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# Recent achievements of the Pd-Ag membrane technologies in tritium extraction system applications

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Main expertise of the Membrane Laboratory of ENEA Frascati is related to the study and development of Pd-based membrane technologies (both permeators and catalytic reactors), which are one of the reference processes in the fuel cycle of nuclear fusion reactors. Principal characteristics of Pd-based membranes are infinitive hydrogen selectivity, elevated hydrogen permeability, continuous operation, modularity, reduced cost and low energy consumption.
In the last few years, the ENEA laboratory has realized two experimental facilities for testing single and multi-tube Pd-Ag membrane modules. Several experimental and simulation activities have been carried out to investigate the possible application of these technologies in the tritium extraction system of the solid breeder blanket concept.
First the paper illustrates the proposal (back-up solution) of a tritium extraction system for HCPB based on membrane technologies and, then, provides the most significant results of water decontamination and He-$H_2$ obtained in two different facilities. Main difference among the two facilities is the number of Pd-Ag tubes installed.
Water decontamination tests have been performed by exploring the effect of different catalysts. The results obtained in the water gas shift tests are discussed in terms of reactor performances and methane production. During the He-$H_2$ permeation tests several operating conditions have been investigated, mainly the effect of the He-$H_2$ feed ratio gives an interesting and unique view of the membrane module performances.

Keywords: tritium extraction system, Pd-Ag membrane, catalytic membrane reactor

## 1. Introduction

In a fusion reactor ultra-pure hydrogen isotopes are "fused" to produce energy according with the follow reaction.

$$D + T \rightarrow {}^4He + n + 17.586\ MeV \quad (1)$$

ITER, the largest fusion experiment currently under construction in Cadarache, has a fusion power of 500 MW, meaning that it has to fuse about $1.78 \times 10^{20}$ T nuclei $s^{-1}$ corresponding to 76 g $d^{-1}$ of tritium. DEMO, the future fusion reactor still at the design phase, has a fusion power of 2.7 GW and will require about 412 g $d^{-1}$ of tritium [1-2]. These few numbers highlight the importance of developing efficient and reliable technologies for the recovery and purification of hydrogen isotopes (mainly tritium). In fact, inside a fusion reactor tritium has to be recovered from several sources (mainly plasma exhaust and breeding blanket, but also neutral beam, pellet injection, etc.) and purified before its reuse in the machine. The systems and technologies dedicated to this scope form the so-called fuel cycle which is composed of an inner and outer part [3-5]. The inner part is responsible for the processing of the hydrogen isotopes coming from the plasma exhaust since only a small fraction of the D-T mixture is burnt, while the outer part has the duty to recover the tritium produced inside the breeding blanket: a Li-based material surrounding the plasma chamber able to "breed" tritium (according with reactions 2 and 3) in order to guarantee the self-sufficiency of the reactor.

$$^7Li + n \rightarrow {}^4He + T + n - 2.47\ MeV \quad (2)$$

$$^6Li + n \rightarrow {}^4He + T + 4.78\ MeV \quad (3)$$

Especially in view of DEMO, there is a large R&D program to investigate most suitable blanket options [6] and related Tritium Extraction Systems (TES) [7]. Particularly, the Helium Cooled Pebble Bed (HCPB) is one of the blanket concepts under investigation; it uses helium as coolant, lithium orthosilicate as tritium breeder and beryllium as neutron multiplier material [8].

This work illustrates most recent achievements of the ENEA membrane laboratory related to the development of a TES for HCPB blanket based on membrane technologies.

## 2. Tritium Extraction System in HCPB: the back-up solution

In the HCPB the produced tritium is recovered with a He purge gas at 0.15-0.20 MPa with an addition of 0.1wt.% of $H_2$ (or $D_2$) as doping agent. In order to

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separate tritium from the purge stream. Two major difficulties have to be taken into account: i) tritium is present only as traces (ppm level) in a huge helium flow and ii) tritium is present in both molecular and oxidized (water) form. Table 1 summarizes the main characteristics of the purge stream leaving the HCPB blanket [8-9].

Table 1. Characteristics of the He purge stream leaving the blanket.

| | Value | Unit |
|---|---|---|
| He purge flow rate | 10000 | $Nm^3\ h^{-1}$ |
| Helium pressure | 0.2 | MPa |
| Average He temperature | 450 | °C |
| $H_2$ swamping gas amount | 0.1 | wt. % |
| T production | 252 | $g\ d^{-1}$ |
| Pulse | 8640 | s |
| Dwell | 2400 | s |

The reference process to recover tritium from the described gas stream relies on the trapping of the $Q_2O$ (Q=H, D and T) on reactive molecular sieve beds and on the adsorption of $Q_2$ over molecular sieve beds at cryogenic temperatures. The so-trapped tritium is recovered afterwards during the regeneration phase: the reactive molecular sieve beds are flushed with $D_2$ which replace the tritium in the water (isotopic exchange), while the tritium blocked in the cryogenic molecular sieve beds is released by increasing the temperature. A great advantage of this process is related to its readiness level, even if activities for the development of optimal sieving materials and for the definition of the $Q_2$ adsorption/desorption behavior are still ongoing [10]. On the other hand, the use of isotopic exchange reactions and of the regeneration phase result in two principal drawbacks: 1) the load of the subsequent isotopic separation systems and 2) the increase of the tritium inventory in the extraction and recovery system of the HCPB blanket due to the non-continuous operation of the process.

In this view, the development of a membrane-based system as back-up solution remains of great interest because of the numerous advantages of such technology: mainly continuous operation, modularity and contained energy consumption. ENEA Frascati and the TLK of KIT are working on a process (see Figure 1) that uses zeolite and Pd-Ag membranes cascade for $Q_2$ separation coupled with a Pd-Ag membrane reactor for $Q_2O$ decontamination.

According with such proposal, the gas stream leaving the HCPB blanket enters a cold trap where $Q_2O$ is removed. At the moment this step is necessary since data about the performances and selectivity of the ceramic and the metallic membranes are known for binary (He-$Q_2$) mixture but still unknown for ternary (He-$Q_2$-$Q_2O$) mixture [11-13]. During cold trap regeneration, the $Q_2O$ is released and processed inside a Pd-Ag membrane reactor. The $Q_2O$ can be processed by performing two types of reaction: isotopic swamping (IS) and water gas shift (WGS), see Eqs. 4 and 5 respectively.

$$Q_2O + H_2 \rightarrow H_2O + Q_2 \quad (4)$$

$$Q_2O + CO \rightarrow CO_2 + Q_2 \quad (5)$$

It is important to notice that the IS reaction provides good performances only when the swamping ratio (i.e. $H_2/Q_2O$) is higher than 1 [14]. This means that the $Q_2$ in the products will contain a large amount of $H_2$ that has to be separated downstream through the isotopic separation system (ISS). On the contrary the $Q_2$ produced in the WGS only comes from the $Q_2O$ fed in the reactor, thus the $H_2$ content, and the subsequent load on the ISS, is largely reduced. The remain He-$Q_2$ stream is routed inside the zeolite membranes cascade in which part of the helium is separated. Finally the gas stream enters the Pg-Ag membranes where $Q_2$ is recovered and sent to the tritium plant. Regarding the two membrane-based processes it is important to recall some of their peculiarities. The zeolite material cannot guarantee very high $Q_2$ selectivity while the Pd-Ag membranes are permeable only to $Q_2$. On the other hand, zeolite membranes can operate also when the $Q_2$ partial pressure is very low (as in the purge stream leaving the HCPB blanket) while, in such conditions, the operation of the Pd-Ag membranes is not possible.

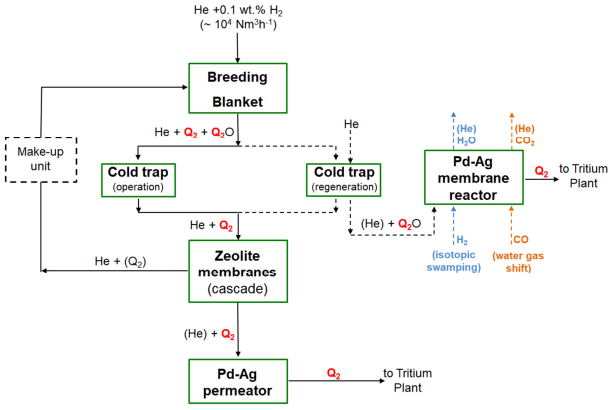


Fig. 1. Block diagram of the back-up solution based on membrane technologies for the tritium extraction and removal (TER) in the HCPB blanket.

In order to explore the feasibility of the back-up solution, two facilities have been constructed in ENEA Frascati. The first, called HyFraMe, has been mainly used to perform water decontamination tests, while the second, named MeSMeR has been completed at the end of 2017 and used for He-$H_2$ permeation tests. With regard the zeolite membrane cascade, the activity is developed by the TLK of KIT.

## 3. Water decontamination tests

Water decontamination tests have been carried out in the HyFraMe facility that hosts a Pd-Ag membrane reactor (single tube). The facility is equipped with several mass flow controllers and pressure transducers to measure the gas and liquid mass flow rates entering and leaving the system and the pressure in the lumen and

shell side of the reactor. The reactor heating is performed via Joule effect; a detailed description of the experimental set-up and of the reactor is provided in [12] and [15].

The tests have been carried out by using $D_2O$ instead of tritiated water. Both IS and WGS tests have been performed with several catalysts (the follow reports only the results of the WGS). In general, compare with the WGS, the IS tests exhibit lower performances in terms of decontamination factor (DF), moreover the $H_2$ amount contained in the produced $Q_2$ is much higher (i.e. higher load for the isotopic system afterwards). On the contrary main drawback of the WGS reaction is the formation of $CQ_4$ as byproduct. In this direction several WGS tests have been performed to measure either the DF and the $CQ_4$ amount in the retentate by varying experimental conditions and also type of catalysts. Table 2 and 3 illustrate the experimental conditions and the main characteristics of the catalysts used during the WGS tests.

Table 2. Operating conditions investigated during WGS tests.

| Parameter | Values |
|---|---|
| $H_2O$ feed flow rate, mol $h^{-1}$ | 0.25 |
| CO feed flow rate, mol $h^{-1}$ | 0.25 |
| Reactor temperature, K | 573-623 |
| Lumen pressure, kPa | 200-300-400-500 |
| Shell pressure, kPa | ~ 1 |

Table 3. Characteristics of the catalysts used in WGS tests.

| Composition | | |
|---|---|---|
| CAT 1 | CAT 2 | CAT 3 |
| Pt(0.62 wt.%), $SiO_2$ (56.63 wt.%), $La_2O_3$ (43.06%) | Pt 1 wt.% on alumina support | Cu based catalyst |
| **Supplier** | | |
| CAT 1 | CAT 2 | CAT 3 |
| Non Commercial catalyst [16] | Commercial catalyst (Produced by BASF) | Commercial Catalyst (produced by HiFuel ®) |

### 3.1 Results

Main results of the WGS tests are illustrated in Figs. 2 and 3. Particularly Fig. 2 provides the DF (see Eq. 6) for each catalyst at several lumen pressures and reactor temperatures, while Fig. 3 gives the amount of methane detected in the retentate (i.e. gas stream leaving the reactor lumen) from the gas chromatographer (GC).

$$DF = \frac{D_2 \text{ in shell}}{D_2 \text{ in } D_2O \text{ fed}} \times 100 \qquad (6)$$

With regard the non-commercial Pt-based catalyst (CAT 1) and the commercial Cu-based catalyst (CAT 3) both exhibit very good methane selectivity (in most of the cases the GC did not detected the presence of methane in the retentate). Of course the performances of CAT 1 are always higher than the ones of CAT 3, but one has to consider that also the cost of CAT 1 (since it is not commercial) is much higher than CAT 3. By comparing the results of the two commercial catalysts, it is evident that the DFs achieved with CAT2 are higher than the ones with CAT 3. However during the tests with CAT 2 some methane has been observed in the retentate, especially when the reactor was operated at 400 kPa.

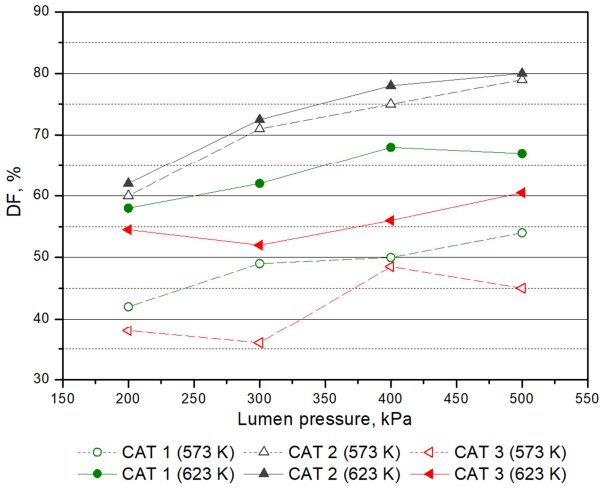


Fig. 2. Efficiency of the WGS tests vs. lumen pressure.

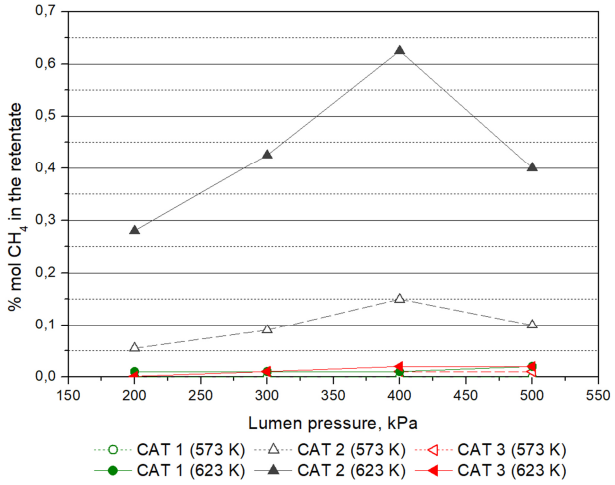


Fig. 3. Methane produced during the WGS tests vs. lumen pressure.

## 4. He-$H_2$ permeation tests

As previously introduced, the Membrane Laboratory of ENEA Frascati currently hosts two experimental facilities, named HyFraMe and MeSMeR, which main difference consists in the number of Pd-Ag membrane tubes installed: the first has only one tube while the second has a membrane module containing 10 tubes in parallel (total surface area of 0.16 $m^2$ and average thickness of 116 µm). He-$H_2$ permeation tests have been carried out in both facilities; the follow describes only the activity performed in MeSMeR whose picture is given in Fig. 4. Table 4 summarizes the parameters varied during the permeation tests.


Fig. 4. Picture of the MeSMeR facility.

Table 4. Parameters varied during the permeation tests.

| Parameter | Values |
|---|---|
| Total feed flow rate, $Nm^3\ h^{-1}$ | 0.12-0.24-0.36-0.6 |
| $He/H_2$ feed ratio | 1-5-10-20 |
| Reactor temperature, K | 573-623-673-723 |
| Lumen pressure, kPa | 300-400-500-600 |

### 4.1 Results

Figure 5 provides an overview of the results obtained in the permeation tests at 623 K for different feed flow rates. The efficiency (%) and the $\Delta P_{H_2}$ ($Pa^{0.5}$) are calculated according with Eqs. 7 and 8.

$$Efficiency = \frac{H_{2,lumen}}{H_{2,shell}} \times 100 \quad (7)$$

$$\Delta P_{H_2} = \sqrt{P_{H_2 lumen}} - \sqrt{P_{H_2 shell}} \quad (8)$$

Where $H_{2,lumen}$ and $H_{2,shell}$ ($Nm^3h^{-1}$) are the hydrogen feed flow rates sent to the lumen and collected in the shell side respectively, while $P_{H2lumen}$ and $P_{H2\ shell}$ (Pa) are the hydrogen partial pressures in the lumen and shell side.

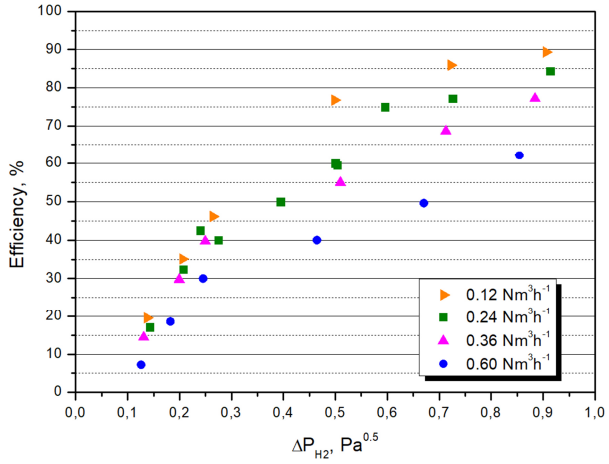


Fig. 5. Permeation efficiency vs. $\Delta P_{H_2}$ of the experiments performed at 623 K.

It is evident that the efficiency increases by increasing the $\Delta P_{H_2}$ and decreases by increasing the total feed flow rate. It seems also that there is a different trend between the results obtained with $\Delta P_{H_2}$ < 0.3-0.4 $Pa^{0.5}$ and the ones above such values. This aspect will be better investigated during future experiments.

## 5. Conclusion

The work illustrates some results of the experimental activities conducted in ENEA Frascati. Water decontamination tests gave the possibility to identify suitable catalyst materials: keeping the absence of methane as major requirement and considering also the availability/cost of the catalyst, CAT3 appears as best candidate. He-$H_2$ permeation tests highlight the importance of the feed flow rate on the separation efficiency.

The entire activity represents an important step to demonstrate the feasibility of a TES for HCPB based on membrane technologies. Of course additional activities are required to evaluate the dimensions and the cost of the entire back-up proposal.

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