

TITLE: ULTRA-HIGH TRITIUM DECONTAMINATION OF SIMULATED FUSION FUEL EXHAUST USING A 2-STAGE PALLADIUM MEMBRANE REACTOR

AUTHOR(S): Stephen a. Birdsell ESA-TSE
R. Scott Willms ESA-TSE
Richard C. Wilhelm ESA-TSE

RECEIVED
OCT 11 1996
OSTI

SUBMITTED TO: FOURTH INTERNATIONAL SYMPOSIUM ON FUSION NUCLEAR TECHNOLOGY
APRIL 6-11, 1997 - MEIKI KINENKAN, TOKYO JAPAN

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED



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. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISCLAIMER

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

CONF-970404--1

Title: ULTRA-HIGH TRITIUM DECONTAMINATION OF SIMULATED FUSION FUEL EXHAUST USING A 2-STAGE PALLADIUM MEMBRANE REACTOR

Author(s): Stephen a. Birdsell ESA-TSE
 R. Scott Willms ESA-TSE
 Richard C. Wilhelm ESA-TSE

MASTER

**Submitted To: FOURTH INTERNATIONAL SYMPOSIUM ON FUSION NUCLEAR TECHNOLOGY
APRIL 6-11, 1997 - MEIKI KINENKAN, TOKYO JAPAN**

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, makes 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.

ULTRA-HIGH TRITIUM DECONTAMINATION OF SIMULATED FUSION FUEL EXHAUST USING A 2-STAGE PALLADIUM MEMBRANE REACTOR

Stephen A. Birdsell, R. Scott Willms and Richard C. Wilhelm
Mail Stop C-348
Los Alamos National Laboratory
Los Alamos, NM 87545
505-667-2138

ABSTRACT

A 2-stage cold (non-tritium) PMR system was tested with the ITER mix* in 61 days of continuous operation. No decrease in performance was observed over the duration of the test. Decontamination factor (DF) was found to increase with decreasing inlet rate. Decontamination factors in excess of 1.4×10^5 were obtained, but the exact value of the highest DF could not be determined because of analysis limitations.

Results of the 61-day test were used to design a 2-stage PMR system for use in tritium testing. The PMR system was scaled up by a factor of 6 and built into a glovebox in the Tritium Systems Test Assembly (TSTA) of the Los Alamos National Laboratory. This system is approximately $1/5^{\text{th}}$ of the expected full ITER scale. The ITER mix was injected into the PMR system for 31 hours, during which 4.5 g of tritium were processed. The 1st stage had $DF = 200$ and the 2nd stage had $DF = 2.9 \times 10^6$. The overall $DF = 5.8 \times 10^8$, which is greater than ITER requirements.

I. INTRODUCTION

A Palladium Membrane Reactor (PMR) system is under consideration for the tritium plant for the International Thermonuclear Experimental Reactor (ITER). The ITER reactor exhaust will contain tritiated impurities such as water and methane. Tritium will need to be recovered from these impurities for environmental and economic reasons. For this purpose a promising device called a palladium membrane reactor (PMR) has been proposed. The PMR is a combined permeator and catalytic reactor. Shift catalysts are used to foster reactions such as water-gas shift, $H_2O + CO \rightarrow H_2 + CO_2$, and methane steam reforming, $CH_4 + H_2O \rightarrow 3H_2 + CO$. 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.

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. Both sets of experiments were conducted at ITER relevant conditions and found to have a decontamination factor ($DF = \text{inlet tritium}/\text{outlet tritium}$) in the 150-400 range.

The earlier experiments used Ni/ γ - Al_2O_3 catalyst which was not stable in the PMR environment. Pellets tended to break up into fine particles, especially when coking occurred. The need for a better catalyst and to avoid coking was apparent.

II. CATALYST EVALUATION AND COKE PREVENTION

Figure 1 shows a schematic drawing of a 1st stage PMR. The PMR in the cold testbench has a Pd/Ag tube which is 61.0 cm long, 0.635 cm in diameter, and has a wall thickness of 0.0178 cm. The stainless steel shell is 66.0 cm long, 2.54 cm in diameter, and has a wall thickness of 0.165 cm. The annular space around the Pd/Ag tube was filled with a catalyst and the performance was tested with an inlet mixture of 40 sccm CH_4 , 50 sccm H_2O , and 44 sccm Ar, which is a simulated fusion fuel exhaust referred to as the "ITER Mix". Reactor temperature and pressure were 510°C and 590 torr, while the permeate pressure was 0.2 torr. Three types of catalyst were tested: Ni/ γ - Al_2O_3 catalyst (United Catalyst C150-8-01), Ni/ α - Al_2O_3 (United Catalyst C11-9-09 EW), Pt/ α - Al_2O_3 catalyst (Engelhard A-16825).

* simulated ITER exhaust

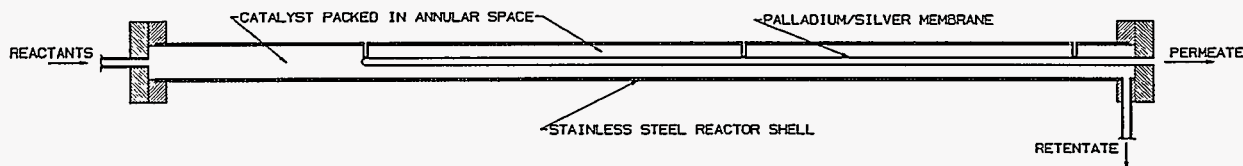


Figure 1. 1st Stage PMR.

Both Ni catalysts exhibited significant pellet degradation after several days of operation. The catalyst was removed and areas of pellet degradation correlated with areas predicted by a numerical model to have coke deposition.³ Pellet degradation was accompanied by increasing DF and increasing pressure drop across the catalyst bed. These observations are consistent with the catalyst being converted from relatively large pellets to small particles. Increasing catalyst surface area results in larger reaction rates and decreasing bed porosity results in larger pressure drops. Pellet degradation occurs due to coke formation in the pores of the catalyst.

In contrast to the Ni catalyst, the Pt catalyst showed no sign of pellet degradation. After several days of operation the DF began to slowly decline, which is apparently due to coke deposition. This coke appears to

be forming on the catalyst surface and blocking the active sites rather than forming in pores and causing structural damage as in the Ni catalysts.

The Pt bed was decoked with dilute O₂ and the coking/decoking cycle was repeated. No loss of performance was observed after the cycling.

Next, to demonstrate that coking can be avoided altogether, 6% O₂ was added to the inlet mixture. This experiment was run continuously for 5 days with no decrease in performance. This result demonstrates that coke formation can be avoided regardless of the inlet CH₄:H₂O by addition of O₂. At the end of these experiments the Pt catalyst had been used for 16 days. The catalyst was removed and inspected. No visual difference was observed between the used catalyst and a fresh sample. The catalyst was reloaded into the PMR

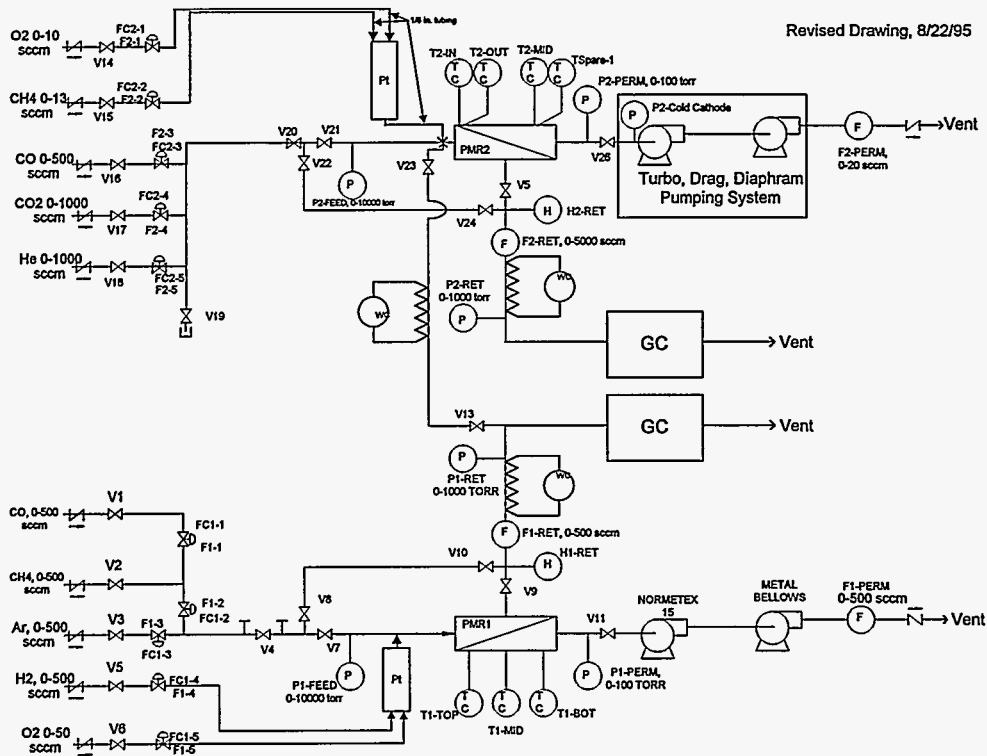


Figure 2. The 2-stage PMR cold test bench.

and has subsequently been used in over 130 days of operation with no decrease in performance.

III. 2-STAGE COLD TESTS

Figure 2 is a drawing of the 2-stage non-tritium PMR testbench. The testbench was designed to do either 2-stage testing or simultaneous independent testing of both the 1st and 2nd stages. A simulated torus exhaust is produced with the mass flow controllers. Water in the simulated exhaust is produced by flowing H₂ and O₂ over a Pt catalyst before injection into the PMR. The combination of the Normatex 15 scroll pump and the Metal Bellows 601 pump is capable of maintaining about a 0.5 torr vacuum at the flow conditions of interest in the 1st stage. In the 2nd stage, the Varian V250 pumping system is capable of about a 5×10^{-6} torr vacuum. The MTI model M200 gas chromatographs have a CH₄ sensitivity of 5 ppm and a H₂ sensitivity of 0.3 ppm. The Endress and Hauser model 2850 humidity probes are calibrated from -80°C to 20°C.

The 1st stage is the same PMR that was used in the catalyst evaluation experiments (figure 1). The shell was packed with 297 g Pt/ α -Al₂O₃ catalyst (Engelhard A-16825). The 2nd stage PMR is a similar design to the 1st stage.

The 2-stage system was tested with the ITER mix. 6.3% O₂ was added to the ITER mix to prevent coking. The temperatures of the 1st and 2nd stages were held at 530 and 500°C, respectively. The 2nd stage retentate was vented to the atmosphere, which is approximately 590 torr. The pressure drop through the 1st and 2nd stages was small. At the highest inlet rates, the inlet pressure was 610 torr.

The overall DF as a function of inlet rate is shown in Figure 3. The DF approaches an asymptote at 1.4×10^5 . This asymptote represents the maximum sensitivity of our gas chromatograph and humidity probe at the outlet of the 2nd stage. Although it was not possible to measure the maximum DF, it is known to occur when the hydrogen in the reaction side of the PMR is in equilibrium with the hydrogen in the permeate side (i.e. at low flow).

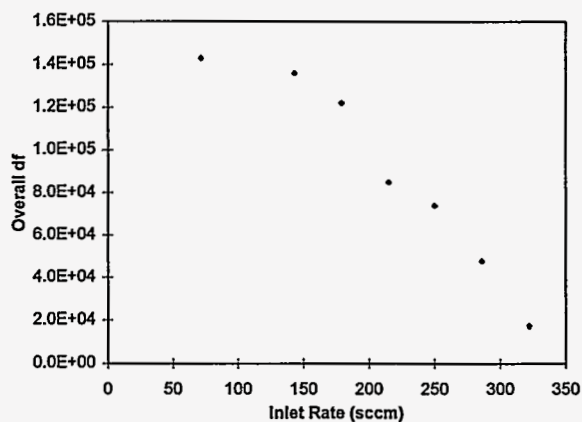


Figure 3. Overall DF for the 2-stage cold tests. Feed composition was 28% CH₄, 35% H₂O, 31% Ar, and 6.3% O₂.

Differentiating the relative contributions of each stage, Figure 4 shows the DF for the 1st and 2nd stages at various 1st stage feed rates. Stage 1 makes its greatest contribution to the overall DF at low stage 1 feed rates. Its DF decreases as more "load" (i.e., flow) is placed on stage 1. Though not apparent on this figure, at even lower feed rates the stage 1 DF would reach a plateau as it became limited by the permeate pressure.

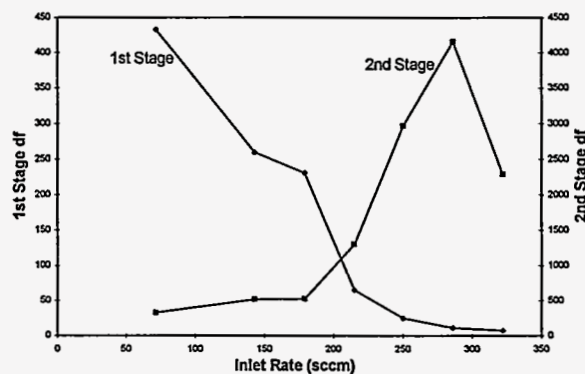


Figure 4. 1st and 2nd stage decontamination factors for the cold tests. Feed composition was 28% CH₄, 35% H₂O, 31% Ar, and 6% O₂.

The stage 2 behavior is more complicated since both the flow rate and composition of its feed is varying. At low stage 1 feed rates the stage 2 DF is low since stage 1 is not leaving much hydrogen for stage 2 to process. As rates increase, more hydrogen reaches stage 2 and it exhibits an increasing DF. At the highest rate, however, stage 2 begins to show signs of rate limitation as its DF starts dropping.



Figure 6. Photograph of the 1st stage (background) and 2nd stage PMRs. Catalyst is not yet loaded around the 1st stage Pd/Ag tubes.

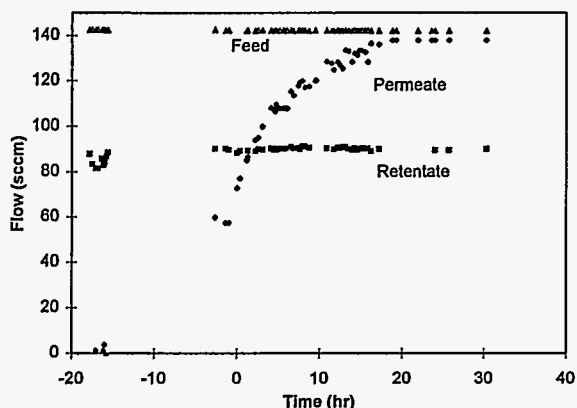


Figure 7. Feed and effluent rates for the 31 hr tritium test of the 2-stage PMR system.

Figure 8 shows the GC analysis for CO and CO₂ in the 1st stage retentate. Ar is not measured with the GC, but is calculated from continuity. Figure 9 shows GC analysis for CQ₄ and Q₂ in the 1st stage retentate. The remaining tritium-containing specie in the 1st stage retentate is Q₂O, which was constant throughout the experiment at a much lower 0.0035%. Decontamination factors were determined from the GC results and also from the ion chamber results for the 1st stage (figure 10). The ion chamber data shows that tritium began breaking through the 1st stage shortly after tritium injection began. The DF was 300 at the end of the experiment, but it was still slowly coming down. The DF calculated from GC data is almost constant at 200 because the GC does not distinguish between hydrogen isotopes. The GC data is considered to be more accurate because the ion chamber was calibrated over a range of 6 orders of magnitude. However, it appears that the 2 methods for measuring DF would agree quite well if the experiment had been run longer.

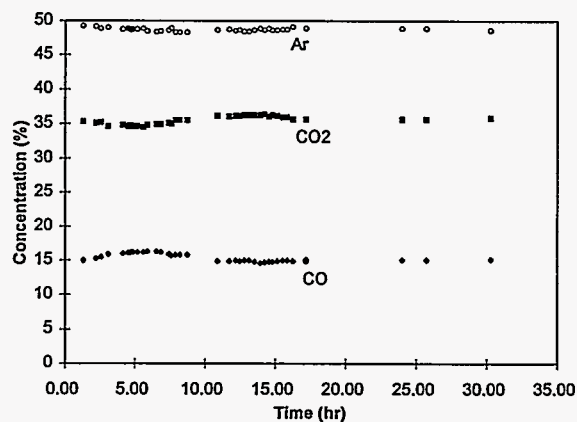


Figure 8. Ar, CO, and CO₂ concentrations in the retentate of the 1st stage.

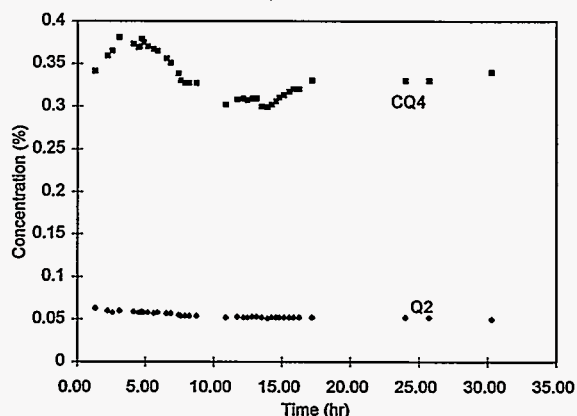


Figure 9. CQ₄ and Q₂ concentrations in the retentate of the 1st stage.

Determination of the DF for the 2nd stage retentate stream proved to be much more difficult than the 1st stage. As in the cold tests, measurement of CQ₄ and Q₂ by GC and Q₂O by humidity probe were not possible because the values were below the range of the instruments. This also proved to be the case for the ion chamber at the outlet of the 2nd stage. Activity never rose above background for this instrument. Therefore, a bubbler method was used to measure the activity of the outlet stream. All retentate flow was oxidized over a CuO bed and bubbled through 200 ml of glycol. A 1.0 cm³ sample was counted on a scintillation counter about every hour beginning with the 23rd hour of the experiment. Accumulation of tritium was constant at approximately 2.5 μCi/hr from the 23rd hour through the end of the experiment. This outlet tritium rate divided into the 1st stage inlet rate of 1440 Ci/hr gives an overall DF of 5.8x10⁸. The 2nd stage DF is 1.9x10⁶ if it is assumed that the 1st stage DF=200 (i.e., GC method).

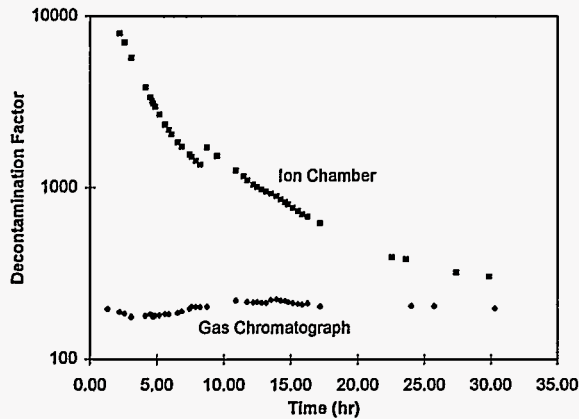


Figure 10. 1st stage decontamination factor calculated by ion chamber and GC measurements.

V. CONCLUSIONS

Catalyst evaluation experiments indicated that Pt/ α -Al₂O₃ catalyst is superior to Ni catalysts. The Pt catalyst was stable in environments where coke formation occurred, while Ni catalysts were severely degraded by coke formation. Also, avoiding coke formation in a PMR by O₂ injection was demonstrated.

A 2-stage system was tested with the non-tritium ITER mix in 61 days of continuous operation. No decrease in performance was observed over the duration of the test. Decontamination factor was found to increase with decreasing inlet rate. Overall decontamination factors in excess of 1.4×10^5 were obtained, but the exact value of the highest DF could not be determined because of analysis limitations.

Results of the 61-day test were used to design a 2-stage PMR system for use in tritium testing. The PMR system was scaled up by a factor of 6 and built into a glovebox in TSTA. The ITER mix was injected into the PMR system for 31 hours, during which 4.5 g of tritium were processed. The 1st stage had a DF ≈ 200 and the 2nd stage had a DF $\approx 2.9 \times 10^6$. The overall DF $\approx 5.8 \times 10^8$, which is greater than ITER requirements.

REFERENCE

1. Willms, R.S., Wilhelm, R., and S. Konishi, "Performance Of A Palladium Membrane Reactor Using An Ni Catalyst For Fusion Fuel Impurities Processing," *Fusion Engineering And Design*, **28**, 397-405 (1995).
2. Willms, R. S. and S. A. Birdsell, "Palladium Membrane Reactor Development At The Tritium Systems Test

Assembly," *Fusion Technology*, **28**, No. 3, Part 1, 772-777 (1995).

3. Birdsell, S. A. and R. S. Willms, "Modeling and Data Analysis of a Palladium Membrane Reactor for Tritiated Impurities Cleanup," *Fusion Technology*, **28**, No. 3, Part 1, 530-537 (1995).