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Sulfur Thermochemical Processes with Inorganic Membranes to Produce Hydrogen

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ABSTRACT

The hybrid and sulfur-iodine (SI) thermochemical processes are the leading candidates worldwide for production of hydrogen (H₂) using nuclear energy. In both processes, water plus high-temperature heat yields hydrogen and oxygen. In each process there is a series of chemical reactions in which all the chemicals, with the exception of water, are recycled. The processes are potentially efficient, scalable to large sizes, and economic.

However, both processes have one major disadvantage: high operating temperatures (800 to 900°C). Both processes have the same high-temperature steps: the equilibrium thermal decomposition of sulfuric acid into H₂O, O₂, and SO₃ followed by the decomposition of SO₃ into O₂ and SO₂. The high temperatures are at the limits of materials of construction for heat exchangers and other components. The peak reaction temperatures can be lowered by ~200°C if the high-temperature decomposition products of sulfuric acid (O₂, H₂O, and SO₂) can be separated from SO₃ as they are formed. Selective separation of reaction products allows the reaction to be driven to completion at lower temperatures. Experiments are under way at Oak Ridge National Laboratory to develop an inorganic membrane to accomplish this task. The preliminary data on the separation of O₂ and SO₂ from SO₃ using an inorganic membrane are reported.

KEY WORDS

Hydrogen, Nuclear Energy, Thermochemical Cycles

INTRODUCTION

The leading candidates for low-cost, large-scale H₂ production using nuclear energy are thermochemical processes. A thermochemical process consists of a set of chemical reactions in which the input is high-temperature heat plus water and the output is H₂ and O₂. Nuclear reactors can provide the heat needed for these processes.

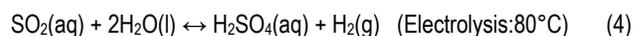
Two [1] of the highest-rated processes have the same high-temperature steps (see Figure 1) that requires heat input at 850°C if the process operates at ~10 bar. The highly endothermic (heat-absorbing) gas-phase reactions in each of these processes are



The two thermochemical processes have different lower-temperature chemical reactions. The sulfur-iodine process [1] has two other chemical reactions (Equations 2 and 3), which, when combined with the reaction in 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 low-voltage electrochemical step (Equation 4) that completes the cycle [2].



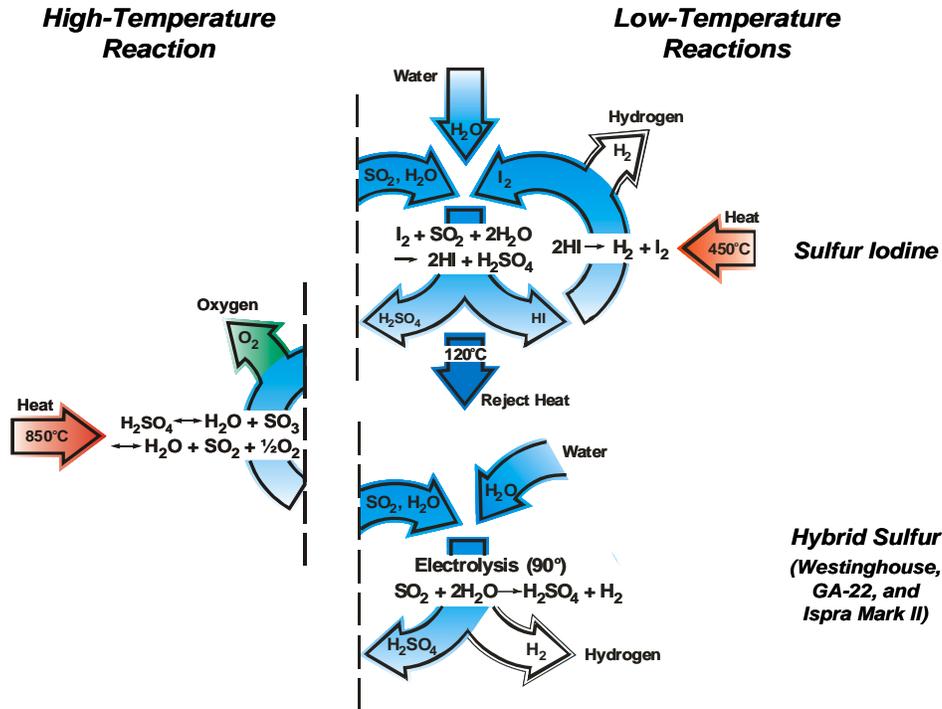


Figure 1. Sulfur-iodine and hybrid sulfur hydrogen thermochemical processes

In each of these cycles, the high-temperature sulfur trioxide (SO₃) dissociation reaction (Equation 1) is an equilibrium chemical reaction that requires a catalyst. High temperatures and low pressures drive the reaction towards completion. Detailed studies have concluded that the required 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 oxygen separated out and released to the atmosphere, the SO₂ sent to the next chemical reaction, and the unreacted sulfuric acid (formed by recombination of SO₃ and H₂O at lower temperatures) reheated 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 result in a very

inefficient and uneconomical process. One recent analysis of one particular SI flowsheet [1] showed that process inefficiencies increased so rapidly with decreasing temperature (incomplete SO₃ dissociation) that the process could not produce H₂ below 700°C.

However, strong incentives [3] exist to lower the temperature and increase the pressure at which SO₃ dissociates—the opposite of the conditions indicated by thermodynamic considerations for the reaction to go to completion.

- Lower temperatures. A major challenge to thermochemical H₂ production is the high-temperature heat required for efficient H₂ production, which is at the limits of nuclear reactor technology. The 850°C process temperature implies that the peak nuclear reactor temperature would need to be significantly higher in order to

account for temperature losses in heat exchangers between the reactor coolant and chemical plant. If this temperature could be lowered to 700°C, current [4] and advanced [5] designs of high-temperature nuclear reactors could be used for H₂ production.

- Higher pressures. If the equilibrium of the SO₃ dissociation reaction can be shifted, higher-pressure operation would improve economics and process efficiency by reducing equipment size and gas compression losses. Higher pressures would improve efficiency for processes such as the hybrid process [2]. In this process, the product SO₂ is separated from O₂ by sorption in water. At low pressures, the water must be refrigerated to absorb the SO₂. At high 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 SO₃ dissociation step by up to 200°C and allow the dissociation process to operate at a higher pressure. This is accomplished by the separation of SO₂, H₂O, and O₂ from the SO₃ at 650 to 750°C. If these reaction product gases are removed, the remaining SO₃ (with a catalyst and heat) will dissociate into its equilibrium concentrations. If the product 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. The 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 SO₂ and O₂ from SO₃. This paper describes the initial analysis, new experimental equipment fabricated to evaluate alternative inorganic membranes, and preliminary experimental results for the first membrane tested.

ALTERING THE DISSOCIATION EQUILIBRIUM

Figure 2 shows a schematic of two 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 H₂O and O₂ to pass through the membrane but blocks all other chemical species. At high temperatures, the H₂SO₄ dissociates into H₂O and SO₃. When these reagents contact the catalyst, the SO₃ partly dissociates into SO₂ and O₂ (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, O₂ and H₂O go through the membrane. The reaction shown in Equation 1 is driven to the right with the resultant greater concentrations of SO₂. A mixture of SO₂, SO₃, and small quantities of oxygen exits the reactor.
- Oxygen and SO₂ separation. The membrane reactor is similar to the first case, except that the membrane selectively allows H₂O, O₂, and SO₂ to pass through the membrane. In this case, a perfect membrane would drive the reaction to completion.

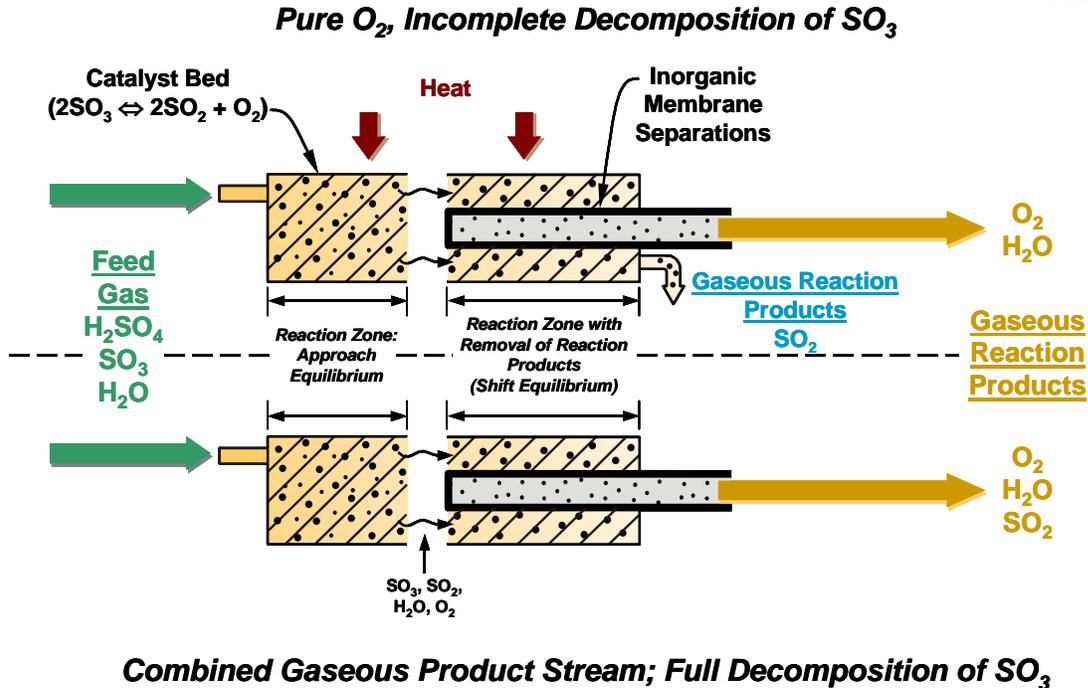


Figure 2. Membrane reactor system

The classical thermodynamic equation for this equilibrium reaction is

$$K(T) = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2} \quad (5)$$

where

$K(T)$ = equilibrium constant (a constant at any temperature but increases with temperature);

$[\text{SO}_2]$ = gas-phase concentration of SO_2 , typically in moles per liter;

$[\text{O}_2]$ = gas-phase concentration of O_2 ;

$[\text{SO}_3]$ = gas-phase concentration of SO_3 .

A parametric study was conducted to determine the potential benefit that the removal of (1) O_2 and (2) O_2 and SO_2 could have on the conversion of SO_3 to SO_2 . Using a thermochemical equilibrium computer program [6] the equilibrium conversion as a function of temperature was calculated (Table 1), assuming an initial quantity of 100 mol of H_2SO_4 .

Next, the effect of the removal of O_2 was studied. Calculations were made by first assuming that the reaction reached equilibrium in the first (theoretical) stage. At that stage, all of the O_2 was assumed to be removed and the remaining SO_3 and SO_2 were allowed to come to equilibrium again (stage 2). The O_2 was again removed, and this process was repeated through six stages. As shown in Table 1, the residual SO_3 at 700°C (21.6 moles) using inorganic membranes is approximately equal to the residual SO_3 at equilibrium at 850°C (21.1 moles) with no membrane separation. The calculations were performed in multiple batch removal stages in this way as an expedient to approximate continuous removal of reaction products to low levels. For the chemical reactor configuration shown in Figure 2, lengthening the tubes would increase the continuous removal of reaction products (i.e., effectively increase the number of hypothetical batch removal stages). (The stages do not represent physical stages of this equipment.)

Table 1. Effect of removal of oxygen and sulfur dioxide from sulfuric acid decomposition reactor using an ideal inorganic membrane at 1 atmosphere

Stage no.	Removal of O ₂ Temperature = 850 °C			Removal of O ₂ Temperature = 700 °C			Removal of O ₂ and SO ₂ Temperature = 700°C		
	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	39.4	78.9	21.1	23.8	47.6	52.5	23.8	47.6	52.5
2	5.4	90.0	10.3	6.8	61.2	38.9	12.5	24.9	27.5
3	1.9	93.6	6.5	3.5	68.2	31.8	6.5	13.1	14.4
4	0.9	95.4	4.6	2.3	72.8	27.2	3.4	6.9	7.6
5	0.5	96.5	3.5	1.6	76.0	24.0	1.8	3.6	4.0
6	0.3	97.1	2.9	1.2	78.4	21.6	0.9	1.9	2.1

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

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 2.1 mol of the SO₃ remained.

Although the analysis indicates that an ideal membrane that separates only O₂ can effectively lower the peak dissociation temperature 150°C and reduce the unreacted SO₃ to 21.6 mol at 700°C, there are strong incentives to remove both SO₂ and O₂. An ideal membrane can reduce the unreacted SO₂ to 2.1 mol with six ideal stages of separations, the same number of separation stages as used in the oxygen separation.

The lowest practical operating temperature of the inorganic membrane is determined by the condensation temperature of H₂SO₄. Membranes are gas separation devices that must operate significantly above the condensation point of components in the gas stream. For operation at 10 bars, the lower temperature limits are near 700°C.

If the pressure in the SO₃ dissociation chemical reactor is increased, the minimum operating temperature of the membrane increases because the condensation temperature of H₂SO₄ increases. In the near term, the incentive for use of inorganic membranes is to lower the peak reaction temperatures in order to reduce the peak temperature requirements on the nuclear reactor. If higher temperatures become available, a strong incentive remains to use inorganic membranes, because such 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 bars. Based on the thermodynamic equilibrium considerations, there are incentives to use inorganic membranes at temperatures to 1000°C.

INORGANIC MEMBRANE PRINCIPLES

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. Multiple gas-transport

mechanisms exist [7]: viscous flow, molecular diffusion, Knudsen diffusion, surface diffusion, capillary condensation, and nanopore diffusion. 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 feature 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. These are 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 that come into operation are covered by the term nanopore diffusion.

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 [$\text{mol}/(\text{m}^2 \text{ s Pa})$]. It is a measure of throughput. The selectivity or ideal separation factor 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 separation factor is generally smaller than the selectivity because of interactions among the gas species and other nonidealities. 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.

For O_2/SO_3 and SO_2/SO_3 separations, high operating temperatures ($\sim 700^\circ\text{C}$) are required, which, in turn, defines the type of physical separation system that is needed—nanopore diffusion. Nanopore separations improve with temperature with the permeance generally proportional to $m^{-1/2} d_p T^{-1/2} \exp[-E_d/RT]$. In contrast, transport mechanisms such as Knudsen diffusion, where the permeance decreases with temperature, are not candidates under these conditions. This finding has been demonstrated in a variety of other systems [3]. However, nanopore diffusion places demanding requirements on the membrane, in which the diameter of pores must be less than three times the diameter of the molecules.

The term “nanopore diffusion” encompasses several distinct mechanisms that take place in nanometer-diameter pores. For larger molecules, the membrane may function effectively as a molecular sieve, eliminating their transport through the membrane and giving very high separation factors. For smaller molecules, the transport exhibits thermally activated behavior. As the temperature is increased, the permeance increases exponentially, rather than decreasing as in Knudsen diffusion [8]. This implies the potential for high separation factors at high temperatures.

One thermally activated nanopore mechanism that has been understood is termed “gas translational diffusion.” It is also referred to as “thermally activated Knudsen diffusion,” in which molecules again 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 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 $d_p \sim 1$ nm, separation factors >100 are possible. For example, Uhlhorn and coworkers [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.

EXPERIMENTS

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 been commercialized.

Based on guidance from 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 or smaller. The results of these tests will be combined with theory to develop a custom membrane designed for this specific separation.

A membrane test system was designed and fabricated (see Figure 3). The system was designed to measure the permeance of pure gases, including N₂, O₂, SO₂, and SO₃, as a function of temperature and pressure. The system is constructed of materials that are compatible with the operating temperatures and gases employed in this system. Because SO₂ and SO₃ are not gases at room temperature, the piping, valves, and gauges are heated by heat tape throughout the complete system where there is a possibility that the gas would be at sufficiently high enough pressures to condense. The membrane holder and membrane are enclosed in a clam-shell heater capable of temperatures of ~900°C. Both the upstream and downstream pressures can be controlled and monitored independently from one another to give maximum flexibility in varying total pressure as well as transmembrane pressure. Lastly, all of the heat zone temperatures, pressures, and gas

flow data are continuously collected and monitored by a computer.

The initial membrane testing is being done by measuring the permeance of pure gases (N₂, O₂, SO₂, and SO₃) as a function of temperature and pressure. The gas flow per unit surface area is measured as a function of pressure drop and temperature. The mutual interactions among gas molecules and of the gas mixture with the membrane will be investigated in the future.

Testing has been completed on the first membrane. Using independent gas measurements, its pore size is estimated to be between 0.6 and 0.8 nm. Because of concerns with SO₂ and SO₃ condensation, only O₂ permeance was measured at room temperature and SO₃ permeance was measured only at 133°C. The results are shown in Figure 4. The plots show the permeance versus the sum of the pressures on the high- and low-pressure sides of the membrane (σP). The data at high σP can have both a molecular and viscous flow component. When the data are extrapolated to $\sigma P = 0$, the permeance should be a more accurate representation of molecular flow. This set of data had too much noise to yield a good estimate of molecular flow at $\sigma P = 0$.

While the data have some noise due to minor initial control problems and the fact that gas flows were very close to the lower detection limits, the bottom chart shows that *the permeance of O₂ increased by a factor of almost 2.5 from room temperature to 133°C*. This phenomenon is consistent with permeance increases observed for He and H₂ in other systems in which nanopore diffusion exhibits a thermally activated behavior. The middle chart in Fig. 4 shows the SO₂ data. It also shows an increase in permeance with temperature over a smaller temperature range.

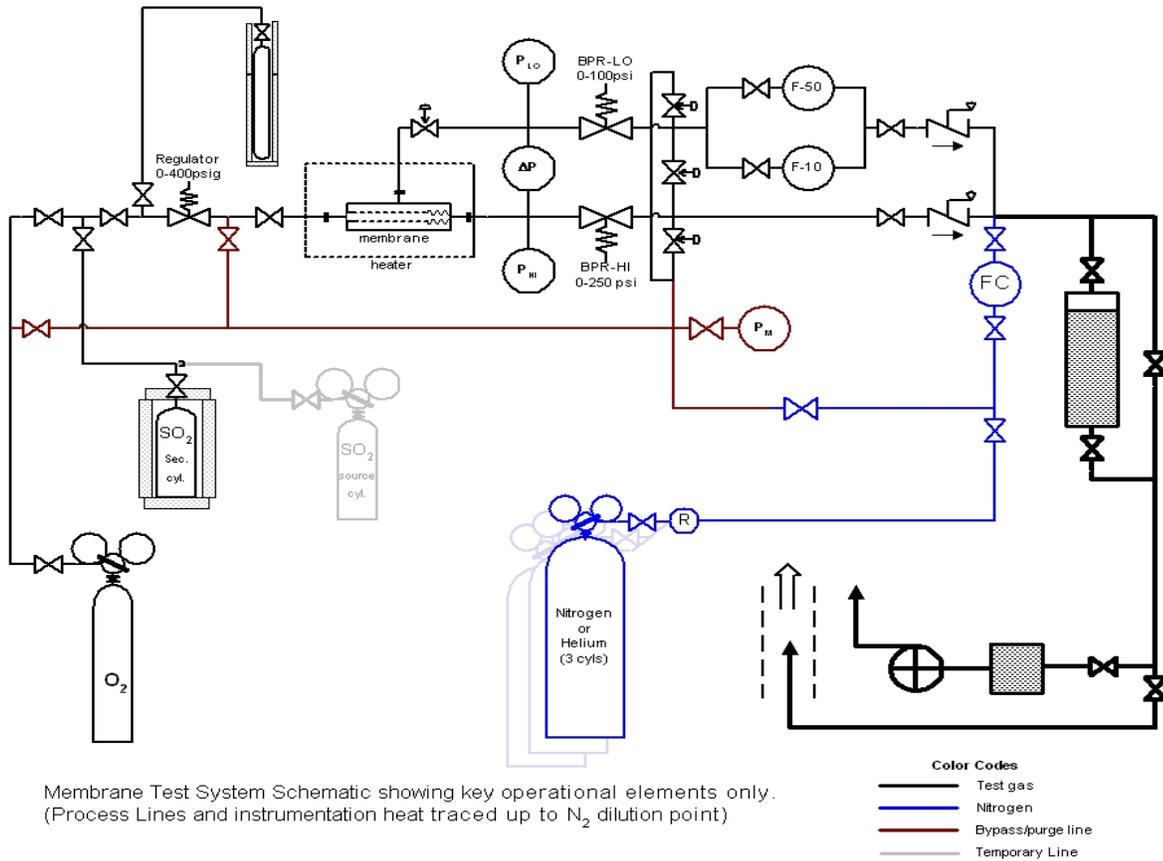


Figure 3. Schematic of membrane test system.

The top graph (Fig. 4) shows the permeance of all three gases at ~133°C. By calculating the ratio of the average permeances, the selectivities (ideal separation factors) of O₂ and SO₂ over SO₃ are ~2.3 and 2.2, respectively. These separation factors are far higher than Knudsen diffusion. It should also be noted that the flow of O₂ was significantly reduced after the membrane was subjected to SO₃. It is believed that although the SO₃ was above its condensation temperature in the membrane, significant gas adsorption occurred, which significantly blocked the pores to flow of the O₂.

Although these are preliminary tests, we can draw several conclusions from this series of experiments.

- Operations. The SO₂ and SO₃ exposure under the present conditions did not induce membrane failure.

- Temperature. The preliminary data show promising results. The flows of SO₂ and O₂ through the membrane increase with temperature (as had previously been observed for He and H₂ in small pores), which suggests a thermally activated diffusion mechanism and improved performance as the temperature is increased toward the required temperatures at which the membranes must operate for use in thermochemical cycles. However, because SO₃ flow has been collected at only one temperature at this time, it is not known how its flow will be influenced by temperature. Therefore, it cannot be predicted whether the separation factor will increase (or by how much) at 600–700°C.

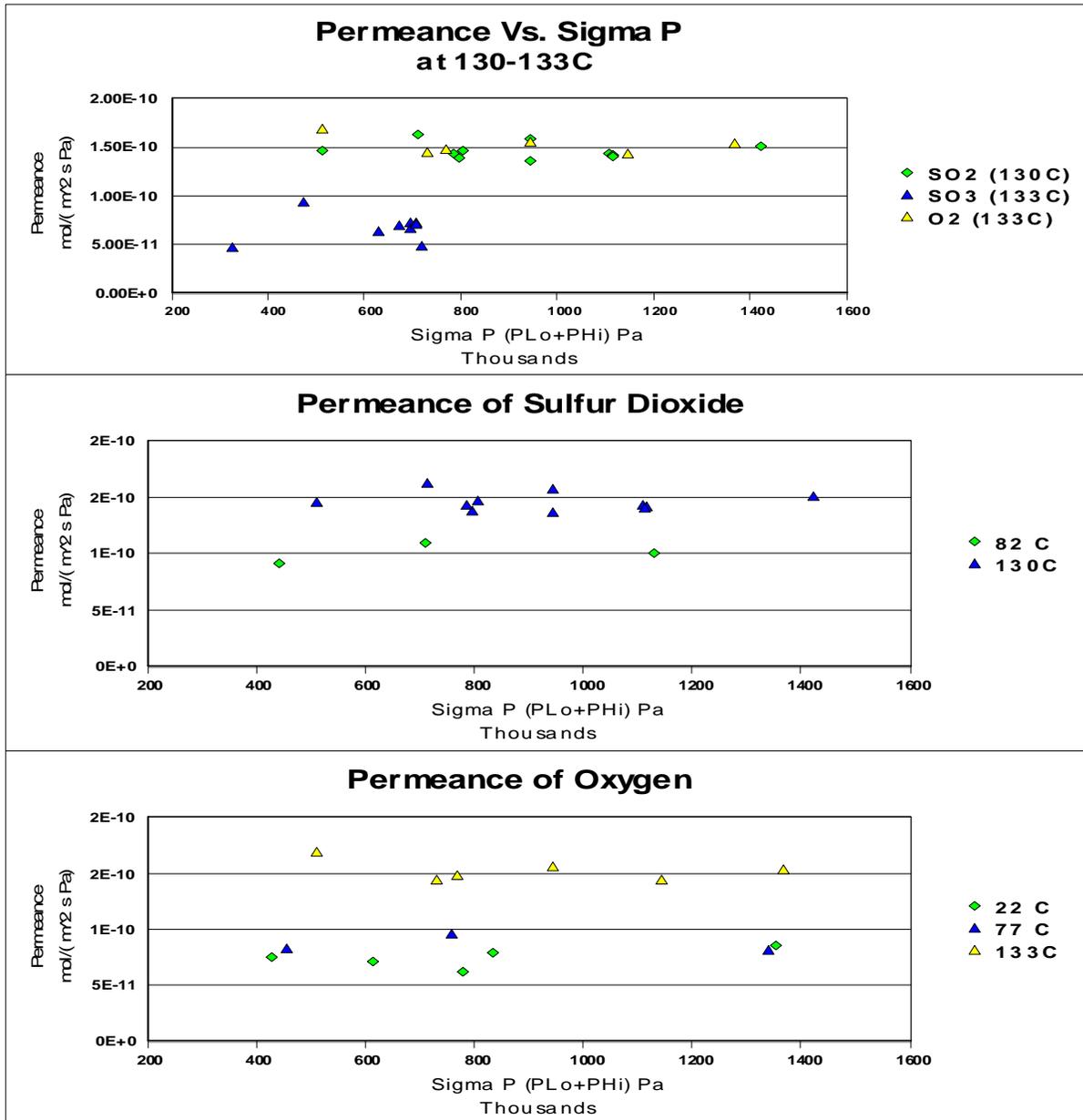


Figure 4. Results of pure gas flows through membrane 101501.

- Separations factors. The separation factors for O₂ and SO₂ from SO₃ are similar. For these chemical processes, it is highly desirable to simultaneously remove these two species to maximize membrane performance and minimize the peak temperatures at which these thermochemical processes are operated. It also suggests that the planar SO₃ has a significantly higher activation energy than the other species and lower transport through the membrane.
- Membrane. A higher-permeance membrane is desirable.

SUMMARY

The initial results at low temperatures on the first membrane tested are encouraging. Based on these results and experience in development of other membranes, the next tests will use a second membrane with a somewhat larger pore size and be operated at higher temperatures. After added tests with multiple membranes and various temperatures, the best membranes (i.e., those having the highest ideal separation factors and high permeance) will be subjected to separation tests using gas mixtures. Results using gas mixtures are expected in 2005.

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