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ABSTRACT
Under a collaborative agreement between US and Japan, two tritium processing components, a palladium diffuser and a ceramic electrolysis cell have been tested with tritium for application to a Fuel Cleanup System(FCU) for plasma exhaust processing at the Los Alamos National Laboratory. The fundamental characteristics, compatibility with tritium, impurities effects with tritium, and long-term behavior of the components, were studied over a three year period.
Based on these studies, an integrated process loop, "JAERI Fuel Cleanup System" equipped with above components was installed at the TSTA for full scale demonstration of the plasma exhaust reprocessing.

I. INTRODUCTION

The Japan Atomic Energy Research Institute (JAERI) and the United States Department of Energy (DOE) agreed a collaborative program for the development of the components, the palladium diffuser and the ceramic electrolysis cell for the Fuel Cleanup System(FCU), which would be applicable to the next generation of fusion experimental devices. Both designed and manufactured by JAERI and shipped to the Tritium Systems Test Assembly(TSTA) at the Los Alamos National Laboratory for the testing with tritium.

A palladium diffuser separates hydrogen isotopes from all other impurity species and produces a pure hydrogen stream that will be handled in the isotope separation system in the fusion fuel loop. The ceramic electrolysis cell decomposes tritiated water vapor without generating solid waste or having a large tritium inventory. Since 1984, preliminary tests on both components with tritium have successfully been performed at the TSTA under an early agreement [illegible] JAERI collaboration. Both components proved to be feasible for tritium service and seemed attractive for application in the processes of the Fuel Cleanup[1-4]. Thus further studies were suggested for development of practical components.

II. EXPERIMENTS

A Palladium Diffuser

The palladium diffuser contains [illegible] fine palladium alloy tubes that selectively permeate hydrogen isotopes. Figure 1 shows the schematic of the diffuser. A mixture of hydrogen isotopes and impurity is separated into a pure hydrogen stream and a bleed stream that contains mostly impurity and some residual unpermeated hydrogen. The diffuser is contained in a double jacket in order to recover tritium permeated from the primary containment that is heated up to 450°C by a heater wire wound on it. The flow diagram of the experiment is shown in Figure 2. One or two metal bellows pumps are used to evacuate the inside of the palladium tubes and recirculate the permeated hydrogen into the feed stream. Impurities such as methane and carbon monoxide were added in order to investigate the chemical effect as well as measure the separation characteristics. Gas samples were occasionally taken from the feed

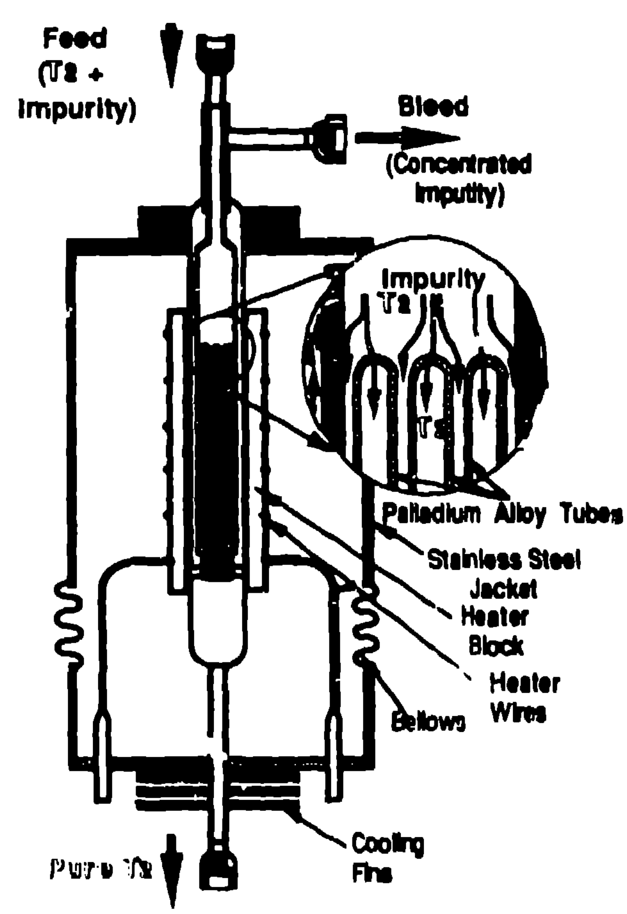

Fig. 1. Schematic of the Palladium Diffuser

or bleed for Raman or mass spectroscopy. Flow rates and pressures were measured at the feed and permeated sides of the diffuser. Tritium was supplied to the experiment from the ZrCo bed. Approximately 2500Ci were used. The experiment was independent of the TSTA main loop and was placed in a separate glovebox.

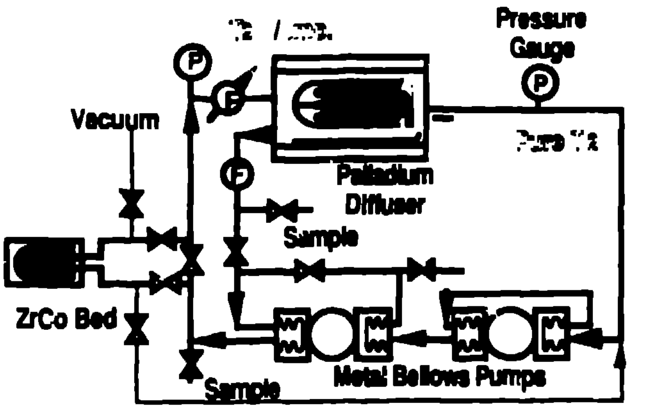

Fig. 2. Flow Diagram of the Palladium Diffuser Experiment.

B Ceramic Electrolysis Cell

The electrolysis cell contains 10 sintered stabilized zirconia tubes that has calcined platinum electrodes at the inside and outside. Figure 3 shows the structure of the cell. Water vapor in the feed gas stream is decomposed at the surface of the inner electrode to form hydrogen/tritium while pure oxygen generates at the outer surface of the ceramic tube.

The test loop consisted of a tritium source, a catalytic reactor filled with hopcalite, a LN2 freezer, the CEC, a metal bellows pump, and a ZrCo tritium storage bed as shown in Figure 4. Pure or high level tritiated water was formed by oxidation of tritium gas at the hopcalite bed. The water vapor was then collected in a freezer so that regeneration of the freezer in the FCU system was simulated. In some tests, vapor was continuously sent to the cell for decomposition followed by recombination with oxygen from the oxygen side of the cell. Inert gas and deuterium was used as carrier gas in the loop. Effects of impurities such as CO and CO_2 were investigated. The experiment was located in a glovebox in an auxiliary laboratory at the TSTA

C. Zirconium Cobalt Bed

The zirconium-cobalt intermetallic compound is a new material developed by JAERI as a substitute for uranium for tritium recovery and storage[5]., and some beds for tritium service are developed[6].

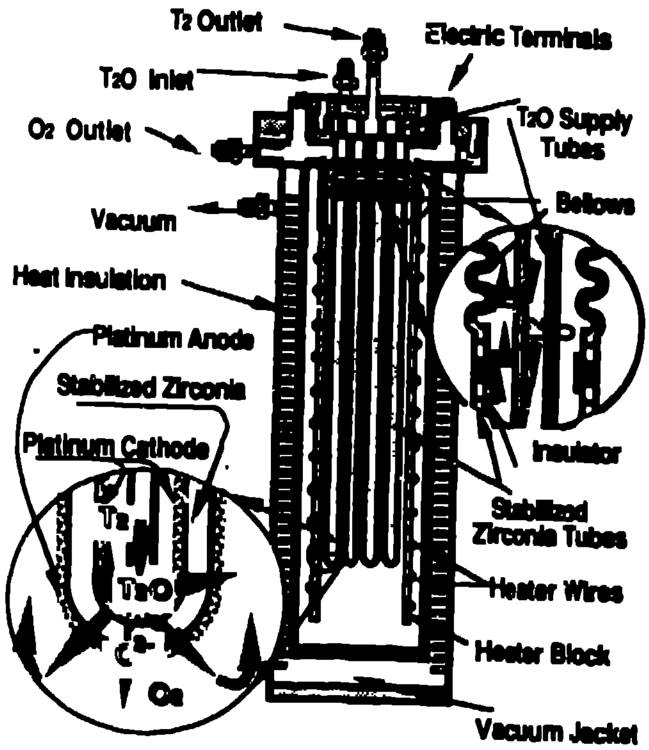

Fig. 3. Schematic of the Ceramic Electrolysis Cell.

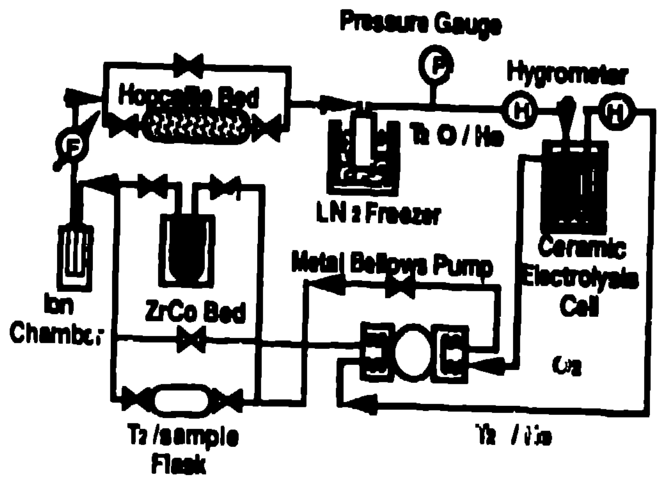

Fig. 4 Flow Diagram of the CEC Experiments.

Both experiments were equipped with ZrCo beds for recovery, storage and supply of tritium as shown in the figures. Some features of the ZrCo beds were tested in practical tritium service.

III RESULTS

A. Palladium Diffuser Experiment

1 Permeability Measurement

The permeation flow rates of pure H_2, D_2 and T_2 were measured as the functions of pressure at various temperatures. Examples at 300°C are summarized in Figure 5. Flow rates are expressed in cm^3 per minutes at 0°C, 103kPa. Linear relations are observed between flow rates and differential square root of pressures across the membrane although some deviation at both high and low pressures appeared. Permeability of tritium was approximately one half of that for hydrogen.

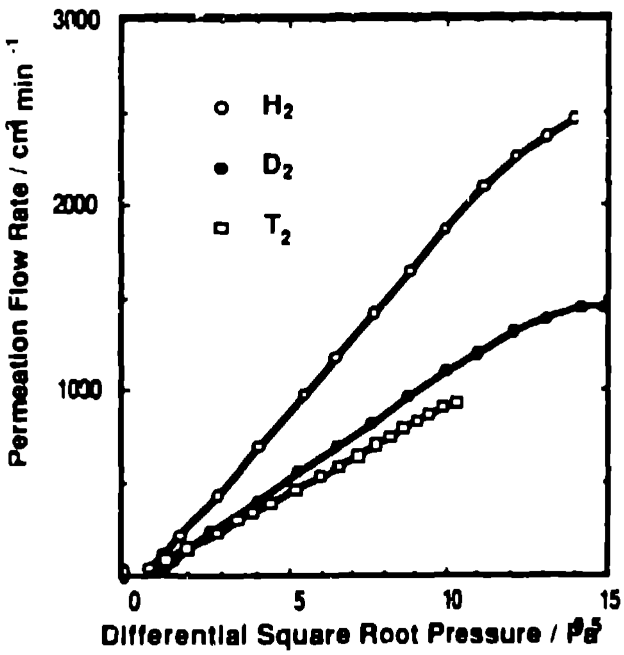

Fig. 5. Permeability of Pure Hydrogen Isotopes through the Diffuser.

2 Separation Characteristics

A mixture of hydrogen and 10% methane was introduced into the system to measure the separation characteristics of the diffuser. Feed and permeation flow rates were measured as a function of the concentration of hydrogen in the feed stream. The result indicates a low concentration of hydrogen at the bleed from a feed containing major amount of hydrogen, however the permeation flow rate is much smaller than in the case of pure hydrogen feed. This is caused by a high partial pressure of impurity in the feed side of the diffuser. Numerical calculation suggests that an increased diffuser length was desirable for achieving low hydrogen concentration in the output impurity stream. The system was left in a continuous operation mode for months and little change in the separation characteristics was observed.

3 Carbon Monoxide Testing

A high concentration of CO in the stream may be encountered in some applications of the diffuser in tritium processing loops. The diffuser was operated for an extended period with a T_2-CO mixture. Approximately a 10% loss of permeability occurred in a 6 month operation. Oxidation treatment of the membrane followed by hydrogen reduction regenerated the permeability as in Fig.6. This result suggests that the reduction of the permeability might have been caused by surface contamination of the palladium alloy membrane. A possible deposit of carbon caused by the radiolysis of CO was suspected.

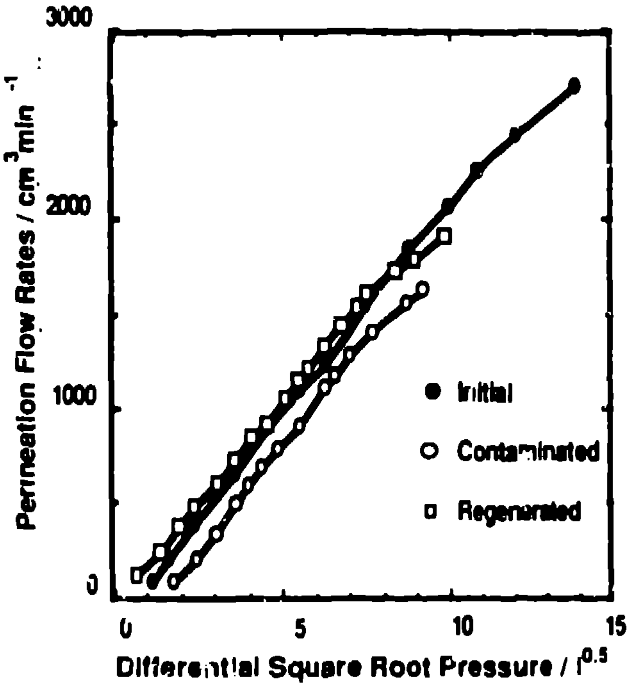

Fig. 6 Regeneration of the diffuser after long-term exposure to T_2-CO.

4 Long term Reliability

The diffuser was operated at relatively low temperature (150°C – 300°C) to investigate the effect of the formed ^3He in the palladium metal. Little degradation of the permeability was observed in more than 1 year of operation.

B. Ceramic Electrolysis Cell Experiment

1 Decomposition Characteristics

Decomposition characteristics of the electrolysis cell was measured with H_2O-N_2, T_2O-N_2, T_2O-D_2 systems under the conditions simulating application for a plasma exhaust process. In the Fuel Cleanup Systems in TSTA or TPL, DTO captured at the DTO freezers should be regenerated and decomposed to recover tritium. Carrier gases such as N_2, He or D_2 may be used for regeneration of the freezers. Carrier flow rate was 400 - 1000cc min, where no effect of the flow rate was observed on the characteristics of the cell. Figure 7 shows the conversion efficiency of water vapor to hydrogen obtained with the cell operated at 600°C. Conversion ratio was determined from the ratio of the inlet and the outlet humidities. The Ir-free voltage is measured between the two electrodes on the cell that composes an open circuit where no current is applied. This value indicates the electrochemical potential across the cell generated by the difference of oxygen potential at the O_2 side and the T_2/T_2O side. The observed conversion efficiency was around 95%. These values are lower than expected, probably due to the error caused by the residual humidity at the outlet of the cell. A small isotopic difference was observed between T_2O and H_2O. The theoretical conversion efficiencies for each system are also shown on the figure. The results show similar trends although marked deviations are observed.

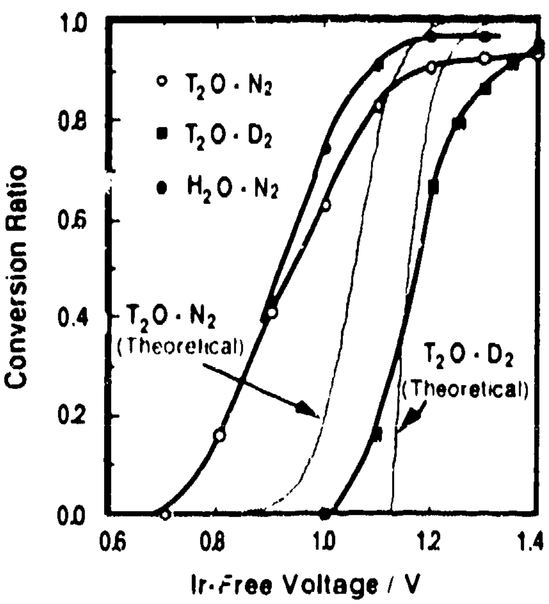

Fig. 7 Conversion efficiency from vapor to hydrogen for H_2O-N_2, T_2O-N_2, and T_2O-D_2 systems at the electrolysis cell. Theoretical results are also shown.

Deuterium was tested as carrier gas for the tritiated water. Use of the D_2 for regenerating the freezer is advantageous because only gaseous hydrogen isotopes $(DT)_2$ is expected to be obtained as product stream from the cell. The experiment proves that T_2O can be decomposed at high efficiency at 1.4V, that is higher than the case with inert carrier as predicted by the calculation.

2 Impurity Testing

Systems of CO_2-N_2 and CO_2-D_2O-N_2 were tested to investigate the effect of CO_2 that might be electrolyzed by the cell while water is decomposed. A thermochemical calculation was made for the electrochemical equilibria of the CO_2, CO, H_2O, H_2, C and O_2 systems in the cell.

Figure 8 shows the relationship between conversion ratios for the reactions discussed above and Ir-free potential at 600°C. For the reactions $CO \leftrightarrow \frac{1}{2}O_2 + C$, and $CO_2 \leftrightarrow C + O_2$, initial concentrations of CO or CO_2 are assumed to be 0.1. Each line shows how the reaction can proceed at the given Ir-free voltage in the cell. As seen in the figure, the decomposition of water is the easiest to occur in the cell, but all the reactions are possible at the potential of 1.3V to 1.4V where the cell is usually operated. Either CO_2 or CO can be decomposed to form carbon as the result of the reaction.

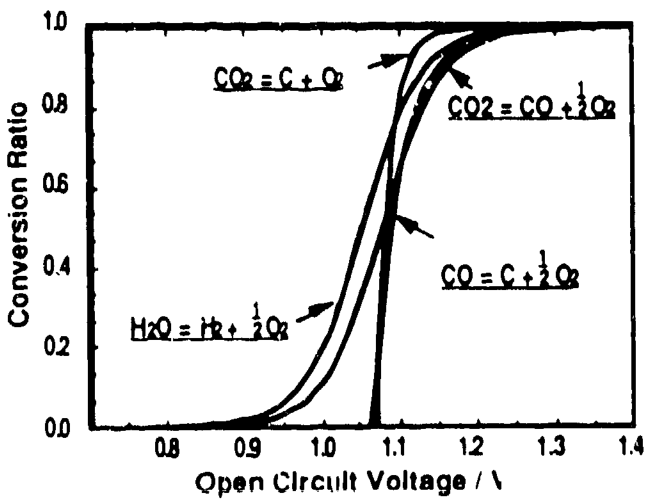

Fig. 8 Theoretical equilibrium conversion of H_2O and CO_x at the electrolysis cell at 600°C. Feed concentration was assumed to be 0.1 for CO and CO_2.

Figure 9 shows the result of the tests with CO_2. The electrolysis of CO_2 starts at about [illegible]V, that is close to the calculated voltage for reaction $CO_2 \leftrightarrow \frac{1}{2}O_2 + CO$, however the conversion ratio was less than 3%. It is understood that the porous platinum electrode does not have catalytic activity for the decomposition of CO_2, while it does for the decomposition of water. Electrolysis of D_2O - CO_2 - N_2 mixture shown in the figure indicates no effect on the electrolysis performance of water. These results suggest that CO_2 impurity in the cell does not have any undesirable effect on the decomposition of water.

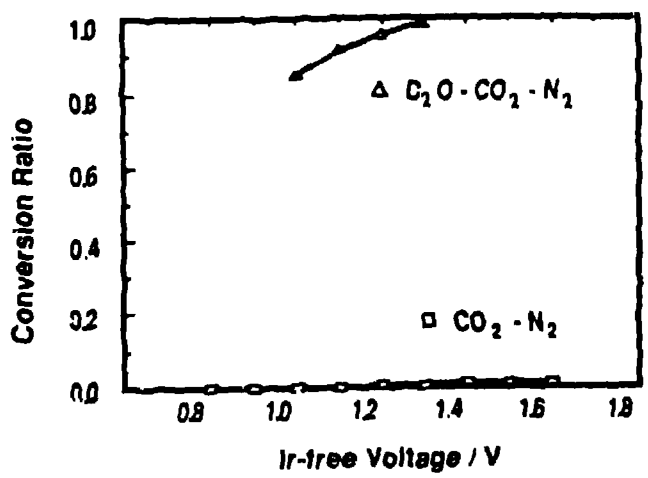

Fig. 9. Electrolysis of CO_2-N_2 and D_2O-CO_2-N_2.

3 Batch Operation

One of the major practical applications of the CEC is the batch processing of a tritiated water gas mixture. In the test, a mixture of tritiated water and carrier was processed with the cold trap, electrolysis cell and a ZrCo bed to convert tritiated water and recover tritium in a closed loop. More than 99.99% of the water was decomposed and tritium was trapped at the bed. It was proved that the CEC is suitable to process relatively small amounts of high level tritiated water in a batch operation.

4 Long-term Reliability

The electrolysis experiment was operated in a closed loop mode in which oxygen generated at the anode is recycled to the catalytic reactor inlet for recombining with electrolyzed tritium. A test with T_2O-CO_2-He was performed as long as one year to evaluate the long term reliability of the cell with tritium and impurity. The cell has successfully worked for the test period, however marked embrittlement of the stabilized zirconia material was observed when the test was completed.

C. Zirconium-Cobalt Bed

1 Equilibrium Pressure of Tritium

Pressure-composition isotherms of the T_2-ZrCo system was measured with the ZrCo bed installed in the CEC experiment. Preliminary results indicated that the equilibrium pressure of T_2 on the ZrCo is higher than that of hydrogen by a factor of less than 2. It is suggested that the isotopic difference was negligible in the practical use of ZrCo for tritium service. Detailed measurement was done by the program and apparatus under the Annex IV agreement.

2 Practical Application

Both palladium diffuser and electrolysis cell experiments were equipped with ZrCo beds of 5 liter of hydrogen in capacity. The beds were used for storage and supply of pure and mixed tritium. The recovery of tritium was performed both by absorption of pure isotopes and recycling of the mixture with inert through the bed. These practical experiences of the beds verified that a ZrCo bed is a suitable substitute for uranium beds.

IV. CONCLUSION

The experimental program on the "process ready components" under Annex III was completed and all of the objectives were achieved experimentally in the tests performed in these three years. Through the tests, it is concluded that the palladium diffuser is applicable to the processing of plasma exhaust to produce pure hydrogen isotopes for as long as 3 years without any maintenance. Use with carbon monoxide was not a problem. The ceramic electrolysis cell was verified as an attractive component for the decomposition of tritiated water in various processes. Carbon dioxide affected it little. Thus, both process-ready components, the palladium diffuser and the ceramic electrolysis cell, were proved to be suitable for fusion fuel processing. Long term reliability and compatibility of the components with tritium and impurity was verified.

Based on the results, an integrated process loop, "JAERI Fuel Cleanup System" that utilizes both components was developed and designed by JAERI for full scale demonstration of the plasma exhaust reprocessing. The system will be tested with simulated fusion fuel in the TSTA main loop in the near future.

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