RECENT PALLADIUM MEMBRANE REACTOR DEVELOPMENT AT THE TRITIUM SYSTEMS TEST ASSEMBLY

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ABSTRACT

The palladium membrane reactor (PMR) is being investigated as a means for recovering hydrogen isotopes (including tritium) from compounds such as water and methane. Previous work with protiated water and methane showed that this device can be used to obtain high hydrogen recovery efficiencies using a single processing pass and with essentially no waste production. With these successful proof-of-principle results completed, recent work has focused on PMR development. This included studies of various geometries and testing with tritium. The results, which are reported here, have led to a better understanding of the PMR and will lead to the ultimate goal of building a production PMR and puting it into practical tritium processing service.

I. INTRODUCTION

The palladium membrane reactor (PMR) is proving to be a simple and effective means for recovering hydrogen isotopes from fusion fuel impurities such as methane and water. This device directly combines two techniques which have long been utilized for hydrogen processing, namely catalytic shift reactions and palladium/silver permeators. Catalytic shift reactions such as water-gas shift, $H_2O + CO \rightarrow H_2 + CO_2$, and methane steam reforming, $CH_4 + H_2O \rightarrow 3H_2 + CO$, are used extensively in the petrochemical industry for producing free hydrogen from water and methane. Thermodynamic equilibrium limitations preclude the simple use of these reactions for the complete recovery of all hydrogen isotopes in a single processing pass. However, if free hydrogen liberated by these reactions is removed from the catalytic reactor, the equilibrium limitation is removed allowing for further free hydrogen generation. Palladium/silver membranes, which have long been used to generate ultra-pure hydrogen, provide a practical means for removing the liberated hydrogen. Such membranes have the fortuitous property of being exclusively permeable to hydrogen isotopes

(∞ separation factor). By combining a catalytic reactor with a palladium/silver membrane, the PMR is capable of recovering essentially all of the hydrogen isotopes from fusion fuel impurities in a single processing pass. The device is relatively easy to construct and operate. It produces essentially no waste and does not require the use of recycle streams or the addition of diluents. Indeed, the elegantly simple PMR is compact, inexpensive and reliable.

A proof-of-principle PMR has been constructed and tested at the Tritium Systems Test Assembly of Los Alamos National Laboratory. The first tests with this device showed that it was effective for the proposed purpose. These initial results and numerous citations of pertinent literature were reported in [1]. This work concluded that a nickel catalyst was an appropriate choice for use in a PMR. More detailed testing of the PMR with such a catalyst was performed and reported in [2]. It was shown that a nickel catalyst-packed PMR did, indeed, recover hydrogen from water and methane with efficiencies approaching 100% in a single processing pass. These experiments were conducted over an extended period of time and no failure or need for regeneration was encountered.

These positive results have prompted further PMR development. Topics addressed include alternate PMR geometries and initial testing of the PMR with tritium. These are the subjects of this paper.

II. EFFECT OF PMR ANNULAR DIAMETER

A scale drawing of the original PMR is shown in figure 1. The inner diameter of this PMR was 0.87" (22 mm). It was expected that the PMR annular diameter would effect performance due largely to the effect on residence time. To quantify this effect a PMR shell with a smaller inner diameter of 0.50" (12.7 mm) was constructed and installed over the original palladium/silver tube
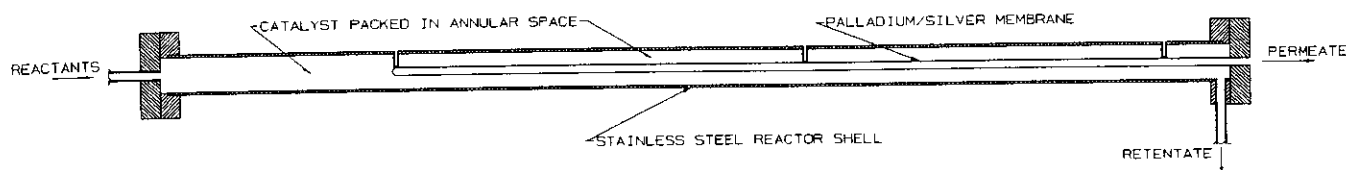
Figure 1 Scale drawing of the original TSTA proof-of-principle PMR

assembly. The smaller diameter PMR was loaded with 0.125" (3.18 mm) diameter catalyst while the original PMR was operated with 0.25" (6.35 mm) diameter catalyst. Except for the outer shell diameter and catalyst size, all other PMR geometry was held constant at the following values: Pd/Ag tube length of 20.9" (530 mm), outer diameter of 0.197" (5 mm) and wall thickness of 0.008" (0.2 mm); and annular space length of 26" (660 mm). The Pd/Ag tube was obtained from Rosemount GmbH and Co. Futher details of the construction and operation of the original PMR may be found in [1,2].

The smaller diameter PMR was operated with a water-gas shift feed composition ratio of $CO:H_2O = 1.8:1$ at 450 °C. Total feed flowrates ranging between 30 and 110 sccm were used. The hydrogen recovery results are plotted on figure 2 along side comparable data collected with the original PMR (see reference [2] for the original data). Hydrogen recoveries approach 100% at the lower flowrates for both the 0.50 and 0.87" diameter cases. As the feed flowrate increases, a point is reached where recoveries fall progressively below the 100% recovery line. However, the two datasets differ in that the 0.50" ID PMR reaches the point of departure from the 100% recovery line at about 60 sccm, while the 0.87" ID PMR reaches this point at about 120 sccm.

A primary design objective for the PMR is to process the highest possible flowrates without degraded hydrogen recovery performance. Within limits, this objective can be
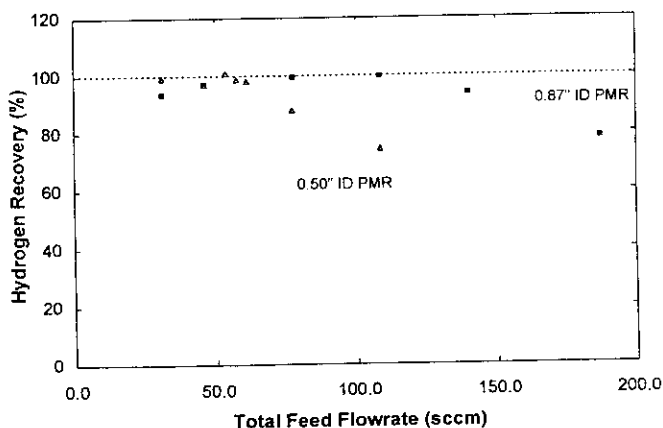

Figure 2 Comparison of hydrogen recoveries using different diameter PMR's

met by increasing the diameter of the PMR shell. This, by increasing the residence time, provides the reactants with more time to react and the liberated hydrogen with more time to permeate through the Pd/Ag tube. This beneficial effect of increased residence time is predominately the phenomenon observed on figure 2. However, it must be recognized that for a given reactor length, as the PMR diameter continues to increase, a point will eventually be reached at which significant amounts of free hydrogen isotopes will exist too far away from the Pd/Ag tube to permeate. There is no evidence of this "diffusion-limited" condition in these experiments. Rather it is concluded that the PMR diameter could likely be increased beyond 0.87" ID with only a further improvement in PMR performance. Experiments designed to test this postulate are being planned. Also, to properly evaluate the effects of geometry and operating conditions, a computer model is useful. Such a model has been developed [3] and has been benchmarked with the data from this study.

III. AN "INSIDE-OUT" PMR

The PMR discussed above is referred to as an "outside-in" PMR since the hydrogen isotopes flow from the outside of the Pd/Ag tube into its center. This geometry seems to be well suited for dealing with the bulk of the hydrogen isotopes that need to be recovered since it provides a large volume of catalyst. Loading the PMR with sufficient catalyst is important to 1) ensure adequate reaction kinetics for the relatively large quantities of reactants encountered and 2) provide plenty of catalyst to assimilate coke which may result from reactions such as methane cracking. However, the degree of hydrogen recovery for the PMR is limited by the vacuum which can be applied to the permeate side of the Pd/Ag membrane. The "outside-in" configuration results in a limited permeate vacuum since the vacuum must be applied to the inside of a relatively small tube with limited conductance.

This limitation has prompted the consideration of an "inside-out" PMR. This configuration uses a Pd/Ag tube and stainless steel shell similar to the previous case, but the catalyst is packed inside the Pd/Ag tube rather than in the annular space. Reactants are fed into the packed tube and hydrogen isotopes are recovered via permeation from within the Pd/Ag tube to the annular space. Due to the relatively large area of the annular space, there is good
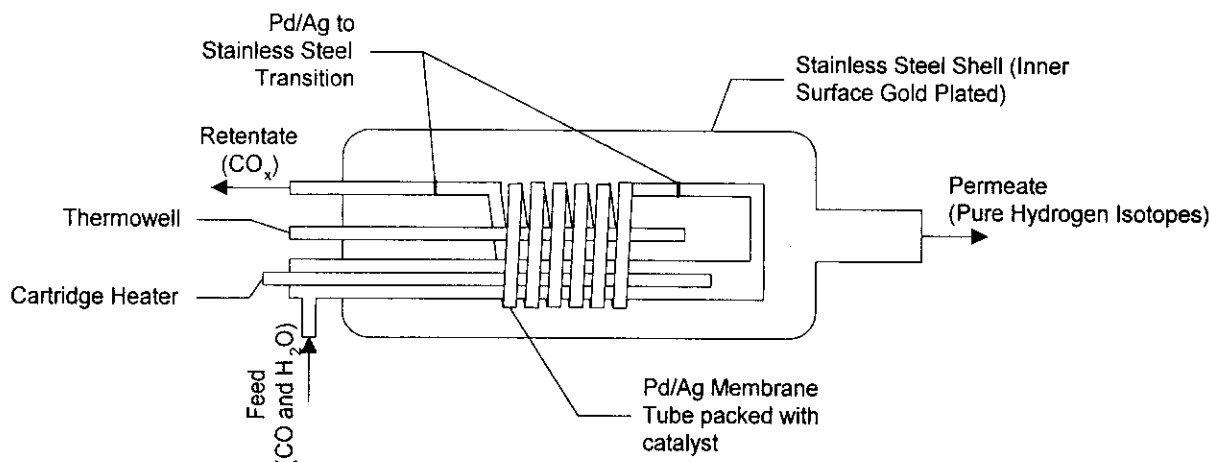
Figure 3 Prototype "Inside-Out" PMR

conductance and high vacuum can be maintained on the permeate side. Since most of the hydrogen isotopes are expected to be removed by the "outside-in" PMR, there will be a rather small hydrogen isotope flux through the "inside-out" membrane, so only a relatively small high-vacuum pumping system will be required.

An example of an "inside-out" PMR is shown in figure 3. This device can be constructed by starting with a straight length of Pd/Ag tube. This can be packed with catalyst then coiled on a mandrel.

An inside-out PMR was constructed using 0.125" (3.18 mm) Pd/Ag tube. Initial testing showed that it worked well for recovering hydrogen isotopes from water and methane. However, due to a combination of factors including the small diameter Pd/Ag tube and small catalyst pellets, excessive pressure drops were encountered on the retentate stream. Also it was found that the cartridge heater radiating heat from within the Pd/Ag tube coil resulted in excessive temperature gradients when vacuum was applied to the shell. External heating which radiated heat inward from the shell walls was found to solve this problem. Learning from this experience, an "inside-out" PMR using larger diameter Pd/Ag tube and larger catalyst pellets is currently being constructed and will soon be tested.
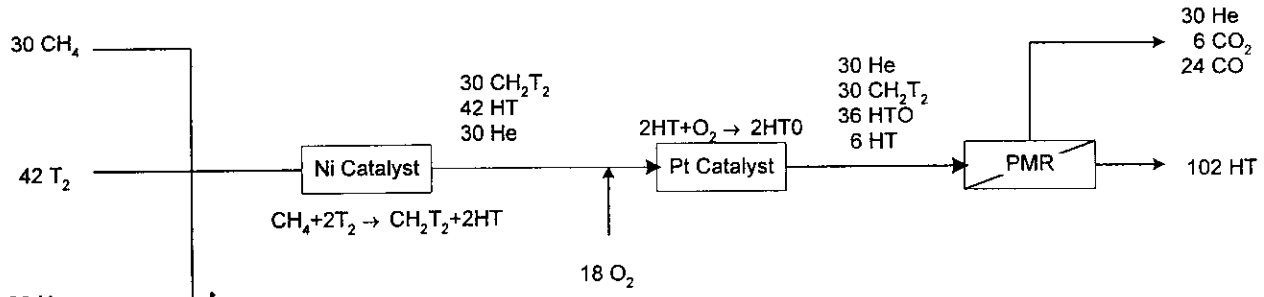
IV. FIRST PMR TEST WITH TRITIUM

To further demonstrate the efficacy of the PMR for recovering hydrogen isotopes from fusion fuel impurities, an effort was mounted to test the original "outside-in" PMR (figure 1) with tritium. It was deemed appropriate to test the PMR using a mixture of impurities which is being considered by the Tritium Plant Team of the International Thermonuclear Experimental Reactor (ITER) Engineering

Design Activity (EDA). As the first step in this undertaking it was necessary to construct a system to generate such a mixture of tritiated methane, tritiated water, Q_2 (hydrogen isotopes) and helium.

For this purpose the system shown in figure 4 was built. The process begins by mixing normal protiated methane, tritium and He. This mixture is passed over a Ni catalyst operated at 400 °C to exchange protium in the methane with the free tritium. Experiments were conducted to ensure that the Ni catalyst bed, at actual operating conditions, did not crack methane. Oxygen is added to this equilibrated mixture before flowing into a 100-200 °C Pt catalyst bed where the HT is oxidized to HTO. This component was also tested with protium to ensure that the HT was oxidized without also oxidizing the methane. Proper design of the oxidation reactor was found to be necessary to avoid hot spots which could lead to unwanted methane oxidation. The end result of these processing steps is a mixture that closely approximates the concentrations specified by the ITER EDA Tritium Plant Team for input to the impurities processing system. This mixture is fed directly to the PMR. If 100% efficient, the PMR will directly recover the HT from the water and methane, producing a stream of ultra-pure HT and a second stream of mostly tritium-free He and carbon oxides, as shown on figure 4.

A basic process and instrumentation diagram for the first PMR test with tritium is shown by figure 5. Standard compressed gas cylinders were used to supply all gases other than tritium which was supplied by a 50 liter product container. Vacuum was applied to the permeate side of the PMR via a Normetex 15 scroll pump backed by a metal bellows pump. The permeate was characterized by its pressure and flowrate and was returned either to a second 50 liter product container or to a 265 liter storage tank.

Figure 4 Processing Steps and Nominal Flowrates Used for the PMR First Test with Tritium

Measurements for the PMR retentate included pressure, flowrate, humidity, gas chromatograph analysis and tritium content via an ionization chamber. The retentate was exhausted to the TSTA Tritium Waste Treatment (TWT) system.

It was a venerable PMR which was used in this system. Indeed, this was the very first 0.87" (22.1 mm) inner diameter PMR which was constructed at TSTA and the one shown in figure 1. This same PMR had undergone over two years of intermittent testing with various catalysts including Cu, Fe and Ni-based materials. Operating conditions ranged from 310 to 600 °C with the most extensive testing occurring at the middle to upper portion of this range. Throughout these campaigns, the Pd/Ag

membrane performance was consistent and no failure of any kind was encountered. This experience has built considerable confidence in the long-term reliability of the PMR.

For the tritium tests the PMR was packed with 134 g of a catalyst obtained from United Catalysts Inc. composed of about 70% Ni on γ-alumina spineled with magnesium. The γ-alumina provides high surface area and the magnesium increases the catalyst stability at higher temperatures. The catalyst was obtained from the manufacturer in the reduced and stabilized form.

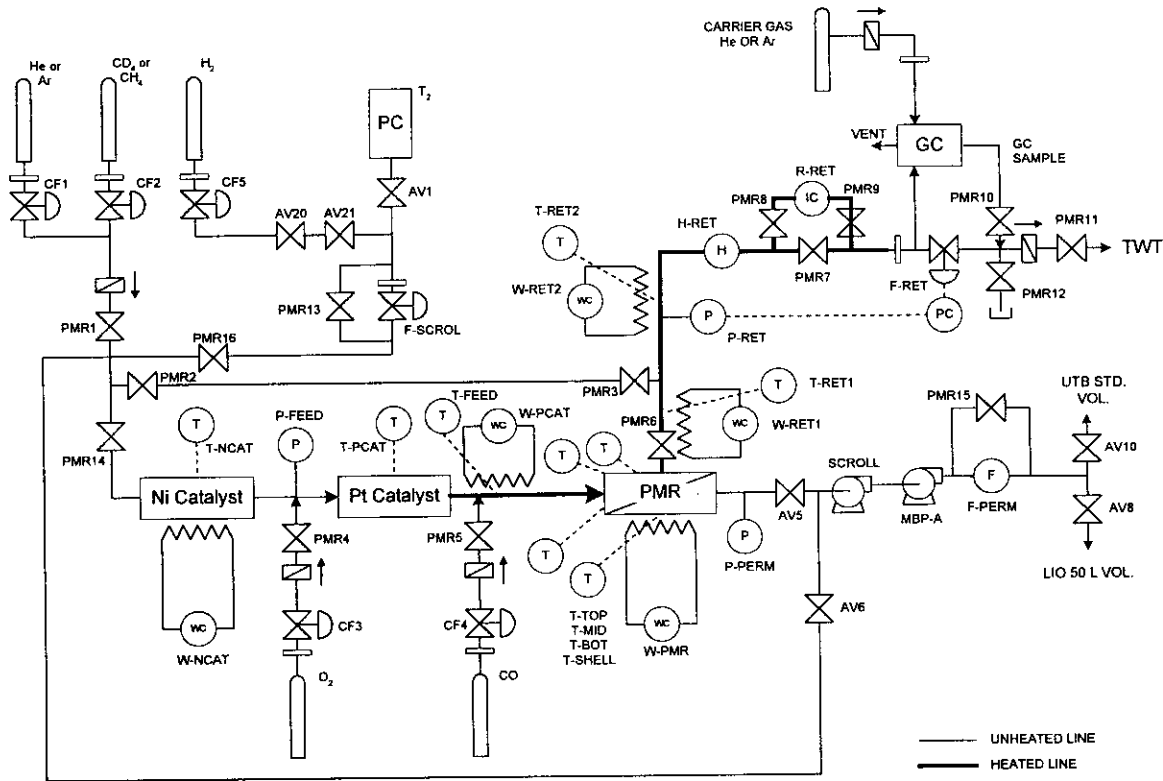Non-tritium tests with the PMR had been conducted in

Figure 5 Process and Instrumentation Diagram for First PMR Test with Tritium

a uniformly heated tube furnace. This, of course, was not practical for use in the glovebox which was required to house the tritium experiments. Thus, the PMR was retrofitted with insulated clamshell heaters. Unfortunately this did not provide the uniform heating of the PMR that was desired. It was observed that the thermocouple located near the PMR exit lines was typically 200 °C cooler than the middle and feed thermocouples. This large difference appeared to be localized to the PMR exit. Nonetheless, it is apparent that the PMR axial temperature profile was not uniform, and a single does not accurately represent each test condition.

The first PMR test with tritium used a limited amount of tritium in the supply product container ("PC" on figure 5). Tritium was diluted with H_2 so that the resulting mixture contained 5% tritium. This was fed to the PMR reactor (using "F-SCROL" for flow control) along with

other gases to make up the ITER-relevant mixture. Test conditions as well as results are shown in Table 1 for Tests 1-3. Relative to Test 1, Test 2 was run somewhat hotter and with a greatly increased tritium concentration. The Q_2 feed was increased from 5% tritium to 80%. In this case the tritium was diluted with ^3He (rather than protium) which resulted from tritium decay. Test 3 used experimental conditions almost identical to Test 2, except that all feed flowrates were reduced.

All readings listed in Table 1 were recorded after a number of hours of PMR operation (generally 2-4 hours) to ensure, in particular, that all isotopic exchange with PMR materials had reached equilibrium. Thus, the values listed are steady state readings.

As shown on Table 1, the PMR feed was composed of nominally 29% inert (Ar and/or He), 28% CQ_4, 36% Q_2O

Table 1 Conditions and Results for First PMR Test with Tritium

Parameter	Test 1	Test 2	Test 3
Input Settings			
T conc. in Q_2 (%)	5	80	80
T_{feed} (°C)	505	570	574
T_{middle} (°C)	503	565	570
T_{exit} (°C)	296	335	340
Inert Feed (sccm)	22.0 (Ar)	20.6 (Ar & He)	12.8
CQ_4 Feed (sccm)	20.0	20.0	13.1
Q_2O Feed (sccm)*	25.2	25.2	17
Q_2 Feed (sccm)*	5.2	5.2	3
CO Feed (sccm)	0	0	0
Feed Pressure (torr)	909	924	930
Output Measurements			
Permeate Pressure (torr)	0.4	0.6	0.5
Permeate Flowrate (sccm)	69.4	78	48
Ret. Humidity (°C dew point)	-6	6.9	-24
Ret. Pressure (torr)	902	901	902
Ret. Flowrate (sccm)	34.2	35.6	25.5
Ret. Inert (mole%)	61.5	55.0	61.2
Ret. CQ_4 (mole%)	0.195	0.590	0.210
Ret. Q_2O (mole%)	0.310	0.824	0.058
Ret. Q_2 (mole%)	0.133	0.185	0.110
Ret. CO (mole%)	2.45	3.29	2.98
Ret. CO_2 (mole%)	35.7	40.1	34.9
Radiation (Ci/m^3)	1400	9300	12000
Radiation background (Ci/m^3)	470	2800	2600
DF (IC calculation)	150	400	260
DF (GC/humidity calculation)	250	90	307
Tritium Processed (g)	0.09	2.4	2.4

*Result of reacting Q_2 and O_2

and 7% Q_2. For all three tests, the retentate was composed of mostly inert, CO_2 and some CO. The other species, CQ_4, Q_2O and Q_2, were each well below 1%.

The ionization chamber which was used in these experiments received only a cursory calibration. During the calibration the chamber was reading lower than would be expected by theoretical calculations. Among various explanations for this is a suspicion that the radiation levels being measured during the calibration were approaching the saturation level for the chamber. Nonetheless, decontamination factors (DF) ranging from 150 to 400 were determined using the cursory calibration. The DF is better at the higher temperatures. Decontamination factors can also be determined using GC compositions and humidity readings. The results of these calculations are also included in Table 1 and are generally higher than those determined by ion chamber readings. The one exception is for test 2. This was caused by higher than normal retentate methane and humidity concentrations. Based on comparisons with the other tritium tests and previous non-tritium testing, this result is believed to be spurious.

It is clear that the PMR was working quite well. Indeed, in each test well over 99% of the tritium was recovered in a single processing pass. To better characterize the PMR's performance further tests with improved diagnostics are in preparation.

V. CONCLUSIONS

Continued PMR development work is elucidating potential design improvements. This will guide the construction and testing of improved devices.

The first PMR test with tritium was a significant milestone. While the tritium results are preliminary, it was observed that the PMR worked well with tritium just as it had in extensive earlier non-tritium tests. The tritium tests showed that the bulk of tritium fed to the PMR was successfully recovered in ultrapure form in a relatively simple, once-through process. Essentially no waste (only carbon oxides and He) was produced in the process. These tests have served to validate the belief that the PMR will become a valued technology for tritium processing systems. These first tests with tritium establish a starting point from which even better performing designs can be developed.

Decontamination factors for the PMR are known to be limited by the quality of the permeate vacuum. For the "outside-in" PMR, pressures below about 0.1 torr do not appear practical. However, an "inside-out" PMR is currently being considered. For this device much lower permeate pressures are practical and can be easily maintained with turbomolecular pumps. Thus, it appears judicious to process impurities with an "outside-in" PMR backed by a scroll pump, followed by an "inside-out" PMR backed by a turbomolecular pump. It is expected that such a system will realize very high, once-through decontamination factors. Experiments are being planned and conducted at TSTA to test such a system.

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