

LA-UR- 97-372

Approved for public release;
distribution is unlimited.

CONF-970404--3

Title: TRITIUM RECOVERY FROM TRITIATED WATER
WITH A TWO-STAGE PALLADIUM MEMBRANE
REACTOR

Author(s): S. A. Birdsell
R. S. Willms

Submitted to: 4th International Symposium on Fusion
Nuclear Technology, Tokyo, April 7-11,
1997

MASTER

RECEIVED
APR 10 1997
OSTI

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ph

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. The Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

TRITIUM RECOVERY FROM TRITIATED WATER WITH A TWO-STAGE PALLADIUM MEMBRANE REACTOR

S. A. Birdsell and R. S. Willms

Los Alamos National Laboratory
Mail Stop C348
Los Alamos, NM

Abstract

A process to recover tritium from tritiated water has been successfully demonstrated at TSTA. The 2-stage palladium membrane reactor (PMR) is capable of recovering tritium from water without generating additional waste. This device can be used to recover tritium from the substantial amount of tritiated water that is expected to be generated in the International Thermonuclear Experimental Reactor both from torus exhaust and auxiliary operations. In addition, this process can be used to recover tritium from tritiated waste water being prepared for disposal in radioactive waste repositories. A large quantity of tritiated waste water exists world wide because the predominant method of cleaning up tritiated streams is to oxidize tritium to tritiated water. The latter can be collected with high efficiency for subsequent disposal.

The PMR is a combined catalytic reactor/permeator. When used to process water, carbon monoxide is injected into the tritiated water stream and catalyst is used to promote the water-gas shift, $\text{HTO} + \text{CO} \rightarrow \text{HT} + \text{CO}_2$. In a typical reactor, this reaction only proceeds to partial completion due to thermodynamic equilibrium. However, by embedding palladium/silver permeator tubes in the reactor, the desired product, HT, can be almost completely removed and recovered from tritiated water, HTO.

Cold (non-tritium) water processing experiments were run in preparation for the tritiated water processing tests. Operating conditions were varied in the cold experiments so that optimal operating conditions could be determined before tritium tests were run. The optimal CO injection rate was found to be in the range of 1.1-1.25 times the water injection rate. The decontamination factor (DF) increased with temperature for the experimental range of 300-530°C. DF also increased with decreasing inlet flow rate for the experimental range of 29-125 std. cm³/min (sccm) of steam. A 1st stage DF of 340 was achieved at the maximum temperature tested of 530°C. Second stage decontamination factors in excess of 1000 were seen, but the exact number could not be determined due to analysis limitations. Therefore, it can only be stated that overall (2-stage) decontamination factors $>1 \times 10^5$ were achieved.

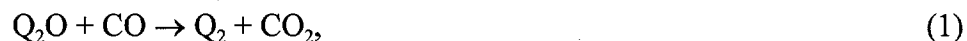
Tritium was recovered from a container of molecular sieve loaded with 2050 g (2550 std. L) of water and 4.5 g of tritium. During this experiment, 27% (694 std. L) of

the water was processed resulting in recovery of 1.2 g of tritium. The maximum water processing rate for the PMR system used was determined to be 0.5 slpm. This correlates well with the maximum processing rate determined from the smaller PMR system on the cold test bench and has resulted in valuable scale-up and design information. Carbon monoxide was injected into the 0.5 slpm steam at a rate of 0.61 slpm, which corresponds to a CO-to-HTO ratio of 1.22. A control method was developed to automatically liberate steam from the molecular sieve and add the desired amount of CO before injection into the PMR system. The system is accurate, reliable, and easy to operate. The maximum DF achieved in the 1st stage ranged from 100-260, depending on the inlet flow rate. The experiments were not run long enough to reach steady state and the DFs were slowly increasing at the end of the experiments. Performance of the 2nd stage could not be measured because the outlet tritium concentration was below the background of the ion chamber used for analysis. Although the DF could not be measured, it is known that the DF was high because no tritium was detected, except during start-up, in the tritium waste treatment system that was downstream from the PMR system.

I. INTRODUCTION

A process to recover tritium from tritiated water has been successfully demonstrated at the Tritium Systems Test Assembly (TSTA) at Los Alamos National Laboratory. The 2-stage palladium membrane reactor (PMR) is capable of recovering tritium from water without generating additional waste. In addition, this process can be used to recover tritium from tritiated waste water being prepared for disposal in radioactive waste repositories. A large quantity of tritiated waste water exists world wide because the predominant method of cleaning up tritiated streams is to oxidize tritium to tritiated water. The latter can be collected with high efficiency for subsequent disposal.

The ITER exhaust will contain tritiated impurities such as water and methane. Tritium will need to be recovered from these impurities for environmental and economic reasons. The PMR is a combined permeator and catalytic reactor. Catalysts are used to foster reactions such as water-gas shift,



and methane steam reforming,



where Q represents the hydrogen isotopes H, D, and T. Due to thermodynamic limitations these reactions only proceed to partial completion. Thus, a Pd/Ag membrane, which is exclusively permeable to hydrogen isotopes, is incorporated into the reactor. By maintaining a vacuum on the permeate side of the membrane, product hydrogen isotopes are removed, enabling the reactions to proceed toward completion.

In the water-processing application, only HTO and CO are injected into the PMR and it might be expected that only reaction (1) would be of importance. However, near the inlet of the PMR, some CQ_4 is formed by the reverse of reaction (2). Therefore, performance of the PMR system at water-processing conditions is similar to that of fusion-fuel processing conditions in which CQ_4 is also present.

Results of a single stage palladium membrane reactor have been reported in previous papers. Willms et al.¹ processed simulated fusion fuels with a PMR, but these early experiments contained no tritium. Willms et al.² and Birdsell and Willms³ report on tritium experiments with a single-stage PMR system and Birdsell and Willms⁴ report on tritium experiments with a two-stage PMR system. The experiments were conducted at ITER relevant conditions and were found to have a 1st stage decontamination factor ($\text{DF} = \text{inlet hydrogen isotopes} / \text{retentate hydrogen isotopes}$) in the 150-400 range for the 1st stage alone and up to 3×10^6 for the 2nd stage alone.

The present study was done to demonstrate that tritium can be recovered from tritiated water. Initially cold experiments were run to determine the effect of inlet rate, temperature, and the optimum CO injection. Tritiated water was then processed at these conditions. To close the loop of tritium recovery, tritium must be adequately separated from hydrogen and deuterium so these non-radioactive components can be stacked to the environment. Isotope separation experiments were run in the cryogenic distillation system at TSTA to demonstrate this separation. Results of these experiments will be reported in a later paper.

II. COLD TESTING

Experimental Apparatus

Figure 1 is a simplified schematic of the PMR cold test bench. Feed gases are injected into the 1st stage using Brooks 5850EM mass flow controllers. Water injection is made by flowing a mixture of H_2 and O_2 over a Pt catalyst. CO is mixed with the H_2O before injection into the 1st stage. The ~ 1 torr vacuum on the permeate side of the 1st stage is generated by a Normatex 15 scroll pump backed by a Metal Bellows 601 pump. In the 2nd stage, the Varian V250 pumping system is capable of about a 1×10^{-6} torr vacuum with the hydrogen rates resulting from these experiments. Two MTI model M200 gas chromatographs are used to measure the performance of the PMRs. The GC at the outlet of the 2nd stage is setup in the "high sensitivity" mode so that a minimum of approximately 5 ppm CH_4 and 0.3 ppm H_2 can be measured. The GC at the outlet of the 1st stage is setup in the "medium sensitivity" mode so that a minimum of approximately 0.01% CH_4 and H_2 can be measured. Endress and Hauser model 2850 humidity probes are used to measure the H_2O concentrations at the outlet of each stage. The probes were calibrated from -80°C to 20°C dew point and have an accuracy of $\pm 1^\circ\text{C}$ dew point.

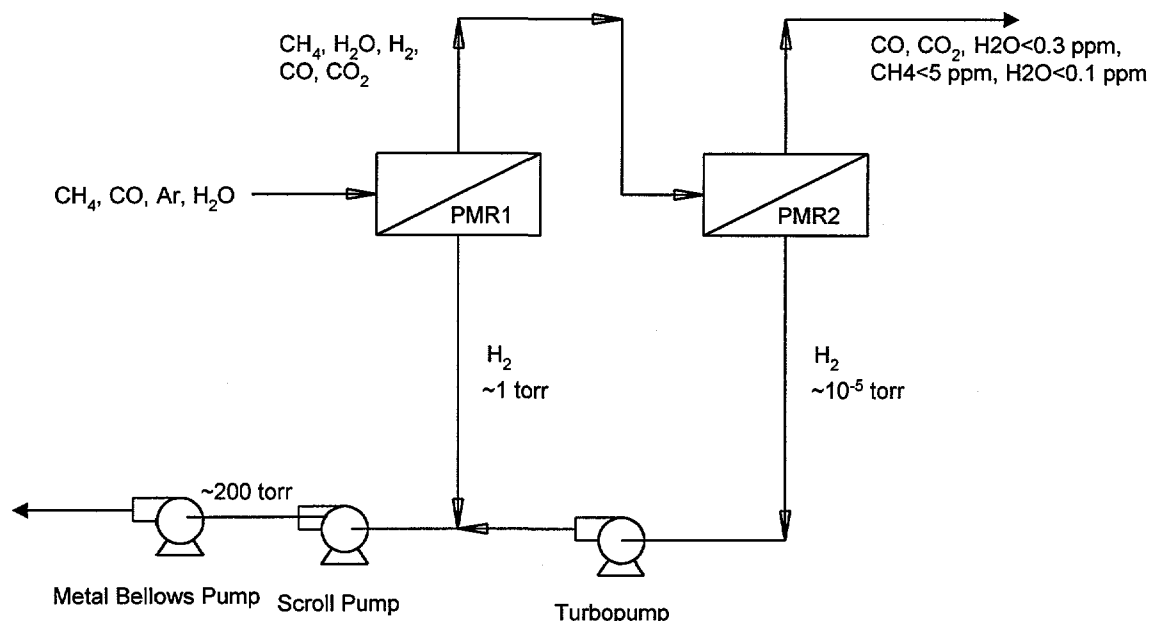


Figure 1. Schematic of cold test bench.

Figure 2 shows a schematic drawing of the 1st stage. This PMR has a Pd/Ag tube which is 61.0 cm long, 0.635 cm in outer diameter, and has a wall thickness of 0.0178 cm. The stainless steel shell is 66.0 cm long, 2.54 cm in outer diameter, and has a wall thickness of 0.165 cm. The annular space around the Pd/Ag tube was filled with 297 g of Pt/ α - Al_2O_3 catalyst (Engelhard A-16825). A vacuum is applied to the inside of the Pd/Ag tube with the pumping system. The PMR is oriented vertically in a tube furnace with the inlet at the top.

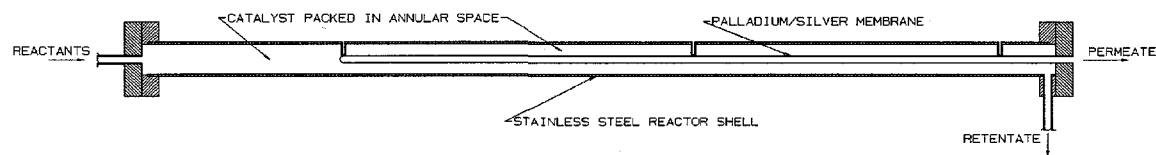


Figure 2. Schematic of 1st stage PMR.

Figure 3 is a schematic drawing of the 2nd stage. One of the $\frac{1}{4}$ in. tubes is a Pd/Ag tube identical to that in the 1st stage, while the other tube is a stainless steel blank. The Pd/Ag tube was filled with 10.3 g of Pt/ α - Al_2O_3 catalyst. The vacuum is applied to the shell side in the 2nd stage because the large 9.83 cm inner diameter is required so that high vacuums of $\sim 10^{-6}$ torr can be uniformly developed down the length of the pipe. Also, a relatively smaller quantity of catalyst is required in the 2nd stage and this quantity can fit on the inside of the Pd/Ag tube. The PMR is oriented horizontally in a tube furnace.

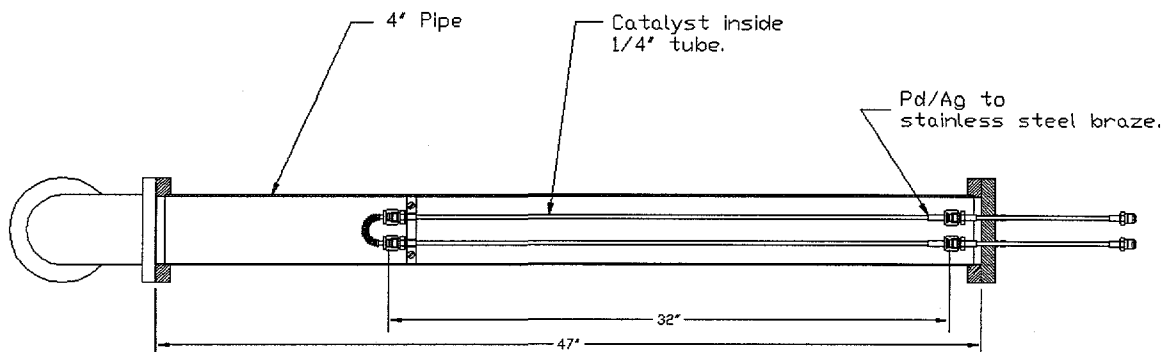


Figure 3. Schematic of 2nd stage PMR.

1st Stage Results

Non-tritium experiments were run on the cold test bench in preparation for the tritium water processing tests. Operating conditions were varied so that optimal operating conditions could be determined before tritium tests were run. H_2O and CO were injected into the system and the hydrogen recovery was measured as a function of temperature, inlet flow rate, and inlet CO -to- H_2O ratio ($\text{CO}:\text{H}_2\text{O}$).

It is believed that, at 530°C , significant fractions of CH_4 are formed near the inlet to the reactor where sufficient hydrogen exists for reaction (2) to proceed in reverse. CH_4 then needs to be converted back into H_2 for separation through the Pd/Ag membrane. To avoid CH_4 formation, the PMR system was tested at 300 and 400°C where little or no CH_4 formation occurs to determine if better performance could be achieved. Although little CH_4 was generated at the lower temperatures, the overall performance of the PMR system suffered due to lower reaction and permeation rates. As can be seen from Figure 4, the PMR has poor performance below about 450°C , and performance improves with increasing temperature above 450°C . The figure shows data up to 600°C , but as will be discussed below, long-term operation of PMRs have not been demonstrated above 530°C .

Experiments were run at inlet H_2O rates of 29, 50, 75, 100, 125, and 150 sccm at 530°C . Data were collected at $\text{CO}:\text{H}_2\text{O}$ ratios of 1.00, 1.10, 1.25, and 1.40 for each of the H_2O inlet rates. Figure 5 shows the 1st stage outlet concentration for CH_4 .

Figure 5 shows that as the $\text{CO}:\text{H}_2\text{O}$ increases, the outlet CH_4 concentration increases. This is believed to be partially because more carbon is available to form CH_4 at higher $\text{CO}:\text{H}_2\text{O}$. Residence time is also a factor. The residence time can be increased in two ways. The first is by decreasing the inlet rate (i.e., moving from, say, the 125 sccm H_2O to the 100 sccm H_2O curve on Figure 5). The second way is by decreasing the $\text{CO}:\text{H}_2\text{O}$ for a given H_2O injection rate. As the residence time in the reactor increases, the outlet CH_4 concentration decreases because more time is available for CH_4 to react and permeate.

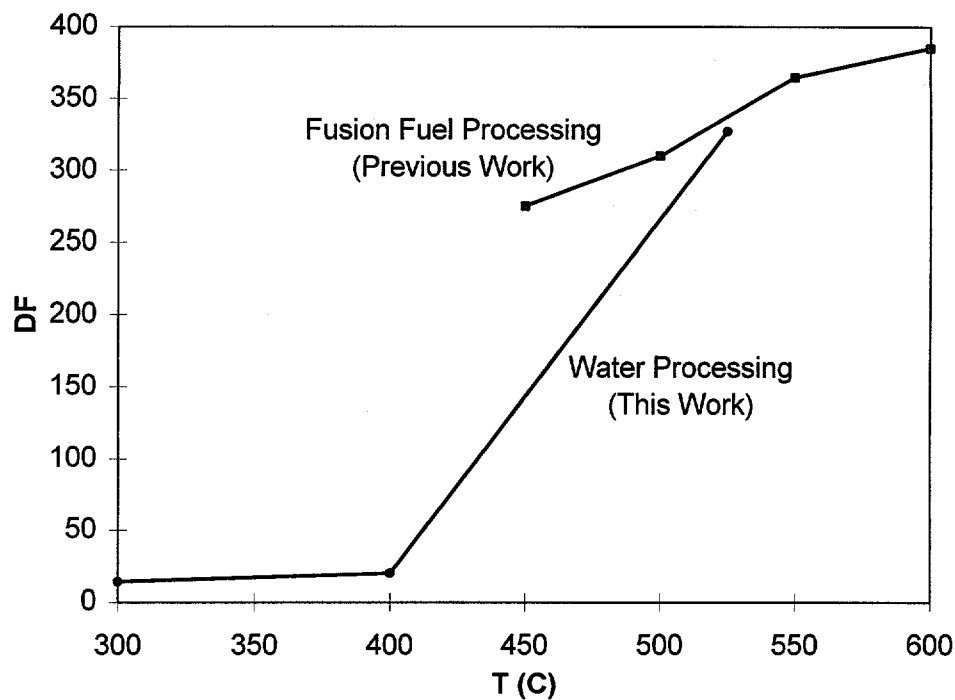


Figure 4. Decontamination factor versus temperature for water processing and fusion fuel processing conditions. Inlet rate is 29 sccm H_2O for water processing. Fusion fuel processing results are for comparable conditions.

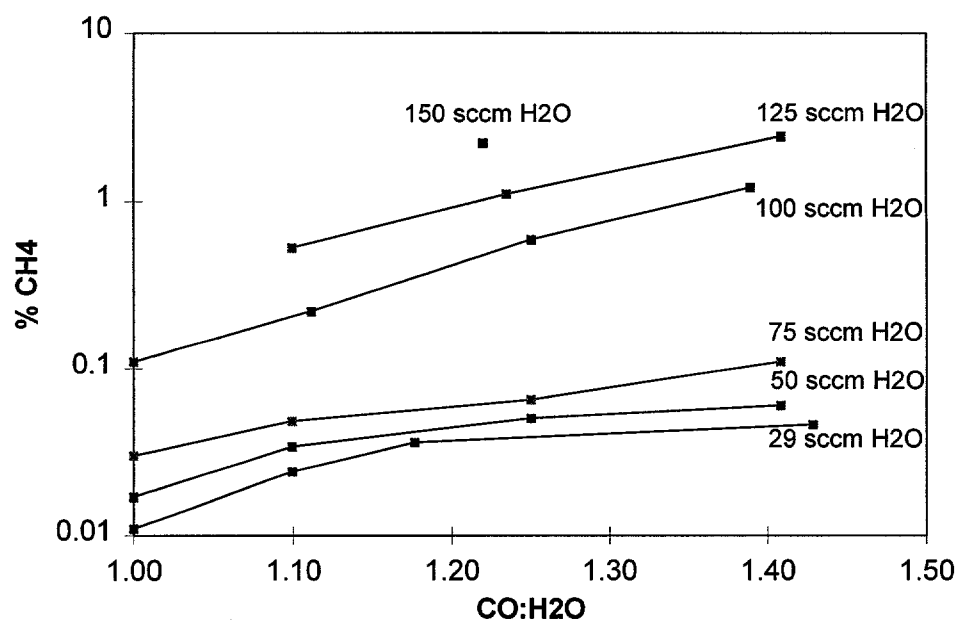


Figure 5. Methane concentration at the outlet of the 1st stage (530°C).

Figure 6 shows the H_2O concentration at the outlet of the 1st stage. These results are similar to the CH_4 results in that increasing the residence time by decreasing the H_2O injection rate results in lower outlet H_2O . However, increasing the residence time by lowering the $CO:H_2O$ (at constant H_2O injection), results in higher outlet H_2O . This is believed to be because as the carbon to oxygen ratio (C:O) becomes smaller, more oxygen is present which favors water formation.

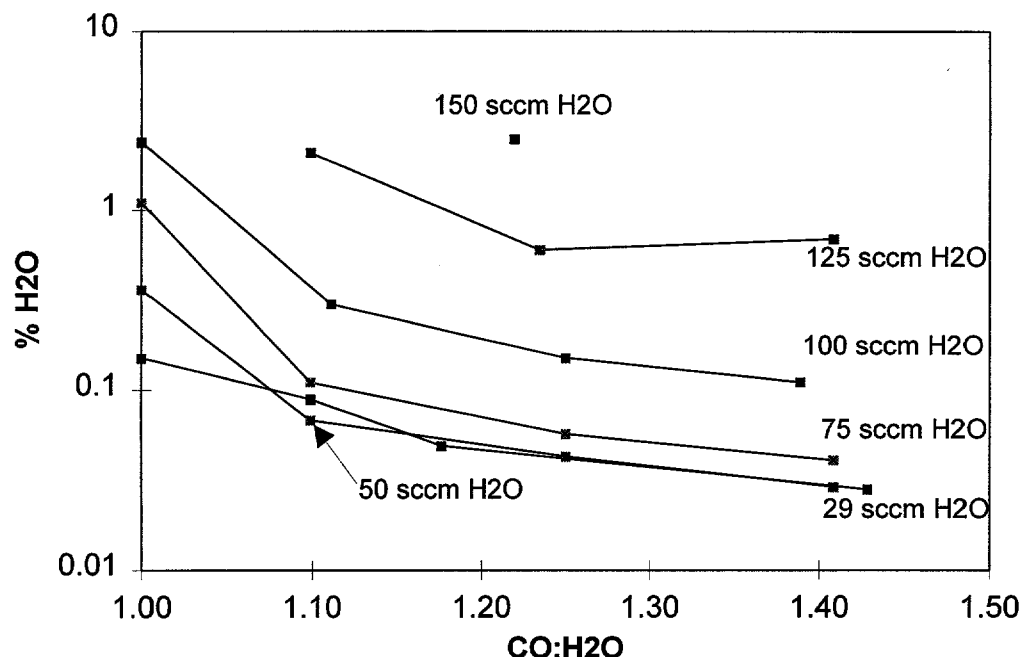


Figure 6. Water concentration at the outlet of the 1st stage (530°C).

Figure 7 shows the H_2 concentration at the outlet of the 1st stage. These curves are relatively flat when compared to Figures 5 and 6 because the H_2 concentration is believed to be controlled by the vacuum on the permeate side of the membrane. Sievert's law

$$Q_{perm} \propto \sqrt{P_H} - \sqrt{P_L} \quad (3)$$

where Q_{perm} is the permeate flow rate and the subscripts H and L represent the high and low pressure sides of the membrane, indicates that the permeate rate should be independent of the $CO:H_2O$, since changing this ratio only slightly changes $\sqrt{P_H}$ and has no effect on $\sqrt{P_L}$. At the lowest H_2O inlet rate of 29 sccm, the H_2 concentration is in nearly in equilibrium with P_L . However, the Pd/Ag membrane area is not large enough for equilibrium to be reached as the H_2O inlet rate is increased. It is believed that this permeation rate is slower than the chemical reaction rates and dominates the performance of the PMR. That is, H_2 concentration is controlled by the permeation rate and this H_2 concentration is in chemical equilibrium with the other components in the retentate

stream. Birdsell and Willms³ analyzed PMR data with a numerical model and determined that the retentate stream is nearly in equilibrium.

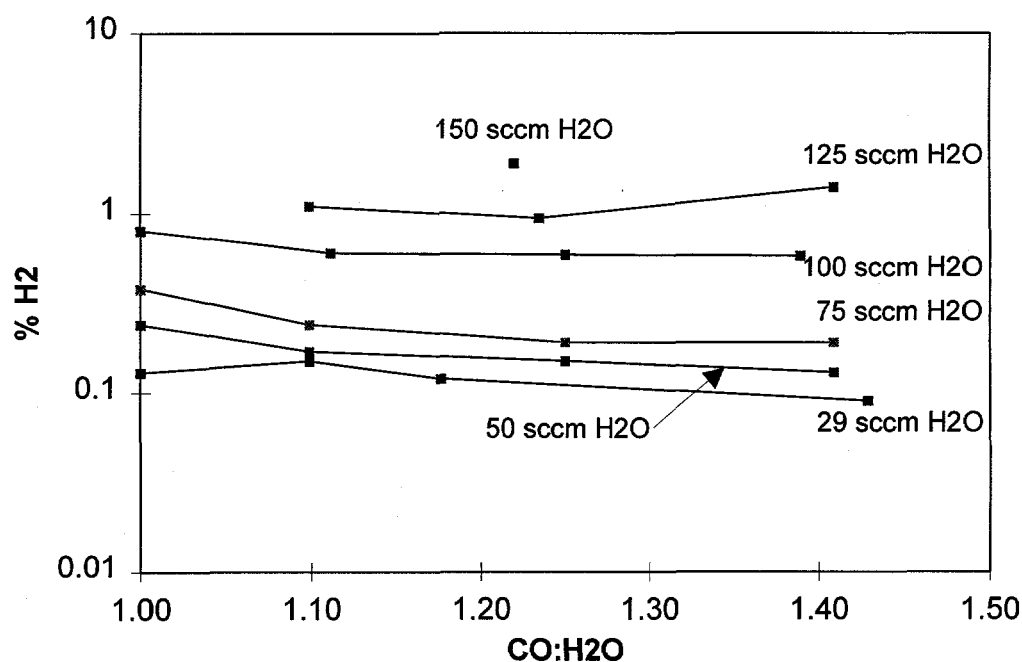


Figure 7. Hydrogen concentration at the outlet of the 1st stage (530°C).

The data of Figures 5, 6, and 7 is shown on a single plot in the form of DF on Figure 8. The optimum CO:H₂O was found to be in the range of 1.1-1.25 at 530°C. These curves are relatively flat near the optimum resulting in a wide range of CO:H₂O where good performance is obtained and, thus, tight control of the CO:H₂O is unnecessary. There are not adequate data to determine the exact optimum value, nor to determine if the value is dependent on the inlet H₂O rate. In the future, experiments will be performed to determine the optimum O₂ and CO injections for any mixture of CH₄ and H₂O that are fed to the PMR.

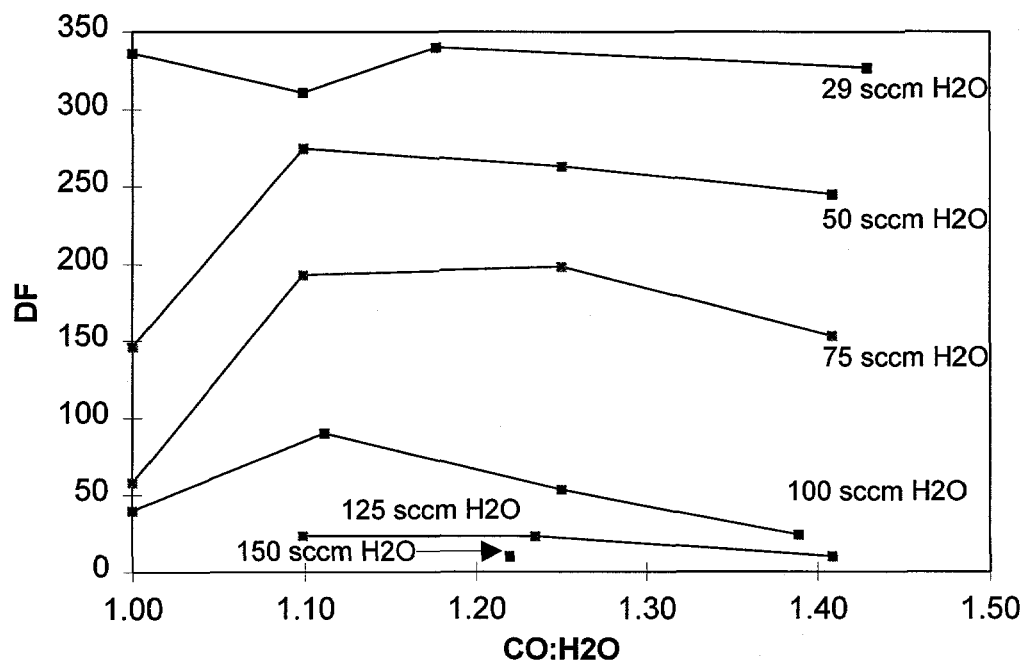


Figure 8. Decontamination factor versus inlet CO-to-H₂O ratio (530°C).

2nd Stage Results

Second stage decontamination factors in excess of 1000 were seen, but the exact number could not be determined due to analysis limitations. In nearly all of the runs, the compositions of all 3 hydrogen bearing species were below detection limits ($H_2 < 0.3$ ppm, $CH_4 < 5$ ppm, $H_2O < -80^\circ C$ dew point). Therefore, overall (1st and 2nd stage) decontamination factors could only be determined to be $> 1 \times 10^5$.

Long-Term Operation and Reliability

These water processing experiments were conducted over a period of 30 days of around-the-clock operation. In addition, fusion-fuel processing experiments have been conducted with the same PMR system for over 100 days, including a single 61 day test. During the operating history of the PMR system, many startups and shutdowns have occurred. No failures or loss of performance have been experienced.

III. TRITIATED WATER PROCESSING WITH THE PMR SYSTEM

Experimental Apparatus

In addition to the cold test bench, a 2-stage tritium compatible PMR system has been constructed within a glovebox. Figure 9 is a schematic drawing of this system. Figure 10 is a photograph of the 1st and 2nd stages. The 1st stage has an outer diameter of 10.2 cm with a 0.165 cm wall thickness and has 7223 g of $Pt/\alpha-Al_2O_3$ catalyst loaded around 6 Pd/Ag tubes. One of the Pd/Ag tubes is located on the centerline and the

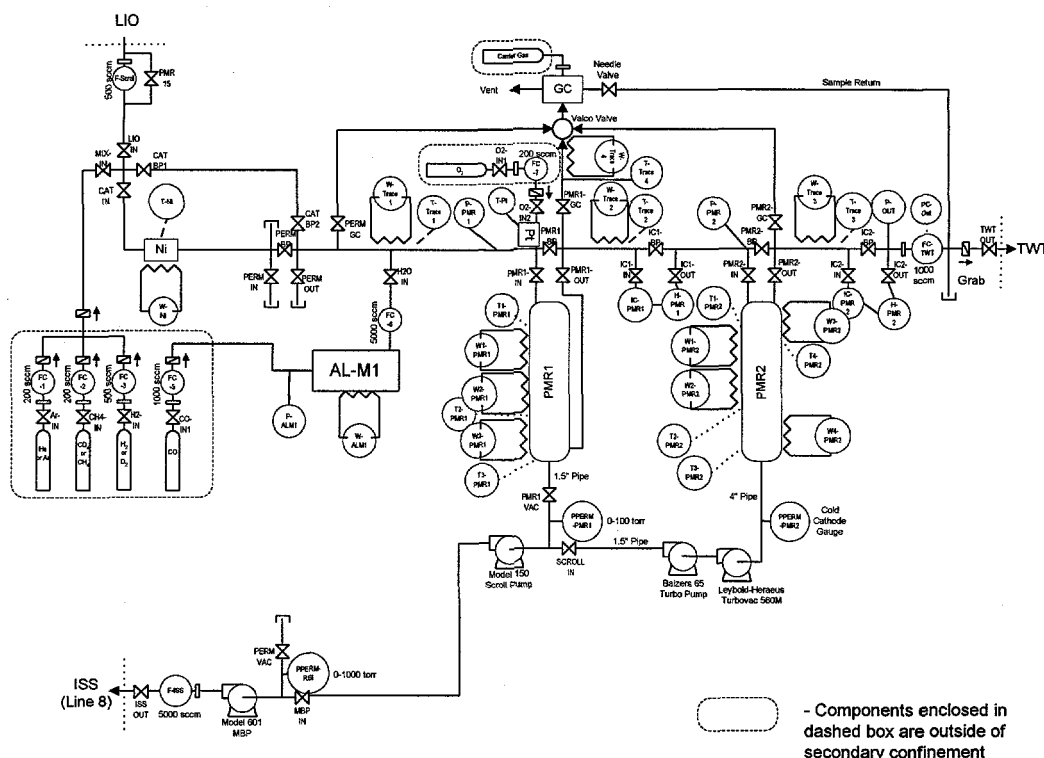


Figure 9. Schematic of the glovebox PMR system

remaining 5 are arranged in a 5.4 cm circle. One end of each of the Pd/Ag tubes is plugged, while the other end is attached to a flange so the inside of the tubes can be pumped. The 2nd stage design is similar to that of the 2nd stage on the cold test bench, but 6 Pd/Ag tubes are arranged in the 9.83 cm inside diameter pipe rather than 1 Pd/Ag tube and 1 stainless steel blank. 61.0 g of Pt/ α -Al₂O₃ catalyst were loaded inside the Pd/Ag tubes.

Both PMRs are similar to those used in the cold tests, but are scaled up by a factor of 6 in the surface area of Pd/Ag tubing. The gas chromatograph and humidity probes are also the same as in the cold test bench. Two Overhoff Technology ion chambers were installed in the process. The ion chamber at the outlet of the 1st stage has a range of 1×10^{-1} to 2×10^6 Ci/m³, while the one at the outlet to the 2nd stage has a range of 3.4×10^0 to 2×10^4 Ci/m³. The inlet and outlet tubing to the PMRs were heat traced so that water condensation would not occur. Both stages were oriented horizontally in the glovebox and heated with Thermcraft, Inc. clamshell heaters.

Seven tritiated water processing tests were run in the period from June-Sept. 1996 (Table 1). These were 1 day tests resulting in a total of 47 hours of operation. The 1st test was run at a low total inlet rate of 0.29 slpm (0.13 slpm HTO) in order to check out the system. The next 4 tests were run at a total inlet rate of 1.11 slpm (0.50 slpm HTO). This is roughly the maximum inlet rate, based on tests from the cold test bench, without causing a sharp decline in the decontamination factor. The inlet rate was increased above 0.5 slpm HTO for short periods of time and the 1st stage DF dropped significantly, thus

confirming that the maximum inlet rate for a PMR system of this size is about 0.5 slpm HTO.

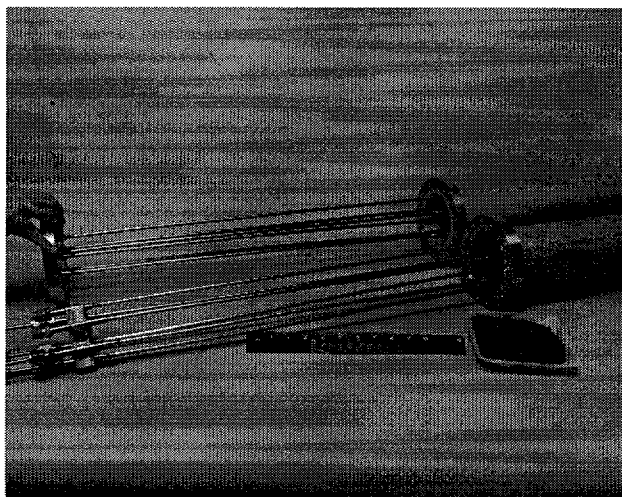


Figure 10. Photograph of the 1st stage (background) and 2nd stage (foreground). Catalyst is not yet loaded around the Pd/Ag tubes in the 1st stage.

Up to 4 hr were required for start up of each test due to the time required to heat the molecular sieve container to a temperature at which it would produce the desired flow of HTO. The temperature was increased slowly in the first few experiments to learn the heat-up versus HTO flow behavior. In later tests, the heat-up time was reduced to about 1 hr.

Table 1. Recovery and processing time during the water processing tests.

Run	Date	Nominal Q ₂ O Injection Rate (slpm)	Processing Time (hr)	Q ₂ Recovery (std. L)	T ₂ Recovery (Ci)
1	6/12/96	0.13	6	28.9	490
2	6/13/96	0.50	8	134	2280
3	7/9/96	0.50	8	91.5	1550
4	7/10/96	0.50	8	158	2680
5	7/11/96	0.50	8	161	2730
6	8/12/96	0.13	4	31.2	530
7	9/27/96	0.13	5	90.3	1530
Total			47	694	11,800 (1.2 g)

To operate properly, the PMR must be fed CO and steam in a proper ratio and at a controlled rate. By heating, a steady rate of steam was produced from the molecular sieve and a method for accurately adding the desired quantity of CO to the HTO stream was demonstrated (Figure 11). The technique consists of manually setting power to the molecular-sieve-bed heater to roughly set the rate of steam generation. Downstream from the molecular sieve bed, a heated mass flow controller from Unit Instruments measures

the combined CO and steam flow rates. The total CO and steam flow rate is sent to a ratio controller which determines the CO flow rate and sends this signal to the CO flow controller. The control scheme has been demonstrated to be accurate, reliable and easy to operate.

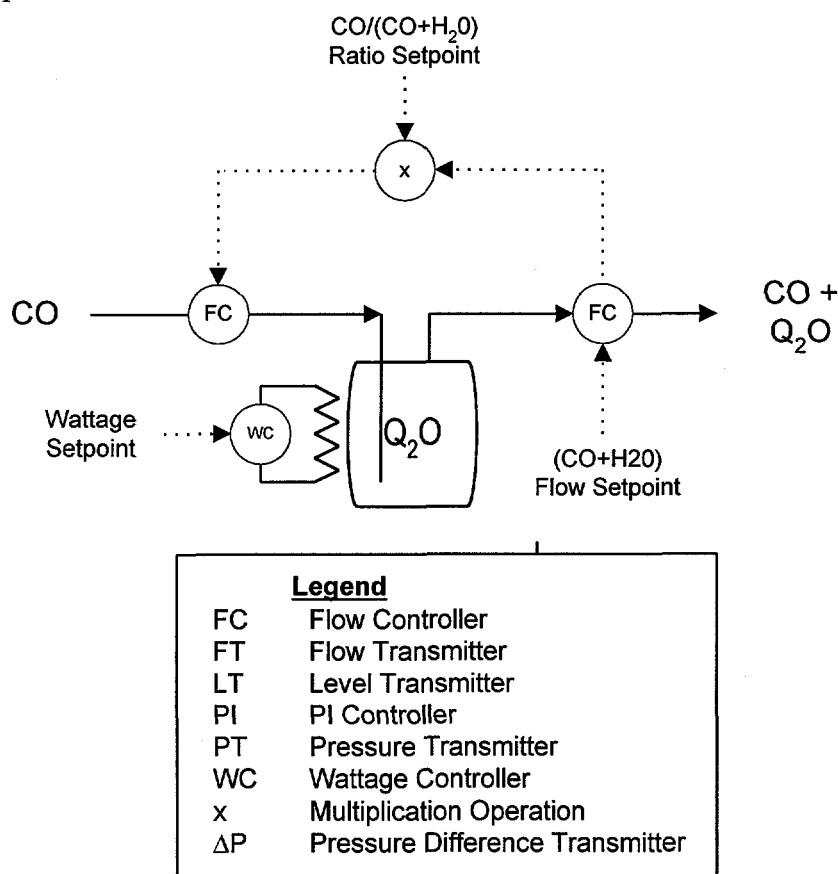


Figure 11. Control scheme for producing water from a molecular sieve bed and injecting the appropriate amount of CO

Steady state was not achieved within the PMR system during any of these tests due to the relatively short run times. The gas compositions measured by GC and the activity measured by the ion chambers were still transient at the end of the tests. A previous experiment indicated that about 30 hr. are required to achieve steady state. The 1st stage initially had a decontamination factor (DF) of about 50 for each of the tests and the DF steadily increased throughout the tests. By the end of the tests, the DF had reached the 100-260 range and was still increasing. The final DF depended on the inlet rate and the length of time the test had been run. This performance is consistent with what was expected from parametric testing on the cold test bench.

Performance of the 2nd stage could not be measured because the outlet tritium concentration was below the background of the ion chamber used for analysis. Although the DF could not be measured, it is known that the DF was high because, except for a brief period at the beginning of each run, no tritium was detected in the tritium waste

treatment system that was downstream from the PMR system. The tritium breakthrough at start-up was due to a slug of gas breaking through the 2nd stage. A start-up method is being developed to avoid this situation.

IV. CONCLUSIONS

- A process to recover tritium from tritiated water has been successfully demonstrated at TSTA. 694 std. L of tritiated steam have been processed at high decontamination factors resulting in recovery of 1.2 g of tritium.
- 30 days of round-the-clock testing were completed on the cold PMR test bench in preparation for tritium tests. Decontamination factors $>10^5$ were routinely observed. The optimum CO injection ratio was determined from these tests. The cold test bench now has about 130 days of operation without failure or decrease in performance.
- A system was developed to control the production of tritiated steam from molecular sieve beds and add the proper amount of CO. The control system is accurate, reliable and easy to operate.

REFERENCES

1. R. S. Willms, R. Wilhelm, and S. Konishi, Performance Of A Palladium Membrane Reactor Using An Ni Catalyst For Fusion Fuel Impurities Processing, Fusion Eng Des. 28 (1995) 397-405.
2. R. S. Willms and S. A. Birdsell, Palladium Membrane Reactor Development At The Tritium Systems Test Assembly, Fusion Tech. 28, No. 3, Part 1 (1995) 772-777.
3. S. A. Birdsell and R. S. Willms, Modeling and Data Analysis of a Palladium Membrane Reactor for Tritiated Impurities Cleanup, Fusion Tech. 28, No. 3, Part 1 (1995) 530-537.
4. S. A. Birdsell and R. S. Willms, Ultra-High Tritium Decontamination of Simulated Fusion Fuel Exhaust using a 2-Stage Palladium Membrane Reactor, to appear in Fusion Tech.