Reducing Peak Temperatures For Thermochemical Hydrogen Production

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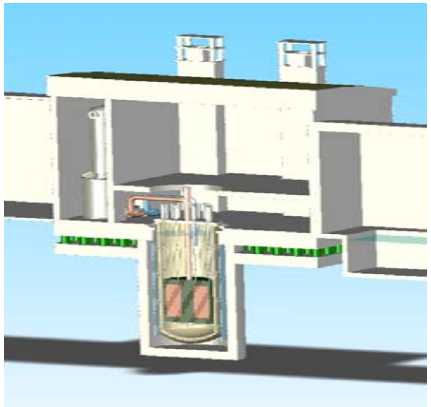

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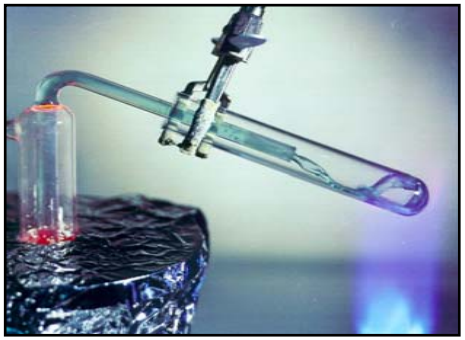


Molten Salts

Inorganic Membranes

The Challenge

Thermochemical Hydrogen Production Methods Require High Temperatures

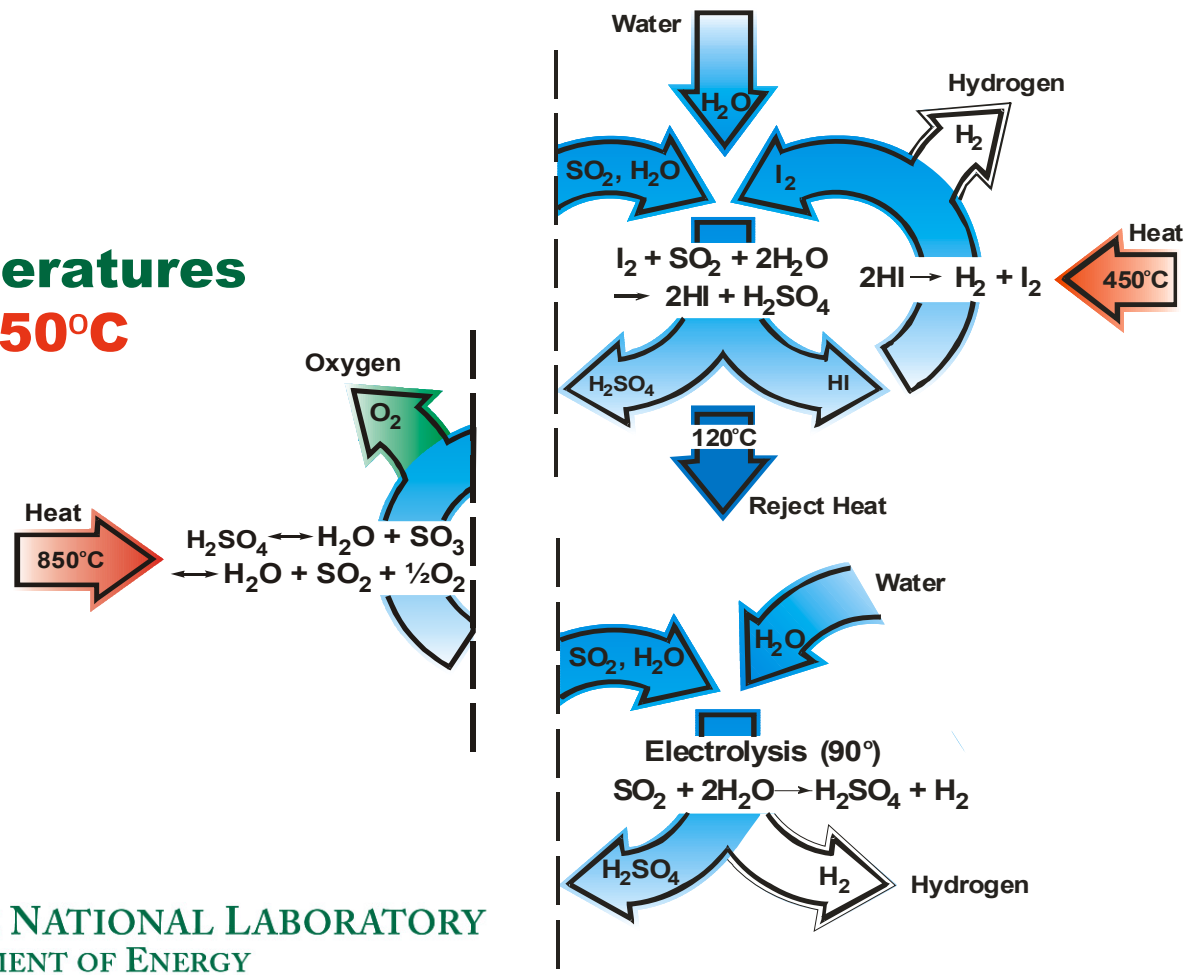
The Sulfur-Cycle Thermochemical Processes Require High-Temperature Heat

Water + Heat → Hydrogen + Oxygen

High-Temperature Reaction

Low-Temperature Reactions

Peak Temperatures
800-850°C



Sulfur Iodine

Hybrid Sulfur

Peak Temperatures are at the Limits of Practical Operations

- Three challenges
  - High nuclear-reactor temperatures at limits of materials of construction
  - Need for efficient heat transport from the reactor to thermochemical hydrogen plant
  - High temperatures in the thermochemical process
- Three solutions are being examined at ORNL
  - The Advanced High-Temperature Reactor
  - Molten-salt-heat transport
  - Inorganic membranes to drive chemical reactions to completion at lower temperatures

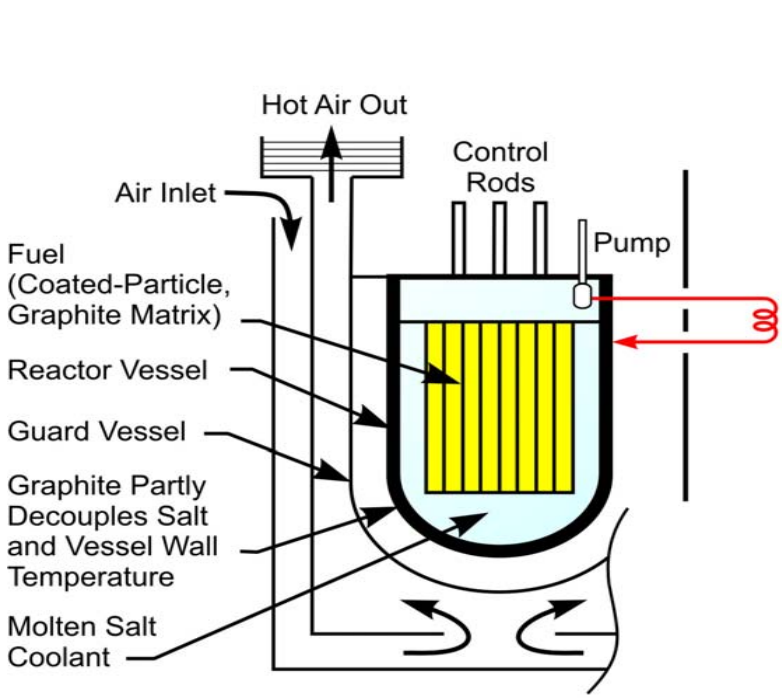
Reducing Reactor Temperatures

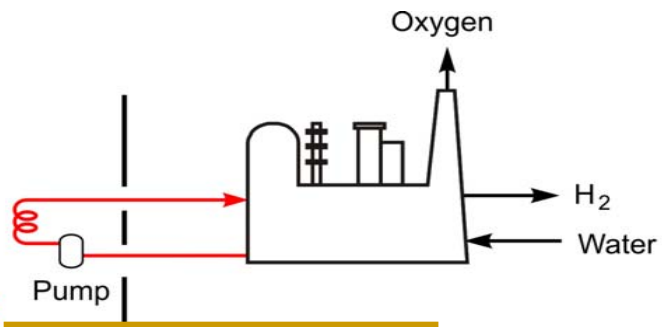
Liquid Cooling Minimizes Reactor Temperatures for Heat Delivered at a Given Temperature

The Advanced High-Temperature Reactor

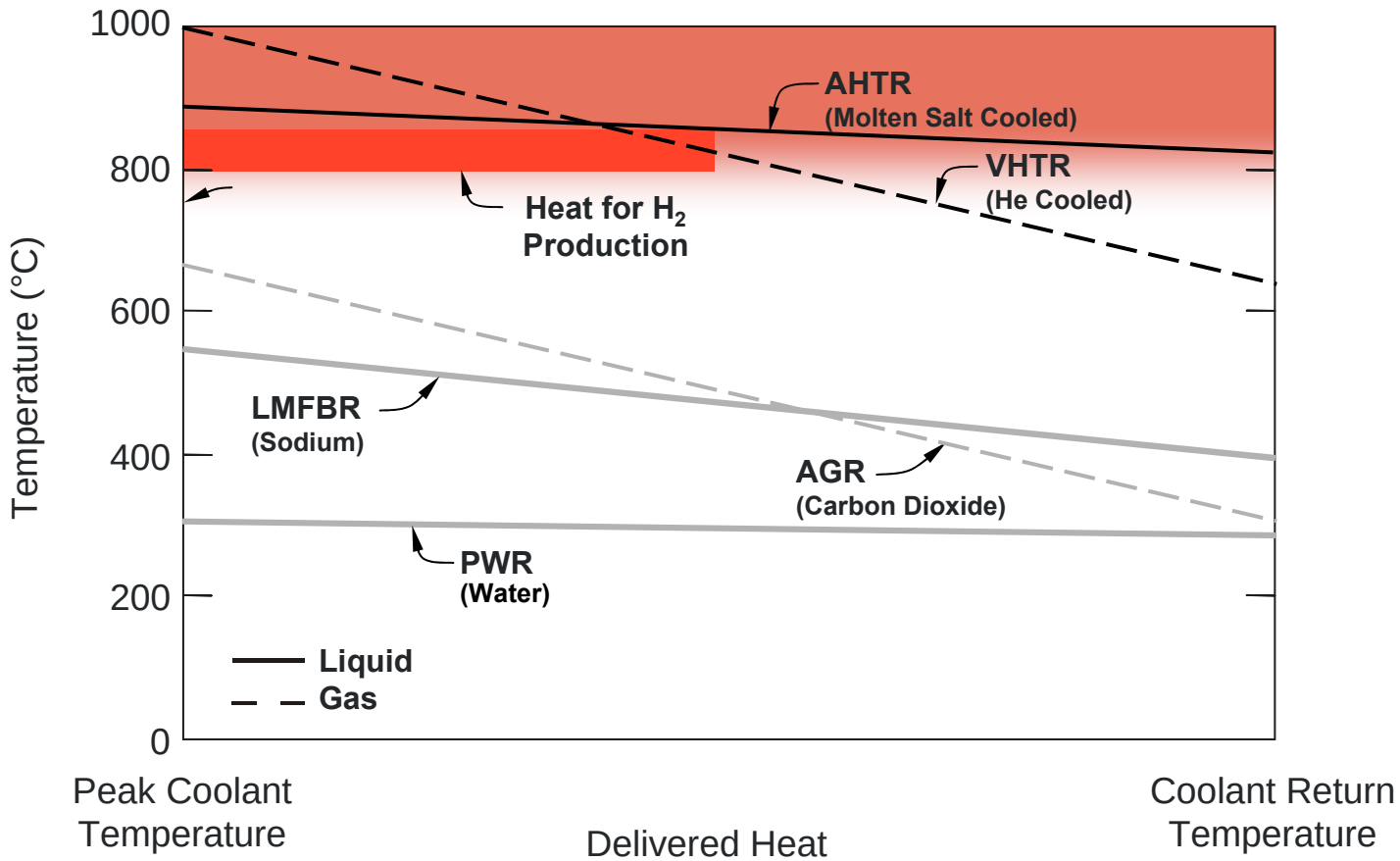
Graphite-Matrix Fuel and Low-Pressure Molten-Salt Coolant

Passive Decay Heat Removal | **Reactor** | **Heat Exchanger Compartment** | **Hydrogen/Electricity Production**

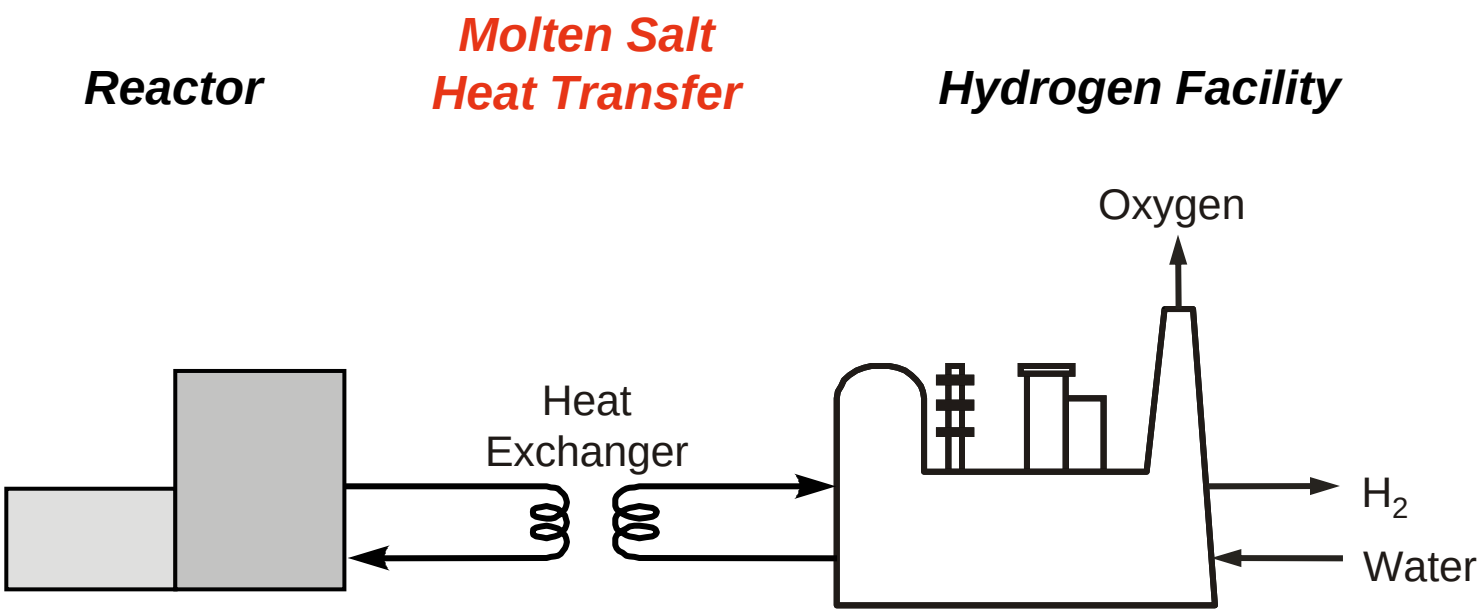




Liquid Cooling Lowers Peak Reactor Coolant Temperatures *for Heat Delivered at Any Given Temperature*



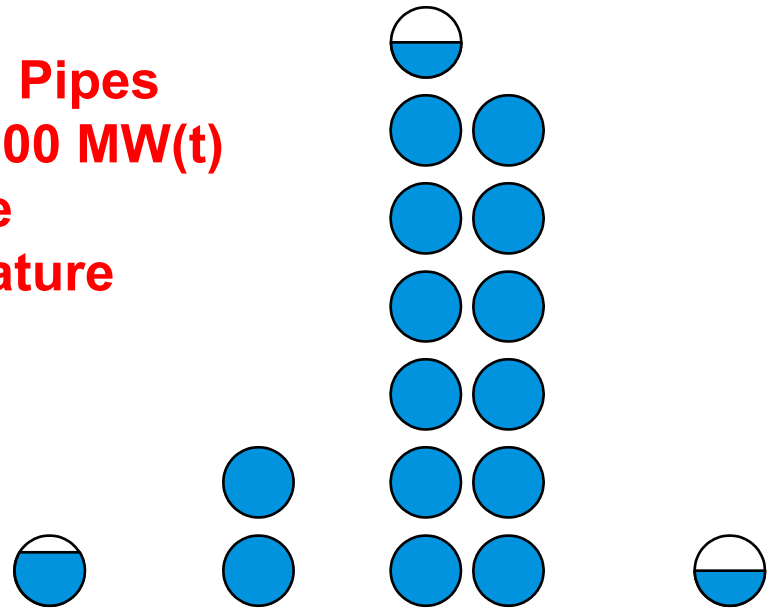
Methods are Required to Reduce Heat-Transport Loses from the Reactor to the Thermochemical Hydrogen Plant



Liquids Are Better Than Gases

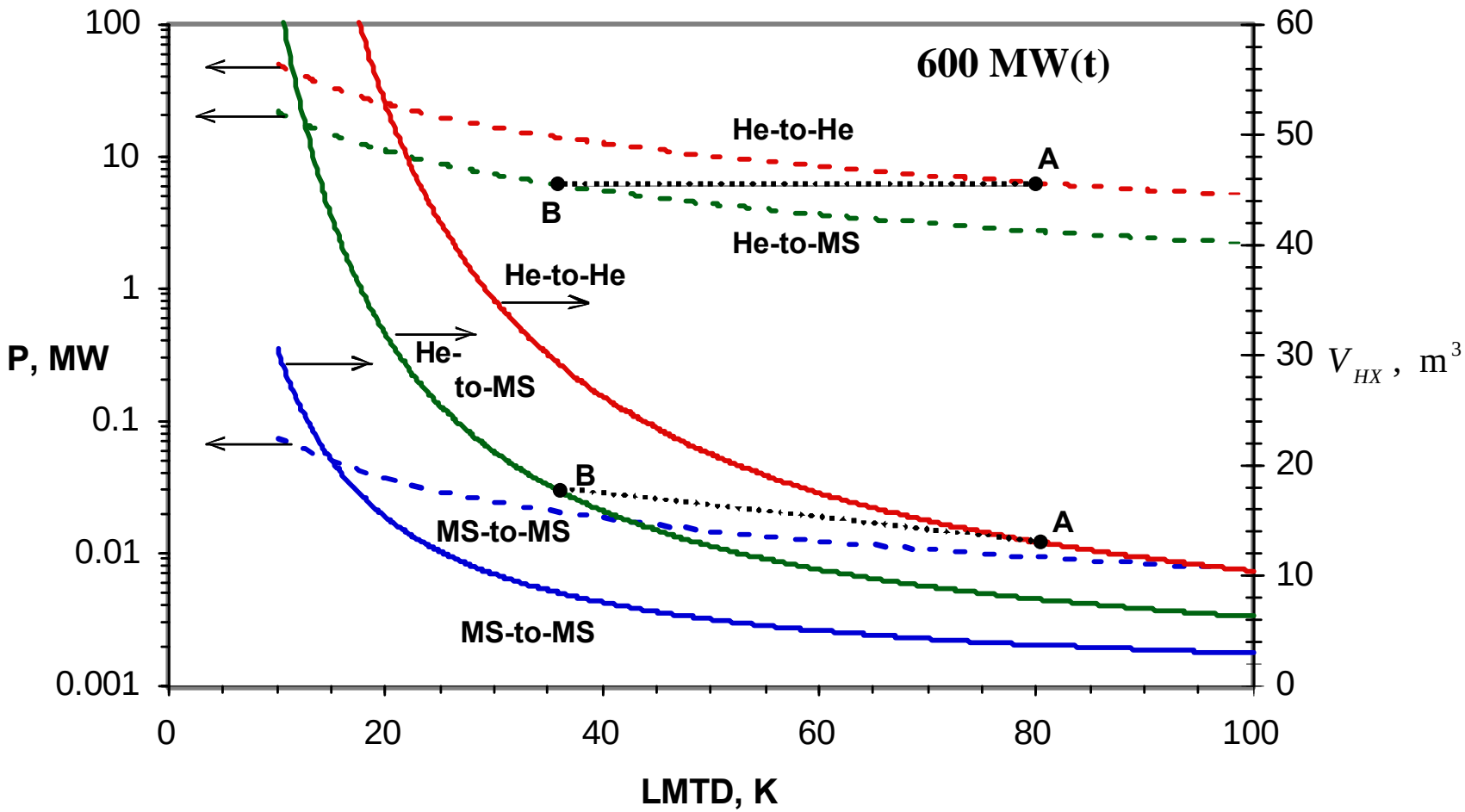
Molten Salts Have Superior Capabilities for Heat Transport

Number of 1-m-diam. Pipes Needed to Transport 1000 MW(t) with 100ºC Rise in Coolant Temperature



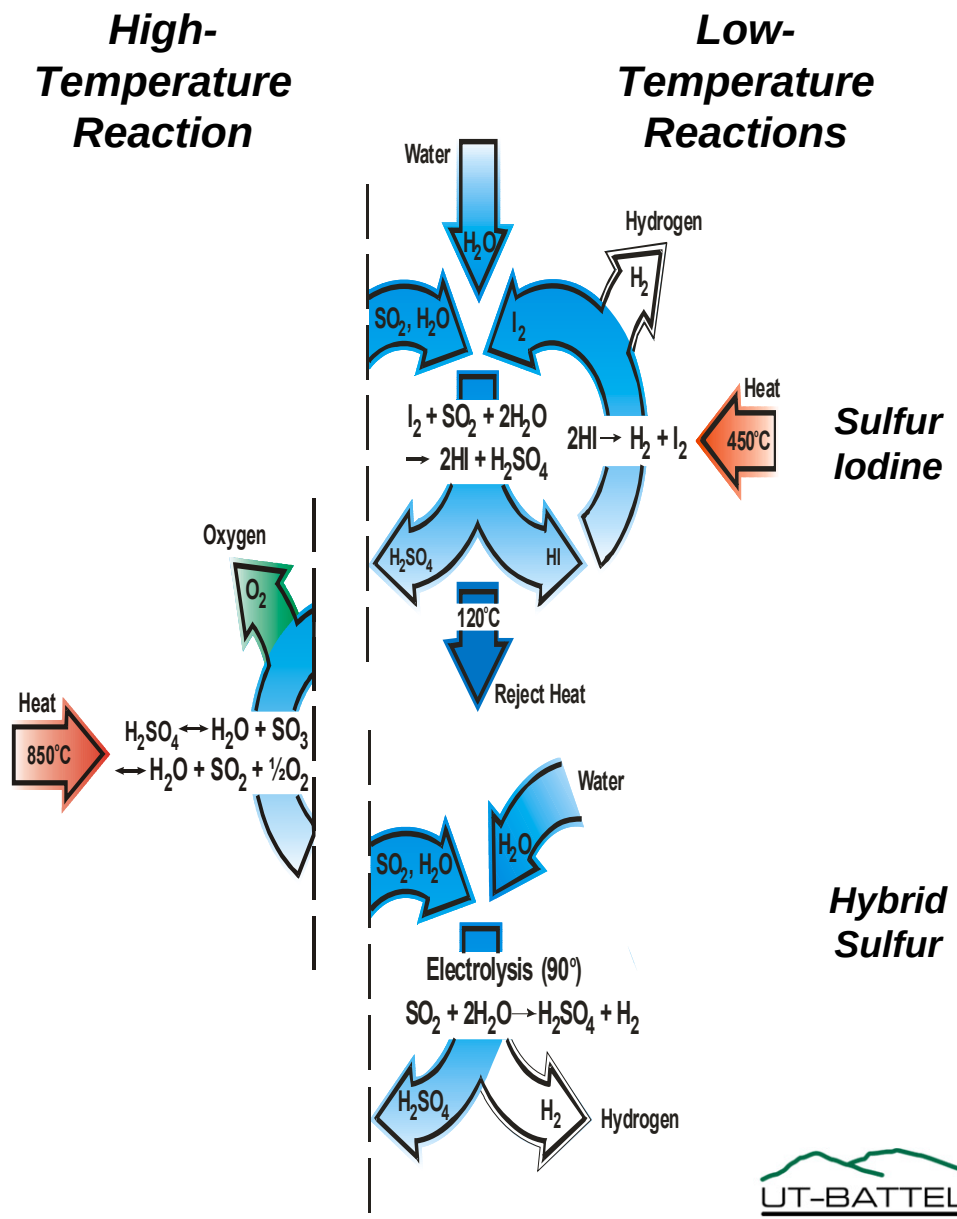
	Water (PWR)	Sodium (LMR)	Helium	Molten Salt
Pressure (MPa)	15.5	0.69	7.07	0.69
Outlet Temp (ºC)	320	540	1000	1000
Coolant Velocity (m/s)	6	6	75	6

Molten-Salts have Lower Temperature Drops than Gases in Heat Exchangers



Inorganic Membranes May Lower Sulfur-Cycle Peak Temperatures

Goal: Lower peak temperatures by 100 to 200ºC



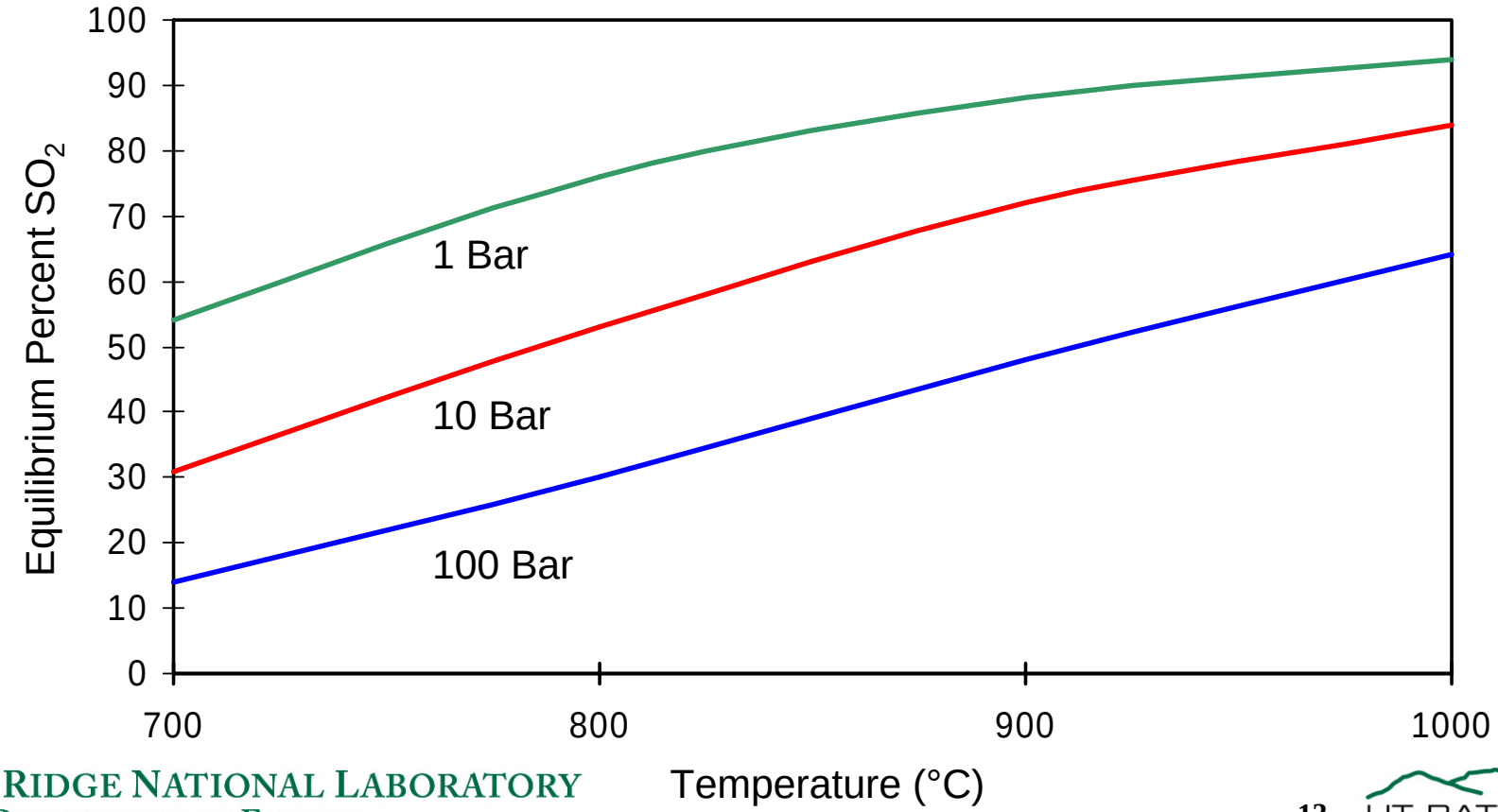
The High-Temperature Step is the Thermal Decomposition of Sulfuric Acid

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

- **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**

High Temperatures and Low Pressures Drive Chemical Reactions to Completion

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



Complete H_2SO_4 Dissociation is Possible at Lower Temperatures

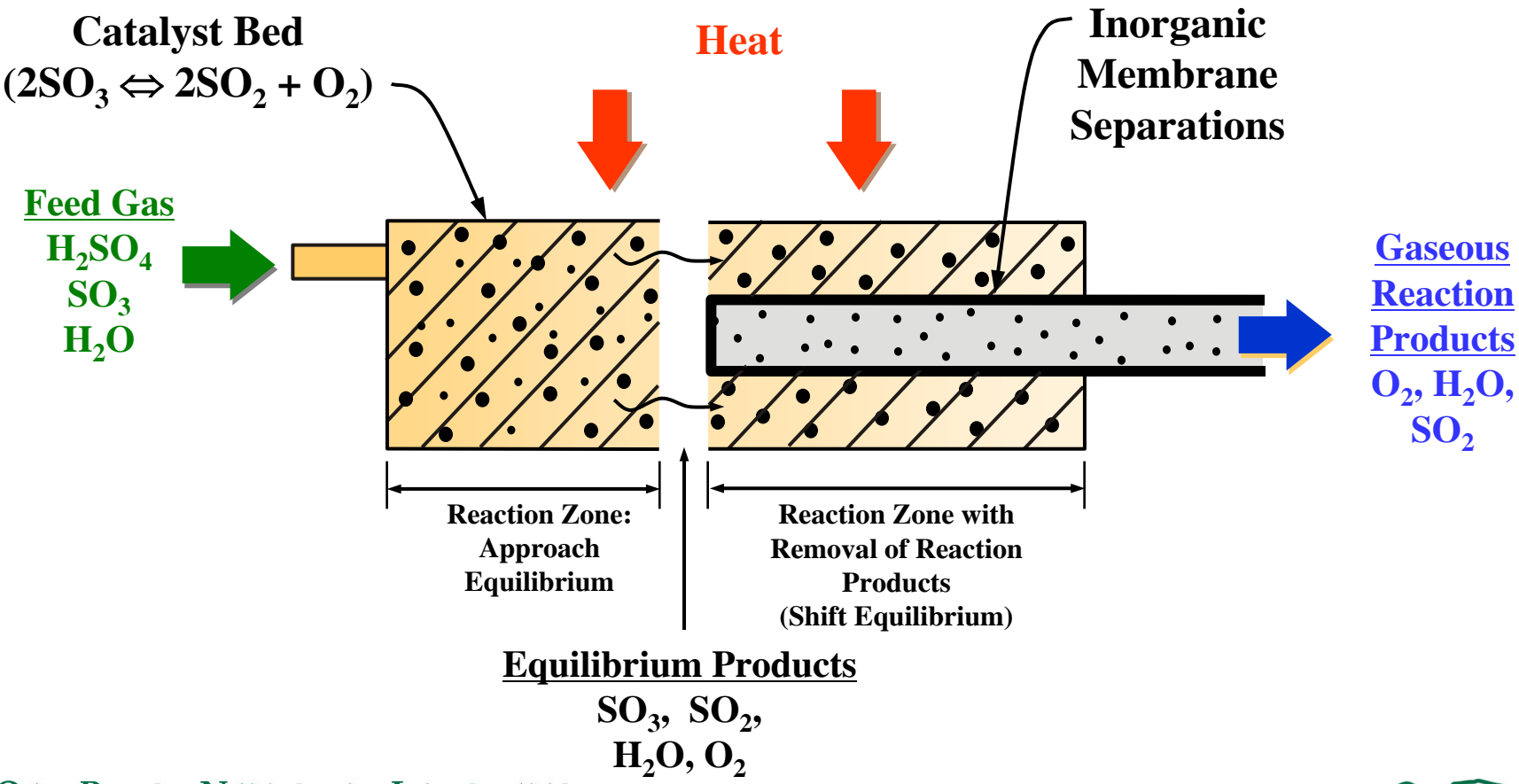
- Push the equilibrium high-temperature reaction to completion by removing the reaction products

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

- Requires membrane separation of O_2, H_2O, and SO_2 from SO_3

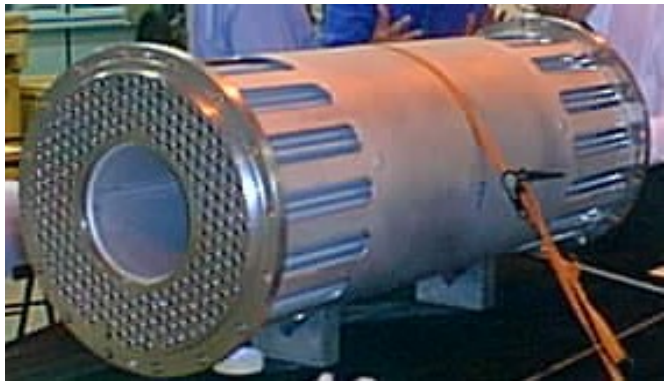
Potential to reduce peak temperature to between 650 and 750°C

Schematic of Membrane Process to Lower Peak Temperatures to 650-750°C



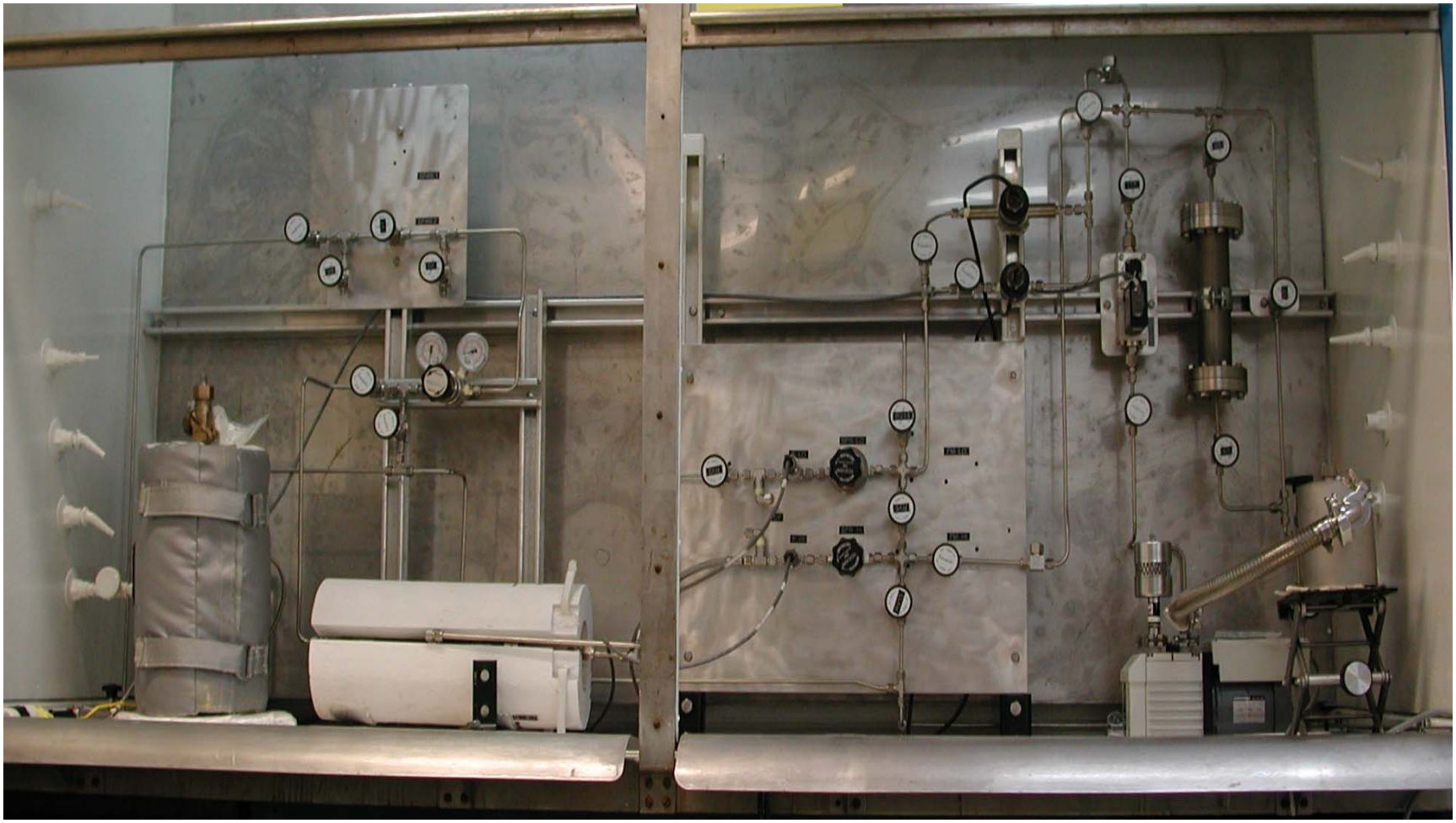
Inorganic Membranes have been Demonstrated for Moderate Temperatures

- Technology utilizes expertise from separation of uranium isotopes by gaseous diffusion
- Pore diameters of 0.5 nm to 20,000 nm
- 1600 psi burst pressure
- Separation layer applied to metal or ceramic support tube
- Layer thickness is 2μm or less yielding high permeance at low pressure drop



Experimental Apparatus to Measure Membrane Performance

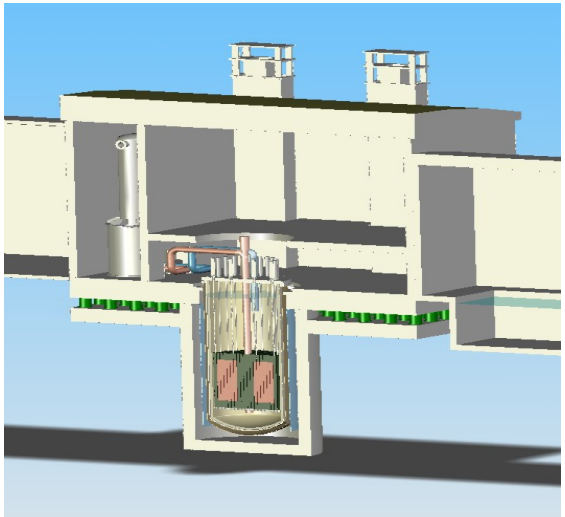
(Before Fully Insulated)



Preliminary Work Suggests Practical Separations Membrane can be Developed

- **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**
  - **These separation factors should significantly increase with increasing temperature**
- *Durability and Performance under Realistic Conditions Must Still Be Demonstrated*

Conclusions: Three Approaches to Reduce Peak Temperatures for H_2 Production



←Advanced High-Temperature Reactor

Molten Salt Heat Transport→

←Inorganic membranes

Backup
Backup
Backup

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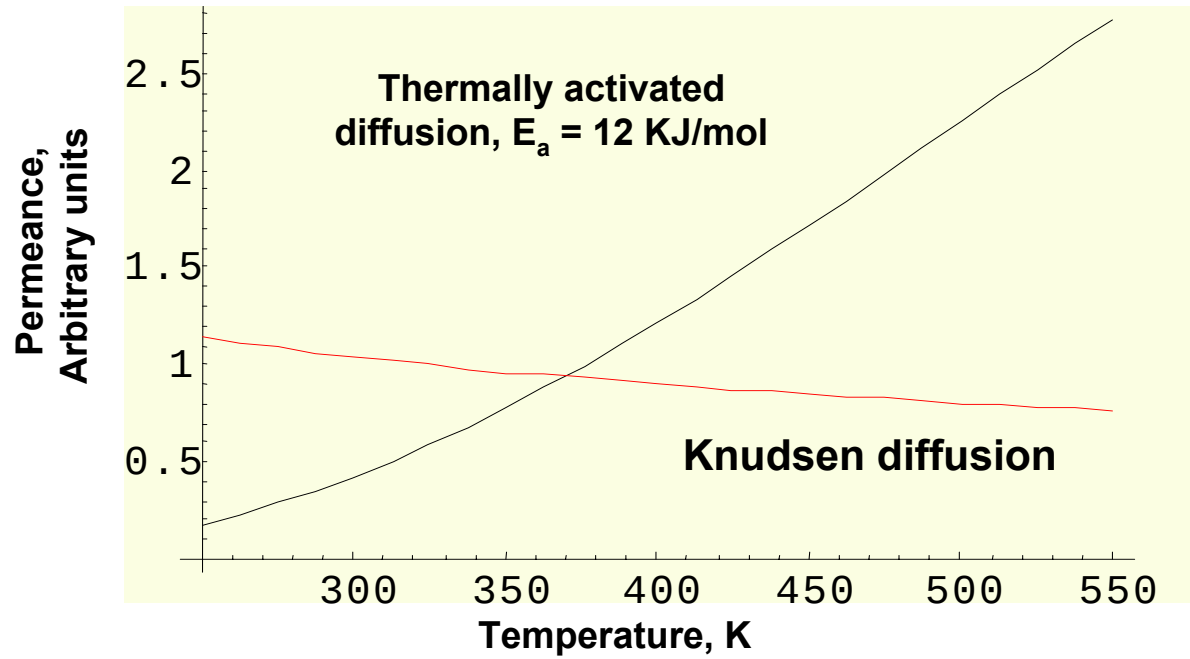
Membrane Gas Transport Mechanisms

Nanopore Diffusion Required for Efficient Sulfur Thermochemical Separations

Mechanism	Pore Diameter	Selectivity	Permeance
Viscous flow	$\lambda < d_p$	None	$d_p^2 P T^{-1}$
Molecular diffusion	$\lambda < d_p$	None	
Knudsen diffusion	$\lambda > d_p$	m-1/2	$m^{-1/2} d_p T^{-1/2}$
Surface diffusion	All d_p	Variable	$d_p^{-1} P \exp[(H_a - E_s)/RT]$
Capillary condensation	f(P)	Variable	
Nanopore diffusion	$3d_m > d_p$	Highest	$m^{-1/2} d_p T^{-1/2} \exp[-E_d/RT]$

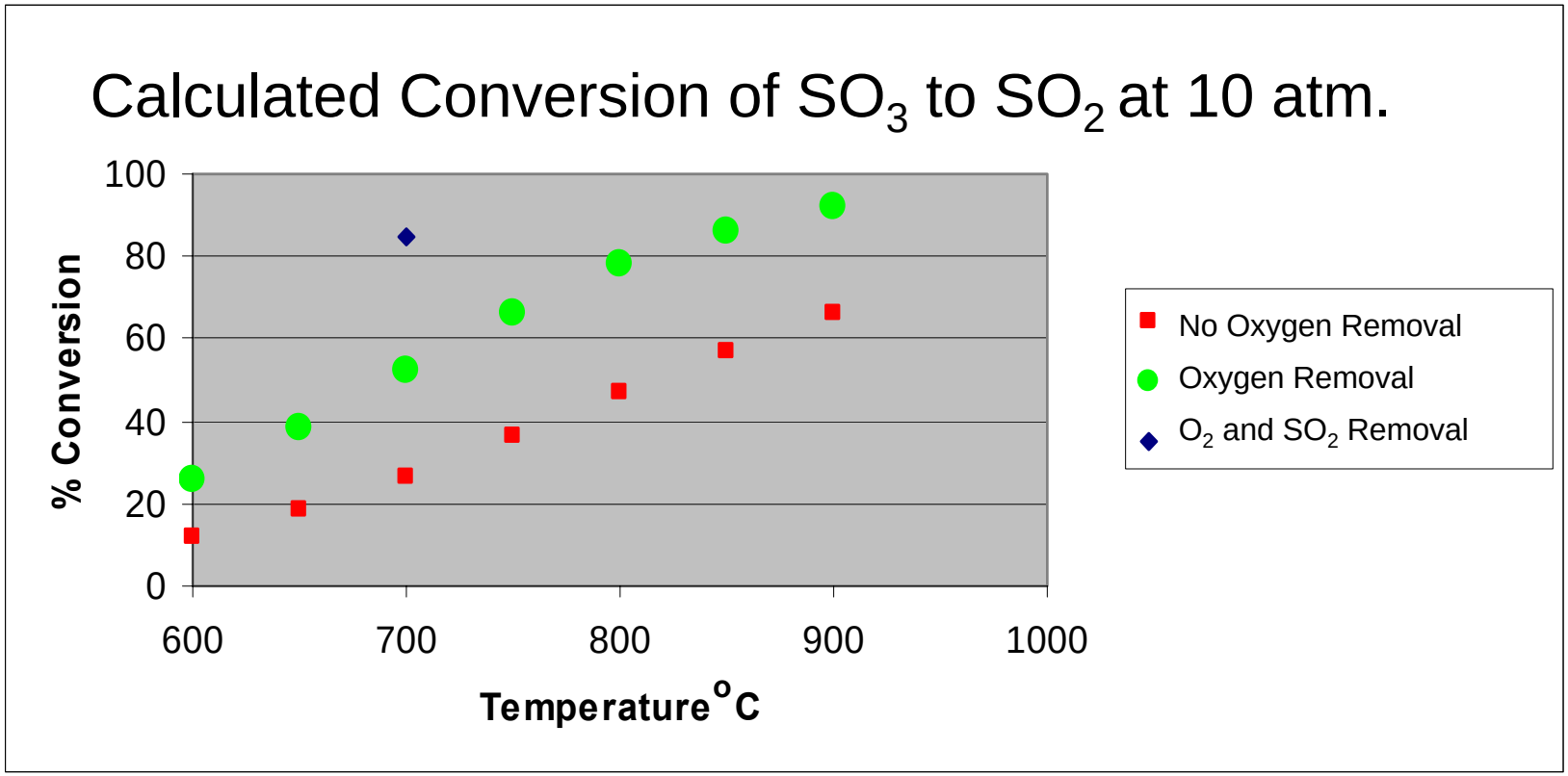
With Nanopore Diffusion, Separation Factors Increase with Temperature

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

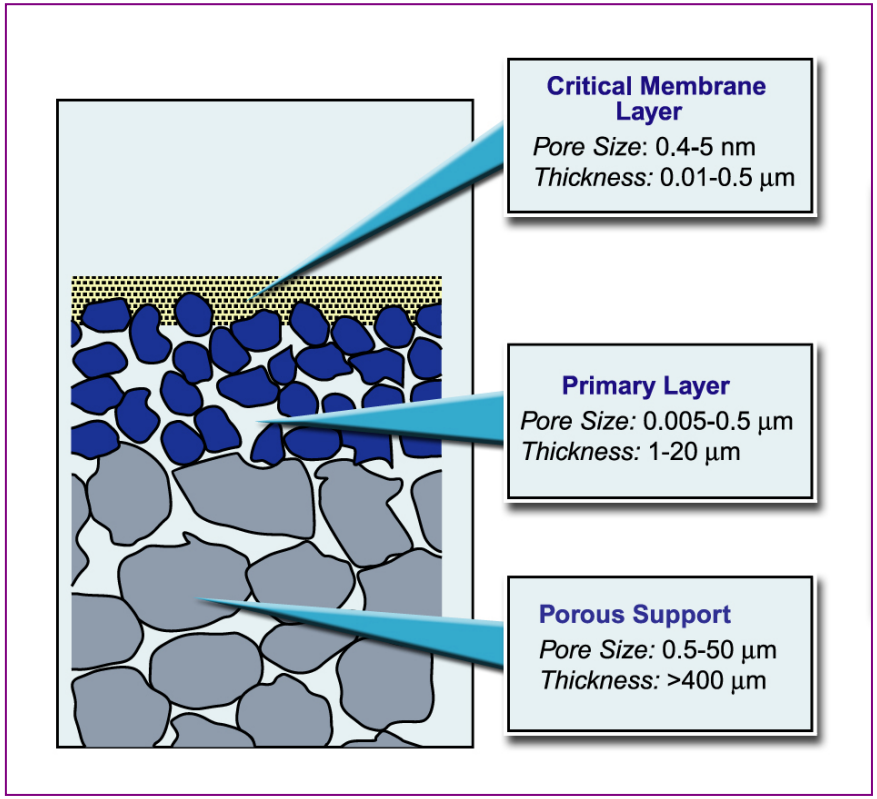


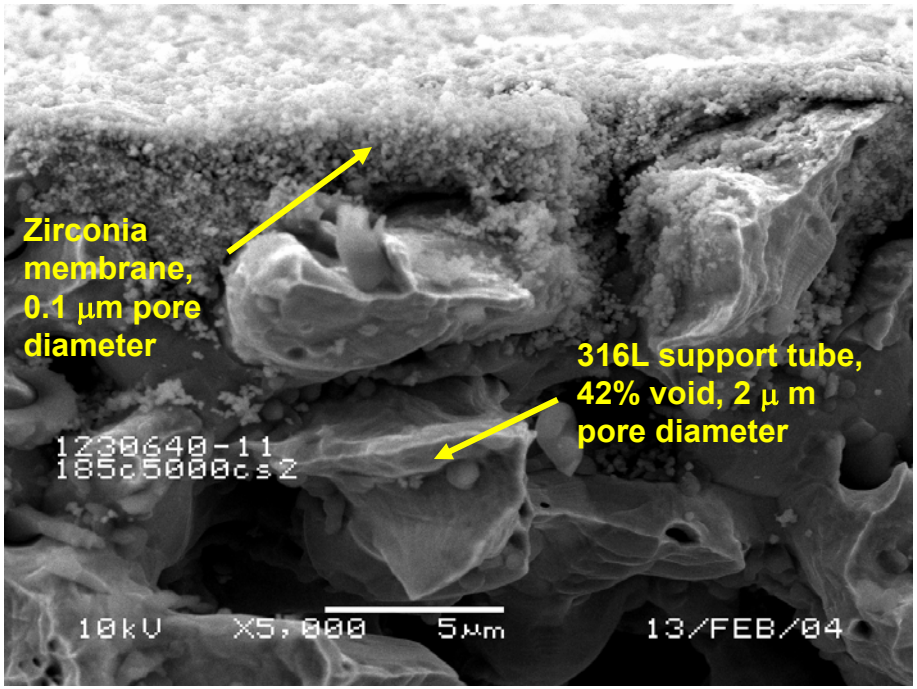
- Rates of increase of permeance with increasing T for both H_2 and He increase with decreasing pore diameter
- Implies that E_{ef} is a strong function of pore radius
- These behaviors are not fully understood on a physical basis

Conversion of SO_3 to SO_2 as Function of Reaction Products Removed



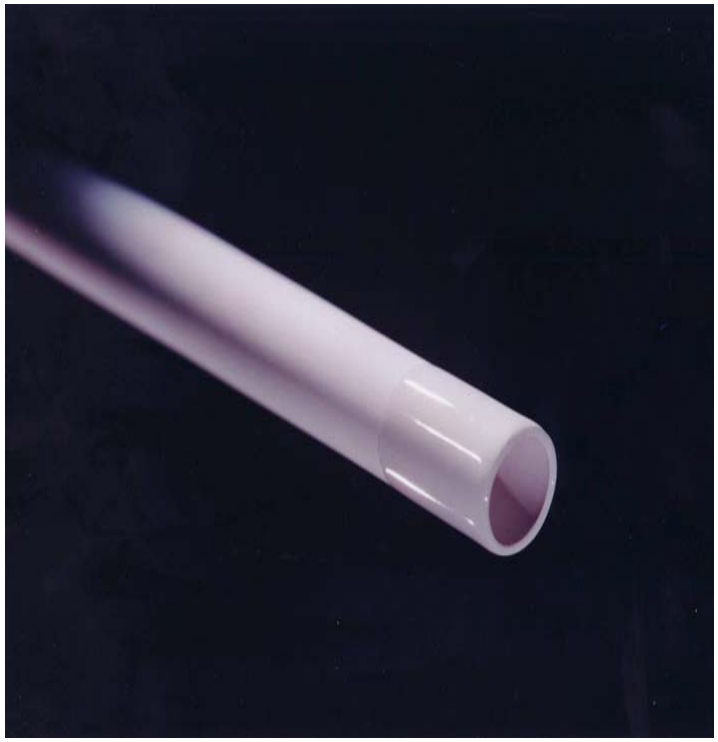
Separation Occurs at the Thin Separation Layer



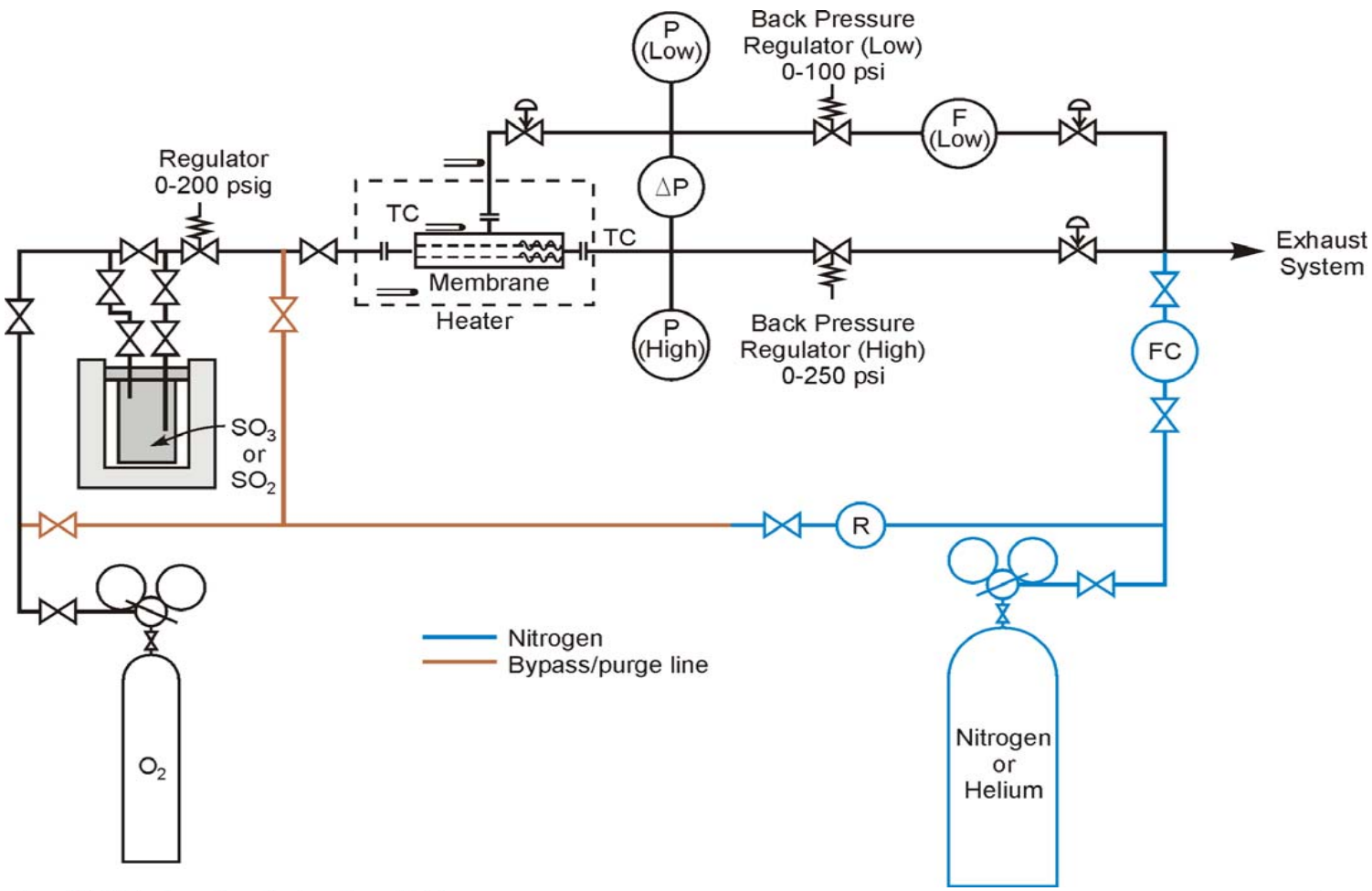


Inorganic Membrane Fabrication Processes are Versatile

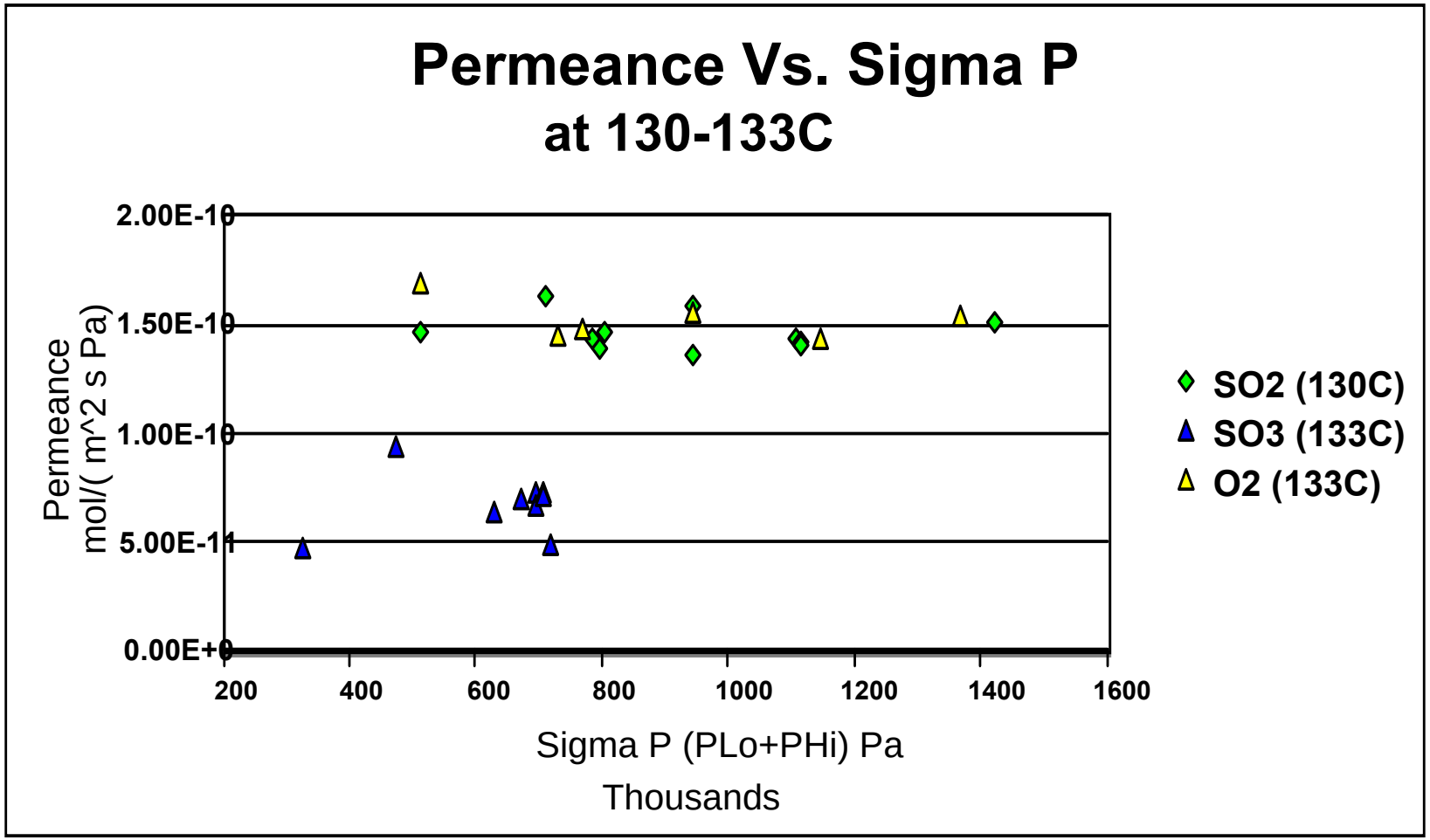
- Choice of pore diameters from 0.5 nm to 20,000 nm
- Support structure and layer made of variety of metals and ceramics
- Mechanical, thermal, and chemical stability
- Membrane layer thickness of 2 µm or less yielding a high permeance at low pressure drop
- Proven scalability



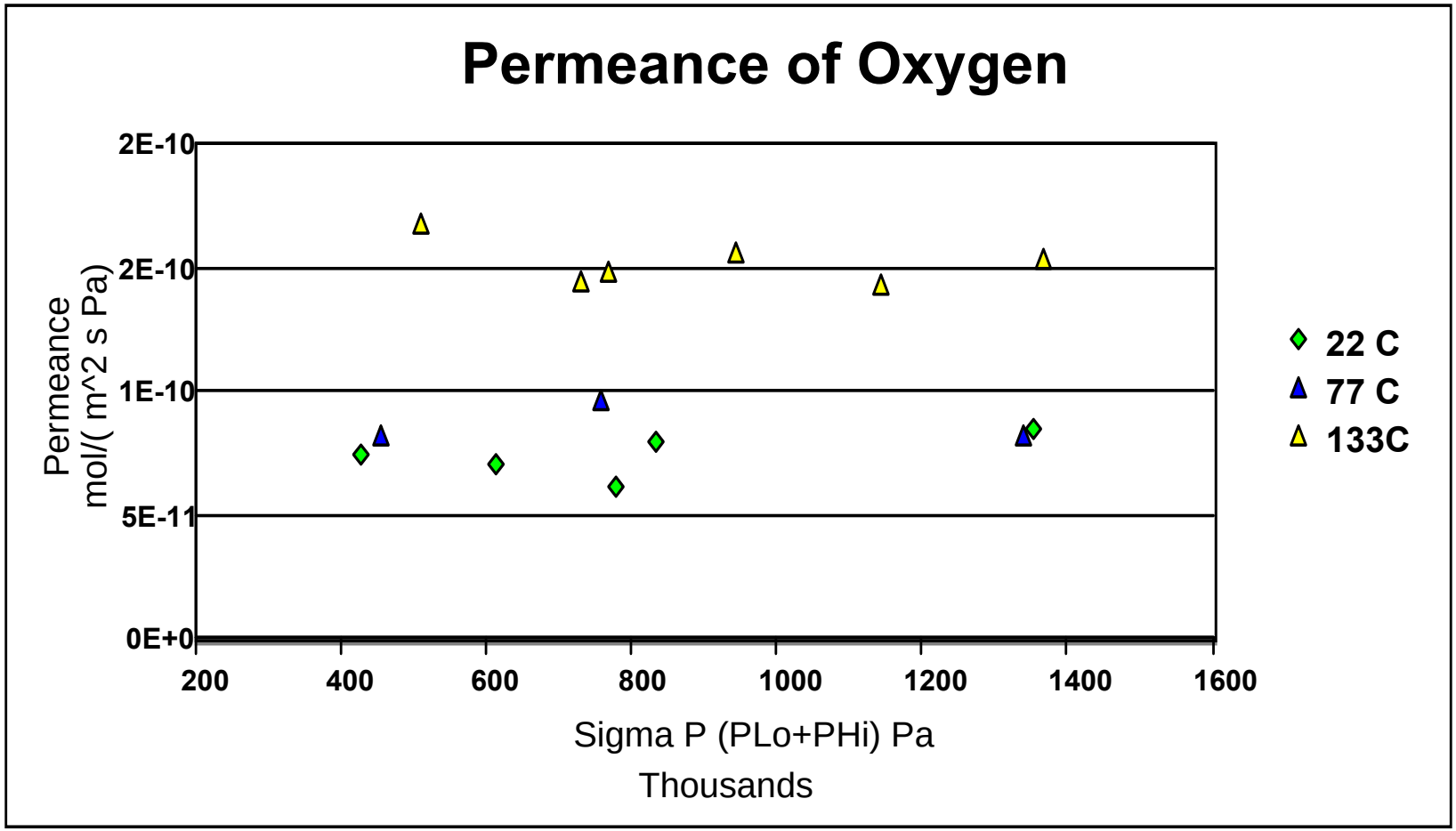
Test Facility Developed for Permeance Measurements at Moderate Temperatures



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



1st Generation Membrane Tests: Oxygen Flow through Membrane Increases with Temperature: Indicative of Thermally-Activated Diffusion



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