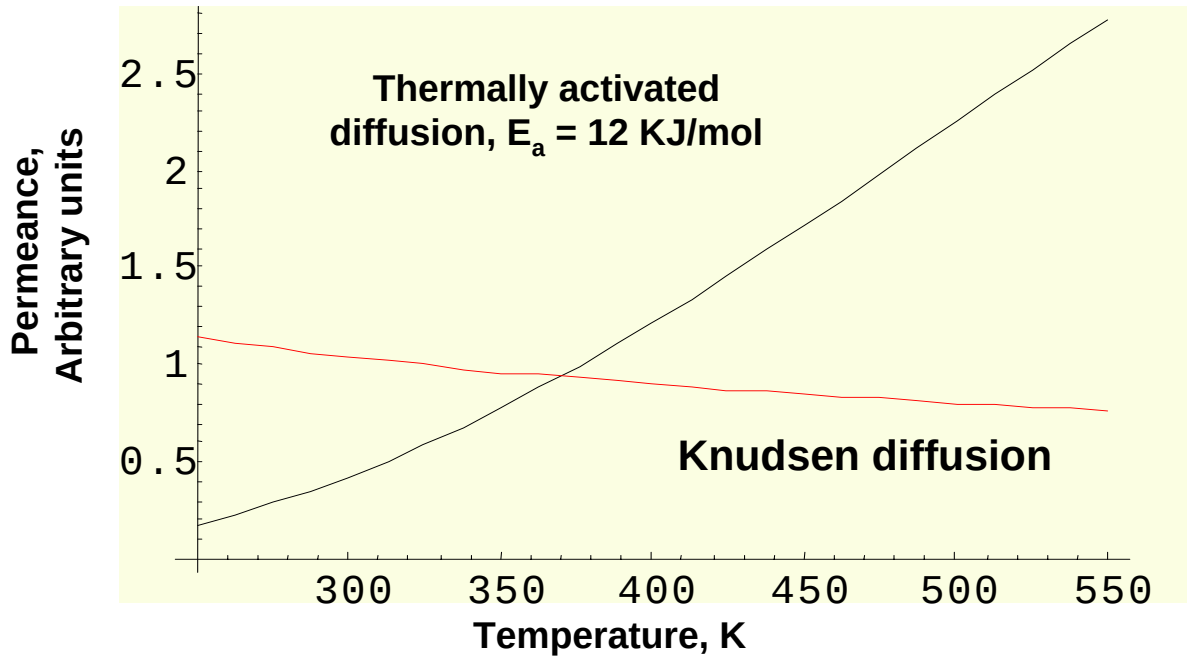
Alternative Sulfur Oxide Decomposition System Design

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



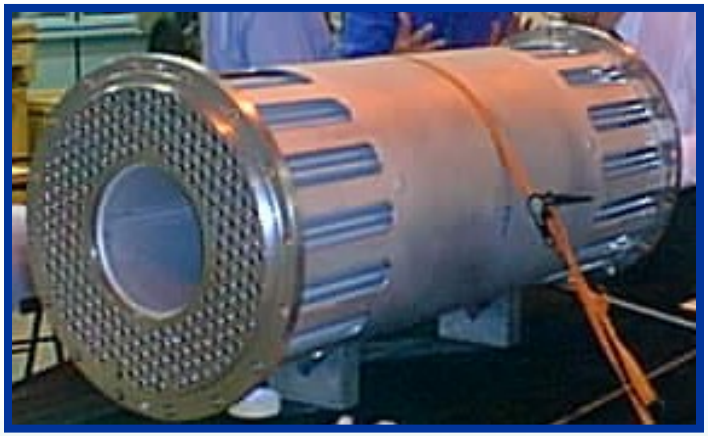
Separation Factors Increase with Temperature in Nanopores Because Gas Permeation Exhibits Thermally Activated Diffusion

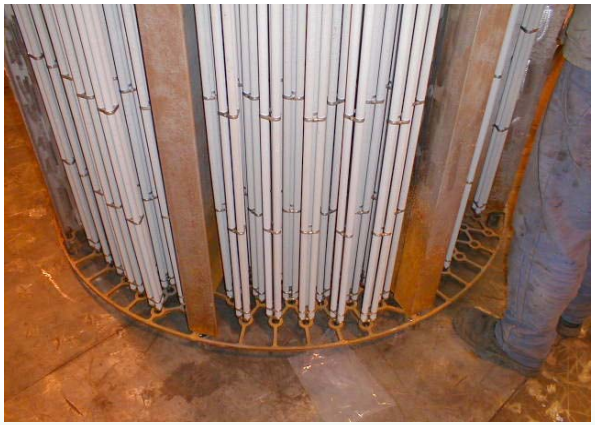
$$Q \sim \exp\left(\frac{-E_{ef}}{RT}\right)$$



- **Rates of increase of permeance with increasing T for both H_2 and He increase with decreasing pore diameter**
- **Implies that E_{ef} is a strong function of pore radius**
- **These behaviors are not fully understood on a physical basis**

ORNL's Industrial Partner, Pall Corporation, Offers Accusep Filters in Several Configurations





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

Path Forward

- Experimental apparatus under construction
- Theory used to select multiple membranes from stocks for testing
- Analysis of experimental results used to define preferred properties for sulfur species separations
- Optimized membrane fabricated
- Test optimized membrane
- Repeat process