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Numerical study and experimental verification of protium permeation through Pd/Ag membranes for fusion applications

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Pd/Ag membranes are one of the reference technologies for the fuel cycle of deuterium-tritium fusion machines. This technology is proposed to be implemented in tritium recovery systems, due to their exclusive selectivity towards molecular hydrogen isotopes. For instance, these membranes are proposed to process and separate Q_2 (Q = H, D, T) species from impurities (e.g., inert gases) coming from the plasma exhaust of ITER and also foreseen for DEMO. In view of up-scaling this technology to a DEMO-relevant case, a one-dimensional simulation code was developed to first predict H_2 permeation efficiencies. In this contribution, a numerical code which computes the permeation efficiency of protium through Pd/Ag membranes at different operating conditions and tubular geometries is presented. –A good agreement between the numerical outcomes and actual experimental results obtained at ENEA is highlighted and discussed.

Keywords: *metal membranes, tritium processing, tritium recovery, numerical simulation*

1. Introduction

Palladium and palladium-based (alloy) membranes have been used since the 1960s for the removal of H_2 molecules from incoming streams [1]. More recently, these membranes have been used in combination with catalysts for instance for methane steam or ethanol reforming [2, 3]. These technologies are routinely used in several major laboratories, such as the Tritium Laboratory Karlsruhe or the JET Active Gas Handling System, for the separation and/or detritiation of Q_2, Q_2O or CQ_4 molecules (Q = H, D, T) [4, 5]. Furthermore, these technologies are foreseen to be used at ITER and DEMO [6, 7]. An example is the use of Pd-based permeators to remove the Q_2 species present in the tokamak exhaust stream. Moreover, Pd-based membrane reactors (i.e., PERMCAT) are proposed to be used in different systems for detritiation purposes (e.g., tritium extraction system) [8]. Therefore, scaling-up studies are required to ensure operation at optimum conditions. For this purpose, a numerical code which is able to predict performance measured at small-scale is thus required. Numerical models simulating metal membranes and membrane reactors with different degrees of detail (e.g., 2-dimensional model) can be found in the literature [9 - 11]. The model presented in [11] aimed at studying the most impacting parameters on the detritiation of an incoming $He/H_2O/HTO$ stream. However, this code has not yet been validated with experiments. Furthermore, the model has to be further upgraded to include surface effects for permeation. An extended discussion on the algorithm is also required. Thus, this contribution presents an extension of the the numerical code presented in [11], and a validation with H_2 permeation experiments.

2. Mathematical description and algorithm

2.1 Mathematical description

The numerical code presented in this paper considers a tubular membrane with a given length L_m (m), inner diameter d_{inn} (m), and thickness t_m (m), as depicted in Error: Reference source not found. These geometric parameters, together with the permeability P_{Q2} (mol m^{-1} s^{-1} Pa$^{-0.5}$) of hydrogen isotopologues (Q_2 = H_2, HD, D_2, HT, DT, T_2) through a Pd-Ag layer are given as input. In addition, the temperature of the membrane T_m (K), the absolute feed p^f (Pa) and shell p^s (Pa) pressures are also an input. Finally, the initial feed and shell flows F^f_{tot} and F^s_{tot} (mol s^{-1}) and corresponding concentrations x^f_i and x^s_i (mol) are also required. The objective of the code is to determine the permeation efficiency (η_{Q_2}, no units) of each Q_2 species (e.g., H_2 and D_2) through the metallic membrane. The permeation efficiency (η_{Q_2} ¿ is given by the ratio of the Q_2 flow $F^s_{Q_2}$ (mol s^{-1}) permeated through the membrane in respect to the Q_2 flow in the feed stream

$$\eta_{Q_2}(\%) = 100 \times \frac{F^s_{Q_2}}{x^f_{Q_2} F^f_{tot}} \qquad (0)$$

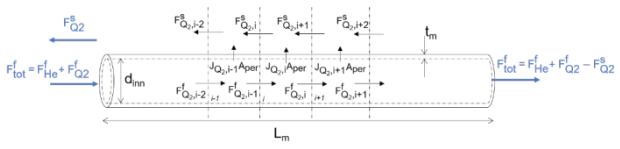

Figure 1 – Schematic diagram of the permeator only permeable to Q2 species (Q = H, D, T), operated in counter-current mode.

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(i.e., $x^{f}_{Q_2} F^{f}_{tot}$), as given in equation Error: Reference source not found.

To simplify, the equations (0)-Error: Reference source not found consider a feeding stream consisting of Q_2 (e.g., H_2) and He. The Q_2-flow $F^{s}_{Q_2}$ permeating the membrane can be calculated by dividing the membrane tube into a number of segments N_{seg}. In each segment i, the flux of protium $J_{H_2,i}$ (mol m^{-2} s^{-1}) permeating each element area A_{seg} (m^2) is given by equation (0), and A_{seg} is defined by equation (0).

$$J_{H_2,i} = \frac{S_{f,i} F^{f}_{H_2,i-1} - S_{s,i} F^{s}_{H_2,i+1}}{\frac{t_m}{P_{H_2}} + \left(S_{f,i} + S_{s,i}\right) A_{seg}} \quad (0)$$

$$A_{seg} = \pi \frac{d_{inn} L_m}{N_{seg}} \quad (0)$$

The terms $S_{f,i}$ and $S_{s,i}$ are the driving-force terms (Pa$^{0.5}$ mol^{-1} s) for gas permeation through the membrane, and they are defined by equations Error: Reference source not found and Error: Reference source not found. The first terms of S_f and S_s are due to the surface contributions. When these contributions are important (e.g., for very thin membranes ≤ 3 µm [11]) they decrease the driving force for permeation of the Q_2 species (i.e., H_2 in this case). K^{f}_{a,H_2} and K^{s}_{a,H_2} are the adsorption constants (in mol m^{-2} s^{-1} Pa^{-1}) for H_2 on the Pd-Ag surface in both feed and shell sides of the membrane [12]. The second terms of these equations are the contributions of the partial pressures of the permeating species (in this case is H_2), which follow the well-known Sieverts' law [13]. These terms include: the sum of the flows of all species (i.e., H_2 and He) present in the feed ($\sum F^{f}_{j}$) and shell ($\sum F^{s}_{j}$) streams, and the sum of all Q_2 species (e.g., H_2) in the feed ($\sum F^{f}_{Q_2}$) and shell ($\sum F^{s}_{Q_2}$) streams. Moreover, these terms are also dependent on the absolute pressures p^f and p^s.

$$S^{f}_{i} = \sqrt{-\frac{J_{H_2,i}}{K^{f}_{a,H_2} F^{f\,2}_{H_2,i}} + \frac{p^{f}}{\sum F^{f}_{j} \left(\sum F^{f}_{Q_2}\right)}} \quad (0)$$

$$S^{s}_{i} = \sqrt{\frac{J_{H_2,i}}{K^{s}_{a,H_2} F^{s\,2}_{H_2,i}} + \frac{p^{s}}{\sum F^{s}_{j} \left(\sum F^{s}_{Q_2}\right)}} \quad (0)$$

The equations above are generically applicable if a stream is sent into the shell side of the membrane (as in the case of a membrane reactor which could be operated under isotope swamping).

In this work, an initial feed flow of H_2 and He is routed into the membrane (i.e., no initial shell flow), and no other hydrogen isotopologues are considered. Eventually, H_2 will permeate through the membrane, and, at each segment i, the mass-balance is respected using

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$$F^{f}_{H_2,i} = F^{f}_{H_2,i-1} - J_{H_2,i} A_{seg} \quad (0)$$

$$F^{s}_{H_2,i} = F^{s}_{H_2,i+1} + J_{H_2,i} A_{seg} \quad (0)$$

equations Error: Reference source not found and Error: Reference source not found. These equations consider the counter-current case, where the feed and shell flows have the opposite direction (as depicted in Error: Reference source not found). For the co-current case, $F^{s}_{H_2,i+1}$ should be replaced with $F^{s}_{H_2,i-1}$ in both equations (0) and Error: Reference source not found.

2.2 Algorithm

The numerical implementation of the above equations for the calculation of η_{H_2} in counter-current mode follows the steps below:

a) for $i = 1$, estimate S^{f}_{1} using equation Error: Reference source not found with the input parameters $x^{f}_{H_2}$, F^{f}_{tot}. Use this value to estimate $J_{H_2,1}$ (equation (0)), assuming $F^{s}_{H_2,2} = 0$, $S^{s}_{1} = 0$ and no surface effects. Then, calculate $F^{f}_{H_2,1}$ and $F^{s}_{H_2,1}$ (equations Error: Reference source not found and Error: Reference source not found);

b) use the $J_{H_2,1}$ and the $F^{f}_{H_2,1}$ values calculated in a) to re-calculate S^{f}_{1} and S^{s}_{1} using equation Error: Reference source not found. Then, new values for $J_{H_2,1}$, $F^{f}_{H_2,1}$ and $F^{s}_{H_2,1}$are obtained using equations (0), Error: Reference source not found and Error: Reference source not found, respectively. In this step, the surface effects shall be also included;

c) repeat b) until the values for S^{f}_{1}, S^{s}_{1}, $J_{H_2,1}$, $F^{f}_{H_2,1}$ and $F^{s}_{H_2,1}$ converge to a pre-defined tolerance ε;

d) repeat steps a)-c) for $i = 2$ with $F^{s}_{H_2,3} = 0$ for a first estimation of $F^{s}_{H_2,2}$;

e) with the non-zero value of $F^{s}_{H_2,2}$, re-calculate the values for $i = 1$;

f) repeat steps a)-e) until $i = N_{seg}$;

g) Using the $F^{f}_{H_2,i}$ values, calculate the profile for the shell flows $F^{s}_{H_2,i}$;

h) calculate η_{H_2} using equation Error: Reference source not found, where $F^{s}_{Q_2} = F^{s}_{H_2,1}$, and $x^{f}_{Q_2} = x^{f}_{H_2}$.

If there are other hydrogen isotopologues present in the streams, the steps a)-h) presented above must be repeated using the corresponding values. It should be mentioned that the condition $F^{s}_{H_2,i+1} = 0$ (see step a)), used to estimate of $J_{H_2,i}$ and $F^{s}_{H_2,i}$, only applies if no flow is initially sent into the shell side of the membrane. If there is an initial flow F^{s}_{tot}, then $F^{s}_{H_2,i+1} = x^{s}_{H_2} F^{s}_{tot}$ should be used instead for step a). The calculations in the co-current mode are more simple. In fact, there is no need to go through steps e) and g), since $J_{H_2,i}$ and $F^{s}_{H_2,i}$ are

both

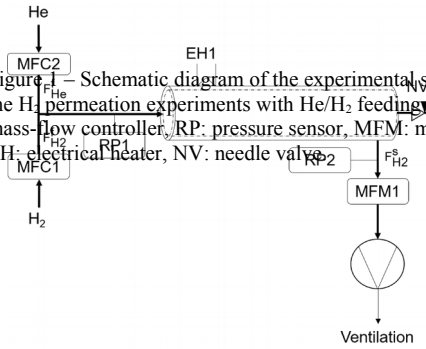

Figure 1 – Schematic diagram of the experimental setup used for the H_2 permeation experiments with He/H_2 feeding mixtures. MFC: mass-flow controller, RP: pressure sensor, MFM: mass-flow meter, EH: electrical heater, NV: needle valve.

calculated with $F^s_{H_2,i-1}$. It has been found that simulations with a number of segments above 50 for the co-current case and 200 for the counter-current produce negligible differences in the outcomes. The reason for the higher number of steps for the latter is due to the additional step e).

The inputs and outputs of this code are summarized in Table 1. From the output values the concentrations of

$$P_{H_2} = \frac{F^s_{H_2}}{\left(\sqrt{p^f x^f_{H_2}} - \sqrt{p^s}\right)} \frac{t_m}{A_{tot}} \qquad (0)$$

the species in the lumen and shell sides of the permeator can be calculated and also the permeation efficiency η_{Q_2}.

Table 1 – Inputs and outputs of the numerical code presented. From the output values several quantities of interest can be determined, such as the permeation efficiency given by Error: Reference source not found.

Inputs	Outputs
L_m, d_{inn}, t_m, P_{Q2}, T_m, p^f, p^s F^f_{tot}, x^f_i, F^s_{tot}, x^f_i	F^f_i, F^s_i, $J_{Q_2,i}$

3. Validation with the H_2 permeation experiments

3.1. Summary of the experimental conditions

Permeation experiments were performed at ENEA-Frascati to determine the H_2 permeation efficiency through a 113 μm thick Pd/Ag membrane at different conditions: different He/H_2 molar ratios (in the feed or lumen side), membrane temperatures and feed pressures. The experimental setup is schematically presented in Error: Reference source not found. The H_2 and He feed flows and absolute inlet pressures are imposed using mass-flow controllers (MFC1 and MFC2) and a needle valve (NV1), respectively. The lumen pressure is measured by RP1. The shell (or permeate) side is continuously evacuated, and its pressure is measured by RP2. The permeated H_2 flow is measured with a mass-flow meter (MFM1). The summary of the experimental conditions is given in Table 2.

Table 2 – Summary of the experimental conditions for the He/H_2 permeation experiments. sccm – standard cubic centimeter.

MFC1	25 – 400 sccm
MFC2	50 – 500 sccm
MFM1	4 – 390 sccm
RP1	100 – 500 kPa
RP2	< 21 kPa
T_m	523 – 673 K

3.2. Determination of the H_2 permeability

The H_2 permeability for a given permeator, with a thickness t_m(m) and surface area A_{tot} (m^2), at a certain temperature, can be determined experimentally by measuring the permeation flow $\left(F^s_{H_2}\right)$ and the pressures across it ($p^f x^f_{H_2}$ and p^s), according to equation Error: Reference source not found). Calculating permeability values at different temperatures, an expression for the permeability, as presented in equation (0), can be deduced. In this equation, E_a (J mol^{-1}) is the activation energy, R (J K^{-1} mol^{-1}) is the ideal gas constant and $P^0_{H_2}$ (mol m^{-1} s^{-1} $Pa^{-0.5}$) a pre-exponential coefficient. However, equation (0) only takes into account the H_2 partial pressure at the inlet of the permeator. In the experimental results, no decrease of the H_2 partial pressure along the permeator is measured or accounted for. Thus, an alternative method is proposed here to take into account the decrease of hydrogen concentration in the lumen side, and therefore provide a correction for the H_2 permeability.

$$P_{H_2}(T_m) = P^0_{H_2} e^{-\frac{E_a}{R T_m}} \qquad (0)$$

The numerical code presented and discussed in section 2 calculates the depletion of H_2 along the permeator tube, and consequently the decrease of its partial pressure in the lumen side. Thus, the strategy is to determine numerically an average lumen pressure $p'^f_{H_2}$ along the tube which can be used as input to equation Error: Reference source not found) (i.e., replacing $p^f x^f_{H_2}$). For this purpose, a permeability expression (equation (0)) must be given as input for the tool at first. Since $P^0_{H_2}$ and E_a are not available for the membrane tested, the values obtained for a thinner (84 μm) and a thicker (150 μm) Pd/Ag membranes reported in [12] are used as input and the outcomes compared. The pre-exponential coefficients and activation energies for these membranes are presented in Table 3. Different values shall be obtained for the 113 μm thick membrane. Two different sets of experimental points are used for this propose, where the He/H_2 molar ratio at the inlet was equal to 0.12 and 1.00. For each membrane temperature, permeation experiments were performed with different absolute inlet pressures in the range 100 – 500 kPa (see Table 2).

Table 3 – Pre-exponential coefficients and activation energies for the H_2 permeability expression for Pd/Ag membranes given by equation (0). The values for 84 μm and 150 μm are from [12] and the values for 113 μm are calculated in this work.

	$P^0_{H_2}$ (10^{-8} mol m^{-1} s^{-1} $Pa^{-0.5}$)	E_a (J mol^{-1})
84 μm	2.95	2531.49

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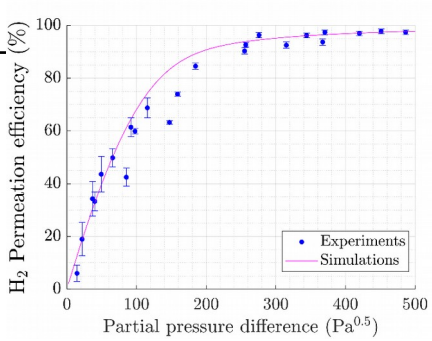
150 µm 5.63 5456.06

113 ± 640.3

When

H_2



depletion is not considered, the permeability values are underestimated. Moreover, the obtained permeability decreases with the absolute feed pressure, which should not occur as the permeability is a characteristic of the material and the permeating gas and it is constant for a given temperature. In contrast, when depletion is considered using the numerical code, a correction is applied on the permeability values, providing more consistent values. These observations can be appreciated in the plot of Error: Reference source not found, obtained for $He/H_2 = 1.0$ at 673 K. The associated uncertainties are within 1% (and thus not visible in the plot). The values obtained without considering depletion are smaller by at least a factor of 2. Moreover, it should be noticed that the discrepancy of the values is reduced after correction using the numerical code: the standard deviation is ~40% when no depletion is considered, and around ~9% with depletion. Similar conclusions apply to the remaining results not shown in this paper.

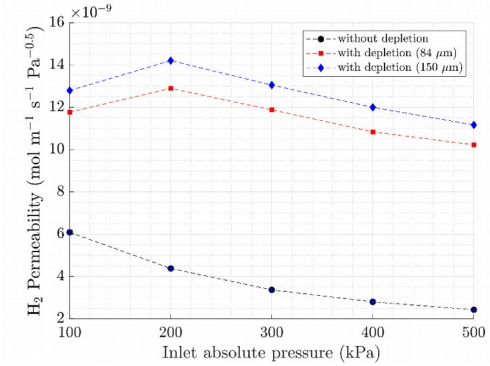


Figure **2** – H_2 permeability as a function of the feed absolute pressure, considering no H2 depletion (black circles) and considering H_2 depletion using the values presented in Table 3 as input for 84 µm (red squares) and 150 µm (blue diamonds). Results obtained for $He/H_2 = 1.0$ and 673 K. The uncertainties associated are within 1%.

Figure 3 – H_2 permeation efficiency as a function of the partial pressure difference obtained from the experiments (blue points) and simulations (solid magenta) thick membranes. The temperature of the membrane was 673 K.

The $P^0_{H_2}$ and E_a values for the membrane used in our experiments (presented in Table 3) are determined by averaging the permeability values obtained at the same temperature, and fitting them using equation (0). They were calculated by averaging the outcomes obtained with both experimental sets (i.e., $He/H_2 = 0.12$ and $He/H_2 = 1.0$) and both membranes (i.e., 80 µm and 150 µm). The errors presented are calculated using the standard deviation of the mean [14].

3.2. Comparison with the experimental results

In the plot of Error: Reference source not found the experimental permeation efficiency values (determined by equation Error: Reference source not found)) for H_2 as a function of the pressure-difference are compared with the outcomes from the numerical code. The results were obtained with a 113 µm-thick membrane, as mentioned above, and at a temperature of 673 K. The curve obtained using the numerical code is also presented (see Table 3). The values of feed flows and pressures given as input were obtained by averaging the corresponding experimental values: $F^f_{H_2} = 224$ ml min^{-1}, $F^f_{He} = 240$ ml min^{-1}, and $p^s = 16.4$ kPa.

It can be observed that a good agreement is obtained between the experiments and the numerical outcomes. These results give confidence to further use the numerical code to predict performances at different operating conditions. In addition, scaling-up studies in view of its application for fusion reactors can be also performed.

5. Conclusions and perspectives

A numerical code was developed to calculate the permeation efficiency of hydrogen isotopologues through a palladium membrane. The model relies on a finite element method, where the permeation through the membrane is calculated. At each segment, mass-balance equations are applied, so that flows profiles in the lumen and shells sides of the membrane are obtained. In this work, the main objective was to calculate the permeation efficiency of H_2 in the presence of He and compare the outcomes with actual experimental results. The numerical code was successfully validated with H_2/He permeation experiments performed at ENEA with a 113 µm palladium tube at different partial pressures.

This code can be further extended to include the kinetics of reactions (e.g., isotope exchange reactions) which occur in a membrane reactor, and thus simulating for instance decontamination via water-gas shift reactions. In addition, scaling-up studies can be done by identifying the most impacting parameters on the separation (or decontamination) performance. For instance, the membrane temperature and feed/permeate pressures are parameters of interest. These activities are required to support the design of DEMO-relevant systems relying on Pd/Ag permeators and/or membrane reactors.

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