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PROCESSING TRITIATED WATER AT THE SAVANNAH RIVER SITE: A PRODUCTION-SCALE DEMONSTRATION OF A PALLADIUM MEMBRANE REACTOR

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The Palladium Membrane Reactor (PMR) process was installed in the Tritium Facilities at the Savannah River Site to perform a production-scale demonstration for the recovery of tritium from tritiated water adsorbed on molecular sieve (zeolite). Unlike the current recovery process that utilizes magnesium, the PMR offers a means to process tritiated water in a more cost effective and environmentally friendly manner. The design and installation of the large-scale PMR process was part of a collaborative effort between the Savannah River Site and Los Alamos National Laboratory.

The PMR process operated at the Savannah River Site between May 2001 and April 2003. During the initial phase of operation the PMR processed thirty-four kilograms of tritiated water from the Princeton Plasma Physics Laboratory. The water was processed in fifteen separate batches to yield approximately 34,400 liters (STP) of hydrogen isotopes. Each batch consisted of round-the-clock operations for approximately nine days. In April 2003 the reactor's palladium-silver membrane ruptured resulting in the shutdown of the PMR process. Reactor performance, process performance and operating experiences have been evaluated and documented. A performance comparison between PMR and current magnesium process is also documented.

I. INTRODUCTION

The Palladium Membrane Reactor (PMR) process was part of a collaborative effort between Defense Program Division, Savannah River Technology Center, Los Alamos National Laboratory and the Accelerator Production of Tritium – Tritium Separation Facility. The PMR system was installed in Building 232-H to perform a production-scale demonstration for the recovery of tritium from tritiated water adsorbed on molecular sieve (zeolite). Unlike the current recovery process that generates depleted magnesium beds, the PMR offers a means to process tritiated water in a more cost effective and environmentally friendly manner.

The PMR was developed at the Los Alamos National Laboratory as a simple and effective means for recovering hydrogen isotopes from fusion fuel impurities such as methane and water, Birdsell and Willms[1, 2] and Birdsell, Willms and Wilhelm[3]. This device directly combines two techniques that have long been utilized for hydrogen processing: catalytic shift reactions and palladium-silver permeators (diffusers). The water-gas shift reaction,

$$H_2O + CO \leftrightarrow H_2 + CO_2$$

is used extensively in the petrochemical industry for providing free hydrogen from water. Thermodynamic equilibrium limitations of this reaction (i.e., H_2 concentration) prevent the complete formation of hydrogen isotopes in a single pass through a catalytic reactor. However, if free hydrogen liberated by the reaction is removed from the catalytic reactor, the equilibrium limitation is reduced, allowing for further free hydrogen formation. Palladium-silver membranes, long used to generate ultra-pure hydrogen, provide a practical means for removing the liberated hydrogen. These membranes are exclusively permeable to hydrogen isotopes. By combining a catalytic reactor with a palladium-silver membrane, the PMR is capable of recovering nearly all of the hydrogen isotopes from water in a single processing step.

II. PROCESS DESIGN & OPERATION

II.A. Magnesium Process

The traditional process used at the Savannah River Site for decomposing tritiated water is a magnesium based process called Z-bed Recovery. This process is a simple circulation loop consisting of a metal-bellows pump train, a zeolite bed furnace, and a heated magnesium reactor. The magnesium reactor is a large cylinder (16.8 cm OD x 88.9 cm long) filled with 5 to 6 kg of reagent-grade magnesium turnings. Recovery operations commence by slowly heating a loaded zeolite bed to drive the tritiated water into the vapor phase so it can be transported to the magnesium reactor running at approximately 500°C. The piping between the zeolite furnace and the magnesium reactor is held at 38°C to limit the partial pressure of water to less than 70 torr. The slow zeolite heat up and the low water partial pressure help to minimize the risk of a rapid and uncontrolled temperature excursion during the exothermic decomposition reaction:

$$Mg + H_2O \rightarrow MgO + H_2$$

The circulation pumps pull the liberated hydrogen molecules from the magnesium chamber and pump them back through the heated zeolite to “pick up” more tritiated water vapor for decomposition. Circulation continues until the loop pressure reaches approximately 730 torr at which time the hydrogen is pumped to one of two large storage tanks leaving approximately 200 torr in the loop continuing operations. Heating and circulation continues until the loop pressure no longer increases, indicating that the zeolite has reached an appropriate level of dryness for reuse or disposal. Zeolite that is reused for additional tritiated water storage is typically heated to 250°C while zeolite being desorbed for disposal is baked out to 500°C.

The magnesium process has operated for many years mainly because it is simple, reliable, and efficient in terms of achieving the zeolite dryness requirements, however, there are a few drawbacks. First, magnesium is a consumable. While magnesium metal is fairly inexpensive the cartridges containing the magnesium are expensive and must be disposed of as radiological waste. Second, the conversion of magnesium to magnesium oxide is not a very efficient process. The average utilization or conversion of magnesium is 59% resulting in frequent maintenance outages to replace the magnesium cartridges during which there is a high potential for tritium release and employee exposure. Low utilization is typically caused by high differential pressure across the magnesium and the corresponding decrease in the hydrogen recovery rate. Evidence of this can be observed in Figure 1 below.

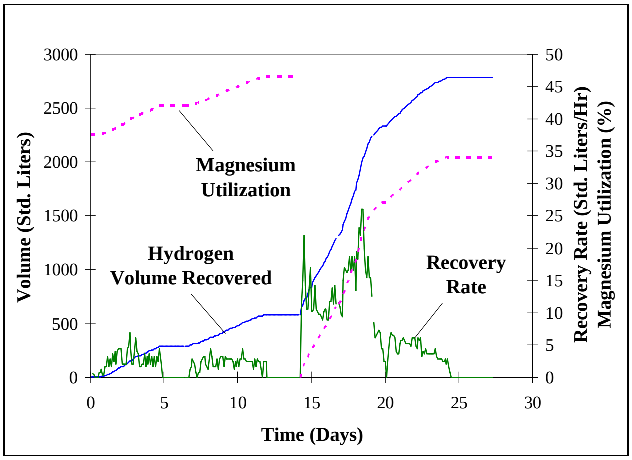

Figure 1: Desorption Data for Bed 524 Using a Magnesium Based Recovery Process

These data above represent the desorption of tritiated water from a fully loaded zeolite bed from which nearly 2,800 liters (STP) of hydrogen isotopes were recovered. Figure 1 shows a relatively low hydrogen recovery rate over the first 12 days. Once the magnesium was replaced (Time = 14 days), the recovery rate increased significantly. The initial low recovery rate is primarily due to the condition of the magnesium, initially at 38% utilization, and not due to the low water desorption rate that is experienced as the zeolite becomes drier towards the end of the operation (Time = 19 – 25 days).

II.B. Palladium Membrane Reactor Process

II.B.1. Process Design

The Palladium Membrane Reactor (PMR) process installed at the Savannah River Site utilized a significant amount of equipment from the traditional magnesium process, such as pumps, storage tanks, and the zeolite furnace. New equipment included the palladium membrane reactor, carbon monoxide supply system including monitoring equipment for personnel safety, three Normetex scroll pumps for removal of hydrogen isotopes from the reactor, and three Unit Instruments mass flow controllers (carbon monoxide supply, tritiated steam supply, and byproduct outlet). An outline flow diagram is provided in Figure 2.

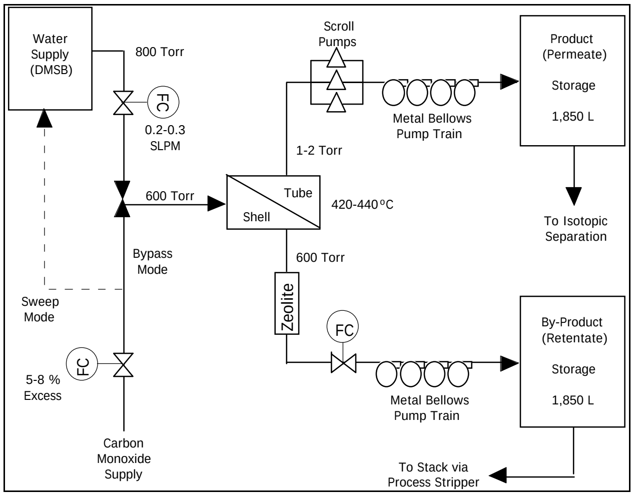

Figure 2: PMR Process Flow Diagram

The process design provided two locations where carbon monoxide could be injected. The primarily location, known as Bypass, is just prior to the reactor. This location is preferred and is seen as the most accurate in terms of reactant flow control as two pure components, water/steam and carbon monoxide, can be individually measured and controlled. The secondary location, known as Sweep, actually injects the carbon monoxide through the heated zeolite. The CO acts as a moisture carrier that is necessary towards the end of a desorption run when steam pressure and high water desorption rates can no longer be maintained. The drawback of using the sweep location is that flow control becomes much cruder. Since the steam flow controller is now measuring a two component mixture, the Programmable Logic Controller must calculate how much of the combined flow is water and how much is carbon monoxide. Reactor performance will likely be affected by potentially feeding non-ideal or non-optimal molar ratios.

II.B.2. Reactor Design

The PMR is a combination of a catalytic reactor and a palladium-silver diffuser. The reactor is constructed of 347 stainless steel with a diameter of 8.9 cm and a total length of 111.1 cm. The reactor is composed of four main sections: feed-end cap, reaction chamber, bleed-end cap, and the vacuum manifold.

The feed-end cap is approximately 2.5 cm long and serves as the entry point for the two reactants. The reactants enter the side of the cap via 9.5 mm diameter tubing and are distributed into the reaction chamber through an eleven square mesh 316 stainless steel screen.

The reaction chamber houses sixteen palladium-silver tubes surrounded by 3.9 kg of reaction catalyst, and is approximately 77.5 cm long. The 3.2 mm diameter pelletized catalyst is platinum on alumina (2 wt. % Pt). The palladium-silver alloy tubes (75 wt. % Pd – 25 wt. % Ag) are arranged in two concentric circles, the inner circle containing five tubes while the outer circle is comprised of eleven. Each tube is 6.4 mm in diameter and 71.8 cm long with a nominal wall thickness of 178 µm. The top of each tube (feed-end cap side) is sealed (Figure 3 – Right). The bottom of each tube is open and passes through the bleed-end cap assembly that is welded to the bottom of the cell body (Figure 3 – Left).

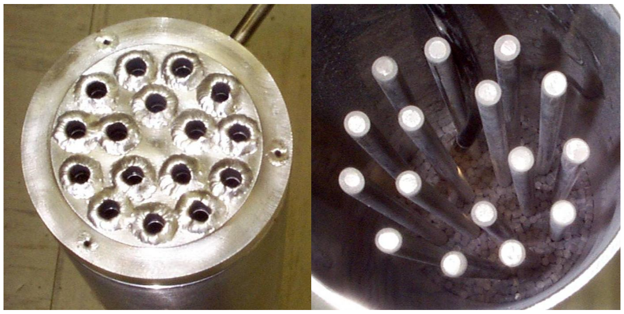

Figure 3: PMR Tube Arrangement

The bleed-end cap is comprised of a ten-micron stainless steel filter on the catalyst side. The cap is configured with a 6.4 mm diameter tube radiating out the side through which the carbon dioxide as well as any unreacted carbon monoxide and water exit the reactor. The palladium-silver tubes penetrate the entire bleed-cap assembly. The open ends of the tubes are welded to outer portion of the assembly (Figure 3 – Left), thus allowing the hydrogen that permeates into the tubes to be removed from the reactor via the vacuum manifold.

The vacuum manifold attaches to the outer portion of the bleed-end cap assembly. The manifold is a transition piece between the reactor body and the vacuum pumping system thus allowing the inside of the palladium-silver tubes to be evacuated.

A heating and insulating jacket surrounds the reactor body. The jacket is composed of three separate heating elements, several thermocouples, and insulation. The three heating element or zone design provides flexibility to vary the temperature along the length of the reaction chamber to account for inlet/outlet cooling effects and heats of reaction. The zone lengths for the top, middle, and bottom portions of the reaction chamber are 15.2, 45.7, and 15.2 cm, respectively. There are two thermocouples associated with each heating zone, one measures the temperature of the heating element while the other measures the skin temperature of the reactor itself.

II.B.3. PMR Process Operations

PMR operations commence by heating a loaded zeolite bed to generate approximately 800 torr steam. Via electrically heated piping (~110°C), the steam is delivered to the reactor at a controlled flow rate. A Programmable Logic Controller (PLC) continuously monitors the process variables and based on the actual steam flow rate, the PLC calculates the required carbon monoxide flow setpoint. All PMR runs were performed with 5 – 8 % excess CO.

Once formed in the reactor, the product (hydrogen isotopes) will permeate through the palladium-silver tubes and be removed by three normetex scroll pumps. The product is then routed to a storage tank where mass balances and accountability are performed. The by-product (carbon dioxide, unreacted or excess carbon monoxide and water, and possibly undiffused hydrogen) are removed from the reactor through the bleed-end cap and routed to a zeolite bed (Type 5A) to remove any unreacted waters prior to being pumped to a storage tank.

Feed pressures to the reactor and throughout the reaction side were approximately 600 torr. The by-product was also controlled to approximately 600 torr using a mass flow controller in the by-product line. Steam flow rates were adjusted to maintain the product pressure (tube side) at approximately 1 torr. The reactor was designed for a steam flow rate of 0.5 standard liters per minute (SLPM) but most runs were fed at 0.2 – 0.3 SLPM due to the inability to maintain adequate vacuum levels at the design flow rate.

The PMR is considered a continuous process but actually operated in batch mode due to the finite amount of water contained on individual zeolite beds. Once the zeolite bed was installed in the furnace the PMR operated continuously until all of the water had been processed, however, there were periods of time during this continuous operation when the water and carbon monoxide flow were temporarily suspended.

III. RESULTS

III.A. Summary of PMR Results

A total of fifteen zeolite beds known as Disposable Molecular Sieve Beds (DMSBs) were desorbed using the palladium membrane reactor process to yield approximately 34,400 liters (STP) of hydrogen isotopes. During these operations the PMR process was found to have several control issues with the most significant being the ability to maintain optimal steam and reactor pressures. The primary reason is the decreasing water desorption rate as zeolite becomes increasingly drier. This resulted in periods of varying pressure on both sides of the reactor (Figure 4).

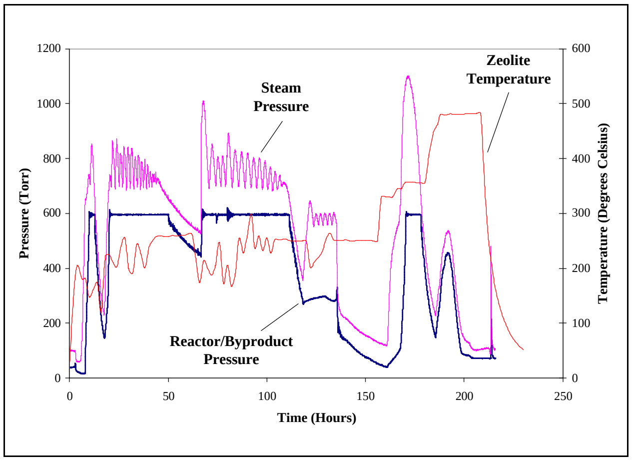

Figure 4: PMR Pressure Profile of Bed 548

Additional problems were encountered with the electrical heat trace on the inlet steam line. Fluctuations in the line temperature adversely affected the high-temperature mass flow controller. Periodically, condensation formed inside the controller giving the false indication of steam flow resulting in improper mixtures of reactants being fed.

The lack of inline or real-time analytical equipment made the 2-year operation of the palladium membrane reactor a guessing game. The byproduct stream exiting the reactor was periodically analyzed by mass spectrometer, however, the time required to deliver the samples via 61 meters long capillaries and the extra processing time necessary to resolve the mass-28 species (N_2 and CO) did not make the results useful for control purposes. Mass spectrometer results were also obtained on the composite hydrogen and byproduct storage tanks which allowed an overall mass balance to be performed.

For typical day-to-day process operations it is not necessary for the mass spectrometer to distinguish between similar masses of waters, X_2O, and methanes, CX_4, where the X represents H, D, or T in any combination. Unreacted water exiting the reactor was expected, however, the magnitude during operations was never known even though there were moisture meter probes installed in the byproduct line. The presence of methane indicates that the steam reforming reaction,

$$3H_2 + CO \leftrightarrow CH_4 + H_2O$$

is occurring and is not being forced back to the left before the reactor outlet. While the gross levels of carbon dioxide and carbon monoxide in the byproduct seem to be relatively inline with expected levels, it is the instantaneous trace quantities of hydrogen, methane, and water that are important for control purposes. Knowing these could have prompted changes in steam flow rates, reactor temperature, and the $CO:H_2O$ molar ratio throughout a desorption run instead of operating in a turn it on and see what you get type of operation.

Very limited adjustments to the amount of carbon monoxide added could be made. Decreasing the amount of carbon monoxide would have resulted in a significant amount of unreacted water while increasing the carbon monoxide would have resulted in higher carbon monoxide and methane levels that could potentially harm the downstream operations through which the byproduct had to be processed prior to release to the environment.

Even with the control problems discussed above the palladium membrane reactor delivered excellent results for a first production-scale demonstration. This process successfully desorbed fifteen zeolite beds to acceptable dryness levels, and recovered 34,400 liters (STP) of hydrogen isotopes while eliminating the generation of nearly 5.7 cubic meters of tritiated magnesium waste. During the first three beds alone an average of 89.5% of the hydrogen known to be present was recovered with only 0.3% in the byproduct stream. The majority of the hydrogen balance is believed to remain on the molecular sieve water source. A small amount of hydrogen is also present on the byproduct zeolite bed as a result of water breakthrough during process operations. Improvement in performance over the next 12 beds did not occur

III.B. Comparison of Magnesium and PMR Performance

As previously shown the hydrogen recovery rate using the magnesium reaction tends to be dependent on the condition of the magnesium. Figure 5 shows the desorptions of similarly sized zeolite beds, approximately 2,400 liters (STP) hydrogen, using new magnesium and the palladium membrane reactor. The hydrogen recovery rates for the first 1,000 liters (STP) are very similar. The magnesium rate begins to slow to approximately 10 liters per hour while the temperature of the zeolite is raised to release more water. Once the zeolite reaches its maximum temperature the recovery rate decreases to around 2 liters (STP) per hour. As for the PMR, the recovery rate stayed nearly constant for the first 1,800 liters (STP) at which time flow was temporarily suspended. When restarted a much lower recovery rate was initially observed (Time = 135 – 165 hours), however, a higher recovery rate returned as the zeolite temperature was raised and the carbon monoxide was changed from bypass to sweep. This change also explains the rapid pressure increase shown at Time = 165 hour on Figure 4 which is the pressure profiles for the same PMR desorption run shown in Figure 5. The higher hydrogen recovery rates for the palladium membrane reactor turned into an overall lower processing time for desorbing zeolite beds when compared to the magnesium process. Although only 91.5% of the hydrogen isotopes were recovered in the above mentioned operation, compared to 97.4% recovery for the magnesium run, recovery occurred in nearly half the time that it took to recover the same volume of hydrogen using the magnesium.

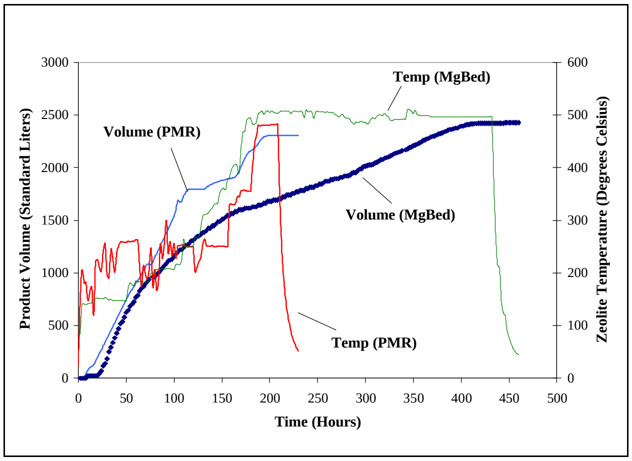

Figure 5: Comparison of PMR (Bed 548) and Magnesium (Bed 532) Desorption Runs

Table I provides a summary of the fifteen DMSB recovery runs using the palladium membrane reactor. This data set indicates that tritiated water can be processed very quickly using a palladium membrane reactor. The processing times indicated include small amounts of non-processing time that was necessary to transfer the product and by-product tank contents to other storage locations. It should be noted that the process data for 3 of the 15 runs was lost. The average processing time for a DMSB turned out to be 9.2 days. Since each DMSB contained varying amounts of tritiated water the processing time was normalizing to the amount of water recovered. The processing times ranged from 71.8 to 185.4 hrs/kg water recovered with an average of 112.5 and a median of 110.0. As expected, the maximum processing time of 14.8 days (185.4 hrs/kg water) was associated with the first recovery run using the palladium membrane reactor. In terms of the completeness of hydrogen isotope recovery, an average of 88.9% of the hydrogen isotopes were recovered as product or permeate using the palladium membrane reactor. The recovery rate ranged from 74.2 to 95.0% with a median for the data set of 89.3%. The recovery percentages were calculated by dividing the actual volume of hydrogen isotopes recovered by the volume of hydrogen isotopes loaded on the DMSB. Loading information was provided by the Princeton Plasma Physics Laboratory.

TABLE I. Summary of DMSB Recovery Runs using the Palladium Membrane Reactor

Run #-DMSB ID	Process Time (Days)	Hrs per Kg Water Recovered	Volume HDT Recovered	Percent HDT Recovered
1-538	14.8	185.4	2,181	87.8
2-537	10.1	124.5	2,224	89.3
3-548	9.0	108.3	2,264	91.5
4-544	Note 1	Note 1	2,529 (Note 2)	90.5 (Note 2)
5-539	Note 1	Note 1	2,575 (Note 2)	90.5 (Note 2)
6-535	Note 1	Note 1	2,161 (Note 2)	90.5 (Note 2)
7-540	11.1	126.1	2,395	87.8
8-517	7.1	71.8	2,693	95.0
9-563	10.0	153.1	1,798	90.5
10-547	10.9	120.2	2,474	93.9
11-545	9.1	82.3	3,092	91.2
12-558	6.5	80.6	2,197	87.0
13-542	7.8	108.1	1,962	88.6
14-534	5.0	77.8	1,750	89.4
15-536	9.1	111.7	2,223	74.2
Avg.	9.2	112.5	2,271	88.9
Med.	9.1	110.0	2,224	89.3
Min.	5.0	71.8	1,750	74.2
Max.	14.8	185.4	3,092	95.0

Note 1: Data not available; Note 2: Based on average percent HDT recovery

Table II provides data on the remaining 43 DMSBs that were processed using the magnesium based system prior to the palladium membrane reactor demonstration. The processing times indicated only include the time that zeolite heating and loop circulation were active and does not include any non-processing time for tank transfers, replacement of magnesium cartridges, or other temporary suspensions of process operations. Using magnesium the average processing time for a DMSB was 15.1 days. Normalized processing times ranged from 120.2 to 604.4 hrs/kg water recovered with an average of 208.8 and a median of 191.8. When including the non-processing time for these 43 runs, the average time increased to 293.3 hrs/kg water recovered.

TABLE II. Summary of DMSB Recovery Runs using the Magnesium Based Process without Downtime

Run #-DMSB ID	Process Time (Days)	Hrs per Kg Water Recovered	Volume HDT Recovered	Percent HDT Recovered
1-533	Note 1	Note 1	1,605	73.7
2-502	Note 1	Note 1	1,546	95.3
3-501	Note 1	Note 1	1,010	Note 2
4-503	Note 1	Note 1	1,738	84.9
5-556	Note 1	Note 1	1,246	82.7
6-552	14.5	315.7	1,260	73.5
7-510	8.2	120.2	1,865	70.4
8-519	11.6	255.7	1,245	88.6
9-515	20.6	410.4	1,392	77.9
10-518	15.1	130.8	3,156	Note 2
11-557	16.2	223.4	1,975	85.0
12-550	13.6	353.5	1,061	96.9
13-506	14.7	140.2	2,836	95.4
14-505	10.7	203.8	1,444	Note 2
15-504	9.9	167.5	1,624	97.7
16-509	18.0	225.8	2,173	93.6
17-513	12.9	240.3	1,478	69.2
18-508	22.5	232.9	2,630	83.7
19-507	17.5	171.7	2,787	99.7
20-521	11.3	143.5	2,149	94.8
21-511	17.3	198.1	2,400	85.1
22-554	11.3	130.8	2,430	98.6
23-553	23.0	234.1	2,677	96.1
24-516	15.5	175.1	2,427	95.4
25-531	23.2	209.9	2,989	98.9
26-514	14.1	224.9	1,717	92.2
27-520	15.6	149.3	2,851	98.7
28-522	16.1	177.4	2,473	89.0
29-546	16.5	178.0	2,519	92.4
30-526	13.8	161.4	2,322	96.1
31-527	11.2	124.4	2,441	95.3
32-524	20.3	201.1	2,744	92.2
33-523	18.3	191.8	2,586	97.0
34-525	13.1	139.3	2,554	92.2
35-528	17.7	232.4	2,072	77.4
36-529	14.2	147.8	2,598	97.5
37-532	17.6	203.4	2,358	97.4
38-530	13.7	138.3	2,684	94.9
39-541	10.1	167.1	1,648	99.7
40-543	13.3	604.4	612	83.2
41-555	11.0	189.0	1,592	96.1
42-549	13.9	212.7	1,787	98.7
43-551	Note 1	Note 1	1,900	99.5
44-559	Note 1	Note 1	1,711	91.5
Avg.	15.1	208.8	2,053	90.7
Med.	14.5	191.8	2,111	94.8
Min.	8.2	120.2	612	69.2
Max.	23.2	604.4	3,156	99.7

Note 1: Data not available; Note 2: Exceeded 100%

IV. CONCLUSIONS

A palladium membrane reactor process has the potential to be useful in large-scale process applications involving the recovery of tritium from tritiated water. This production-scale demonstration was very useful as it confirmed the need for real-time analytical measurements for optimal control as well as other process control enhancements. Additional improvements in performance could be gained if the desorption of water from the zeolite could be decoupled from the direct feeding of the reactor. This could be accomplished by a two-stage operation that first condenses the desorbed water and secondly heats the liquid water to generate the steam feed. This type of operation could possibly eliminate 1) the end-of-run pressure variations observed as the zeolite drying progresses and 2) the need for the hard-to-control sweep mode which is necessary at the end of the desorption. While the overall hydrogen isotope recovery was slightly lower than the existing magnesium based system, the palladium membrane reactor installed at the Savannah River Site delivered processing rates nearly two times as fast per kilogram of water recovered.

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