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Author 1: BIRDSELL, SA

Author 2: WILLMS, RS

Author 3: WILHELM, RC

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## 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  $1.4 \times 10^5$  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 1<sup>st</sup> stage had  $DF=200$  and the 2<sup>nd</sup> 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.<sup>1</sup> processed simulated fusion fuels with a PMR, but these early experiments contained no tritium. Willms et al.<sup>2</sup> and Birdsell and Willms<sup>3</sup> 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  $Ni/\gamma-Al_2O_3$  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 1<sup>st</sup> 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

\* simulated ITER exhaust

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the permeate pressure was 0.2 torr. Three types of catalyst were tested: Ni/ $\gamma$ - $Al_2O_3$  catalyst (United Catalyst C150-8-01), Ni/ $\alpha$ - $Al_2O_3$  (United Catalyst C11-9-09 EW), Pt/ $\alpha$ - $Al_2O_3$  catalyst (Engelhard A-16825).

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

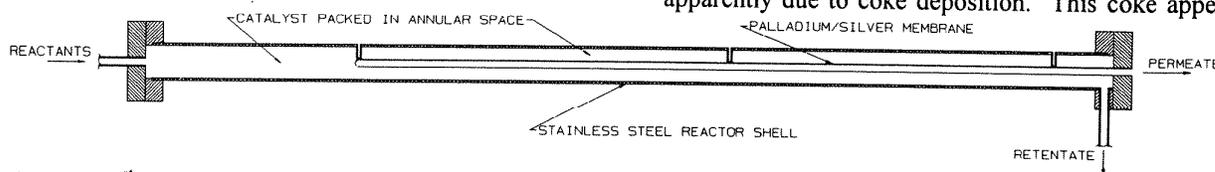


Figure 1. 1<sup>st</sup> Stage PMR.

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.<sup>3</sup> 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.

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  $O_2$  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%  $O_2$  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

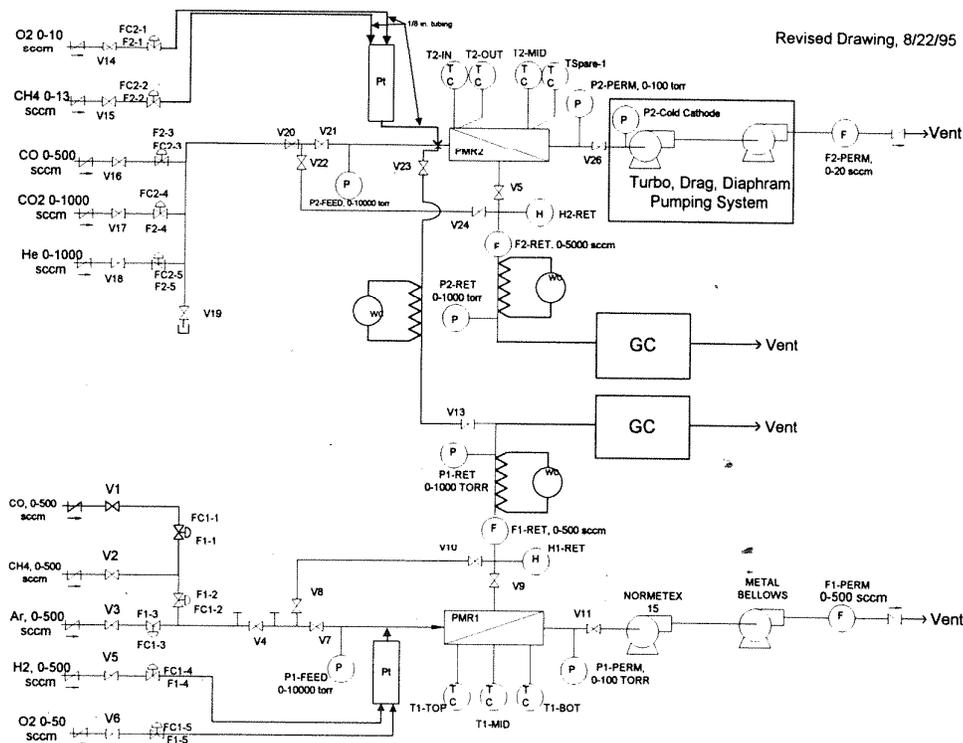


Figure 2. The 2-stage PMR cold test bench.

$\text{CH}_4:\text{H}_2\text{O}$  by addition of  $\text{O}_2$ . 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 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 1<sup>st</sup> and 2<sup>nd</sup> stages. A simulated torus exhaust is produced with the mass flow controllers. Water in the simulated exhaust is produced by flowing  $\text{H}_2$  and  $\text{O}_2$  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 1<sup>st</sup> stage. In the 2<sup>nd</sup> stage, the Varian V250 pumping system is capable of about a  $5 \times 10^{-6}$  torr vacuum. The MTI model M200 gas chromatographs have a  $\text{CH}_4$  sensitivity of 5 ppm and a  $\text{H}_2$  sensitivity of 0.3 ppm. The Endress and Hauser model 2850 humidity probes are calibrated from  $-80^\circ\text{C}$  to  $20^\circ\text{C}$ .

The 1<sup>st</sup> stage is the same PMR that was used in the catalyst evaluation experiments (figure 1). The shell was packed with 297 g Pt/ $\alpha\text{-Al}_2\text{O}_3$  catalyst (Engelhard A-16825). The 2<sup>nd</sup> stage PMR is a similar design to the 1<sup>st</sup> stage.

The 2-stage system was tested with the ITER mix. 6.3%  $\text{O}_2$  was added to the ITER mix to prevent coking. The temperatures of the 1<sup>st</sup> and 2<sup>nd</sup> stages were held at  $530^\circ\text{C}$  and  $500^\circ\text{C}$ , respectively. The 2<sup>nd</sup> stage retentate was vented to the atmosphere, which is approximately 590 torr. The pressure drop through the 1<sup>st</sup> and 2<sup>nd</sup> 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  $1.4 \times 10^5$ . This asymptote represents the maximum sensitivity of our gas chromatograph and humidity probe at the outlet of the 2<sup>nd</sup> 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).

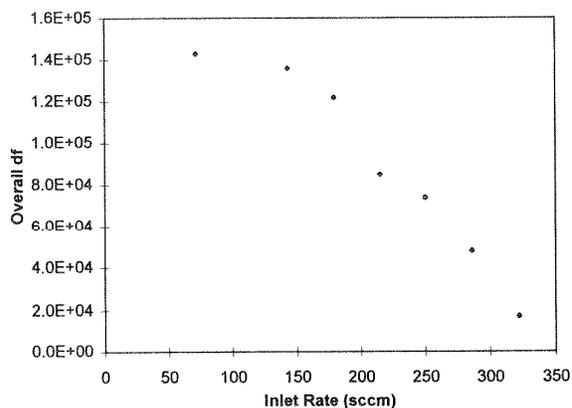


Figure 3. Overall DF for the 2-stage cold tests. Feed composition was 28%  $\text{CH}_4$ , 35%  $\text{H}_2\text{O}$ , 31% Ar, and 6.3%  $\text{O}_2$ .

Differentiating the relative contributions of each stage, Figure 4 shows the DF for the 1<sup>st</sup> and 2<sup>nd</sup> stages at various 1<sup>st</sup> 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.

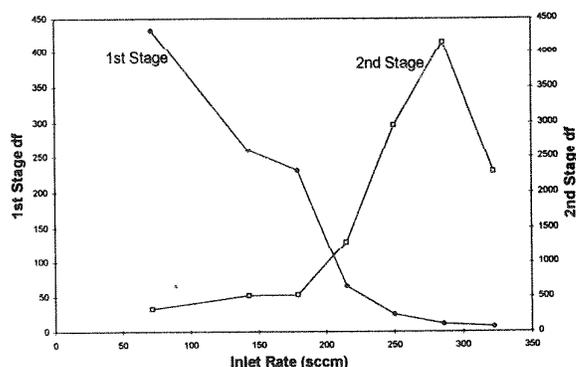


Figure 4. 1<sup>st</sup> and 2<sup>nd</sup> stage decontamination factors for the cold tests. Feed composition was 28%  $\text{CH}_4$ , 35%  $\text{H}_2\text{O}$ , 31% Ar, and 6%  $\text{O}_2$ .

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.

IV. 2-STAGE TRITIUM TESTS

In addition to the cold test bench, a 2-stage tritium compatible PMR system has been constructed within a glovebox. Figure 5 is a drawing of this system. Figure 6 is a photograph of the 1<sup>st</sup> stage. The 1<sup>st</sup> stage has an outer diameter of 10.2 cm with a 0.165 cm wall thickness and has 7223 g of Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst loaded around 6 Pd/Ag tubes. One of the Pd/Ag tubes is located on the centerline and the 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 passes through a flange so the inside of the tubes can be pumped (figure 6). The 2<sup>nd</sup> stage is a similar design.

The 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 testbench. Two Overhoff Technology ion chambers were installed in the process. The ion chamber at the outlet of the 1<sup>st</sup> stage has a range of  $1 \times 10^{-1}$  to  $2 \times 10^6$  Ci/m<sup>3</sup>, while the one at the outlet to the 2<sup>nd</sup> stage has a range of  $3.4 \times 10^0$  to  $2 \times 10^4$  Ci/m<sup>3</sup>.

The 1<sup>st</sup> and 2<sup>nd</sup> stage PMRs were heated to 530 and 500°C, respectively and a mixture of 40 sccm CH<sub>4</sub>, 50

sccm H<sub>2</sub>, 44 sccm Ar, and 34 sccm O<sub>2</sub> were injected into the system. When steady state was reached, the H<sub>2</sub> flow was replaced with a 50 sccm mixture of hydrogen isotopes containing 18% tritium, 75% deuterium, and 7% protium. The CH<sub>4</sub>, Q<sub>2</sub> (Q=H,D, or T), and Ar mixture passed through a Ni catalyst bed at 400°C. This process equilibrates the hydrogen isotopes between the CQ<sub>4</sub> and Q<sub>2</sub> form. O<sub>2</sub> is injected to the mixture before the Pt bed. The temperature of the Pt bed is controlled so that essentially all of the Q<sub>2</sub>, but none of the CQ<sub>4</sub>, is oxidized. Thus, a mixture of 40 sccm CQ<sub>4</sub>, 50 sccm Q<sub>2</sub>O, 44 sccm Ar, and 9 sccm O<sub>2</sub> is injected into the PMR system. The outlet pressure was held at 900 torr and the corresponding inlet pressure was only slightly higher.

A 31 hour experiment was run at the conditions described above. 4.5 g of tritium were processed during this experiment. Figure 7 shows the feed, permeate and retentate rates for the PMR system. Before time zero, near steady state conditions had been established with protium as the only hydrogen isotope. As can be seen from the figure, the permeate flow was not yet stabilized. However, all the other rates and the effluent concentrations had stabilized. At time zero, the protium flow was replaced with the mixture of hydrogen isotopes.

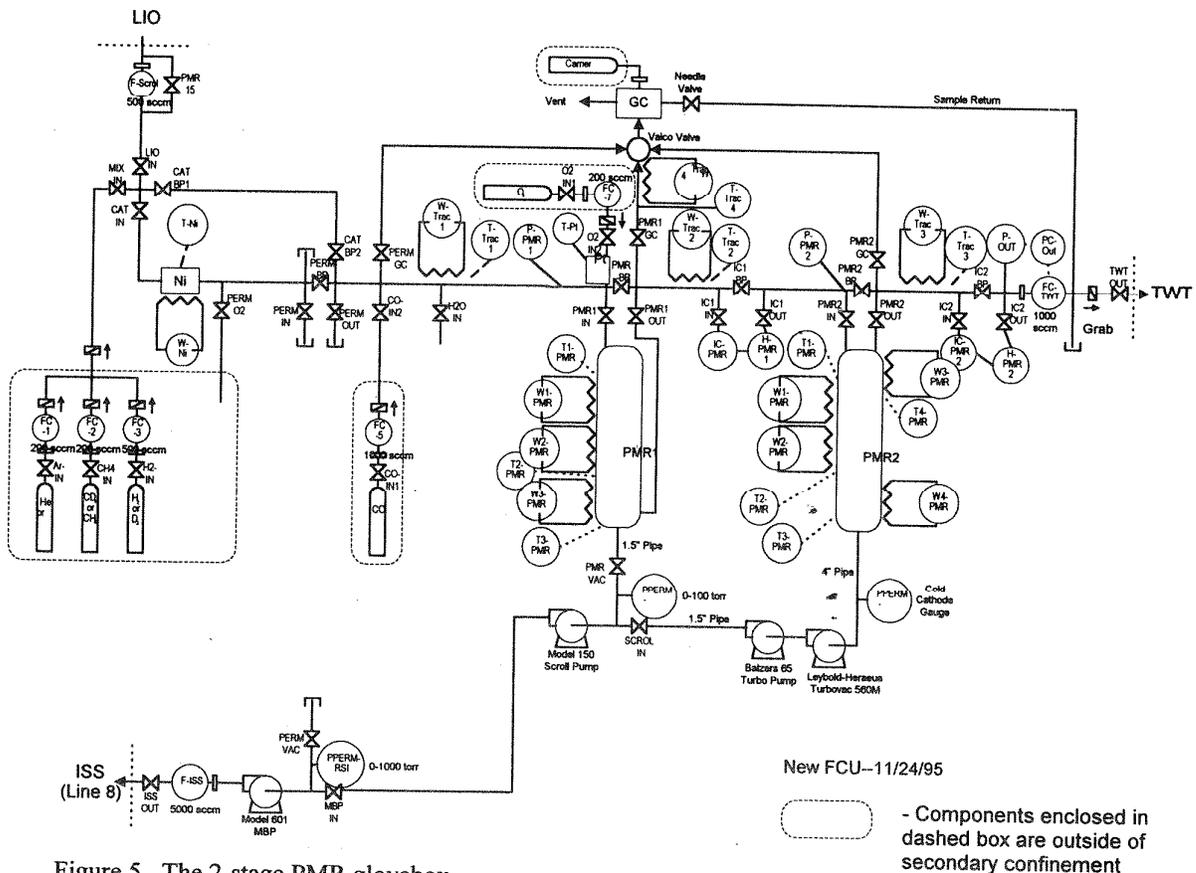


Figure 5. The 2-stage PMR glovebox.

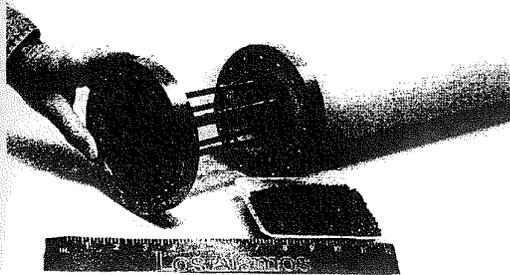


Figure 6. Photograph of the 1<sup>st</sup> stage (background) and 2<sup>nd</sup> stage PMRs. Catalyst is not yet loaded around the 1<sup>st</sup> stage Pd/Ag tubes.

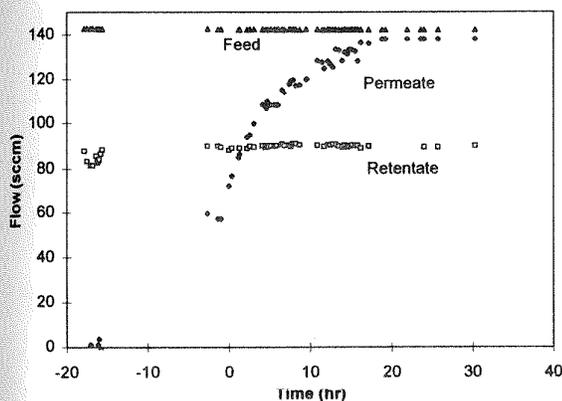


Figure 7. Feed and effluent rates for the 31 hr tritium test of the 2-stage PMR system.

Figure 8 shows the GC analysis for CO and CO<sub>2</sub> in the 1<sup>st</sup> stage retentate. Ar is not measured with the GC, but is calculated from continuity. Figure 9 shows GC analysis for CQ<sub>4</sub> and Q<sub>2</sub> in the 1<sup>st</sup> stage retentate. The remaining tritium-containing specie in the 1<sup>st</sup> stage retentate is Q<sub>2</sub>O, 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 1<sup>st</sup> stage (figure 10). The ion chamber data shows that tritium began breaking through the 1<sup>st</sup> 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.

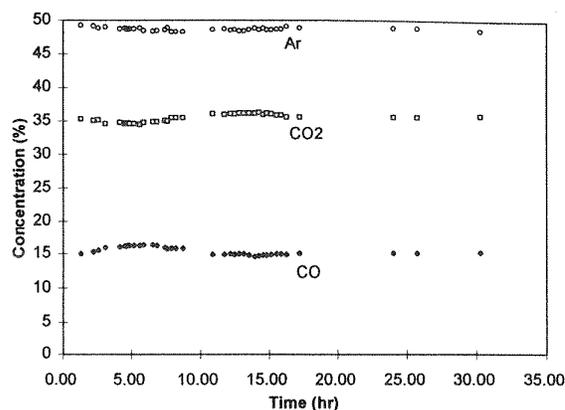


Figure 8. Ar, CO, and CO<sub>2</sub> concentrations in the retentate of the 1<sup>st</sup> stage.

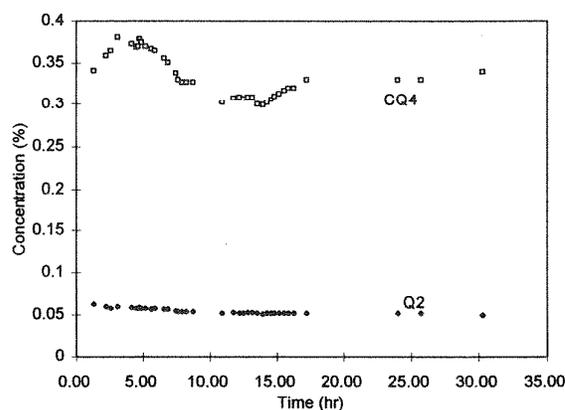


Figure 9. CQ<sub>4</sub> and Q<sub>2</sub> concentrations in the retentate of the 1<sup>st</sup> stage.

Determination of the DF for the 2<sup>nd</sup> stage retentate stream proved to be much more difficult than the 1<sup>st</sup> stage. As in the cold tests, measurement of CQ<sub>4</sub> and Q<sub>2</sub> by GC and Q<sub>2</sub>O 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 2<sup>nd</sup> 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 cm<sup>3</sup> sample was counted on a scintillation counter about every hour beginning with the 23<sup>rd</sup> hour of the experiment. Accumulation of tritium was constant at approximately 2.5 μCi/hr from the 23<sup>rd</sup> hour through the end of the experiment. This outlet tritium rate divided into the 1<sup>st</sup> stage inlet rate of 1440 Ci/hr gives an overall DF of 5.8 × 10<sup>8</sup>. The 2<sup>nd</sup> stage DF is 1.9 × 10<sup>6</sup> if it is assumed that the 1<sup>st</sup> stage DF = 200 (i.e., GC method).

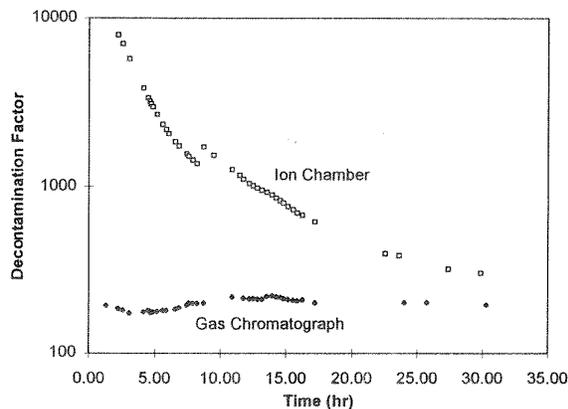


Figure 10. 1<sup>st</sup> stage decontamination factor calculated by ion chamber and GC measurements.

## V. CONCLUSIONS

Catalyst evaluation experiments indicated that Pt/ $\alpha$ - $\text{Al}_2\text{O}_3$  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  $\text{O}_2$  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  $1.4 \times 10^5$  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 1<sup>st</sup> stage had a DF = 200 and the 2<sup>nd</sup> stage had a DF =  $2.9 \times 10^6$ . The overall DF =  $5.8 \times 10^8$ , which is greater than ITER requirements.

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