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# Experimental assessment of palladium-silver membrane for isotope separation, rebalancing and protium removal

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ABSTRACT

The isotope separation, isotope rebalancing, and protium removal are critical functionalities for the fuel cycle of a fusion machine. Nowadays, cryogenic distillation and thermal cycling temperature swing absorption are considered the reference technologies for these tasks, but they are both characterized by high tritium inventory. In the past, the palladium-silver membranes were considered as an option with reduced inventory although some challenges were identified, mainly related to the efficiency of the separation process. This work aims at experimentally investigate the capabilities of this technology for the above-mentioned functionalities in the improved HyFraMe facility at ENEA Frascati laboratories. To do this, the Pd-Ag membrane is preliminary characterized with pure protium and pure deuterium and the permeability and the breakthrough curves are obtained for both the isotopes. After that, the isotope separation tests are performed with different protium-deuterium mixtures. The isotope separation remains a challenging task for the palladium-silver membrane, mainly due to the low efficiency of the process. On the contrary, looking at the isotope rebalancing and protium removal functions, the results obtained in the present campaign are in line with the requirements of a typical fusion machine. Both the functions can be fulfilled with a single and compact permeator which allow to reduce tritium inventory, encumbrances and energy consumption.

## 1. Introduction

Deuterium and tritium are the most promising fuel mixture for the future nuclear fusion machines. Regardless the concepts i.e., magnetic confinement (e.g., Tokamak and Stellarator) and inertial fusion, all the devices have the need of a fuel cycle able to continuously fuel the machine with a pure deuterium-tritium mixture at the desired composition. Therefore, inside the fuel cycle, systems devoted to hydrogen isotopes purification, separation, rebalancing and protium removal must be considered and, with the aim of minimizing tritium inventory, technologies with reduced volume and continuous operation must be preferred.

Purification of the hydrogen isotopes from impurities is the step in which the fusion product, helium, and other seeding gases, like neon, argon, xenon, etc., are separated from hydrogen. Given their high hydrogen permeability and infinite selectivity, membrane-based technologies, such as palladium-silver permeators and/or metal foil pumps, are commonly considered for such process [1,2]. The separation of the different hydrogen isotopes is a function always necessary inside the fuel cycle, but the load on the isotope separation system can largely vary according to the required flexibility in the composition of the D-T mixture and to the presence of a neutral beam injection as method to heat the plasma [3–5]. Cryogenic distillation, exploiting the small difference in the boiling temperatures of the three isotopes, is the reference method for the isotopes separation system [6,7]. To avoid unnecessary hydrogen isotope separation, functions devoted to isotope rebalancing and protium removal are introduced with the aim of restoring the desired D-T composition (i.e., 50–50) and removing the excess of protium. In fact, isotope rebalancing process is a convenient way to directly reuse the unburned fuel that leaves the machine partially disproportionated [8]. Finally, in a deuterium-tritium machine protium acts as a poison for the fusion reaction, contributing to the dilution of the fuel. Although with a low rate, it is continuously produced in the reaction chamber due, for example, to secondary fusion reactions or outgassing from the walls. An excessive increase of protium content in the fuel would lead to the shutdown of the fusion reaction, thus its removal is mandatory [9,10]. Referring to the fuel cycle architecture of the EU-DEMO [11], the above-mentioned tasks are accomplished by the

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system named Isotope Rebalancing and Protium Removal (IRPR) which relies on the thermal cycling temperature swing absorption based on anticyclical operation of two absorption columns with reversed isotopic effects [8].

All the mentioned technologies present clear capabilities to fulfil their task, but cryogenic distillation and temperature swing adsorption are characterized by a common drawback that is the immobilization of tritium and thus, the high tritium inventory. Tritium inventory is a key driver for the development of the fuel cycle of fusion machine both for the safety operation of the plant and for the issue related to the tritium availability for its start-up. The reduction of the whole tritium inventory has recently led the review of the EU-DEMO fuel cycle architecture and the selection of reference technologies within it [11].

To pursuit in this direction, this work experimentally investigates the isotope effect of hydrogen permeation through palladium silver membranes. The intent is to exploit the isotope effects of the permeation process and, benefiting of the continuous operation and the low tritium inventory, evaluate the applicability of this membrane technology in systems dedicated to the isotope separation, isotope rebalancing and protium removal. Regarding the hydrogen isotope separation function, Luo et al. investigated the feasibility of a palladium membrane separator cascade. They measured an H-D separation factor between 1.4 and 1.8 in a temperature range between 473 and 673 K and, based on these results, estimated that the palladium membrane separator cascade concept is both reasonable and practicable for large-scale hydrogen isotope separation [12]. On the other hand, Glugla et al. carried out a numerical study concluding that separation of hydrogen isotopes with Pd-based membranes is not convenient due to the low separation efficiency and the high impact on the auxiliaries (i.e., pumping unit and process control system) [13]. This study poses criticalities in the application of this technology for separation purposes, but the assessment of this process may change moving from the separation task towards the isotope rebalancing and protium removal functionalities. In these cases, the required efficiency of the process is lowered, and the design concerns relaxed making the palladium-silver membrane a possible candidate to replace the temperature swing absorption or to establish a pre-enrichment phase before the cryogenic distillation.

## 2. Experimental apparatus and methodology

The ENEA Frascati laboratories have experience in the development and characterization of palladium-silver membranes. Several research were conducted to optimize the membrane materials [14], to study the joining of this thin-walled tubes with stainless-steel components [15], to characterize the hydrogen purification capabilities of a single-tube permeator [1] and to test the scalability of this unit [16].

Fig. 1 shows the HyFraMe (Hydrogen Frascati Membrane) facility [1], updated to investigate the hydrogen isotopic effect on the permeation. The core of the facility is the permeator, a single-tube palladium-silver membrane (Ag 25 wt. %), and the main improvement concerns the installation of a mass spectrometer, the HPR-20 R&D by Hiden Analytical, for the measurement of the gas composition. The facility can work with protium, deuterium and inert gases such as helium, nitrogen, and argon.

The schematic view of the HyFraMe facility is presented in Fig. 2. The membrane consists of a 500 mm long tube (grey tube in Fig. 2) with an outer diameter of 10.16 mm and a thickness of 0.15 mm. It is fed with a gas mixture prepared with three Mass Flow Controllers (MFC01, MFC02, and MFC03 in Fig. 2) connected to the pure gas cylinders. The MFCs, belonging to the 1179B and to the GE50A series by MKS Instruments, cover the range between 1 and 5000 ml min$^{-1}$. The desired gas mixture passes through the pre-heating feed line (red in Fig. 2) and enters the membrane via a 1 mm stainless steel feeding pipe (yellow in Fig. 2). Permeation is a temperature activated process thus the membrane exploits direct resistive heating as presented by Tosti et al. [17]. Once in contact with the membrane walls, the throughput is divided in two streams, namely the permeate and the retentate. Hydrogen isotopes permeating through the palladium-silver membrane compose the permeate stream that is collected inside the shell and evacuated via the scroll pump. On the retentate line, the throughput is measured by a Mass Flow Meter (MFM01, 1179B series by MKS Instruments) and the pressure regulator allows to fix the desired pressure providing, along with the scroll pump on the permeate side, the driving force to the permeation. Before exhausting, a small fraction of the flow (around 20 ml min$^{-1}$) is sampled by the mass spectrometer to analyze the mixture composition. Once calibrated with a proper certified mixture, representative of the test conditions, the mass spectrometer ensures a measurement with accuracy of around 5 ppb. To do this, a calibration line via the MFC04 (1179B series by MKS Instruments) is foreseen.

The instrumentation setup is completed with thermocouples (TCs) and pressure transducers (PTs). Three thermocouples allow the temperature control of the membrane, being installed in contact with the outside wall of the palladium-silver tube. Further thermocouples are installed along the feed line and on the outside wall of the permeator shell. Thermocouples type-K are adopted with an accuracy of ±1.5 K. Upstream the permeation, the pressure is monitored in the feed line and in the retentate line (PT01 and PT02, respectively) with Baratron® Type 722B by MKS Instruments (accuracy: ±0.5 % of reading), whereas on the permeate side the use of three different PTs allows the measurement of the full range pressure: a Baratron® Type 722B by MKS Instruments (PT03, accuracy: ±0.5 % of reading), a CMR 261 by Pfeiffer Vacuum (PT04, accuracy: ±0.2 % of reading), and a Baratron® Type 127AA by

**Fig. 1.** HyFraMe: the experimental apparatus.

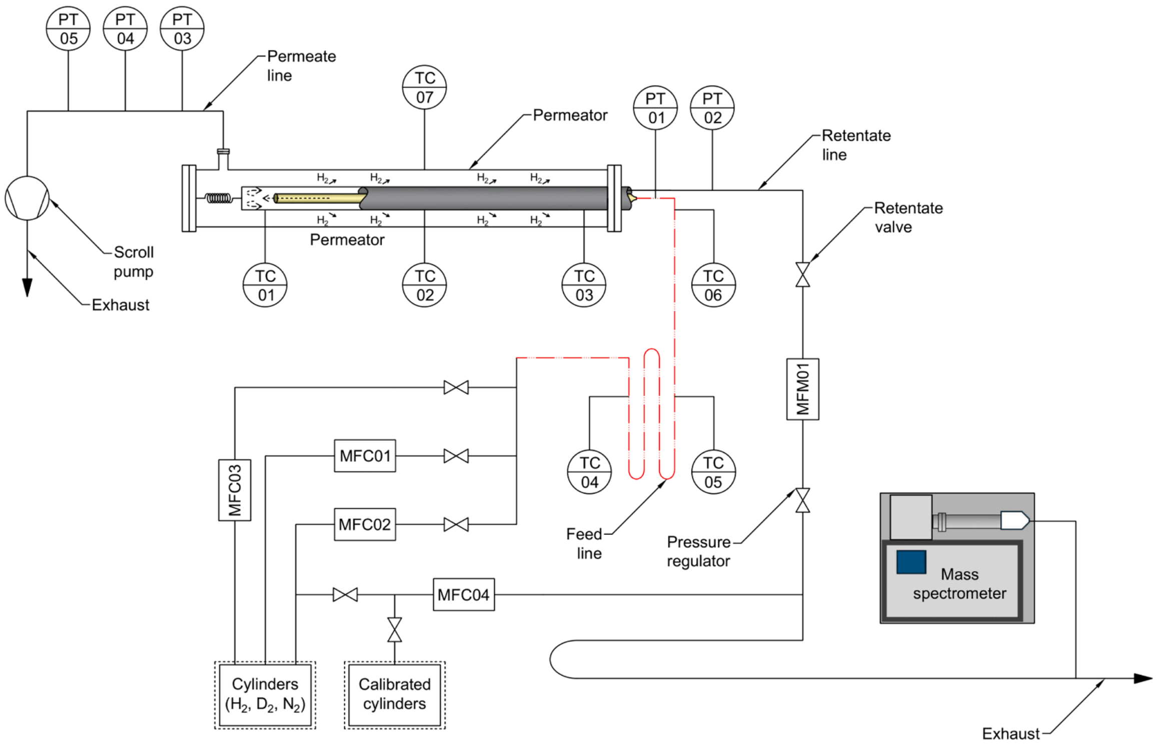


**Fig. 2.** Schematic view of the HyFraMe facility: components and instrumentation.

MKS Instruments (PT05, accuracy: ±0.25 % of reading).

The experimental campaign is divided into three phases: the permeability test, the breakthrough measurement, and the isotope separation test. The procedures and the methodologies adopted are presented in the following sub-sections where the word “hydrogen” is used to identify any mixture of protium and deuterium.

### 2.1. *Permeability test*

According to the permeation theory [13,18] and considering the geometrical characteristic of the membrane and the typical operational conditions adopted in the HyFraMe facility (i.e., retentate side pressure higher than 1 bar), the permeation process through the palladium-silver membrane can be expressed by the Richardson equation [19]:

$$J = \frac{Pe}{s}\left(p_{high}^{0.5} - p_{low}^{0.5}\right) \quad (1)$$

where $J$ is the hydrogen permeation flux (mol m$^{-2}$ s$^{-1}$), $s$ is the membrane thickness (m), $p$ is the hydrogen partial pressure (Pa) and the subscripts *high* and *low* represent the high-pressure side and the low-pressure side of the membrane i.e., the retentate and the permeate side. The proportional coefficient is the permeability ($Pe$), expressed in mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$, which is defined as the product of the diffusivity and the solubility. The permeability, characteristic of the membrane material binary system and the permeating gas, is commonly expressed by an Arrhenius-type behaviour:

$$Pe = Pe_0 \cdot e^{-\frac{E_a}{R \cdot T}} \quad (2)$$

where $\mathrm{Pe}_0$ is the pre-exponential factor (mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$), $E_a$ is the apparent activation energy (J mol$^{-1}$), $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ is the membrane temperature (K).

The objective of the permeability test is to experimentally evaluate the $\mathrm{Pe}_0$ and the $E_a$ for both the protium and the deuterium through the palladium-silver membrane. To do this, the retentate valve is kept close (see Fig. 2) and the membrane is fed with pure hydrogen (protium or deuterium depending on the test) so that all the hydrogen is forced to permeate through the membrane and is evacuated via the scroll pump. Once the steady state is reached, the $Pe$ can be calculated with Eq. (1) from the measured values of pressure in the permeate and retentate side and of the feed flow rate. The measurement is repeated for different temperatures (i.e., 573 K, 623 K, and 673 K) and the $\mathrm{Pe}_0$ and the $E_a$ are derived from the linear regression of the experimental data.

### 2.2. *Breakthrough measurement*

Depending on the magnitude of the feed throughput, the permeation process can fall in two operative regions. For low feed flow rate, almost all the hydrogen permeates and the retentate gas is mainly composed of the remaining impurities. For high feed flow rate, the impurities and the part of hydrogen which does not permeate are evacuated via the retentate line and the hydrogen content in the retentate gas raises with the increase of the feed throughput. A critical feed flow rate can be individuated for which the hydrogen content in the retentate starts to be observed, this is usually indicated as the breakthrough condition.

Most of the applications (i.e., the hydrogen purification) involves the use of the membrane below the breakthrough conditions, ensuring a maximum yield in terms of pure hydrogen separation. Above the breakthrough, the permeator is operated beyond its capacity leading to an undesired loss of hydrogen via the retentate. Nevertheless, conditions above the breakthrough can be explored to assess the isotopic separation capability of the membrane. It is well known that heavier isotopes present lower permeability [20], meaning that the permeate gas is enriched in the lighter component and the retentate gas in the heavier component [13].

The objective of the breakthrough measurement is to identify the two permeation regions of the HyFraMe permeator for protium and for deuterium, and to individuate the best conditions for the isotope separation test. To do this, the retentate valve is kept open and the membrane is fed with a proper gas mixture consisting alternatively in protium and nitrogen or in deuterium and nitrogen. Especially below the breakthrough, the presence of nitrogen ensures a sufficient flow rate to the pressure regulator (see Fig. 2) needed to control the pressure inside the permeator. The mixture is prepared with the multiple MFCs imposing the set point for the pure gases and the retentate flow rate is measured with the MFM01. The scope is to correlate the hydrogen throughput at the retentate, calculated subtracting the nitrogen feed flow rate from the MFM01 measurement, with the hydrogen feed throughput and to compare the breakthrough curves of protium and deuterium.

### 2.3. Isotope separation test

The isotope separation test aims at investigating the capability of the palladium-silver membrane for different purposes: i) to separate protium and deuterium, ii) to rebalance their content in the mixture, and iii) to remove traces of protium.

The feed flow conditions are derived from the breakthrough measurements and different isotopic $H_2$-$D_2$ compositions are considered i.e., 99–1, 75–25, 50–50, 25–75, and 1–99. Among these, all the compositions are relevant for the separation and the rebalancing tasks whereas only the 1–99 is of interest for the protium removal since 1 % is the order of magnitude of protium expected in the plasma exhaust. The feed mixture contains the desired H-D composition plus a fixed relative amount of nitrogen to allow the pressure regulation in the retentate line. The retentate valve is kept open, the flow rate measured by the MFM01 and a portion of it is sampled by the mass spectrometer to provide a quantitative measurement of the molar composition.

To assess the performance of the membrane for separation and rebalancing purposes, two figures of merit are selected, namely the enrichment ratio (*ER*) and the yield (*Y*), defined as:

$$ER = \frac{\left(\frac{D}{H}\right)_r}{\left(\frac{D}{H}\right)_f} \tag{3}$$

$$Y = \frac{(D+H)_r}{(D+H)_f} \tag{4}$$

where *D* and *H* are deuterium and protium atomic molar flow rates (mol $s^{-1}$) and the subscripts *f* and *r* stand for the feed and retentate lines. The throughputs of each isotope in the retentate line are calculated from the MFM01 measurement and from the analysis of the mass spectrometer. Looking at a separation or rebalancing process, the heaviest isotope is enriched in the retentate line, and this explain the choice of this throughput in the definition of ER and Y. Furthermore, it is not enough to guarantee a certain enrichment in one isotope (the heaviest in this case) but it is also important to enrich a consistent amount of the throughput and to consider these two aspects, simultaneously. For this reason, the *ER* gives the information about the enrichment of the deuterium in the retentate line, and the *Y* quantify the recovery ratio in term of flow rates. Based on the specific goal of the process, an optimum between these two parameters can be found.

For protium removal purpose, being 1 % the protium content in the feed flow rate the *ER* loses relevance since the variation of the atomic fraction between deuterium and protium is too small. In this case, the *ER* is replaced by the Protium Removal ratio (*PR*), defined as:

$$PR = 1 - \frac{H_r}{H_f} \tag{5}$$

The *PR* quantifies the capability of the membrane to remove protium from the retentate line and must be considered with the *Y*, simultaneously.

All the above-mentioned parameters require the knowledge of the isotopologues composition in the retentate to calculate the atomic flow rates. In presence of protium and deuterium the possible hydrogen isotopologues are $H_2$, $D_2$ and HD, whose reference equilibrium is:

$$H_2 + D_2 \leftrightarrow 2HD \tag{6}$$

The corresponding equilibrium constant $K_{HD}$, defined as:

$$K_{HD} = \frac{[HD]^2}{[H_2][D_2]} \tag{7}$$

can be calculated as function of the absolute temperature *T* with Eq. (8):

$$K_{HD} = K_{HD,0} e^{\frac{C_{h,HD}}{T}} \tag{8}$$

where $K_{HD,0}$ and $C_{h,HD}$ assumes the values of 4.207 and −75.316 K, respectively [21].

The quantitative analysis of the mass spectrometer implies the calibration of the instrument with respect to the compounds to be detected. For this reason, a direct quantitative measurement of the HD is not possible since the mass spectrometer is calibrated with certified mixture containing $N_2$, $H_2$, and $D_2$. However, under the assumption that $N_2$, $H_2$, $D_2$, and HD are the only compounds present in the retentate line (such an assumption is preliminary verified with a qualitative measurement with the mass spectrometer), the HD throughput can be calculated by knowing the nitrogen feed flow, the measurement of the retentate total throughput (MFM01), and the quantitative analysis of the mass spectrometer. This latter is performed on specific compounds requested by the user. In this case, the instrument is calibrated for $N_2$, $H_2$, and $D_2$ and thus, each molar fraction (*mf*) is calculated as:

$$mf_{N2} = \frac{p_{N2}}{p_{N2} + p_{H2} + p_{D2}} \tag{9}$$

$$mf_{H2} = \frac{p_{H2}}{p_{N2} + p_{H2} + p_{D2}} \tag{10}$$

$$mf_{D2} = \frac{p_{D2}}{p_{N2} + p_{H2} + p_{D2}} \tag{11}$$

where *p* is the partial pressure and the compound is specified by the subscript. It is worth noting that the molar fractions are calculated referred to the sum of the partial pressure of $N_2$, $H_2$, and $D_2$, not referred to the total pressure that includes also $p_{HD}$. Knowing the nitrogen throughput at the retentate ($\Gamma_{N2}$, it is equal to the nitrogen feed flow rate due to the infinitive selectivity to hydrogen of the palladium-silver membrane), the sum of the throughput of $N_2$, $H_2$, and $D_2$ ($\Gamma_{N2,H2,D2}$) is given by:

$$\Gamma_{N2,H2,D2} = \frac{\Gamma_{N2}}{mf_{N2}} \tag{12}$$

and the HD flow rate ($\Gamma_{HD}$) is calculated as:

$$\Gamma_{HD} = \Gamma_{MFM01} - \Gamma_{N2,H2,D2} \tag{13}$$

where $\Gamma_{MFM01}$ is the total throughput at the retentate measured by MFM01.

Such an approach has a limitation related to the MFC and MFM accuracy. In particular, the methodology is not able to provide reliable HD quantification when one or more hydrogen isotopes are present only in traces in the retentate mixture since the uncertainty in the calculated value is higher than the absolute feed throughput of that element.

## 3. Experimental results

### 3.1. Permeability test

The permeability data of protium and deuterium for the palladium-silver membrane are presented in the Arrhenius plot in Fig. 3 comparing values obtained in this work and data of Serra et al. [20]. The comparison provides a satisfactory agreement with the literature data both for the slope of the fits and for the relative difference between

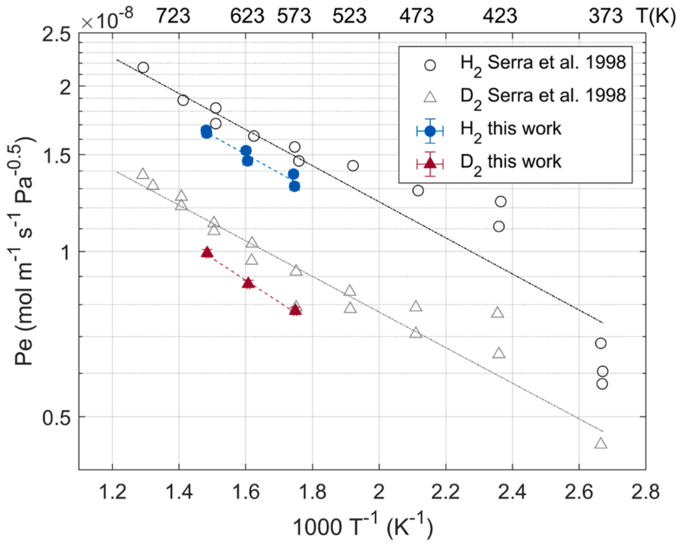


**Fig. 3.** Arrhenius plot of the protium and deuterium permeabilities for palladium-silver membrane.

protium and deuterium permeability. In this regard, Serra et al. found a permeability ratio between protium and deuterium in the range of 1.55 and 1.58 which is a bit smaller than the values obtained in this work, in the range of 1.66±0.1 and 1.73±0.1. The permeability data of this work are slightly lower than those obtained by Serra et al. and a possible explanation can be related to the used membrane. Serra et al. performed the experimental campaign with a well characterized and well-polished small sample, consisting of a disc 7.82 mm in diameter and 0.198 mm in thickness for which the temperature can be accurately controlled with a resistance furnace [20] whereas in this work a preliminary polishing procedure is not carried out and the membrane is subjected to a reducing environment before the experiment in order to remove oxides on the surface. Furthermore, the direct resistive heating does not allow a uniform temperature along the membrane. These can lead to the discrepancy observed in Fig. 3 that, in any case, can be considered acceptable.

The pre-exponential factor and the apparent activation energy of the protium and deuterium permeability derived from the Arrhenius fit (see Fig. 3) are collected in Table 1 along with other literature data. A general good agreement is observed in the comparison.

### 3.2. *Breakthrough measurement*

The operative conditions of the breakthrough experiments are summarized in Table 2. The parameters are kept as much as possible unvaried for protium and deuterium although the scroll pump exhibits a higher pumping speed for deuterium determining a slightly lower pressure in the permeate side compared to the case of protium. Nevertheless, being the permeate pressure two order of magnitude lower than the retentate pressure and considering Eq. (1), the effect of this difference can be considered negligible. Regarding the feed flow rate, the higher throughput for the case of deuterium is lower than the case of protium since in the first case the breakthrough is expected earlier due to the lower permeability.

**Table 1**

The pre-exponential factor and the apparent activation energy for the protium and deuterium permeability: comparison between the present results and literature data.

| | $Pe_0$ (mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$) | $E_a$ (J mol$^{-1}$) | Reference |
|---|---|---|---|
| $H_2$ | $5.20\ 10^{-8} \pm 7.31\ 10^{-9}$ | 6444.51 ± 724.81 | This work |
| | $5.58\ 10^{-8}$ | 6304.00 | Serra et al. [20] |
| | $3.85\ 10^{-8}$ | 1370.00 | Yoshida et al. [22] |
| | $2.45\ 10^{-8}$ | 3332 | Narcisi et al. [1] |
| $D_2$ | $3.94\ 10^{-8} \pm 3.92\ 10^{-9}$ | 7744.16 ± 512.36 | This work |
| | $3.43\ 10^{-8}$ | 6156 | Serra et al. [20] |
| | $2.52\ 10^{-8}$ | 1470 | Yoshida et al. [22] |
| | $5.03\ 10^{-8} \pm 4.00\ 10^{-9}$ | 10,700 ± 400 | Fuerst and Taylor [23] |

**Table 2**

Boundary conditions of the breakthrough experiments.

| Parameter | Unit | Value | |
|---|---|---|---|
| | | $H_2$ | $D_2$ |
| Average membrane temperature | K | 623 | 623 |
| Retentate pressure | bar | 1.35 | 1.35 |
| Permeate pressure | mbar | 40 | 15 |
| Total feed throughput | ml min$^{-1}$ | 200 – 1000 | 200 – 600 |
| Nitrogen mole fraction in the feed | – | 10 % | 10 % |

The breakthrough curves of protium and deuterium are reported in Fig. 4 where the flow rate of the specific hydrogen isotope in the retentate is presented as function of its feed throughput, alternatively for protium (blue circles) and deuterium (red triangles). To better visualize the breakthrough, the plot does not contain the nitrogen amount in the feed and retentate flows.

The plot shows an anticipated bleed in the retentate for the case of deuterium. The breakthrough occurs for a value of deuterium feed between 270 and 360 ml min$^{-1}$ whereas for the case of protium it is observed between 450 and 540 ml min$^{-1}$. Starting from the results reported in Fig. 4, the experimental test matrix of the isotope separation test is derived. Temperatures, pressures, and nitrogen mole fraction are kept equal to the values reported in Table 2 whereas some considerations are made regarding the feed throughput. For a protium-deuterium mixture feed flow rate lower than 270 ml min$^{-1}$ a negligible hydrogen content is expected in the retentate line and, thus, the yield of the separation and rebalancing process should be too low. Concerning the deuterium enrichment in the retentate, the maximum is expected around the breakthrough of protium, where almost all the protium permeates and a considerable fraction of deuterium remains in the retentate (refer to the hydrogen feed throughput of 450 ml min$^{-1}$ in Fig. 4). Increasing the hydrogen feed flow, the enrichment ratio is expected to decrease due to a larger amount of protium in the retentate, but the yield of the process increases. Further considerations are made for the case of the protium removal. In this case, the hydrogen feed consists mainly of deuterium thus it is reasonable to believe that a considerable amount of protium still permeate for higher feed throughput and thus the yield of the process can be increased more than

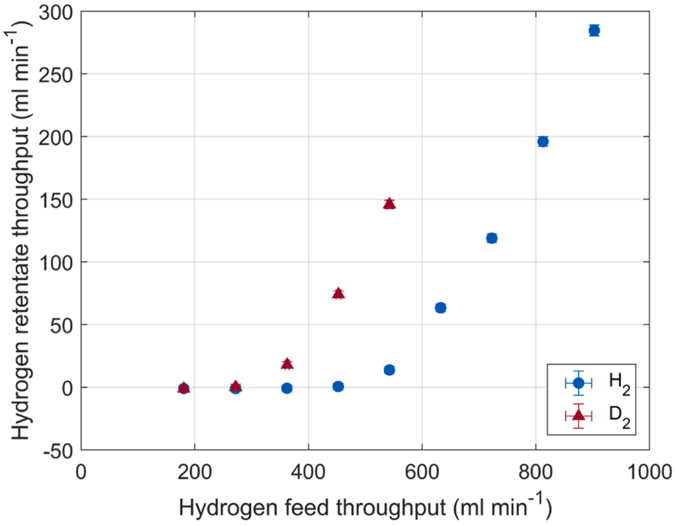


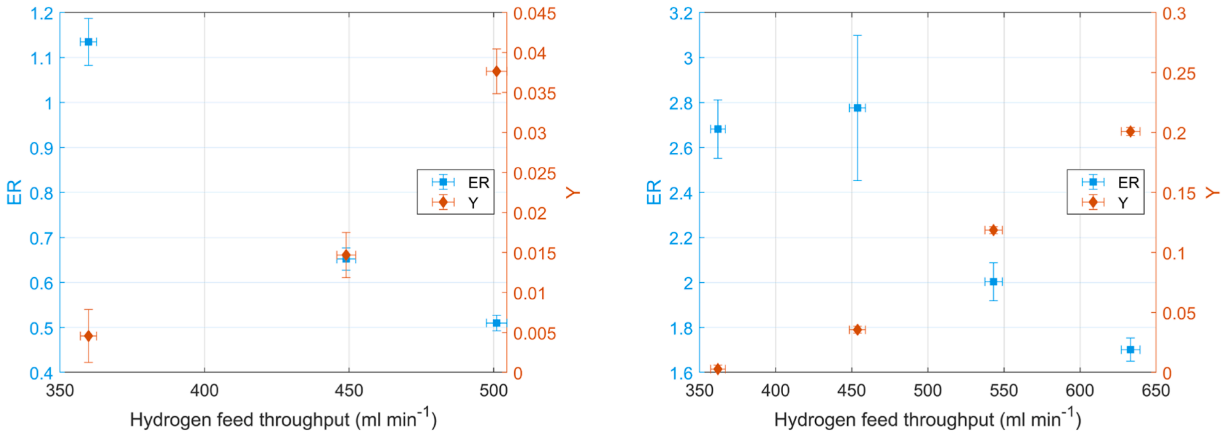
**Fig. 4.** Breakthrough curves of the protium and deuterium bleed in the retentate line.

the separation and rebalancing processes.

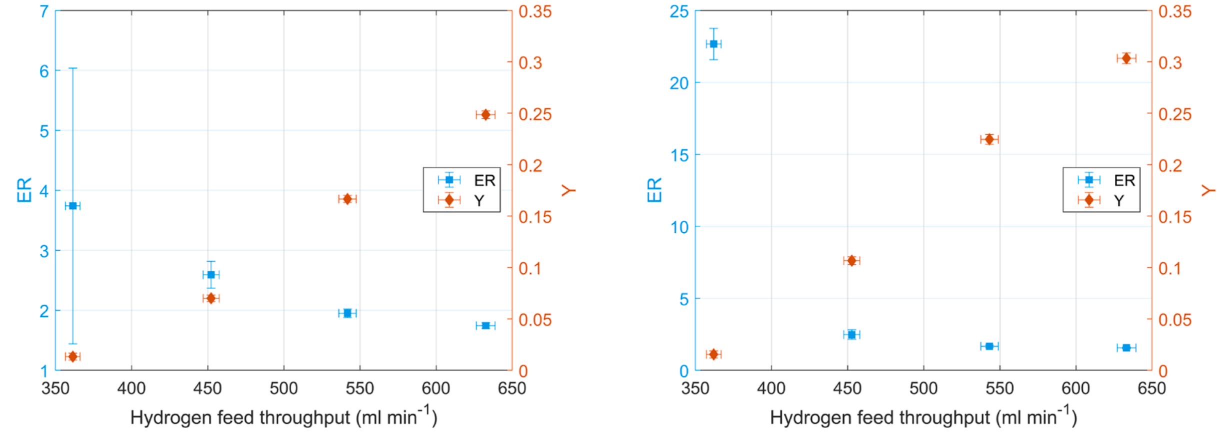
### 3.3. Isotope separation test

Based on the considerations made in the previous section, the separation and rebalancing experiments are performed with the total feed flow rate (hydrogen isotopes plus nitrogen) ranging between 400 and 700 ml min$^{-1}$ whereas the protium removal experiments are extended up to 3900 ml min$^{-1}$. Isotopic compositions and HD evaluation procedure are the same as reported in Section 2.3, the *ER* and the *Y* are evaluated including the contribution of HD formation, except for the 99–1 and the 1–99 cases. The results obtained with the presence of nitrogen, needed to regulate pressure, poses potential inconsistencies with real application scenarios where it is not present. As a consequence, the hydrogen partial pressure and thus, the permeation driving force, will be reduced but the isotopic effect over the permeation, namely the topic of the present paper, will not be affected.

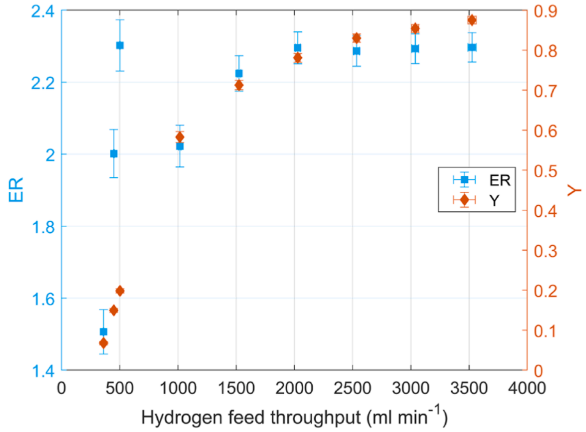
Fig. 5 shows, for each composition, the superposition of the *ER* and the *Y* at the retentate, plotted versus the total hydrogen (protium plus deuterium) feed flow rate. The composition with the highest protium content is presented in Fig. 5(a). As expected, the *ER* decreases when the feed flow rate rises, but for throughputs higher than 400 ml min$^{-1}$ a



(a) H-D: 99-1 (b) H-D: 75-25



(c) H-D: 50-50 (d) H-D: 25-75



(e) H-D: 1-99

**Fig. 5.** Superposition of the enrichment ratio and the yield plotted versus the hydrogen feed throughput for different protium-deuterium molar fractions.

deuterium dilution (i.e., *ER* <1) is observed in the retentate. This could seem inconsistent with the breakthrough measurement since for higher feed throughputs the deuterium permeation is expected to reduce more than the protium. Nevertheless, the low deuterium content in the feed may lead to transport phenomena that could move away from the permeability theory, considering that the permeation surface remains oversized for deuterium. Therefore, the increase of feed throughput may lead to a higher protium bleed in the retentate while keeping unvaried deuterium contribution. In addition, in this case the HD contribution in the retentate is not considered, due to the abovementioned limitations in the measurement and calculation Due to its abundance, this contribution can be neglected for protium, but it could be relevant for deuterium and thus, the ER could remain higher than unity also for higher flow rates. Further investigations are need and, for this reason, the maximum feed flow rate is limited to 600 ml min$^{-1}$ for the 99–1 case and only the lowest feed throughput can ensure a positive *ER* even if this is not of interest for engineering applications because of the extremely low *Y*.

The expected qualitative trends of the *ER* and the *Y* are obtained with the intermediate compositions i.e., 75–25, 50–50, and 25–75 (from Fig. 5(b) to (d)). The increase of the feed flow rate leads to the reduction of the *ER* and to the *Y* raise. The *ER* decreases to around 2 in each case whereas the maximum yield ranges between 0.2 (the 75–25 case) and 0.3 (the 25–75 case). The *ER* for the lowest feed flow is the main difference between these cases. It rises by decreasing the initial content of protium. Nevertheless, these points have a scarce engineering interest due to the low *Y* associated to them.

Finally, the composition with the highest deuterium content i.e., 1–99 (Fig. 5(e)), presents a quick *ER* increment at low flows and then stabilizes at around 2.3 whereas the *Y* continues to increase over the whole flow range. The *ER* profile could seem inconsistent with the breakthrough measurements, since a decrease would be expected by increasing the feed flow. The same evaluations done for the 99–1 composition can be extrapolated for this case, assuming protium as the less abundant element.

Although a remarkable *ER* is shown in Fig. 5(e), along with a very high *Y*, in absolute terms the separation and rebalancing processes for the 1–99 case is not so efficient. As a matter of fact, protium content in the hydrogen mixture passes from 1 % in the feed to 0.44 % in the retentate. Nevertheless, the assessment of the capabilities of the palladium silver membrane for the composition with the higher deuterium content changes if moving to the protium removal function. Fig. 6 shows, for the case 1–99, the superposition of the *PR* and the *Y* versus the hydrogen feed throughput. A very high *PR* is observed for the lowest flow rates, although it is associated to a low *Y* ranging between 0.05 and 0.2. The increase of the feed throughput leads to a considerable raise of the *Y* and to the reduction of the *PR* even if it keeps a considerable value. Depending on the requirements of the protium removal system, the palladium-silver membrane offers several operative points derived from an optimization of the two characteristic parameters.

Concerning the isotopologues composition in the retentate, the results of the analysis are reported in Fig. 7. For the cases 75–25, 50–50, and 25–75, the isotopologues compositions are shown as function of the hydrogen feed throughput and for each composition the coefficient of the reaction $K_c$, calculated with Eq. (7) using the concentration derived from the mass spectrometer analysis, is indicated. For sake of comparison, the equilibrium coefficient $K_{HD}$, calculated with Eq. (8), is equal to 3.73 at 623 K. In general, the presence of $H_2$ rises with the increase of the feed throughput and the opposite trend is observed for $D_2$. This behaviour agrees with the trend of *ER* and can be also used to explain the behaviours in Fig. 5(a) and (e). Concerning the HD, it represents always a not negligible part of the retentate and, comparing $K_c$ with $K_{HD}$, the Eq. (6) is slightly shifted towards the reacts and the products for the lowest and highest feed flow rate, respectively, except for the case 75–25 for which the $K_c$ approaches $K_{HD}$ for high feed throughputs.

## 4. Discussion

The experimental outcomes presented in Section 3.3 are used to evaluate the possibility to adopt palladium-silver membrane for isotope separation, isotope rebalancing, and protium removal functions. For this purpose, benefiting of the experimental data, the evaluation summarized in Table 3 can be derived relevant for a fusion power plant like the EU-DEMO.

In agreement with Glugla et al. (2006) [13], the permeator shows limited performances for the isotope separation task which shall be characterized by a very high *ER* and a reasonably *Y*. The plots presented in Fig. 5 show that the requirement on the two figures of merit is not simultaneously achievable, requiring an increase in the complexity of the system to fulfil the task. In fact, a cascade of permeators should be adopted to increase the *ER* and a nested structure of membranes, able to process both the retentate and the permeate at different level of concentrations, is necessary to allow better performance in terms of *Y*. Moreover, highest is the purity required of one of the isotopes, highest is the complexity of the nested permeators cascade. A system like this is

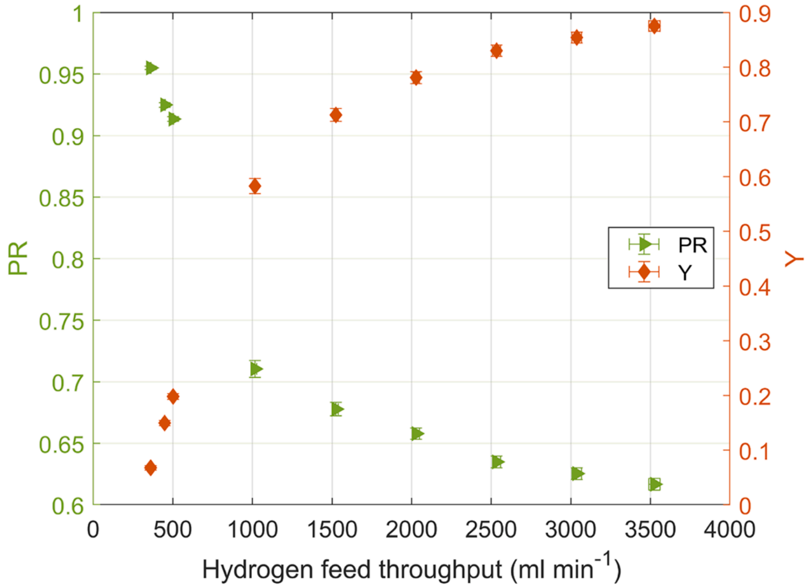
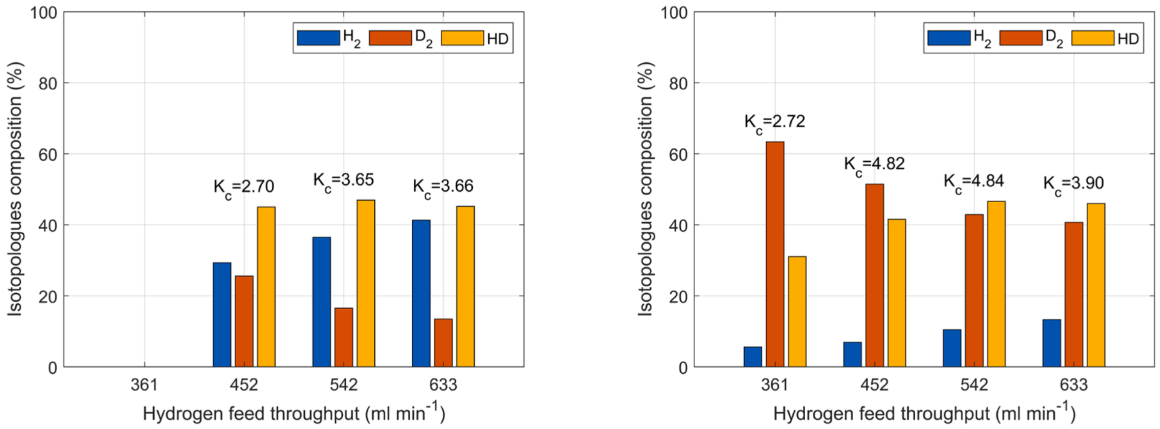
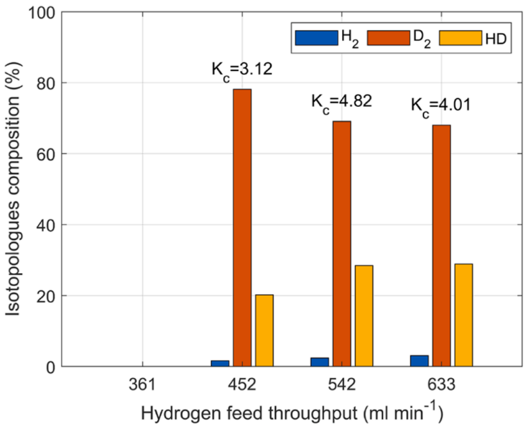


**Fig. 6.** Superposition of the protium removal ratio and the yield plotted versus the hydrogen feed throughput for the H-D composition of 1–99.



(a) H-D: 75-25 (b) H-D: 50-50



(c) H-D: 25-75

**Fig. 7.** Isotopologues composition in the retentate and calculated $K_c$ versus the hydrogen feed throughput for the cases 75–25, 50–50, and 25–75.

**Table 3**
Qualitative evaluation of Pd-Ag permeators applicability in different systems under EU-DEMO requirements.

| System | Reference Technology | Permeator Applicability | Performance Evaluation |
|---|---|---|---|
| Isotope Separation | Cryogenic Distillation | No | Very limited |
| Isotope Rebalancing | Thermal Cycling Adsorption Process | Feasible | Good |
| Protium Removal | Thermal Cycling Adsorption Process | Feasible | Very Good |

characterized by a low controllability and is challenging to be operated. Furthermore, a large palladium-silver surface would be required affecting the cost and the inventory would increase due to the multiple recycles in the nested permeators structure.

The performance assessment improves for the isotope rebalancing. The objective is to rebalance a portion of the feed flow rate to the isotopic composition of 50–50. Considering a feed mixture consisting of 75 % of deuterium and 25 % of protium and the results presented above, it can be estimated that six permeator stages are required, connected in series along the permeate side. This process allows the rebalance of a flow rate that is 11 % of the feed throughput. The outcome remains similar for the mixture with75 % of protium and 25 % of deuterium, for which it is possible to rebalance 9 % of the feed throughput. But the rebalance process is more efficient, and the goal can be achieved with two permeator stages connected in series along the retentate side. In both the cases, the feed throughput decreases along the stages allowing for increasingly more compact permeators. Looking at a system consisting of a single stage of permeators, the allowable concentrations in the feed are 56 % deuterium and 44 % protium, for the deuterium rich stream, and 34 % deuterium and 66 % protium, for the protium rich stream. Referring, as an example, to the EU-DEMO, the expected disproportion between the heavier and the lighter isotope (i.e., tritium and deuterium, respectively) is within 1 %, making the rebalancing task feasible and less challenging with a single permeator. The typical flow rate is around 6500 ml min$^{-1}$, that can be compatible with the operation of a multitube permeator module composed of ten membranes. A representative example of this component has been tested by Narcisi et al. (2024) for the hydrogen purification [16].

It is worth emphasizing that the rebalancing task can be beneficial also for a preliminary isotope separation stage to be coupled with the reference technology i.e., the cryogenic distillation. This latter suffers of the high tritium inventory, mainly due to the demanding separation efficiency which needs a high reflux ratio and thus, large column diameter. This process can benefit of a preliminary isotope separation stage which exploits a rough separation producing enriched streams to be sent in specific portions of the cryogenic columns.

Finally, the palladium-silver membrane shows interesting capabilities for the protium removal task. The results presented in Section 3.3 are in line with the requirements of a protium removal system of a typical fusion machine, allowing a certain ductility in terms of *PR* and *Y*. Referring to the latest updates of the EU-DEMO, the protium removal system must allow a *PR* equal to 0.44 while ensuring a *Y* of 0.55. These conditions are achievable with a single stage of permeators and, considering the target flow rate of 67,000 ml min$^{-1}$ and the outcomes of the present campaign, the task can be fulfilled with seventeen membranes equal to the one adopted in this work.

It is worth noting that for the isotope rebalancing and for the protium removal tasks, the permeator works beyond the breakthrough, meaning that it operates with a higher specific feed flow rate compared to the typical applications of the hydrogen purification. Thus, the permeator can be more compact than the typical membrane modules reducing cost, energy consumption, and encumbrance. A further improvement would be the coupling of the isotope rebalancing and of the protium removal functionalities in a single permeator, for which an optimize design should be derived.

## 5. Conclusions

The activity aims at investigating the possibility to exploit palladium-silver membranes for the isotope separation, isotope rebalancing, and protium removal functions, relevant for the future fusion machines. To do this, the HyFraMe facility at the ENEA Frascati laboratories is revamped to host an experimental campaign with protium and deuterium.

In the past, the attention was posed to the separation task, and the main conclusion was that adoption of palladium-silver membrane is too challenging making its application not convenient compared to the other technologies. The main issues, confirmed in this experimental study, are the required number of stages and the complexity to operate and control the cascade of permeators. Nevertheless, a new interest grows up in the application of this technology for isotope rebalancing and protium removal. The experimental investigation shows promising results of the palladium-silver membrane that demonstrates to fulfil the tasks with a small number of stages and with a convenient ratio between the permeate and the retentate flow rate. This solution is able to solve the issues of inventory and energy consumption of other technologies.

Further analyses are needed to optimize the operational conditions in terms of temperature and flow rate and to verify the operability of a cascade of permeators. In this regard, in 2024 a new facility was designed and constructed at ENEA Frascati laboratories. The objective was to have a better control of the membrane temperature, to improve the vacuum on the permeate side, and to allow the coupling with the existing Medium-Scaled Membrane Reactor (MeSMeR) facility [16] to study the operability of a cascade of permeators. The first hydrogen purification tests are expected in the 2025 which should highlight the capabilities of the facility. After that, the facility will be implemented to study the isotope separation, the isotope rebalancing, and the protium removal functions.

## CRediT authorship contribution statement

**Vincenzo Narcisi:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Linda Sansosti:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Alessia Santucci:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

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