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Charles Forsberg, Brian Bischoff, Louis K. Mansur, Lee Trowbridge, and P. Tortorelli

Oak Ridge National Laboratory*
P.O. Box 2008
Oak Ridge, TN 37831-6165
Tel: (865) 574-6783
Fax: (865) 574-0382
E-mail: forsbergcw@ornl.gov

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Oak Ridge National Laboratory
P.O. Box 2008; Oak Ridge, TN 37831
Tel: (865) 574-6783; Fax: (865) 574-0382
E-mail: forsbergcw@ornl.gov

Abstract—Thermochemical processes are the primary candidates to produce hydrogen (H_2) using nuclear energy. In a thermochemical process, a series of chemical reactions occur in which the net result is heat plus water yields oxygen (O_2) and H_2 . The leading thermochemical processes [Westinghouse (hybrid), sulfur–iodine, and Ispra Mark 13] require heat inputs at temperatures of $\sim 850^\circ\text{C}$. Each of these processes has the same chemical reaction (dissociation of sulfuric acid into H_2O , O_2 , and SO_2) that requires high-temperature heat but different lower-temperature chemical reactions. The high temperatures are at the upper limits of high-temperature nuclear reactor technology. The use of inorganic separations membranes is proposed to drive the dissociation reaction to completion at lower temperatures and higher pressures. If peak temperatures can be reduced by 100 to 150°C , existing reactor technology can be used to provide the necessary heat for H_2 production. Hydrogen produced using nuclear reactors then becomes a much more viable near-term industrial option. If process pressures can be increased, there are expected to be reductions in capital cost and improvements in efficiency.

I. INTRODUCTION

The leading candidates for low-cost, large-scale H_2 production using nuclear energy are thermochemical processes. A thermochemical process consists of a set of chemical reactions in which the net result is high-temperature heat plus water yields H_2 and O_2 . Two factors make thermochemical H_2 production costs (with nuclear reactors providing the heat) potentially lower than those for electrolysis.

- *Efficiency.* Thermochemical processes have potentially greater efficiency than electrolysis because conversion of heat to H_2 requires fewer steps than conversion of heat to electricity and electricity to H_2 .

- *Capital costs.* The economics of scale for chemical processes (function of volume) is better than the economics of scale for electrolytic processes (function of area).

Three (Fig. 1) of the four highest-rated processes (hybrid, sulfur–iodine, and Ispra Mark 13) have the same high-temperature step that requires heat input at 850°C at ~ 10 bar.¹ The highly endothermic (heat-absorbing) gas-phase reaction in each of these processes is as follows:

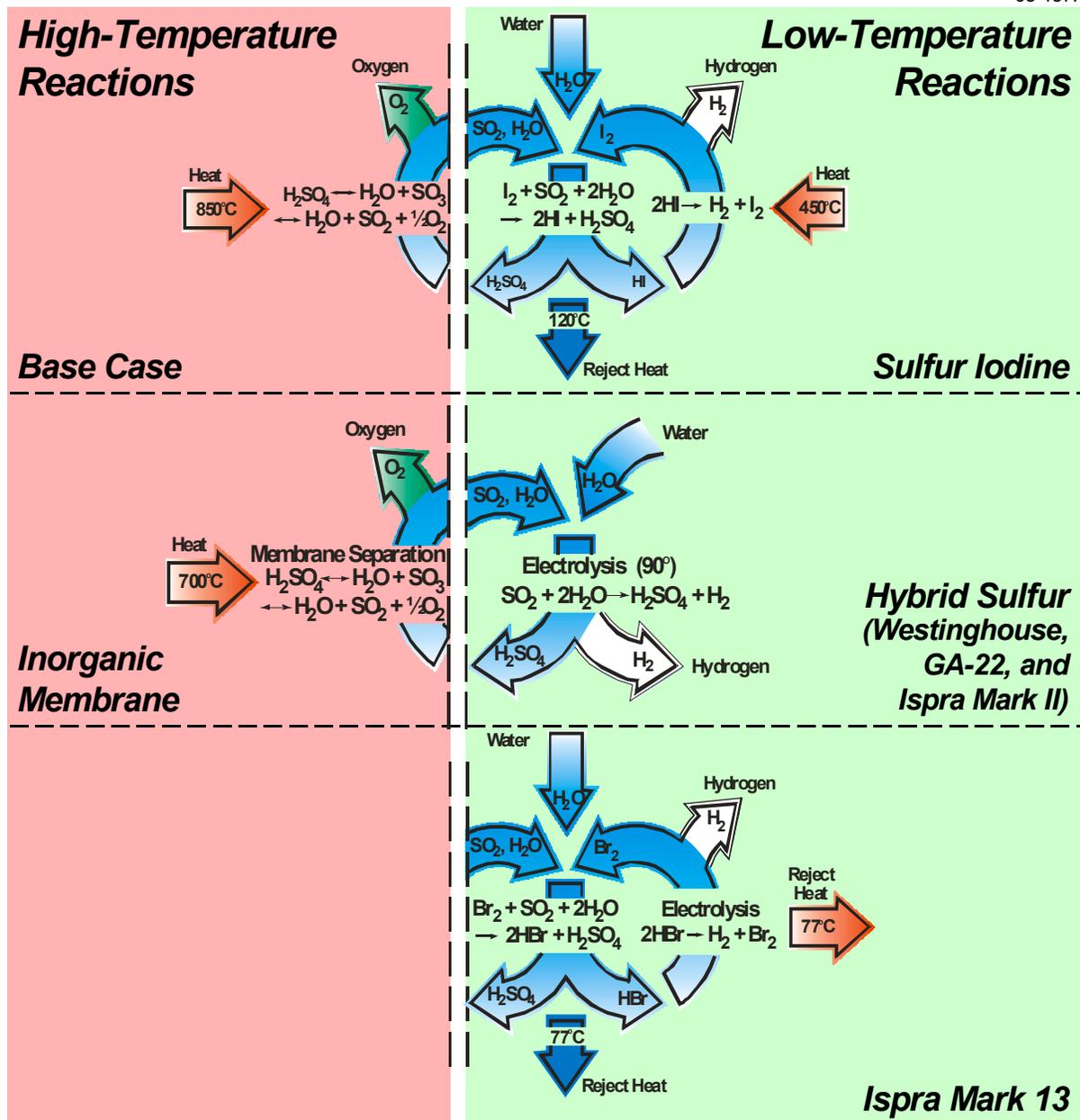
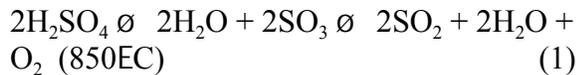
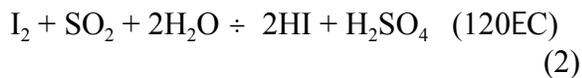


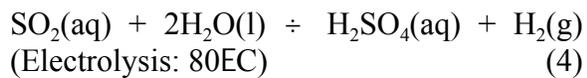
Fig. 1. Sulfur family of thermochemical cycles.



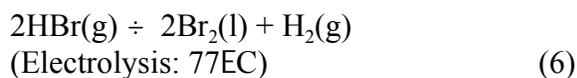
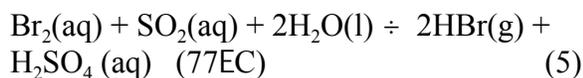
The three thermochemical processes have different lower-temperature chemical reactions. The sulfur–iodine process¹ has two other chemical reactions that (Equations 2 and 3), when combined with Equation 1, (1) yield H₂ and O₂ from water and heat and (2) recycle all other chemical reagents.



The hybrid sulfur process (also known as Westinghouse, GA-22, and Ispra Mark 11) has a single electrochemical step (Equation 4) that completes the cycle.²



The Ispra Mark 13 process has one chemical reaction (Equation 5) followed by one electrochemical reaction (Equation 6) that completes the cycle.



In each of these cycles, the high-temperature sulfur trioxide (SO₃) dissociation reaction (Equation 1) is an equilibrium chemical reaction that requires heat and a catalyst. Table I shows this equilibrium³ as a function of temperature and pressure. *High temperatures and low pressures drive the reaction towards completion.*

Detailed studies have concluded that the peak temperatures need to be very high (850°C) to drive the SO₃ decomposition to near completion. After the high-temperature dissociation reaction, all the chemicals must be cooled to near room temperature, the SO₂ separated out and sent to the next chemical reaction, and the unreacted H₂SO₄ (formed by recombination of SO₃ and H₂O at lower temperatures) reheated back to high temperatures. Unless the chemical reactions go almost to completion, the energy losses in separations and the heat exchangers to heat and cool all the unreacted reagents (H₂SO₄) result in a very inefficient and uneconomical process. This phenomenon is illustrated in Fig. 2, in which the overall efficiency of one variant of the sulfur–iodine process⁴ is shown as a function of temperature. In this flowsheet, the process inefficiencies increase so rapidly with decreasing temperature (incomplete SO₃ dissociation) that the process can not produce H₂ at temperatures below 700°C.

There are strong incentives to lower the temperature and increase the pressure at which SO₃ dissociates—the exact opposite of the conditions required by thermodynamic considerations.

- *Lower temperatures.* A major challenge to thermochemical H₂ production is the high temperature required for efficient H₂ production, which is at the limits of reactor technology. After the temperature losses in heat exchangers between the reactor coolant and chemical plant are accounted for, the 850EC process temperature implies that the peak nuclear reactor temperature will be significantly higher. If this temperature could be lowered to 700°C, current⁵ and advanced⁶ designs of high-temperature reactors could be used for H₂ production.

TABLE I. Thermodynamic Equilibrium for H₂SO₄ Decomposition

Pressure (bar)	Temperature (EC)	Equilibrium fraction of sulfur as		
		% SO ₂ (g)	% SO ₃ (g)	% H ₂ SO ₄ (g)
1	650	41	59	0.3
1	700	54	46	0.1
1	750	66	34	0.05
1	800	76	24	0.02
1	850	83	17	0.01
1	900	88	12	0.004
1	950	92	8	0.002
1	1000	94	6	0.001
10	650	22	75	3.5
10	700	31	67	1.7
10	750	42	57	0.8
10	800	53	46	0.4
10	850	63	37	0.2
10	900	72	28	0.1
10	950	79	21	0.05
10	1000	84	16	0.03
100	650	9	65	27
100	700	14	69	17
100	750	22	69	10
100	800	30	64	6
100	850	39	58	3
100	900	48	50	2
100	950	57	42	1
100	1000	64	35	1

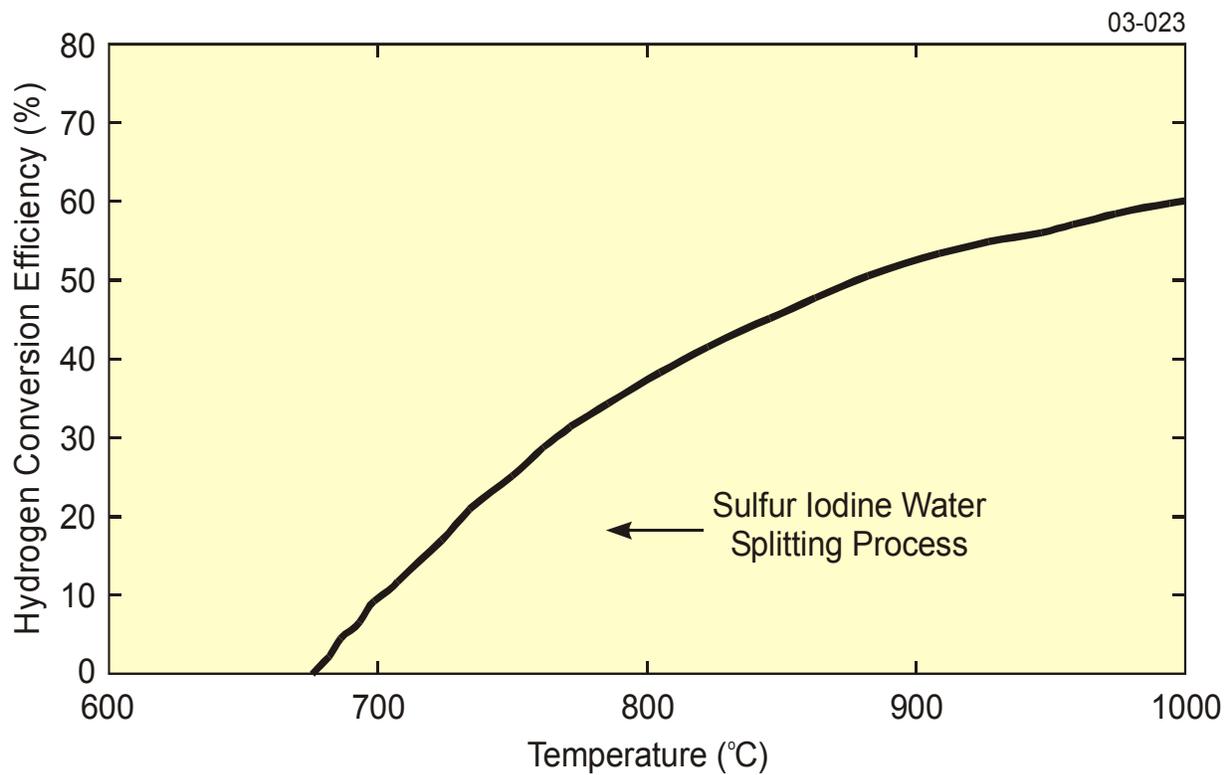


Fig. 2. Efficiency of the iodine–sulfur process vs temperature.

- Higher pressures.* If the thermodynamics of SO_3 dissociation could be overcome, higher-pressure operation would improve economics and process efficiency. Higher pressures would reduce equipment size and gas compression losses. Moreover, higher pressures would improve efficiency for processes such as the hybrid process, in which the product SO_2 is separated from O_2 by sorption in water. At low pressures, the water must be refrigerated to absorb the SO_2 . At higher pressures, this absorption occurs above room temperature and no refrigeration plant is required.

An inorganic membrane process is proposed to reduce the peak temperature of the SO_3 dissociation step by up to 150EC and allow the dissociation process to operate at a higher pressure. This is accomplished by the separation of SO_2 , H_2O , and O_2 from the SO_3 at 650 to 750EC. If these reaction product gases are removed, the remaining SO_3 (with a catalyst and heat) will disassociate into its equilibrium concentrations. If the reaction gases can be selectively removed, the chemical reaction can be driven to completion. The membrane operates with high pressure on one side and a lower pressure on the other side, and this pressure difference drives the separation process.

Inorganic membranes have historically been used to separate uranium isotopes by gaseous diffusion. In recent years, Oak Ridge National Laboratory has developed several inorganic membranes for chemical separations. These membranes are now commercial products. Work has been initiated on inorganic membranes to separate SO_2 , H_2O , and O_2 from SO_3 . This paper describes the initial analysis and characteristics of these membranes. Experimental test systems are currently being constructed to test these alternative membranes.

II. ALTERING THE EQUILIBRIUM SO_3 DISSOCIATION

Figure 3 shows a schematic of two different ideal high-temperature chemical reactors with inorganic separation membranes. Each option consists of two zones:

- Oxygen separation.* The top membrane reactor shows the operation of a perfect membrane that allows H_2O and O_2 through the membrane but blocks all other chemical species. At the high temperatures, the H_2SO_4 dissociates into H_2O and SO_3 . When these reagents contact the catalyst, the SO_3 partly disassociates into SO_2 and O_2 (Equation 1). This is a highly endothermic reaction; thus, heat must be added to enable the reaction. The dissociation is limited by its equilibrium. As the gas mixture flows to the right (past the membrane), the O_2 and H_2O go through the membrane. The reaction is driven to the right (Equation 1) with the resultant greater concentrations of SO_2 . A mixture of SO_2 , SO_3 , and small quantities of O_2 exits the reactor. Removal of oxygen alone can-not drive the reaction to completion (see below).

- Oxygen and SO_2 separation.* The bottom membrane reactor is similar to the first case, except that the membrane selectively allows H_2O , O_2 , and SO_2 to pass through. As the SO_3 dissociates, all the reaction products are removed by going through the membrane. The SO_3 has nowhere to go until it decomposes. In this case, a perfect membrane would drive the reaction to completion.

A thermodynamic analysis of the separation process was undertaken to understand the ideal theoretical performance of these systems. The classical thermodynamic equation for this equilibrium reaction is.

$$K(T, P) = [\text{SO}_2] [\text{O}_2]^{1/2} / [\text{SO}_3] \quad (7)$$

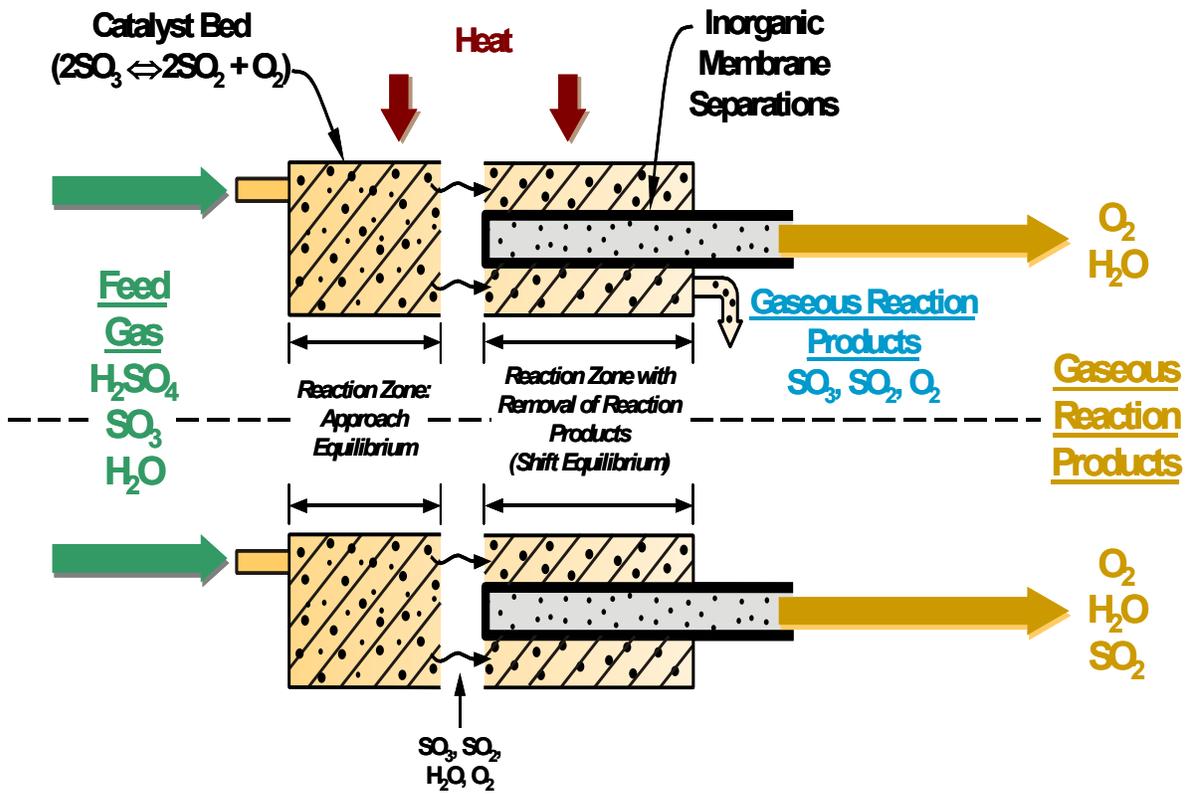
where

$$\begin{aligned} K(T, P) &= \text{equilibrium constant} \\ [\text{SO}_2] &= \text{gas-phase concentration of } \text{SO}_2, \text{ typically in moles per liter} \\ [\text{O}_2] &= \text{gas-phase concentration of } \text{O}_2 \\ [\text{SO}_3] &= \text{gas-phase concentration of } \text{SO}_3 \end{aligned}$$

As can be seen from the equation, as SO_2 and O_2 are removed from the catalyst bed, more of the SO_3 must dissociate to maintain the required equilibrium. However, if only the O_2 is removed, the concentration of SO_2 increases as the SO_3 decreases. With the removal of only one reaction product, the reaction can go far toward, but not all the way to, completion.

A parametric study was conducted to determine the potential benefit that the removal of O_2 and SO_2 could have on the conversion of SO_3 to SO_2 . Using the FactSage computer program,³ the equilibrium conversion as a function of temperature was calculated (Table II), assuming an initial quantity of 100 moles of

Oxygen Separation Membrane



Oxygen and Sulfur Dioxide Separation Membrane

Fig. 3. Membrane reactor systems: Upper system depicts operation assuming that only O_2 and H_2O could be separated; Lower system depicts system assuming that O_2 , H_2O , and SO_2 could be separated.

Table II. Effect of Removal of O₂ and SO₂ from H₂SO₄ Decomposition Reactor Using an Ideal Inorganic Membrane at 1 Atmosphere*

Stage no.	Removal of O ₂ Temperature = 850EC			Removal of O ₂ Temperature = 700EC			Removal of O ₂ and SO ₂ Temperature = 700EC		
	O ₂	SO ₂	SO ₃	O ₂	SO ₂	SO ₃	O ₂	SO ₂	SO ₃
0	0	0	100	0	0	100	0	0	100
1	39.42	78.87	21.13	23.78	47.55	52.45	23.78	47.55	52.45
2	5.43	89.74	10.26	6.8	61.16	38.85	12.47	24.94	27.51
3	1.91	93.55	6.45	3.54	68.24	31.76	6.54	13.08	14.43
4	0.92	95.4	4.6	2.26	72.76	27.24	3.38	6.86	7.57
5	0.53	96.49	3.54	1.6	75.97	24.03	1.8	3.6	3.97
6	0.34	97.14	2.86	1.21	78.4	21.6	0.94	1.89	2.08

*Initial value for SO₃ = 100 moles. The table shows the number of moles of various components remaining in the reaction chamber after each stage.

H₂SO₄. Next, the effect of the removal of O₂ was studied. Calculations were made by first assuming that the reaction reached equilibrium in the first (theoretical) stage. At that stage, all of the O₂ was assumed to be removed and the remaining SO₃ and SO₂ were allowed to come to equilibrium again (stage 2). The O₂ was again removed, and this process was repeated through six stages. As shown in Table II, when inorganic membranes are used the residual SO₃ at 700EC (21.6 moles) is approximately equal to the residual SO₃ at equilibrium at 850EC (21.13 moles) with no membrane separation. For the chemical reactor configuration shown in Fig. 3, lengthening the tubes increases the number of theoretical stages. (The stages do not represent physical stages of this equipment.)

Lastly, the effect of the removal of both O₂ and SO₂ was studied. Calculations were made by first assuming that the reaction reached equilibrium in the first stage. At that stage, all of the O₂ and SO₂ were assumed to be removed and the remaining SO₃ was allowed to dissociate and come to equilibrium again (stage 2). The O₂ and SO₂ were again removed and this process was repeated through six stages. After six stages, only 2.08 moles of the SO₃ remained.

Although the analysis indicates that an ideal membrane that separates only H₂O and O₂ can effectively lower the peak dissociation temperature by 150EC and reduce the unreacted SO₃ to 21.6 moles at 700EC, there are strong incentives to remove both SO₂ and O₂. An idealized membrane

can reduce the unreacted SO₂ to 2.06 moles with six ideal stages of separations.

III. PRINCIPLES OF INORGANIC MEMBRANE OPERATIONS

Membrane separation processes operate by having a higher pressure on one side of the membrane and lower pressure on the other. The relative rates of transport of different molecules through the membrane determine the capability of the membrane to separate different gases. There are multiple gas-transport mechanisms.⁷ The precise transport mechanism that is dominant for each gas depends upon a variety of physical factors including temperature (T), pressure (P), molecular mass (m), pore diameter (d_p), molecular size and shape, pore surface composition, pore morphology, and mutual interactions between molecules traversing the membrane.

The most important characteristic of membranes that dictates the dominant transport mechanism is the pore diameter or, more precisely, the ratio of the pore diameter to one of the important physical characteristics of the gas: λ , the mean free path for molecule–molecule interactions in the gas, and d_m, the effective kinetic diameter of the gas molecule. Most gases of interest have kinetic diameters between one-fourth and two-thirds of a nanometer. Generally, for pore diameters >2 nm, important permeation mechanisms in operation are Knudsen diffusion and surface transport, together with molecular diffusion and viscous flow (Poiseuille or laminar flow) at larger pore diameters. For pore diameters about 1 nm and smaller, other mechanisms which are covered by term “nanopore diffusion,” come into operation. Some important mechanisms of gas transport through a membrane are listed in Table III. Expressions for selectivity and

permeance also are given in the table, where the dependencies on important variables are expressed in simple form without extensive statements or qualifying conditions.

The performance of a membrane is measured by two parameters: permeance and selectivity. The permeance, defined as flow of the pure gas in question per unit membrane area per unit time per unit pressure, is expressed in moles per square meter per second per pascal [mol/(m² s Pa)]. The selectivity is defined as the ratio of the permeances of two pure gases. The separation factor for a mixture of two gases is defined as $[y/(1-y)] [(1-x)/x]$. Here, y is the concentration of the fastest-permeating component on the permeate side of the membrane and x is the concentration of the fastest-permeating component on the feed side. The product of the separation factor and permeance is often taken as the figure of merit by which to judge a particular membrane–gas mixture combination.

The mechanisms for gas transport through the membrane include the following:

- *Viscous flow.* Viscous flow results in no separation and thus is to be avoided.
- *Molecular diffusion.* Molecular diffusion, where gas molecule–molecule interactions dominate, results in no separation and thus is to be avoided.
- *Knudsen diffusion.* In Knudsen diffusion,⁸ light molecules travel faster and therefore bounce off the pore wall more often than heavy molecules. As a consequence, they travel through the pore more quickly. There is assumed to be no interaction with the pore wall other than elastic reflection. This is the mechanism used to separate isotopes in

TABLE III. Characteristics of Different Membrane Gas-Transport Mechanisms
(Symbols Defined at Beginning of Section III)

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 Transport	All d_p	Variable	$d_p^{-1} P \exp[(H_a + E_s)/RT]$
Capillary Condensation	$f(P)$	Variable	
Nanopore Diffusion	$3 d_m > d_p$	Highest	$m^{-1/2} d_p T^{-1/2} \exp[-E_d/RT]$

gaseous diffusion uranium enrichment plants. The separation factor by Knudsen diffusion is proportional to the inverse square root of the molecular weight ratio, 1.58 for the O₂/SO₃ gas pair. Permeance in Knudsen diffusion has inverse parabolic temperature dependence (higher temperatures produce lower performance) in addition to its inverse square root dependence on molecular mass. The process is important when the pore diameter is smaller than the mean free path for molecule–molecule interactions. However, as the pore size of the membrane is decreased to about 1.5 nm, and especially below 1 nm, Knudsen diffusion is no longer possible and other mechanisms come into play that generally depend on molecular size rather than molecular mass.

- *Surface diffusion.* With this mechanism, the gas is adsorbed onto the membrane and then undergoes surface diffusion in which it hops randomly from surface site to surface site. For the surface-transport processes, the separation factor is

dependent in detail on a number of factors and cannot be expressed in a universal form. However, a simplified result can be derived for a model of random walk diffusion in two dimensions, which expresses permeance in terms of pressure, temperature, pore diameter, heat of absorption (H_a), and the activation energy for the diffusion step (E_s). High separation factors are possible for permeation governed by surface transport.

- *Capillary condensation.* Capillary condensation may occur when surface adsorption reaches a stage at which the adsorbate can be considered a liquid phase. Selected molecules sorb onto the surface and flow through the pores to the other side of the membrane.
- *Nanopore diffusion.* This is a term that encompasses several distinct mechanisms that take place in nanometer–diameter pores. For larger molecules, the membrane may function effectively as a molecular sieve, eliminating the transport of molecules

through the membrane and giving high separation factors. For smaller molecules, the transport exhibits thermally activated behavior—that is, as the temperature is increased, the permeance increases exponentially, rather than decreases as in Knudsen diffusion. One thermally activated mechanism that has been understood is termed “gas translational diffusion.” It is also referred to as “thermally activated Knudsen diffusion,” where again molecules jump between pore walls but with an activation barrier that must be overcome in order to make a diffusion jump. This thermally activated characteristic is similar to the diffusion of defects or atoms in the solid state in the presence of traps,⁹ with an activation energy (E_d). Physically this is plausible, since the lower limit on size of a pore must correspond to interatomic spacing in the solid state. In the regime for $d_p \sim 1$ nm regime, separation factors >100 are possible. For example, Uhlhorn et al.¹⁰ report that a separation factor > 200 has been measured for a mixture of H_2 and C_3H_6 gases using a supported amorphous silica membrane with a pore diameter of ~ 1 nm.

For O_2 – SO_3 separations, high operating temperatures are required. This defines the type of physical separation system that is required—nanopore diffusion. Nanopore separations improve with temperature. In contrast, separation processes such as Knudsen diffusion, which decrease with temperature, are not candidates under these conditions. The experimentally measured temperature effects for a simple system are shown in Figs. 4 and 5. Figure 4 shows how the separation factor for a nanoporous membrane separating helium from SF_6 changes with temperature, while Fig. 5 shows the dramatic increases in membrane

permeability (throughput) as the temperature of such membranes increases.

IV. PROCESS EFFICIENCY

From a thermodynamic perspective, lower temperatures would be expected to reduce the process efficiency because mechanical work is required to provide the pressure difference (a few bar) across the inorganic membrane to drive the separation process. In practice, it is unclear whether the process will be more efficient or less efficient. The irreversible losses in heat exchangers to heat and cool reagents are the primary source of inefficiencies between an ideal process and the real process. Inorganic membranes reduce these inefficiencies by driving the high-temperature reactions to completion and thus reduce the quantities of unreacted chemicals recycled in the process. Ongoing work is under way to quantify these effects.

The lowest practical operating temperature of the inorganic membrane is determined by the condensation temperature of H_2SO_4 . Membranes are gas-separation devices that must operate significantly above the condensation point of components in the gas stream. For operation at 10 bar, the lower temperature limits are near 700EC. If the pressure in the SO_3 dissociation chemical reactor is increased, the minimum operating temperature of the membrane increases, because the condensation temperature of H_2SO_4 increases. In the near term, the incentive for the use of inorganic membranes is to minimize peak temperatures and thus reduce the peak temperature requirements on the nuclear reactor. If higher temperatures become available, a strong incentive remains to use inorganic membranes, because the membranes allow the dissociation reaction to proceed at higher pressures. Higher

pressures reduce equipment size and improve efficiency. Economics drive many chemical processes to operate near 100 bar. Based on the thermodynamic equilibrium considerations, there are incentives to use inorganic membranes at temperatures to 1000EC.

V. PATH FORWARD

The current state of technology does not allow design of an inorganic membrane from first principles. Rather a combination of experiment and theory is used to develop new membranes. Lower-temperature inorganic membranes are commercially used for a variety of applications; however, high-temperature membranes have not yet been commercialized.

Based on theory, a series of existing inorganic membranes have been selected for testing. Most of these membranes have pore sizes on the order of 1 nm. Nanopore diffusion is expected to be the primary separation mechanism. The results of these tests will be combined with theory to develop a custom membrane designed for this specific separation.

The initial testing of these membranes is done by measuring the permeance of pure gases (H_2O , O_2 , SO_2 , and SO_3) as a function of temperature and pressure. The gas flow per unit surface area is measured as a function of pressure drop and temperature. Under most conditions, the interactions between molecules are small. Consequently, the measured permeance of the individual gases can be used to predict the separation performance. The best membranes are then subjected to separation tests using gas mixtures. After the initial selection of the membranes, tests will be conducted on gas mixtures. The test loop for these corrosive materials is under construction and will be operational in the

fall of 2003. Initial experimental results will be available in early 2004.

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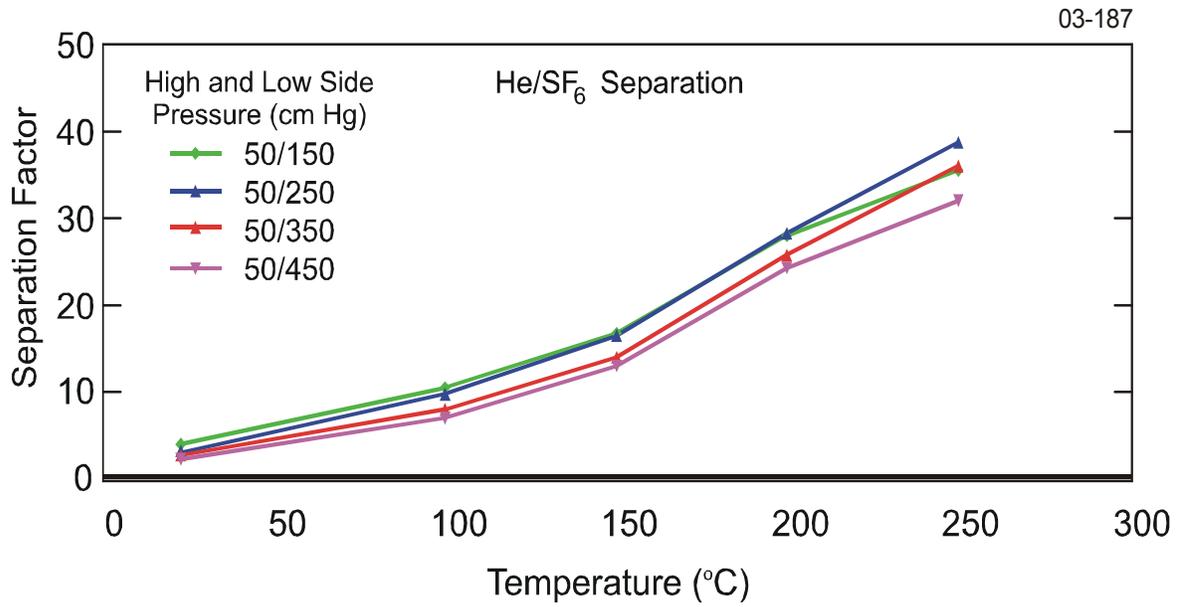


Fig. 4. Separation factors for the He/SF₆ system vs temperature at different pressures for membrane 2528.

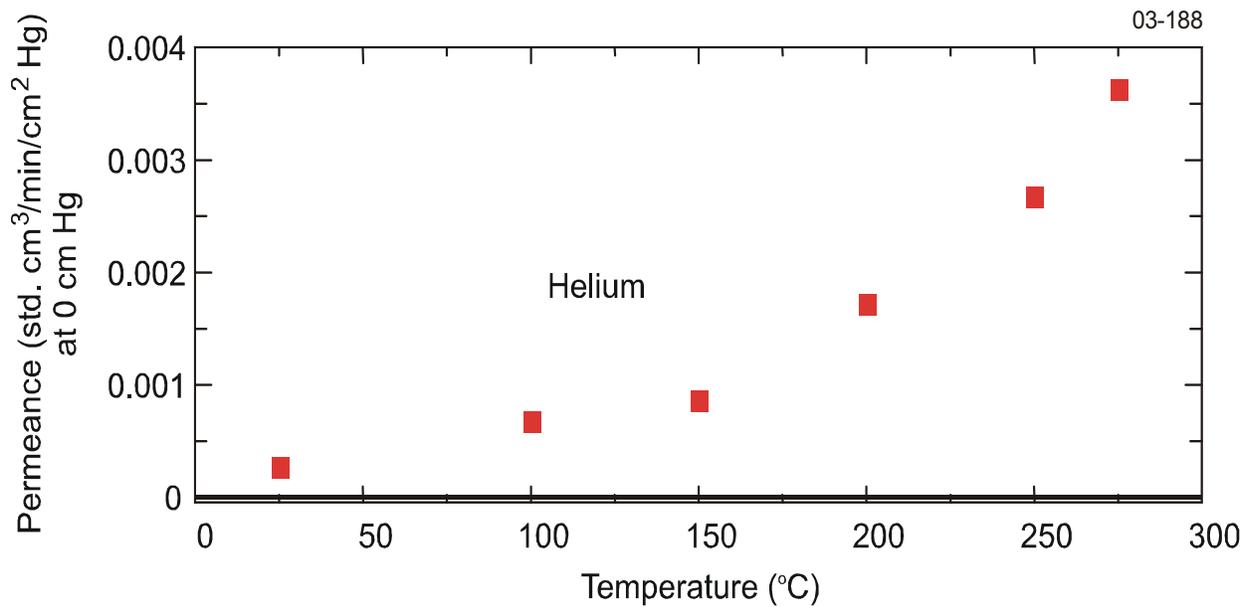


Fig. 5. Helium permeance vs temperature for membrane 1230252-8a.