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Catalytic membrane reactor for tritium extraction system from He purge

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In the Helium Cooled Pebble Bed (HCPB) blanket concept, the produced tritium is recovered purging the breeder with helium at low pressure, thus a Tritium Extraction System (TES) is foreseen to separate the produced tritium (which contains impurities like water) from the helium gas purge. Several R&D activities are running in parallel to experimentally identify most promising TES technologies: particularly, Pd-based Membrane Reactors (MR) are under investigation because of their large hydrogen selectivity, continuous operation capability, reliability and compactness.

The construction and operation under DEMO relevant conditions (that presently foresee a He purge flow rate of about 10000 Nm^3/h and a H_2/He ratio of 0.1%) of a medium scale MR is scheduled for next year, while presently preliminary experiments on a small scale reactor are performed to identify most suitable operative conditions and catalyst materials.

This work presents the results of an experimental campaign carried out on a Pd-based membrane aimed at measuring the capability of this device in separating hydrogen from the helium. Many operative conditions have been investigated by considering different He/H_2 feed flow ratios, several lumen pressures and reactor temperatures. Moreover, the performances of a membrane reactor (composed of a Pd-Ag tube having a wall thickness of about 113 μm, length 500 mm and diameter 10 mm) in processing the water contained in the purge gas have been measured by using a commercial (Ni-based) catalyst. Two different reactions have been investigated: isotopic swamping and water gas shift. The presence of methane among of the water gas shift reaction indicates that a catalyst with higher selectivity is required.

Keywords: tritium technology, extraction system, membrane reactor.

1. Introduction

In future fusion machines, the required tritium has to be produced by the means of a breedering blanket. Such tritium together with the one not burned in the plasma has to be opportunely recovered and purified through dedicated systems which form the so-called Fuel Cycle (FC). Currently the FC comprises an inner and outer part. The inner part consists of the fuelling systems (gas puffing, pellet injection, etc.), the vacuum pumping systems (primary and rough pumping) and the tritium plant systems (tritium recovery, isotope separation, storage and delivery, water detritiation and atmosphere detritiation). The outer part includes the breeding blankets, their tritium extraction and recovery systems (TES) and their coolant purification systems (CPS) [1]. With regard to ITER, its operation should demonstrate the high reliability of the technologies used in the inner cycle, conversely tritium technologies of the outer cycle will be tested only at a small scale by considering the large difference between the tritium production between ITER Test Blanket Modules and DEMO blanket (about 3 order of magnitude) [2]. Therefore several technologies for tritium extraction from breeder are still under evaluation.

In case of a solid breeding blanket (Helium Cooled Pebble Bed, HCPB), helium at low pressure is used as purge gas to remove the tritium from the pebbles bed and carry it in the TES. In the past, several TES concepts have been proposed; most of them based on the combination of technologies such as cold traps, molecular sieve beds and Pd-Ag diffuser [3]. A main drawback of such processes is the non-continuous operation thus the high tritium inventory. Among the technologies able to guarantee the continuous operation of the TES, membranes cover a very important role. However, due to the very low tritium partial pressure in the purge gas, the possibility to feed the blanket gas directly to Pd-Ag diffuser is not practicable.

Recently a novel concept that uses membranes and catalytic membrane reactors, has been proposed by Demange et al [4]. This advanced solution relies on the combination of zeolite membranes for the pre-concentration stage and Pd-Ag diffuser and/or reactor for Q_2 extraction (Q=H, D and T). Demange et al. suggest several options for the pre-concentration stage (that produces a gas stream enriched in Q_2 and/or Q_2O) with zeolite membranes also considering the presence of pre-treatments such as preliminary collection of Q_2O or Q_2 oxidation to form Q_2O. In all cases, the Q_2 or Q_2O enriched gas stream has to be treated inside a Pd-Ag module downstream to the process for tritium extraction.

This paper describes the results of two experimental activities: in the first one, the ability of a Pd-Ag diffuser in hydrogen removal from helium has been measured at different He/H_2 feed flow ratios, while the second one reports the performance of a Pd-Ag membrane reactor

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(tubular Pd-Ag membrane filled with catalyst) in decontaminating tritiated water (simulated by using heavy water).

2. H_2 removal from He via Pd-Ag diffuser

2.1 Experimental

Pd-based membranes are selectively permeable to hydrogen isotopes. The permeability of this dense membrane is described by the Sieverts' law (Eq. 1) and the dependence of the permeability coefficient from the temperature is ruled by an Arrhenius-type behavior (Eq. 2).

$$Pe = \frac{J \quad t}{\left(\sqrt{p_{lumen}} \quad \sqrt{p_{shell}}\right)} \qquad (1)$$

$$Pe = Pe_0 e^{\ (E_a/RT)} \qquad (2)$$

Where Pe is the hydrogen permeability (mol m^{-1} s^{-1} $Pa^{-0.5}$), t the metal wall thickness (m), p_{lumen} and p_{shell} the hydrogen partial pressure inside (upstream) and outside (downstream) the membrane, Pe_0 the pre-exponential factor (mol m^{-1} s^{-1} $Pa^{-0.5}$, E_a the apparent activation energy (J mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T the absolute temperature (K).

In this activity, hydrogen removal tests have been performed by using a Pd-Ag (25% wt.) single tube having a wall thickness of 113 μm, length of 500 mm and diameter of 10 mm. The lumen side has been fed with a gas mixture containing helium and hydrogen while the permeated hydrogen has been collected in the shell side by vacuum pumping. The block diagram of the experimental set-up is reported in Figure 1, while a detailed description of the membrane module is illustrated in [5].

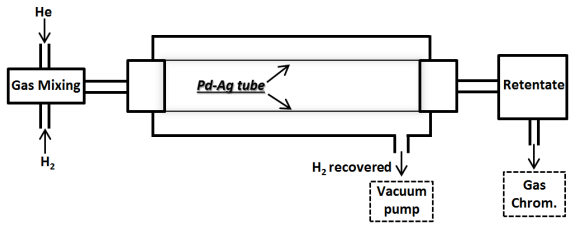

Fig. 1. Block diagram of the experimental set-up of hydrogen recovery tests.

He/H_2 feed flow rate ratio, lumen pressure and membrane temperature are the parameters varied during the tests (see Table 1). In order to operate at the desired He/H_2 feed ratio, the membrane was fed with the He and H_2 flow rates reported in Table 2.

Table 1. Operative conditions of the hydrogen removal tests.

Parameter	*Values*
He/H_2 feed flow rate ratio, a.u.	5, 10, 15, 20
lumen pressure, kPa	100, 200, 300, 500, 700
temperature, K	573, 623, 673,723

Table 2. He and H_2 flow rates used during the tests at several feed flow ratios.

He/H_2 feed flow ratio, a.u.	*He flow rate, L min^{-1}*	*H_2 flow rate, L min^{-1}*
5	0.45	9×10^{-2}
10	0.5	5×10^{-2}
15	0.45	3×10^{-2}
20	0.5	2.5×10^{-2}

A total of 80 tests have been performed each one having a duration of about 1 h. After each test, the leak tightness of the membrane has been checked by pressurizing the lumen with helium. Within the entire experimental campaign, none leak has been detected in the membrane module.

2.2 Results

A typical set of tests is performed by heating the membrane module at a certain temperature and feeding the lumen side with the proper He/H_2 feed flow ratio. Then, starting form 100 kPa, the lumen pressure is increased to 200, 300, 500 and 700 kPa. Figure 2 reports the permeated hydrogen flows for the tests at 623 K.

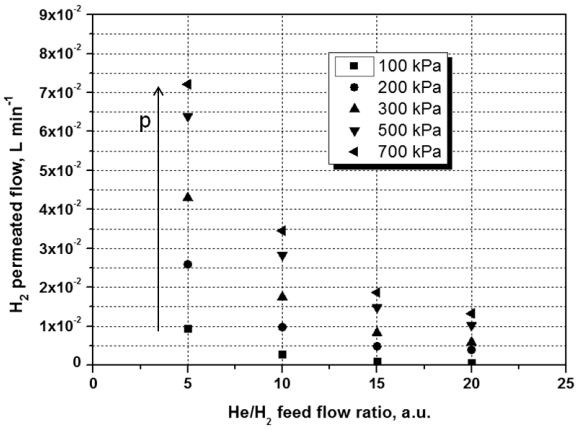

Fig. 2. Hydrogen permeated flow for tests at 623 K (lumen pressure few kPa).

The efficiency of the Pd-Ag diffuser in removing hydrogen from helium can be expressed by the ratio between the hydrogen flux entering the membrane lumen ($F_{H2,\,in}$) and the one collected in the shell side ($F_{H2,\,out}$).

$$= \frac{F_{H2,in}}{F_{H2,out}} \quad 100 \qquad (3)$$

To appreciate the effect of the operative conditions on the efficiency of the system, in the follow three different plots are reported. Figure 3 illustrates the efficiency as a function of the reactor temperature measured at different lumen pressures for a fixed He/H_2 feed flow ratio (He/H_2 = 15), Figure 4 provides the efficiency along several lumen pressure values of the tests performed at different feed flow rates and constant temperature (T = 623 K) and Figure 5 gives the efficiency along the He/H_2 feed flow ratios of tests at different reactor temperature and constant lumen pressure (few kPa).

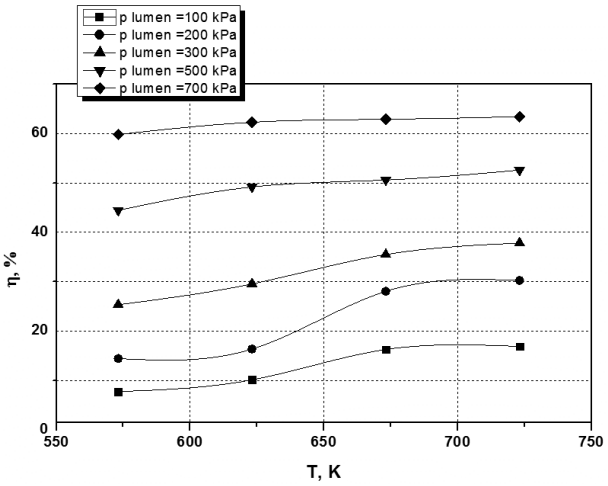

Fig. 3. Efficiency (η) of hydrogen removal tests for the He/H_2 feed flow rate ratio of 15 (lumen pressure at about few kPa).

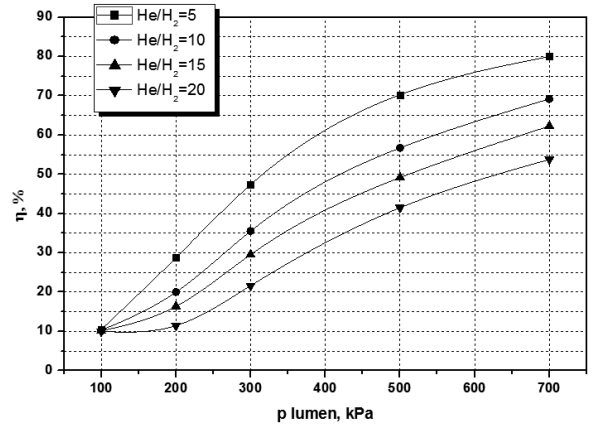

Fig. 4. Efficiency (η) of hydrogen removal tests along lumen pressure for several He/H_2 feed flow rate ratio at reactor temperature of 623 K (lumen pressure at about few kPa).

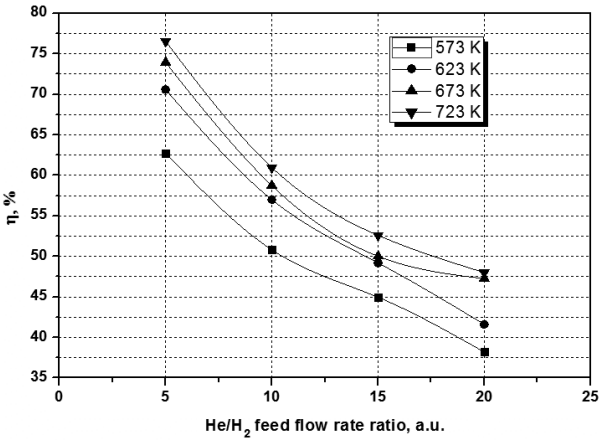

Fig. 5. Efficiency (η) of hydrogen removal tests along He/H_2 feed flow ratios for several reactor temperature at lumen pressure of 500 kPa (lumen pressure at about few kPa).

In agreement with equations 1 and 2, by increasing lumen pressure or reactor temperature, the efficiency of the system increases as well. The only singularity has been measured in the tests at 700 kPa where the efficiency reaches a plateau for temperature above 623 K. Another aspect that has to be highlighted is that for all the tests performed at lumen pressure of 100 and 200 kPa, the efficiency decreases along the time (see Fig. not reported) due to helium accumulation inside the membrane.

3. Water decontamination via Pd-Ag membrane reactor

3.1 Experimental

A Pd-Ag membrane reactor combines a Pd-Ag membrane with a catalyst; in this way permeation and chemical reaction can occur in the same device (more compact and more efficient). Decontamination of tritiated water via Pd-Ag membrane reactor can be achieved in several way. Particularly, this activity has studied two types of reactions: Isotopic Swamping, IS (3), and Water Gas Shift, WGS (4).

$$D_2O + H_2 \quad H_2O + D_2 \qquad (3)$$

$$D_2O + CO \quad CO_2 + D_2 \qquad (4)$$

The block diagram of the experimental set-up used for IS and WGS is illustrated in Figure 6.

In case of IS, a stream of D_2O coming from a vaporizer and mixed with nitrogen is fed into the lumen of the reactor, while in the shell side a pure H_2 stream is counter-currently sent. The Pd-Ag membrane allows the selective permeation of hydrogen isotopes from the shell to the lumen side (and vice versa). The catalyst inside the membrane enhances the isotopic swamping, so that the permeated hydrogen can replace the deuterium in the water. The released deuterium permeates into the shell side of the reactor, it is measured via a mass flow meter and recovered downstream of the process. At the outlet of the membrane reactor, the water is collected in a cold trap operated at 270 K and analyzed via infrared spectroscopy to assess the amount of deuterium present in such a water.

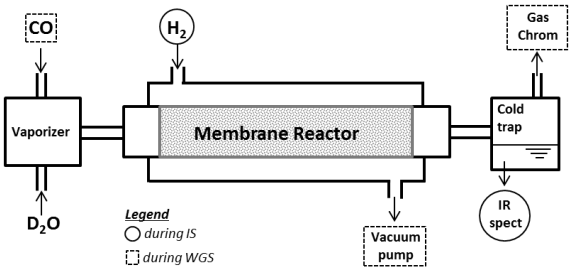

Fig. 6. Block diagram of the experimental set-up used for IS and WGS tests.

With regard to the WGS, the reactants, CO and D_2O vapor have been fed inside the tubular membrane reactor; the D_2 produced by reaction (4) and permeated through the membrane has been collected in the shell side by vacuum pumping and measured via a mass flow meter. At the outlet of the membrane reactor, the non-permeated stream (retentate) has been driven inside a cold trap for water condensation; the gas stream leaving

the cold trap has been sent to a gas chromatograph (Agilent 7820) for gas composition analysis. The efficiency of the processes has been evaluated in term of Decontamination Factor (DF), defined as:

$$DF = \frac{D_2O_{in}}{D_2O_{out}} \qquad (5)$$

Where D_2O_{in} and D_2O_{out} are the heavy water moles entering and leaving the lumen side of the membrane, respectively. More precisely, in case of WGS the D_2O_{out} directly refers to the non-reacted heavy water while in case of the IS, D_2O_{out} refers to the amount of O-D bond contained in the HDO collected downstream of the process and analyzed by infrared spectroscopy.

3.2 Results

The IS tests have been performed by feeding the lumen side with 10 g h^{-1} of D_2O at a pressure of 150 kPa, reactor temperatures of 573 and 673 K and shell pressure of 100 kPa. A parameter that significantly affects the reactor performances is the H_2/D_2O_{in} sweep ratio (i.e. the ratio between the protium moles fed in shell side and the water moles fed in the lumen). Therefore, several sweep ratio values (between 0.5 and 2) have been investigated. Table 3 reports the operating conditions and results of four different IS experiments.

Table 3. IS results in terms of DF values (D_2O_{in}=10 g h^{-1}, p_{lumen} and p_{shell} about 150 kPa and 100 kPa, respectively).

	Operative conditions		*Results*
	H_2/D_2O_{in}	*T, K*	*DF*
Ex 1	1	573	1.64
Ex 2	1	673	1.82
Ex 3	2	573	2.52
Ex 4	½	573	1.38

By increasing the hydrogen sweep flow rate, the decontamination capability of the membrane reactor is larger: however, higher is the hydrogen sweep flow rate and higher is the workload of the isotopic separation units downstream the membrane unit. Therefore, suitable H_2/D_2O_{in} values arise from a compromise, that should take into account the overall design of the detritiation system.

Table 4. WGS results in terms of DF values (D_2O_{in}=10 g h^{-1} and D_2O_{in}:CO = 1).

	Operative conditions		*Results*
	P_{lumen}, *kPa*	*T, K*	*DF*
Ex 5	100	600	1.84
Ex 6	100	700	2.06
Ex 7	100	740	2.41
Ex 8	150	600	1.85
Ex 9	150	700	2.12
Ex 10	150	740	2.48

The WGS tests have been carried out by feeding 10 g h^{-1} of D_2O inside the reactor with a stoichiometric amount of CO. During the tests, the reactor temperature has been varied between 600 and 740 K, while the investigated lumen pressure range was between 100 and 150 kPa. Table 4 collects the operating conditions and results of different WGS experiments.

As regard the possible side-reactions, mainly the formation of methane could significantly reduce the decontamination ability of the process. The CO methanation (6) consumes CO and Q_2 to form CQ_4 while the Sabatier's reaction (7) produces additional CQ_4 from CO_2 and Q_2 (where Q=H, D and T) [6].

$$CO + 3Q_2 \quad CQ_4 + Q_2O \qquad (6)$$

$$CO_2 + 4Q_2 \quad CQ_4 + 2Q_2O \qquad (7)$$

In this view, important information occurs from the gas composition analysis of the gas stream leaving the membrane reactor (retentate). Figure 7 shows the results in term of $D_{2,recovered}$ (left y-axis) and the gas composition in the retentate stream (right y-axis) versus the reactor temperature for the experiment carried out at p_{lumen} of 100 kPa. Particularly, the $D_{2,recovered}$ is the ratio between the D_2 moles permeated in the shell side and the D_2O moles feeding the reactor. Similar analysis (not showed) has been carried out for the tests at 150 kPa, where none significant difference has been detected.

The GC analysis reveals that in the retentate stream, the amount of CO_2 is always around 80%, D_2 is negligible and CO is present in small amounts (1-2 %). This means that most of the CO fed has reacted and all the D_2 produced via the reaction (4) has permeated through the membrane. However, the presence of methane reveals that part of the CO fed has not been consumed by the WGS reaction but by the methanation (6).

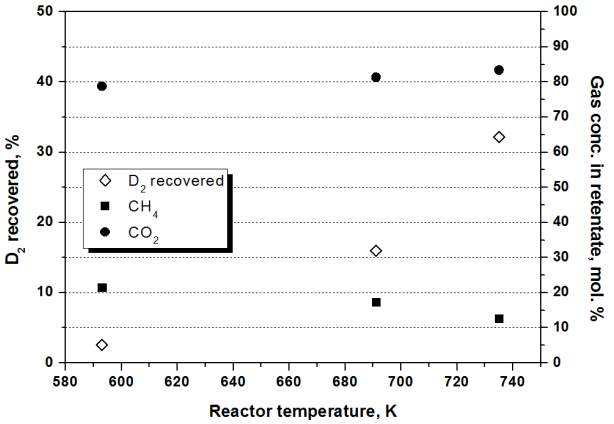

Fig. 7. $D_{2,recovered}$ values and retentate composition for the WGS tests at different reactor temperature (D_2O_{in}=10 g h^{-1}, D_2O/CO=1, p_{lumen} of 100 kPa).

4. Conclusion

Tritium produced inside the blanket of future fusion machines has to be recovered via a dedicated tritium extraction system. With regard the solid breeder, HCPB,

most of the proposed tritium extraction processes relies on the use of Pd-Ag diffuser and membrane reactor.

This activity reports the results of two experimental campaigns. In the first, the performance of a Pd-Ag diffuser has been measured in a wide range of operative conditions. The reported results provide very useful information that can be used either for the dimensioning of the membrane itself and also for more general considerations like the assessment of suitable pre-concentration factor. Moreover, it has been observed that to achieve a reasonable and constant hydrogen removal efficiency value, especially at high He/H_2 feed ratio, the Pd-Ag diffuser should work at lumen pressure higher than 300 kPa to avoid helium accumulation. The second experimental activity investigates the ability of a Pd-Ag membrane reactor in decontaminating tritiated water (simulated by using heavy water) via two different reactions: isotopic swamping and water gas shift. From the tests, both processes exhibited modest decontaminations factors. The efficiency of the IS is significantly favored by high H_2 sweep ratios and slightly promoted by the increase of the temperature however, higher is the hydrogen sweep flow rate and higher will be the workload of the isotopic separation units downstream the membrane unit Although the experiments have not showed significant differences, in principle the WGS process is much more efficient than the IS as demonstrated in previous activity by means on simulation [7]. Therefore the development of highly selective catalyst for the WGS able to reduce the formation of methane is expected to increase significantly the decontamination capability of this process. This aspect is the topic of the next tests in which high selective catalysts for WGS will be tested.

Acknowledgments

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