

Testing of a Practical Low Pressure Permeator

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Abstract Palladium membrane permeators have long been used in tritium processing to separate gas mixtures into a pure-hydrogen permeate fraction, and a hydrogen-depleted retentate fraction. However, the retentate fraction has previously always required further purification (generally by oxidation followed by adsorption) to reach tritium concentrations low enough for environmental release. This report describes the development and testing of a practical-scale, low-pressure permeator to produce a hydrogen-depleted retentate fraction that can be stacked directly to the environment without further processing. This performance is attained by linking the permeator to a high vacuum system and by constructing the permeator with high vacuum conductance. The permeator incorporated three 1/8" Pd/Ag tubes in a 6" shell. The pumping train consisted of turbomolecular pump, followed by a diaphragm pump. For this phase of testing only H₂ performance was measured with tritium operation planned for later. This device has been tested with total feed flowrates up to 20 SLPM and various feed hydrogen concentrations. Permeate pressures were in the range 10⁻⁵ to 10⁻² torr range. Temperatures used were 350 to 450 C. Presented are the design features of the permeator, and the results of testing this prototype device. Retentate hydrogen concentrations in the low ppm range were routinely achieved.

INTRODUCTION

Palladium (or Palladium/Silver alloy) permeators, have been employed in tritium processing operations for many years to remove hydrogen isotopes (Q₂), i.e., protium, deuterium, and tritium from other gases. Practically, Pd/Ag is only permeable to Q₂; a gas mixture is fed to one side of a Pd/Ag membrane and a vacuum is applied to the other side of the membrane. The difference in hydrogen isotope partial pressure across the membrane is the driving force that generates a flow of Q₂ from one side to the other. To date such devices have been used extensively to reduce the Q₂ partial pressure in the retentate gas down to around 1 torr. This is insufficient for stacking the resulting gas if tritium was the isotope. However, previous work [1] suggested that a Pd/Ag permeator could be used effectively at much lower partial pressures. Recently proposed projects would require operating conditions beyond the range of past experience. These operating conditions would require either higher feed flowrate, increased permeation rate, lower hydrogen concentration in the retentate, or some combination of these. The present work was undertaken to demonstrate a new permeator design, intended to achieve these types of operating conditions.

EXPERIMENTAL APPARATUS

Permeator: The permeator tested was manufactured by Resource Systems, Inc. of East Hanover, NJ, to patented design modifications of a commercial RSI-100 permeator. Figure 1 shows a diagram of the permeator.

The new design features are aimed at reducing the pressure on the exterior (shell-side) of the palladium membrane, in order to reduce the upper limit of the retentate composition. To this end, the permeate exhaust port has been increased to a 6 inch nominal diameter. This is closely

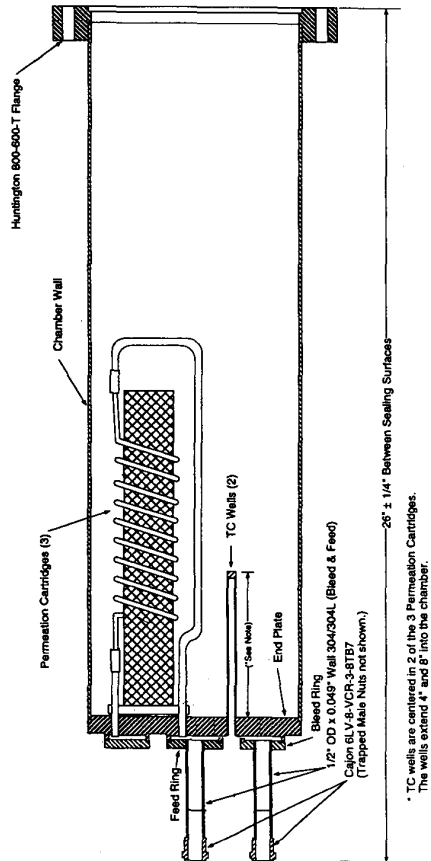


Figure 1 Low Pressure Permeator

coupled to the inlet port of a turbomolecular pump. The large diameter exhaust port and close coupling to the pump increase the conductance of the vacuum piping and reduce any pressure drop from the interior of the permeator shell to the pump inlet. The interior of the permeator has also been opened up to eliminate obstructions that might reduce the conductance down the bore of the permeator shell. To this end, heating is accomplished with exterior clamp-on heaters.

The heart of the permeator are 3 helices of thin-wall palladium/silver tubing, each of which is supplied from a common feed plenum by a long stainless-steel tube which runs down the length of the permeator axis before discharging into the palladium tubing. The helices in the low-pressure design are spaced on a 1/2 inch pitch. This is intended to reduce the pressure of the permeated hydrogen in the exterior

vicinity of each turn. The helices are supported on a perforated (63% open area) cylindrical shell, which permits the permeated hydrogen to also flow radially inward away from the palladium tubing.

Test Manifold: Feed gases (hydrogen and nitrogen) were injected using Brooks 5850EM mass flow controllers supplied from gas cylinders. Outlet retentate flow was measured with a Brooks 5850EM mass flow meter. The pressure of the feed and retentate were measured with Baratron transducers. The permeate vacuum pressure was measured with a cold cathode gauge. Feed and retentate compositions were measured by an MTI model M200 gas chromatograph using a 10 m molecular sieve column and a thermal conductivity detector (TCD). Calibration showed that the TCD could detect down to 0.3 ppm H₂. Discharge pressure of the retentate was controlled using a backpressure regulator. A Varian Turbo-V250 turbomolecular pump backed by a diaphragm pump was used to maintain the permeator shell-side vacuum.

Procedure: The shell of the permeator was pumped down and the permeator heated to and maintained at a fixed operating temperature of 350-400 C. Two types of test were performed: 1) a fixed flowrate of H₂ (0.4 - 135 sccm) was maintained during an experimental run, while the flowrate of the nitrogen was varied (30 - 20,000 sccm); or 2) the feed H₂ composition was maintained at a fixed value (25 ppm - 30%) during the experimental run, while the total feed flowrate was varied (30 - 20,000 sccm). The first procedure using a fixed H₂ flowrate was more convenient, as a fixed load of permeate was sent to the turbomolecular pump, resulting in a fixed permeate pressure, easing the data interpretation. For each flowrate combination the pressures, temperature, flowrates and gas composition were recorded when conditions reached steady state (generally about 2 hours after changing input conditions). Duplicate GC measurements were made until a minimum of 5 measurements were made.

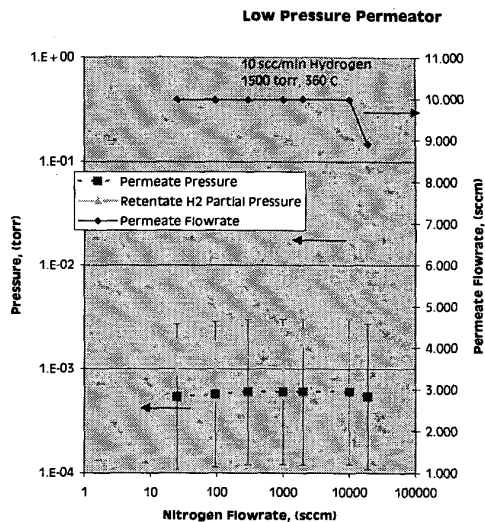
Using the retentate gas composition and total pressure, the retentate H₂ partial pressure could be calculated. Since the permeate was only H₂, the shell-side H₂ partial pressure was the same as the total vacuum pressure. The vacuum pressure was measured after a right-angle elbow connected to the permeator shell; the temperature at that point was measured to be approximately 34 C. Also this cold cathode gauge was calibrated for N₂ rather than the H₂ gas of the permeate. Thus, the following correction was applied to determine the permeate pressure at the membrane:

$$P_{AtMembrane} \square P_{Measured} K_{GasFactor} \sqrt{\frac{T_{AtMembrane}}{T_{ColdCathodeGauge}}}$$

The cold cathode gauge manufacturer listed the gas factor as 0.43. No attempt was made to correct for conductance pressure losses, but order-of-magnitude calculations have indicated this to be negligible.

RESULTS

Figure 2 shows a set of typical results obtained by feeding a constant flow of about 10 sccm of hydrogen to the permeator mixed with nitrogen of feed rates varying from 25 sccm to 19,000 sccm (hydrogen feed concentrations from 30% to 500 ppm) at 360 C. The permeate pressure (permeator shell-side pressure) remained essentially constant at about 6×10^{-4} torr, but the retentate partial pressure, although exhibiting a considerable amount of experimental error, was somewhat higher, averaging about 2×10^{-3} torr, until feed rates exceeded 2000 sccm where the retentate hydrogen partial pressure increased dramatically. At about 2000 sccm feed flowrate the retentate partial pressure begins to rise dramatically above the permeate pressure. This point is referred to as "breakthrough". At higher flowrates, ever-increasing amounts of hydrogen remain in the retentate. It is clear that significant dis-equilibrium exists between the retentate and permeate partial pressures at flow rates Figure 2



Typical Results from Low Pressure Permeator

exceeding 2000 sccm, but the state of equilibrium below 2000 sccm is unclear.

Figure 3 shows a set of typical results where the results are more clear-cut. These measurements fed a constant flow of about 1.5 sccm of hydrogen to the permeator mixed with nitrogen of feed rates varying from 25 sccm to about 7000

sccm (hydrogen feed concentrations from about 6% to 225 ppm) at a temperature of 400 C. The permeate pressure (permeator shell-side pressure) remained essentially constant at about 1×10^{-4} torr, but the retentate partial pressure was more than an order of magnitude higher, averaging about 5×10^{-3} torr, until feed rates exceeded 2000 sccm at which point the retentate hydrogen partial pressure increased even further. The hydrogen partial pressure in the retentate corresponds to a hydrogen concentration of about 1.5 ppm, below 2000 sccm feed flowrate.

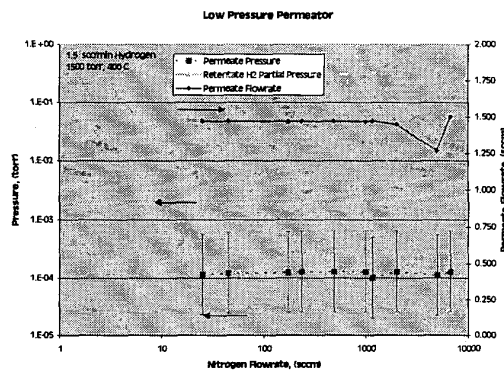


Figure 3 Permeator Performance at 400 C, 1500 torr, and 1.5 sccm Hydrogen Feed

For this experimental run it is clear that the retentate partial pressure of hydrogen is NOT in equilibrium with the permeate pressure; there is a significant difference in partial pressures between the retentate and the permeate (shell-side).

The error bars on the data points show the estimated experimental uncertainty in the measurements. The difference in the partial pressures exceeds the uncertainty. The behavior of the differential between the retentate hydrogen partial pressure and the permeate pressure shown here is typical of all conditions tested.

DISCUSSION

Prior to these tests, there was concern that a permeator would be unable to remove hydrogen isotopes from other gases to the extent that would allow direct venting of the retentate gas when operating at a "practical" flowrate. A criteria for direct venting is often set at less than 5 ppm of tritium, and "practical" flowrates of 1 - 10 liters per minute are often required. These tests have conclusively demonstrated that very low hydrogen concentrations (1 - 5 ppm) can be reached at flowrates up to several 10's of liters per minute in a small permeator. This work demonstrates the practicality of a permeator system for such applications, and provides the basis for designing such permeators. Such a system would probably employ 1 or more "conventional" high-pressure permeators using higher-capacity, higher-pressure vacuum pumps upstream of this low-pressure permeator. Such a system would remove the bulk of the hydrogen in the first stages, and use the low-pressure permeator to "clean-up" the retentate to levels suitable for venting. Such multi-stage permeator systems for several applications are currently in early stages of design.

CONCLUSION

These experiments demonstrate the practicality of this permeator as part of system for applications to produce a very high purity retentate which can be directly vented, or to remove large quantities of tritium from very high flow rate feeds. It was found that this type of permeator can produce a retentate containing less than 5 ppm of hydrogen at flowrates up to 20,000 ppm. Similar results were obtained at temperatures from 360 - 440 C, and permeate pressures from 10⁻⁶ to 10⁻² torr.

REFERENCES

- [1] S. A. Birdsell, R. S. Willms and R. C. Wilhelm; "Ultra-High Tritium Decontamination Of Simulated Fusion Fuel Exhaust Using A 2-Stage Palladium Membrane Reactor", Proceedings of the ANS 12th Topical Meeting on Technology of Fusion Energy, Reno, June 16-20, 1996.