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S. Tosti, C. Rizzello, F. Borgognoni, N. Ghirelli, A. Santucci
and JET EFDA contributors

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S. Tostia, C. Rizzellob, F. Borgognonia, N. Ghirellic, A. Santuccia
and JET EFDA contributors*

JET-EFDA, Culham Science Centre, OX14 3DB, Abingdon, UK

[1]Associazione ENEA-Euratom sulla Fusione, C.R. ENEA Frascati, Via E. Fermi 45, 00044 Frascati (RM), Italy
[2]Tesi Sas, Via Bolzano 28, Roma, Italy
[3]CEA Cadarache, DEN, DTN/STPA/LIPC, F-13108 Saint Paul-lez-Durance, France
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ABSTRACT

The development of a Pd-based membrane reactor to be applied in processes for tritium removal from various gaseous streams of tokamak systems has been carried out. In particular, the membrane reactor has been designed for decontaminating soft housekeeping wastes of JET.

This membrane reactor consists of Pd-Ag permeator tube fixed in a finger-like mode into a stainless steel shell. The feed stream (gases to be detritiated) is fed inside the membrane lumen where the isotopic exchange takes place on to a catalyst bed while pure hydrogen (protium) is sent in countercurrent mode in the shell side. The feed stream consists of 200 Ncm^3 min^{-1} of helium with 10 % of tritiated water (tritium content 1.11×10^8 Bq h^{-1}).

The membrane reactor design has been based on a simplified calculation model which takes into consideration the very low tritium content of the gas to be processed and the complete oxidation of the tritiated species in the feed stream. The model considers a tubular Pd-Ag membrane divided into finite elements where the mass balances are performed according to both the thermodynamic equilibrium reactions and permeation rates through the membrane of the hydrogen isotopes.

The reactor model has permitted to verify that a Pd-Ag commercial tube of diameter 10mm, 500mm of length and 0.150mm of wall thickness is capable to attain a decontamination factor larger than 10.

A new mechanical design of the Pd membrane reactor has been also developed: especially, harmful mechanical stresses of the long permeator tube consequent to the hydrogenation and thermal cycling has been avoided. Furthermore, an innovative effective heating system of the membrane has been also applied.

1. INTRODUCTION

Pd and Pd alloy dense membranes are capable to separate hydrogen and its isotopes from gas mixtures. In fact, hydrogen can selectively permeate a defect-free metal wall and, especially, the Pd-Ag alloy with Ag 20-25 wt% is commercially available for hydrogen purification applications. An extensive literature has been written on laboratory and industrial applications of Pd-based membranes and membrane reactors [1-4].

A membrane reactor (PERMCAT) consisting of tubular Pd-Ag membranes has been studied at Tritium Laboratory of Karlsruhe for the final clean-up of the plasma exhausts [5-8] and Tosti et al. presented an innovative mechanical design of a PERMCAT-kind membrane reactor [9,10]. Based on these experiences, a new membrane reactor has been designed and built for a decontamination process of tritiated housekeeping wastes [11,12]. These materials are produced during the whole life and also during the dismantling of tritium handling facilities and fusion machines. The production of housekeeping waste is assessed around 0.2 kg h^{-1} $worker^{-1}$ in a nuclear facility. The housekeeping wastes are mainly gloves, over shoes, over clothes, personal gas filters, papers, etc.. In particular, the studied decontamination process permits simultaneously the detritiation of the laboratory wastes (decategorization) and the recovery of tritium in gaseous form (valorization).

This paper describes a model study which permits to analyze the behavior of the membrane reactor

under the operating conditions of the housekeeping wastes detritiation process and an improved new design of the membrane module.

2. TRITIUM REMOVAL VIA PD-BASED MEMBRANES

Detritiation of gas mixtures containing tritium can be carried out by isotopic exchange with a pure hydrogen (protium) stream through a dense Pd-based membrane. Isotopic exchange reactions are promoted by the presence of a catalytic bed. A commercial Pd-Ag (with Ag 23-25 wt.%) tube of wall thickness 0.150 mm, diameter 10 mm and length 500 mm with catalyst in the lumen side has been considered to perform the detritiation process studied for decontaminating soft housekeeping wastes of JET (task JW10-FT-2.35).

2.1 DETRITIATION PROCESS

The soft housekeeping wastes (100 g) are treated at 120°C in an oven where an inert gas stream (200 $Ncm^3\ min^{-1}$ of helium with 10 % of water) operates the removal of the tritium at an estimated rate of 1.11×10^8 Bq h^{-1}. Then the helium is fed into the lumen side of the membrane reactor while a pure hydrogen stream is sent in the shell side in counter current mode. The hydrogen isotopes permeate selectively through the dense metal membrane: as a consequence of the isotopic exchange reactions which take place on the catalyst, the tritium transfer from the liquid (tritiated water in the lumen side) to the gas (shell side) occurs.

2.2 SIMULATION CODE

In order to study the behavior of the membrane reactor a simulation code based on a finite element method has been implemented. Main hypotheses at the basis of the study are:

- plug flow fluid dynamic regime,
- perfect gas behavior,
- isothermal conditions,
- negligible pressure losses,
- tritium in elemental form always in equilibrium with tritium in tritiated water.

Particularly, the membrane tube is divided into a number of finite volume elements: the differential axial mass balances are carried out by assuming as inlet boundary conditions for each element the outlet values of the previous one. For a generic finite element (i), the calculation procedure consists of the following steps.

i) To evaluate the amount of HT formed from HTO, according to the exchange reaction:

$$HTO + H_2 \Leftrightarrow H_2O + HT \qquad (1)$$

(equilibrium conditions are considered to be reached, i.e. infinite catalyst efficiency).

ii) To assess the partial pressures of hydrogen and tritium in both lumen and shell sides of the membrane:

$$p_{H_{2f}(i)} = \frac{N_{H_{2f}(i)}}{N_{H_{2f}(i)} + \sum_j N_{jf}} \times p_f \tag{2}$$

$$p_{H_{2s}(i)} = \frac{N_{H_{2s}(i)}}{N_{H_{2s}(i)} + \sum_j N_{js}} \times p_s \tag{3}$$

where P is the total pressure (Pa), pH2(i) is the partial pressure of hydrogen feed side(Pa), NH2(i) is the molar flow rate of hydrogen (mol s^{-1}), Σ Nj is the sum of molar flow rates extended to all the non permeating gases (mol s^{-1}). The subscript f refers to the feed (lumen) side and the subscript s refers to the strip (shell) side. Then same equations are calculated for tritium.

iii) To evaluate the protium permeation flux JH2(i) (mol m^{-2} s^{-1}) on the basis of the partial pressures at the two sides of the membrane according to the equation:

$$J_{H_2(i)} = \frac{\phi}{d}\left(\frac{p_{H_{2f}(i)}}{\sqrt{p_{H_{2f}(i)}} + \sqrt{p_{T_{2f}(i)}}} - \frac{p_{H_{2s}(i)}}{\sqrt{p_{H_{2s}(i)}} + \sqrt{p_{T_{2s}(i)}}} \right) \tag{4}$$

where Φ is the protium permeability (mol m^{-1} s^{-1} Pa0.5), d the tube wall thickness (m). Then the permeation flux of tritium is evaluated accordingly to a similar formula

iv) To perform mass balance over a finite element feed side:

$$N_{H_2 f}(i) = N_{H_2 f}(i-1) = J_{H_2}(i) \tag{5}$$

v) To perform a mass balance over the same finite element at permeate side:

$$N_{H_2 s}(i) = N_{H_2 s}(i-1) = J_{H_2}(i) \qquad \text{(co-current case)} \tag{6}$$

$$N_{H_2 s}(i) = N_{H_2 s}(i+1) = J_{H_2}(i) \qquad \text{(counter-current case)} \tag{7}$$

vi) To compare protium and tritium flow rates obtained in both sides of the membrane NH2f(i) and NH2s(i) with the ones found in the previous iteration and used in the step 1 of the calculation. Then define a set of new flow rates and iterate until convergence is reached.

2.3 MODELING RESULTS

The simulation has been aimed at studying the effect of the main operating parameters such as the temperature (300 and 400°C) and the flow rate of protium which is fed counter-currently in the shell side (10, 50 and 100 Ncm^3 min^{-1}). The analysis has been performed by using 20 finite elements

with lumen and shell pressure of 900 and 50 mbar, respectively.

When operating at temperature of 300°C with protium feed flow rate (shell side) of 50 $Ncm^3\ min^{-1}$, the profiles of the flow rates along the reactor axis are reported in logarithmic graphs in the figures 1 and 2 for the lumen and shell side, respectively. In the lumen side (fig.1) the tritiated water and tritium concentration decreases along the reactor axis while the protium increases as a consequence of the permeation from the shell side. Due to the high dilution, the water flow rate remains quite constant (in logarithmic scale). In the shell side (fig.2) where the gas stream is counter-currently fed (then it moves from left to right in the graph) the tritium concentration increases due to the permeation from the lumen side where the tritium is formed by the reaction (1).

The decontamination capability of the membrane reactor is given by a detritiation factor which takes into account the tritium transferred from the tritiated water (lumen side) to the gas phase into the shell side. Especially, two detritiation factors can be defined:

$$DF1 = \frac{HTO_{in}}{HTO_{out}} \tag{8}$$

$$DF2 = \frac{HTO_{in}}{HTO_{out} + HT_{out}} \tag{9}$$

where HTOin and HTOout are the moles of HTO entering and leaving the membrane reactor, respectively, and HTout are the moles of HT leaving the lumen side of the membrane reactor.

The effects of temperature and protium feed flow rate can be considered through the values of DF1 and DF2, see the Tables I and II. The increase of the temperature affects very slightly the detritiation capability: moving from 300 to 400°C the tritium activity of the tritiated water leaving the reactor increases a little (i.e., DF1 decreases) while a larger amount of tritium leaves the reactor in gaseous form (DF2 increases). Furthermore, from this analysis it is evident that low values of the protium feed flow rate (10 $Ncm^3\ min^{-1}$) strongly reduce the decontamination factors.

The effect of the membrane tube wall thickness has been also considered. Accordingly to the formula (4) the hydrogen isotopes permeation increases by reducing the tube wall thickness. Pd-Ag tubes of wall thickness 0.050 mm are produced by a diffusion and cold rolling technique: for such a tube the model analysis has shown an increase of the detritiation factors by about 5 times with respect to the case of wall thickness 0.150 mm. In fact, for a membrane tube of wall thickness 0.050 mm, diameter 10 mm and length 500 mm operating at 300°C with protium feed flow rate of 50 Ncm3 min-1 the values 58.7 and 30.6 for DF1 and DF2 have been assessed, respectively.

3. MEMBRANE REACTOR DESIGN

In the proposed new design the permeator tube is assembled into the module in a “finger-like” configuration and the heating of the tube (300-400°C) is obtained by direct resistive heating. The innovative design mainly consists of the use of a special device applied to the closed end of the permeator tube. It is a bi-metallic spring which has two functions:

- to apply a traction force to the permeator tube in order to avoid its contact with the inner walls of the membrane module and to prevent deformations due to thermal and hydrogenation cycles,
- to ensure the electrical continuity between the closed end of the permeator tube and the outside of the membrane module thus allowing the heating of the tube via Joule effect.

In the designed reactor, this bi-metallic spring is composed by:

- an Inconel wire able to guarantee the required mechanical performances even at the working temperature (i.e. capable to apply to the permeator tube a traction force sufficient to drive it along a straight direction during its thermal/hydrogenation expansion),
- a silver wire, to ensure the electric current passage with a low electrical resistance in order to avoid the heating of the spring.

In order to avoid excessive deformations of the permeator tube (also considering "creep" phenomena which may occur at the operative temperature 300-400°C), the applied tensile strength has been set at 5% of the Ultimate Tensile Strength (UTS) referred at the temperature of 400°C. The UTS value of 280MPa has been calculated from literature data [13], for the Pd-Ag alloy (23-25% wt. of Ag). Accordingly, the traction force value (calculated at about 5% of UTS) for a permeator tube with wall thickness of 0.150 is 60N.

Direct ohmic heating has the advantage to heat only the membrane by reducing the heating of the process streams and saving power. Furthermore, the traction force applied by the Inconel spring avoid the bending of the long (500 mm) Pd-Ag tube thus ensuring the membrane long life.

CONCLUSIONS

A Pd-Ag tubular membrane reactor has been developed for a process of detritiation of soft housekeeping wastes. A model analysis based on a finite element method permitted to simulate the behavior of the reactor: effect of the main operating parameters such temperature and feed flow rates have been studied. As a main result, the temperature effect in the range 300–400°C has been found very negligible while much more relevant is the influence of the protium feed flow rate (at 10Ncm^3 min^{-1} the detritiation capability gets insignificant). It has been verified that under the foreseen operating conditions (300°C, lumen side feed of 200 Ncm3 min-1 of helium with 10 % of water with tritium content of 1.11×10^8 Bq h^{-1}) the decontamination factor of the tritiated water is larger than 10 as required by the process specifications. Significant improvement of the detritiation capability can be obtained by the reducing the membrane tube wall thickness: at 300°C a Pd-Ag tube of wall thickness 0.050mm presents decontamination factors about 5 times higher than membrane tubes of wall thickness 0.150mm do.

A new design of a finger-like membrane reactor has been also presented: main characteristic are the direct ohmic heating of the Pd-Ag tube and the use of an Inconel spring for applying a traction force to the membrane.

Next work will consider the manufacturing of the innovative membrane reactor which will be tested at JET for decontaminating soft housekeeping wastes.

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Protium feed flow rate $Ncm^3\ min^{-1}$	300°C	400°C
10	1.98	1.79
50	13.3	12.1
100	19.1	18.4

Table I: DF1 values assessed versus temperature and protium feed flow rate.

Protium feed flow rate $Ncm^3\ min^{-1}$	300°C	400°C
10	≈1	≈1
50	5.85	5.99
100	8.46	9.23

Table II: DF2 values assessed versus temperature and protium feed flow rate.

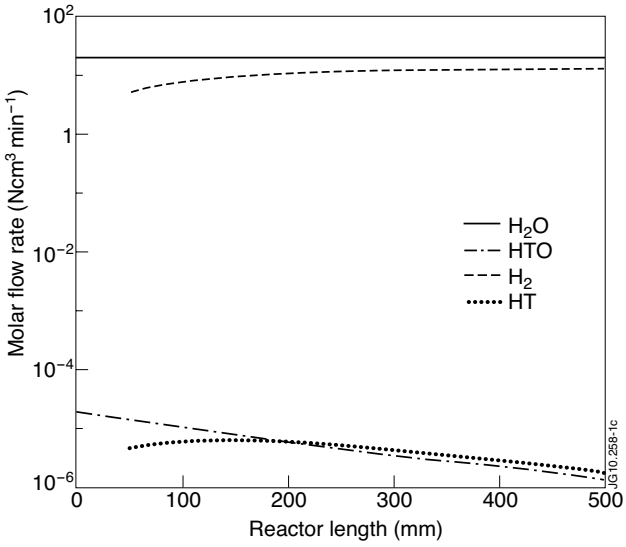

Figure 1: Flow rate along the reactor axis, lumen side: 300 °C, protium feed flow rate of 50 $Ncm^3\ min^{-1}$.

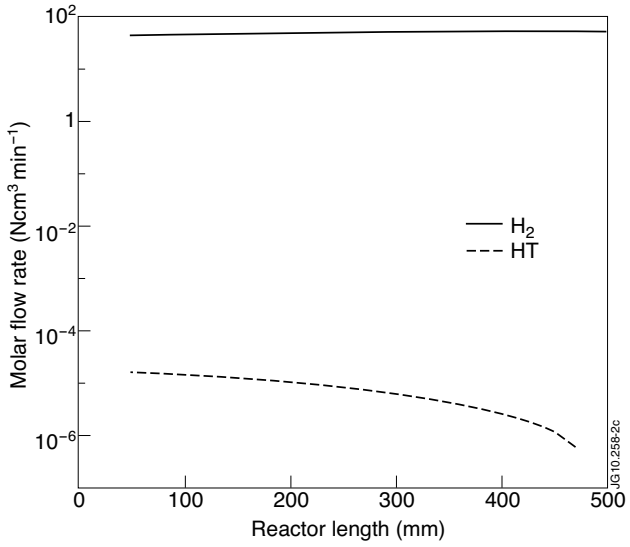

Figure 2: Flow rate along the reactor axis, (shell side: 300°C, protium feed flow rate of 50 $Ncm^3\ min^{-1}$.

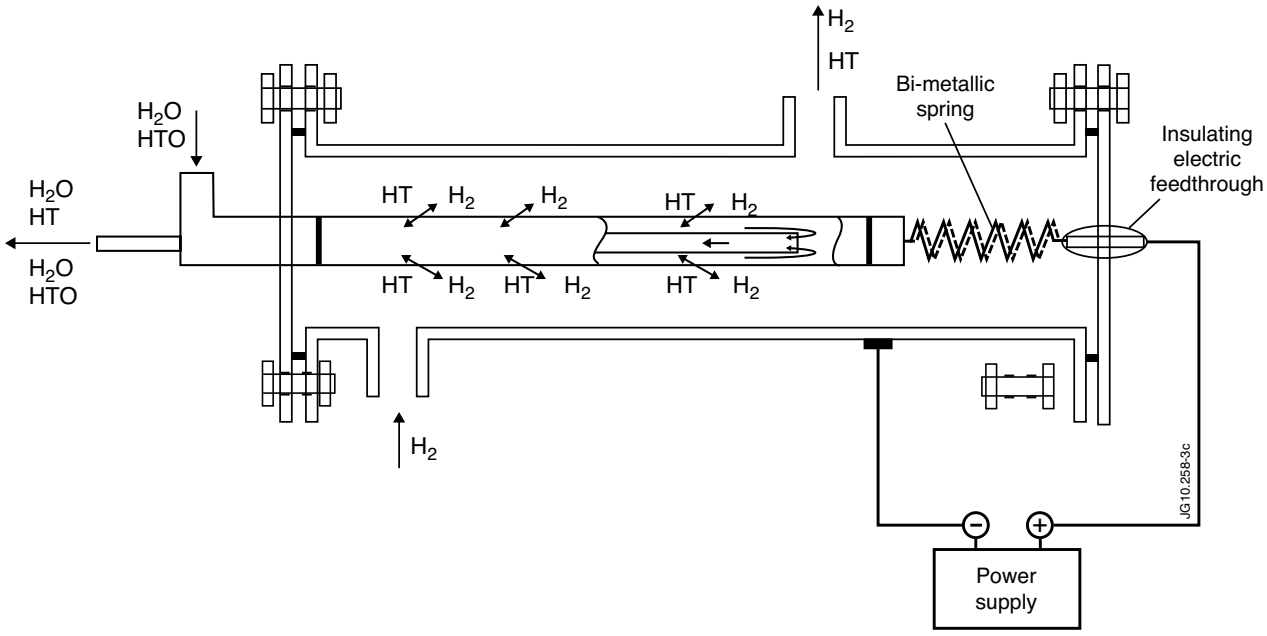

Figure 3: Scheme of the membrane reactor.